



# Nanochemistry Views

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# 33. Is Semiconductor Photocatalysis Photochemical or Thermochemical or Both and Do We Care?

Around 35 years ago in a classic paper (Journal of Catalysis, 1980, 66, 383-390), Childs and Ollis asked a profound question: 'Is Photocatalysis Catalytic?'

They wanted to understand (i) whether or not a photocatalytic reaction was truly catalytic rather than stoichiometric from knowledge of turnover numbers or turnover frequencies and (ii) how these photocatalytic reactions compare to thermocatalytic ones, accessed from reaction rates per unit surface area.

This question is just as applicable today, even after the publication of more than 17,000 papers on semiconductor-based organic photooxidation, water photolysis and carbon dioxide photoreduction reactions.

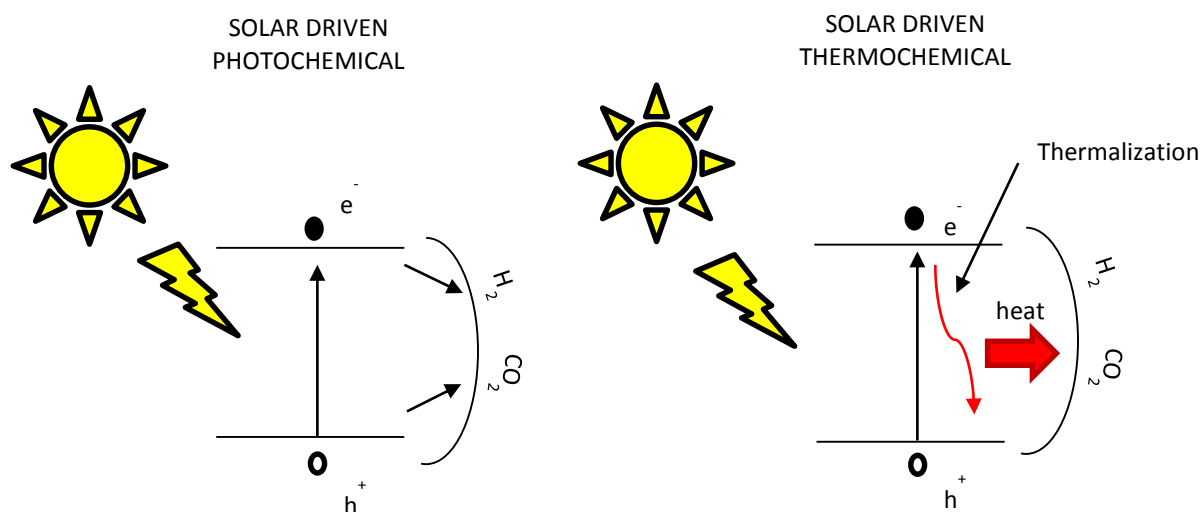


Figure 1 Photocatalysis: light, heat or a combination of both?

An equally important question relevant today, especially in the rapidly emerging field of solar fuels and solar chemicals, is what proportion of a claimed photocatalytic reaction is light driven, heat powered or a combination of both?

This important issue is encapsulated in Figure 1 which illustrates light driven versus heat driven contributions to these 'light-assisted' processes. On the left side of Figure 1, excited charge carriers interact with adsorbed surface species to enhance reaction rates. On the right side of

Figure 1, excited charge carriers thermalize and supply heat energy to enhance reaction rates. The questions are which of these processes dominate and what their contributions are? This is especially pertinent for the case of gas-phase photocatalysis where conduction and convection heat losses are expected to be small compared to the aqueous phase analogue.

The efficiency of most photocatalytic reactions will increase with the intensity of the light and the number of photogenerated electron-hole pairs. This implies the requirement of strong absorption of light by the photocatalyst. Subsequently, photoexcitation at energies higher than the electronic band-gap will result in heating of the photocatalyst from rapid phonon relaxation, with an accompanying increase in the local temperature. Excitation below the energy of the band-gap should have no effect unless sub-gap defect states abound. This is likely the scenario operating in reported research of CO<sub>2</sub> photoreduction on 'black' catalysts, exemplified by Ru-RuO<sub>x</sub> and Ni-NiO<sub>x</sub> nanomaterials, which begs the question whether they are light powered or heat driven or both?

As most photocatalysts these days are high surface area nanoscale particulate materials, it may be the local temperature of the nanoparticle that controls the reaction rate and efficiency rather than the global temperature of the support of nanoparticle film. The latter is usually measured with a thermocouple and can be very different from the local temperature.

An especially pressing question is how to decide on the best way to go scientifically, technologically and economically in the production of solar fuels and solar chemicals using greenhouse gas (CO<sub>2</sub>) as the feedstock. This is particularly urgent as we are currently in the midst of an intense international effort to develop technologies capable of converting CO<sub>2</sub> into a fuel or a chemical. Discovering materials able to positively improve this process on a large scale, driven thermochemically and/or photochemically, is a critical step towards ameliorating greenhouse gas emissions and enabling a carbon-neutral, renewable energy, sustainable economy.

In current industry practice there are many catalysts and processes known for making fuels and chemicals from CO<sub>2</sub> some of which are shown below:

Sabatier Reaction:  $\text{CO}_2 + 4\text{H}_2 \rightarrow \text{CH}_4 + 2\text{H}_2\text{O}$

Methanol Synthesis:  $\text{CO}_2 + 3\text{H}_2 \rightarrow \text{CH}_3\text{OH} + \text{H}_2\text{O}$

Reverse Water Gas Shift:  $\text{CO}_2 + \text{H}_2 \rightarrow \text{H}_2\text{O} + \text{CO}$

Methane Synthesis:  $\text{CO}_2 + 2\text{H}_2\text{O} \rightarrow \text{CH}_4 + 2\text{O}_2$

Methanol Synthesis:  $\text{CO}_2 + 2\text{H}_2\text{O} \rightarrow \text{CH}_3\text{OH} + 3/2\text{O}_2$

Carbon Dioxide Splitting:  $\text{CO}_2 \rightarrow \text{CO} + 1/2\text{O}_2$

Methane can power electricity-generating stations and provide heating for buildings. Methanol can drive fuel cells, run automobiles and act as a precursor for ~30% of industrial chemicals. Lastly, carbon monoxide can be used as a precursor for making hydrogen, methanol and liquid hydrocarbons according to the reactions:

Water Gas Shift:  $\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2$

Methanol Synthesis:  $\text{CO} + 2\text{H}_2 \rightarrow \text{CH}_3\text{OH}$

Fischer-Tropsch Synthesis:  $(2n + 1)\text{H}_2 + n\text{CO} \rightarrow \text{C}_n\text{H}_{2n+2} + n\text{H}_2\text{O}$

The energy required to drive these processes is dominated by fossil fuels. However, increasing amounts of renewable energy, from wind and solar, tidal and hydroelectric, nuclear and geothermal are coming on stream to minimize the depletion of legacy resources and cut back on associated carbon dioxide emissions.

The idea of utilizing power from the sun to make electricity has a long history in the annals of solar cells whereas the vision of making solar fuels and chemicals from the sun is of a more recent vintage. While great scientific and technological strides have been made over the past four decades towards the realization of a renewable energy resource from the photolysis of  $\text{H}_2\text{O}$  to  $\text{H}_2$ , the photocatalytic reduction of  $\text{CO}_2$  remains a significant challenge and has been studied to a much lesser extent. This is especially true for gas-phase  $\text{CO}_2$  photoreduction, which is increasingly being considered as the only practical way of scaling the process to sufficient proportions to have a significant impact on decreasing global greenhouse gas emissions.

As the heterogeneous catalytic reactions listed above for converting  $\text{CO}_2$  to fuels and chemicals are thermally activated, the pursuit of using light and/or heat from the sun to drive these reactions has become an active area of research. In both cases, research has been aimed at the development of optimized photochemical or photothermal catalytic materials, photo-thermal reactors and solar-light concentrators.



While the construction of the most efficient reactors and concentrators are engineering obstacles, the ongoing process of discovery for the most active materials is a chemical challenge. Hence, deciding whether the chemical reactions are light driven, heat driven or both is an important issue, as illustrated in Figure 2. In this respect, experiments need to be devised that would permit the disentanglement of photochemical and thermochemical contributions to observed heterogeneous reaction rates and efficiencies. This can be done by monitoring the temperature, wavelength and intensity dependence of the reactions in the dark versus in the light.

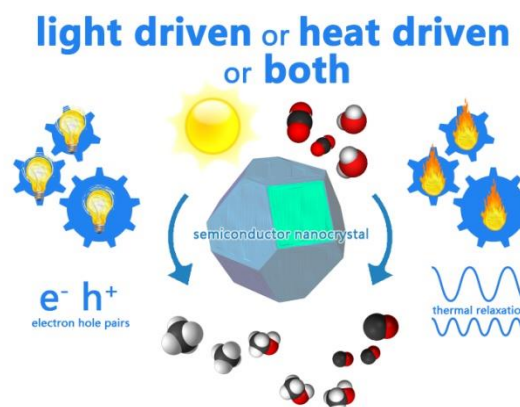


Figure 2 Is your photocatalytic reaction powered by light or heat or both? Graphical illustration courtesy of Chenxi Qian

It is worth noting photon to chemical conversion efficiency in principle can reach 10-20 % whereas thermal to chemical conversion efficiency is usually lower, so from this point of view photocatalysis is advantageous. Also exothermic reactions can be easily catalyzed thermally whereas for endothermic ones catalysis by light can be an efficient way to supply the energy needed to drive the reaction.

The heat is now on the implementation of a new CO<sub>2</sub> economy for the production of solar fuels and solar chemicals using light from the sun!

# 34. This is your Brain on Art: Metaforming Nature

## Boulder Museum of Contemporary Art Lecture Series



The collaboration between arts scientist Todd Siler and nanoscientist Geoffrey Ozin [www.artnanoinnovations.com](http://www.artnanoinnovations.com) began with a shared interest in how the integration of art and science can generate innovative frameworks for a sustainable future. With the global population predicted to reach 9.6 billion by 2050 accompanied by mounting demand for fossil fuels to spur economic growth, the fate of humankind seems tenuous at best. Ozin's research into nanochemistry, however, suggests an

antidote to the fear of environmental collapse and mass extinction. If nanotechnology can mimic a process like photosynthesis in plants then carbon dioxide ceases to be a noxious gas and becomes a resource. Siler's art gives form to these concepts, particularly how the brain interacts with nature as it connects and transforms everything nature creates in personally meaningful and purposeful ways.

At the CU Art Museum, Siler's large-scale installation *Metaphorming Nature* features a selection of artworks that interpret what nature makes and what we make of nature, Figure 1. The

installation replicates the limbic system - the heart of the human brain - where intuitions, feelings and emotions, including fear, are integrated and interpreted. The immersive environment presents a mosaic of interrelated paintings, sculptures, drawings, and photomontages produced over the last four decades. Other artworks visualize nano-scale and macro-scale processes and physical matter, in which sparks

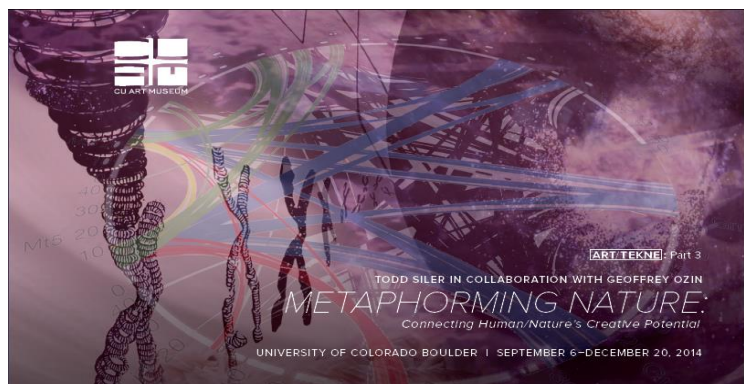


Figure 1 Courtesy of the Colorado Museum of Modern

between atoms seem to transform into a cosmos of possibilities. With no stabilizing horizon line, the large swathes of fiery reds and cool blues at play in these paintings impact cognition and also activate in the mind fear of the unknown and the boundless represented by the infinitesimal and infinite. Likewise, Ozin's research into new nanotechnology with global ramifications on renewable energy solutions to climate change through the paradigm of a new carbon dioxide economy is at once hopeful and a little bit scary.

## 35. Do We Have a Plan B?

The Intergovernmental Panel on Climate Change (IPCC) reported in October 2013 that it is 95% certain humans are the cause of anthropogenic climate change from the increasing concentrations of carbon dioxide greenhouse gas emitted into the atmosphere from the combustion of fossil fuels. In March 2014 the IPCC announced that our planet now faces irreversible climate change and our only choice going forward is an assessment of risk, vulnerability, mitigation, adaptation and cost (see reference: <http://www.ipcc.ch/>).

Let's refer to this 'burn-and-adapt' scenario as Plan A. It appears to me that what is missing from the ongoing greenhouse gas climate-change debate, is a credible Plan B, namely an alternative course of action for use if Plan A should fail.

What I mean by Plan B is a science-based solution with an accompanying action road-map to enable a global scale energy transition from our current one – which is dependent on the finite supply of oil, coal and gas - to one founded on a new energy source that would be able to sustain a global society; particularly after the emission of an estimated Trillion tons of CO<sub>2</sub> into the atmosphere through the burning of fossil fuels (see references: <http://trillionthtonne.org/>, <http://www.climatecommuniques.com/>, <http://www.carbontracker.org/>).

CO<sub>2</sub> is the thermodynamic 'default molecule' of fossil fuel combustion. Hence, I believe a Plan B strategy can be built around a 'New CO<sub>2</sub> Economy', the premise of which is (i) CO<sub>2</sub> is not a waste product to fear, (ii) CO<sub>2</sub> is a bounteous carbon resource, (iii) CO<sub>2</sub> belongs to all and (iv) through innovative chemistry CO<sub>2</sub> could provide a sustainable supply of fuels and chemicals for the rest of time.

In the energy transition to Plan B, the fossil fuel industries can continue their exploration for oil, gas and coal in order to replenish the atmospheric CO<sub>2</sub> feedstock. These CO<sub>2</sub> emissions are needed for Plan B in order to maintain sustained petrochemical and chemical production using CO<sub>2</sub> driven by light and heat from the sun. Once this transition is completed, atmospheric CO<sub>2</sub> can provide a sustained source of feedstock for fuel production via sunlight and depletion of legacy fossil fuels from the earth could then be stopped. At steady state, a closed energy cycle can be reached whereby CO<sub>2</sub> is converted to solar fuels, which is consumed to produce CO<sub>2</sub>, which then can be used to convert to solar fuels again.

In order to expand upon the above statement, we direct our attention to well-documented large scale, gas-phase, heterogeneous catalytic processes which are already able to convert CO<sub>2</sub> into fuels and value-added chemicals in the petrochemical and chemical industries. However, these processes are invariably thermally driven and require an initial input of energy. More often than



not, the energy used to power these processes are usually generated through the burning of fossil fuels, either to produce electricity or heat, which in themselves produce more CO<sub>2</sub>.

I would argue therefore that the infrastructure exists for the development of a global scale CO<sub>2</sub> capture and conversion economy, which leads to recycling of CO<sub>2</sub> from the atmosphere to fuels and value-added chemicals. It can however only be sustained until the point in time when fossil fuels are depleted and the only thing left is a plentiful supply of CO<sub>2</sub> in the atmosphere.

What is missing in the transition from a fossil fuel based economy to one based on CO<sub>2</sub> is a globally sustainable supply of clean energy to enable the heterogeneous catalytic processes that can transform CO<sub>2</sub> into fuels and value-added chemicals. In this, nothing can match the massive scale, pristine nature and essentially infinite lifetime of Nature's fusion reactor, the sun.

The grand challenge for science and engineering is to discover novel materials and processes that can efficiently and economically capture CO<sub>2</sub> and harvest both light and heat from the sun and convert CO<sub>2</sub> into fuels and chemical feed stocks. This can be exemplified by the economically viable production of CO, CH<sub>4</sub> and CH<sub>3</sub>OH at a relevant rate and scale.

To place this grand challenge into perspective, a conversion rate of 10 moles of CO<sub>2</sub> per hour per gram of catalyst translates into a conversion rate of 1 Gigaton of CO<sub>2</sub> per year per ton of catalyst when placed in 250 sunny locations. In practical terms, this can be achieved through the use of 20,000 solar panels with an area of one square meter, containing a 10 micron thick catalyst film made from a MO<sub>x</sub> nanomaterial with average density of 5 g.cm<sup>-3</sup>.

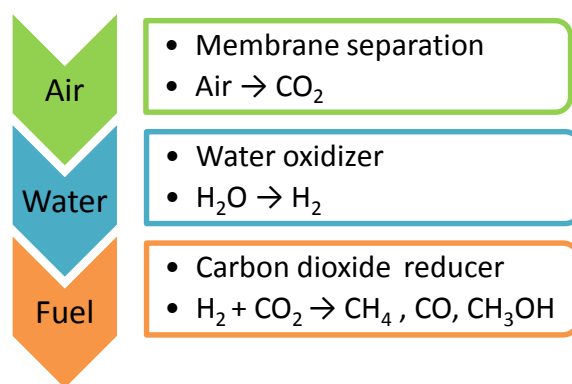
One can appreciate from this 'back-of-the-envelope' calculation that the development of a global scale CO<sub>2</sub> economy could readily handle the yearly global emission of 40 to 50 Gigaton of CO<sub>2</sub>. This conversion rate is sufficiently high in that it can maintain a steady-state concentration of CO<sub>2</sub> in the atmosphere as well as produce the carbon equivalent of fuels and chemicals, thereby solving our climate and energy dilemma in one fell swoop.

In this context it is worth noting that Ivanpah - the world's largest solar thermal power station located in the Mojave Desert (<http://www.brightsourceenergy.com/>) - is currently producing high-value electricity and steam from sunlight. Their product is used in power, petroleum and industrial-process markets worldwide. Its deployment area of 330,000 mirrors is roughly equivalent to the surface area calculated for the envisioned CO<sub>2</sub> conversion process mentioned above.

Integrating an earth abundant and cost effective catalyst with existing chemical and petrochemical industrial infrastructure could provide a practical, economical and sustainable alternative to fossil fuels and its perceived climate change consequences. The beneficiaries of

this will be the oil, coal, gas, and chemical and petrochemical industries, the engines of our global economy.

To further build upon this proposal, a Plan B vision for a sustainable future is to make the solar fuels technology (i.e. capturing and utilizing CO<sub>2</sub> in both air and in concentrated localized sources) compatible with existing infrastructure on land and sea around the world. The scheme illustrates the envisioned Air-to-Fuel technology, which utilizes solar-assisted heterogeneous catalysis materials science and chemical engineering methods. The three-step process involves CO<sub>2</sub> separation or capture. Next gaseous water is split into H<sub>2</sub>. Then this H<sub>2</sub> is utilized to reduce gaseous CO<sub>2</sub> to CO, CH<sub>4</sub> and CH<sub>3</sub>OH fuels and chemicals. This model provides an example of how we can transition the most promising solar fuels materials from a laboratory scale prototype to a CO<sub>2</sub> capture and conversion technology that will enable the creation of a new and sustainable CO<sub>2</sub> economy. If the economics (energy and cost) and the timeline (lab-to-market) of the process both work, we may be able to circumvent the predicted consequences of greenhouse gas climate change.



What will it take to make this energy transition a reality? I believe what I have proposed is a positive message that circumvents the controversy and negativity of the climate debate. It is an appealing vision and a scientifically plausible idea that everyone would appreciate, from high school students to academics, from industrialists to investors and from economists to policy makers.

A solar fuels technology that would enable an energy transition to a sustainable future would begin as a small piece of the energy puzzle that is expected to grow overtime. The end goal is to power the world using renewable energy, with solar fuels generated from CO<sub>2</sub> being a critical component of the energy endgame.

The goal of a new CO<sub>2</sub> economy envisioned in this article presents a credible science and engineering paradigm, with a calculable cost, assessable risk and definable benefit over a quantifiable development time period. By contrast, the protracted climate change debate with its opposing forces appears to be grid-locked, increasing the economic and human cost of not having a credible Plan B.

## 36. Jarring Fears – Have We Covered Everything



Jarring Fears, Courtesy of Todd Siler

We are sensing increasingly escalating fear and angst amongst the public about the environmental uncertainties they must face in the next 10-20 years as a consequence of the relentless emission of carbon dioxide (CO<sub>2</sub>) from the combustion of legacy fossil fuels into our atmosphere, and the havoc the global temperature rise, caused by the associated greenhouse gas effect, is expected to wreak on the climate and their fragile existence.

In 2011 the International Panel on Climate Control (IPCC) announced a “carbon budget” for our atmosphere that was calculated to keep the rise in global temperatures to no greater than

2°C above pre-industrial levels; in 2011 they announced we have used up 67% of that budget!

Todd Siler’s transparent artwork “Jarring Fears” shows a glass jar of potentially deadly weather conditions, which contrasts with Roz Chast’s insightful cartoon “Is Everybody Happy?”, (Fuzzy Logic, in *Scientific American*, 2003), which depicts a tin can full of some unknown, but, presumably, “safe,” consumable goods that’s smothered with popular health-conscious labels, designed to give us a peace of mind.

Crammed within this jar of fears are all the terrifying weather conditions that we dread will result from greenhouse gas climate change. The conditions range from more forceful and frequent hurricanes to record-breaking tornadoes; from rising temperatures to relentless forest fires, famine, drought and disease; from ice cap melting that causes loss of permafrost and the escape of methane, exacerbating sea level rise with ensuing floods of epic proportions. Picture this disquieting image looming over our heads like some proverbial black cloud. That’s the public’s perception of the state of the world that we would be wise to better understand.

The double-entendre title on the lid of this jar "Have we covered everything?" aims to prompt politicians and policy-makers to learn more about the complexity of this whole messy climate change challenge. Currently, they seem not to be "covering" the complexity - or simply fearing it - like so many world citizens experience who feel overwhelmed and frightened by the prospect of living on an ecologically bleak planet.

It humbles and saddens us all just imagining the extinction of the human race.

Is this really what we can look forward to understanding, by accepting the severity, pervasiveness and irreversibility of climate change, its impact on people and the ecosystem and adopting Plan A? This plan implies a global strategy whereby the finite supply of legacy fossil fuels will continue to be combusted and depleted with its associated emissions of CO<sub>2</sub> spewed into our atmosphere. The cost of the risk against the benefits will be estimated and appropriate measures will be put in place to reduce the effects of the vulnerabilities and prepare for the consequences of CO<sub>2</sub> driven climate change. In the absence of any aspirations on mitigation of CO<sub>2</sub> emissions the future appears bleak.

Our most trusted experts assure us that our most well-established advanced technologies (wind, solar cells, biomass and geothermal) will save-the-day. But how exactly they'll fulfill this promise remains a deep source of anxiety for many people who follow this developmental work closely. These experts assure us that hopefully very shortly we'll have the ways and means to create a sustainable future with these renewable forms of energy operating synergistically. To date, these renewable forms of energy continue their remarkable growth and are becoming cost competitive with fossil fuels.

In 2012 global power generation from the four renewable forms of energy mentioned above provided nearly 0.5GW with almost \$250B in investments, ahead of fossil fuels for the third year running. This begs the question; will the current targets for the proportion of renewable forms of energy versus the total energy demand be met? While 0.5GW sounds impressive, keep in mind the 20-30TW global demand for energy, which amounts to about 50 times the energy generated by renewable, most of which still comes from gas, oil and coal. This means current carbon dioxide emissions of around 40-50GTons per year continue unabated and will most likely continue for the foreseeable future.

Some would like us to believe natural gas will rescue us from the abyss as we are told there is plenty of it for at least 250 years. Is this "really" the best we can do for Plan B?

Burning natural gas adds 0.2kg CO<sub>2</sub>/kWh into our atmosphere compared to 0.4kg CO<sub>2</sub>/kWh from coal, 0.28kg CO<sub>2</sub>/kWh from oil, 0.05kg CO<sub>2</sub>/kWh from biomethane, and from wind and solar a mere 0.01kg CO<sub>2</sub>/kWh. Moreover, natural gas provides a stable energy supply, which integrates

well with intermittent renewable forms of energy. Natural gas and biomethane can be readily stored, easily transported and is able to power our homes, industries and transportation.

While this all sounds quite promising it does not solve the problem of our burgeoning obsession with burning fossil fuels and the incessant emissions of greenhouse gas CO<sub>2</sub> it churns out into our atmosphere.

In the future, excess electricity from wind and solar can be stored as synthetic natural gas obtained through electrolysis of H<sub>2</sub>O where the H<sub>2</sub> so produced can be used to reduce CO<sub>2</sub> to CH<sub>4</sub> with known thermally powered heterogeneous catalytic industrial processes.

So the conversion of renewable electricity to natural gas does seem to integrate seamlessly into the existing gas infrastructure and might reduce some of the CO<sub>2</sub> emissions in the process but globally CO<sub>2</sub> from the combustion of fossil fuels will continue to be disgorged into our atmosphere.

The big question is whether natural gas and its synthetic replacement built into an integrated energy system will in the foreseeable future be enough to stop climate change in its tracks? In this context, the recently published book, *Sustainable Energy: Without the Hot Air* by Cambridge University Professor of Engineering, David MacKay, quantitatively defines the enormity of the challenge of replacing fossil fuels by renewable forms of energy. Clearly, the current plan to burn the estimated 24 trillion tons of CO<sub>2</sub> equivalents of fossil fuels that remain in the ground is neither desirable nor sustainable.

MacKay makes it clear in his reality study of a sustainable future that in order to address the crucial issues of climate change and energy security, new global scale renewable energy technologies beyond those mentioned above must be discovered and implemented to achieve CO<sub>2</sub> emission targets and energy demands.

We believe a viable Plan B could be based on a materials technology that can simultaneously harness abundant solar energy - capturing and reducing gaseous carbon dioxide into fuels and chemical feed stocks, while addressing issues of energy security and climate change.

An appealing vision is an energy transition from one based on unsustainable fossil fuels to a sustainable solar fuels energy technology founded on capturing and utilizing CO<sub>2</sub> – from both thin air and more concentrated localized sources. This strategy could be made compatible with existing CO<sub>2</sub> emitting industries around the world.

Achieving this vision of a carbon-neutral-cycle technology necessitates developing compact, tandem, concentrated solar powered photochemical reactors for efficiently splitting gaseous water into H<sub>2</sub> and then using the H<sub>2</sub> to reduce gaseous CO<sub>2</sub> to fuels and chemicals.



With major breakthroughs in conversion rates and efficiencies anticipated over the next five years, the time it should take to transform solar fuels laboratory-scale science to a global technology could be short enough to circumvent the predicted adverse consequences of greenhouse gas climate change. More to the point: this strategy will enable a timely energy transition from unsustainable fossil fuels to sustainable solar fuels.

Is this a credible Plan B? Does it deserve strong support from the fossil fuel producing and consuming industries around the world? Will countries with major concentrated sources of CO<sub>2</sub> be among the main benefactors of Plan B?

If we adopt Plan B, a key question that will be raised, is at what point in time would the total amount of CO<sub>2</sub> in the atmosphere start to reduce; when would the crossover point occur? This calculation would likely depend on how quickly the scaled-up solar fuels plants could be built around the world. Even at the crossover point, we may not see an immediate change in the climate – it might take some further time before an observable change in the climate takes place or the detrimental effects of climate change are halted. We also have to accept that even if climate change is halted, the climate at that point may not be the same as the climate we experience now because of changes which have occurred, such as icecaps and tundra melting.

We think Plan B could prove to be an important component of the renewable energy mix. And we're certain it's worth "covering" in-depth.

## 37. CO<sub>2</sub>: War and Peace



**Figure 1** Every day we influence the dynamic balance between The CO<sub>2</sub> War and Peace, by messing with the equilibrium level and steady-state concentration of CO<sub>2</sub> and O<sub>2</sub> in the atmosphere through the relentless combustion of fossil fuels. If left unchecked and out of balance, this fragile equilibrium - by virtue of photosynthetic bacteria, algae, and plants - can become our nemesis, rather than sustain our genesis and growth. Our well-being and health of collective future now rests on some basic choices and conscious civil actions. Will we choose to flow with Nature, or not, and if not, why not? Choose wisely, and be at peace. Courtesy Todd Siler, [www.artnanoinnovations.com](http://www.artnanoinnovations.com)

this astonishing event, a symbiotic balance and synergy evolved between the O<sub>2</sub> required to sustain life and the life needed to sustain O<sub>2</sub>. In this biological era - and up until recent times - a delicate equilibrium was established that maintained a steady-state concentration of CO<sub>2</sub> and O<sub>2</sub> in the atmosphere. This equilibrium enabled all life processes to flourish on Earth. Essentially, **life was at peace with CO<sub>2</sub>**, and has remained so ever since, **Figure 1**.

**At War with CO<sub>2</sub>** It started around the period of the industrial revolution (1760-1840) as the concentration of CO<sub>2</sub> in the Earth's atmosphere, which had remained at a stable concentration of around 300 ppm for about 2 billion years, began to be disturbed by the combustion of fossil fuels. At this time coal, oil and natural gas harvested from the earth's crust was regarded as a miraculous and seemingly infinite supply of stored chemical energy and certainly have proven to be an able provider of power for a growing global population.

This event, which may be referred to as the "Carbon Dioxide Catastrophe", has caused the concentration of CO<sub>2</sub> in the Earth's atmosphere to gradually increase from its equilibrium level of

**At Peace with CO<sub>2</sub>** Over its 4.7 billion year history the chemical composition of the Earth's atmosphere has changed a number of times from its inhospitable chemical origin into the pre-biological era through the microbial era to the biological era that created an atmospheric environment and ecology suitable for sustaining the co-existence of all life forms on earth today.

About 2 billion years ago, oxygen appeared in the earth's atmosphere for the first time, produced by photosynthetic bacteria that evolved to utilize energy absorbed from ambient sunlight to oxidize water to form molecular oxygen. As a result of

around 300 ppm to the current level of around 400 ppm. And there is no sign of its abatement in the foreseeable future.

The human race has recently been issued an ultimatum by the United Nations Intergovernmental Panel on Climate Change, IPCC. Science has spoken. Pump no more than a trillion tons of CO<sub>2</sub> into the atmosphere to keep global warming below 2°C or face the consequences (note that by 2011 we had pumped 1.9 trillion tons of CO<sub>2</sub> into the atmosphere and at today's increased emission rate of 40-50 billion tons of CO<sub>2</sub> per year we are on track for a 2°C rise). Cut global CO<sub>2</sub> emissions by half within the next fifteen years or be prepared for a temperature rise of between 2-5°C. At that dire level, we'll all be forced by nature to face the resulting dangerous effects of climate change.

In this context, the IPCC strongly recommended that low carbon sources must be used to generate the majority of the world's electricity by 2050. They insist on seeing rapid growth of renewables from their current 30% share of the power sector to 80% by 2050. And they believe electricity from fossil fuels - minus carbon capture and storage - should be essentially eliminated by 2100.

Of course, there will always be climate change skeptics who will hawk the heterodox view arguing the massive cost of the transition from fossil fuels to renewable forms of energy and the adverse effects this will have on national and global economies.

Naturally all sorts of economics and ethics related questions will be raised, such as who should pay for climate cleanup and who should welcome climate refugees forced to relocate because of extreme weather conditions: Those countries that have put most of the CO<sub>2</sub> into the atmosphere since the industrial revolution or those nations currently emitting the greatest amount of CO<sub>2</sub> per capita with willful blindness?

The consensus in the scientific community is crystal clear: If we want to avoid the risk of climate change from a greenhouse gas induced 2-5°C temperature rise our addiction to fossil fuels must be curbed immediately; the pumping of CO<sub>2</sub> into the atmosphere must be reduced immediately, and it must be done fast, effectively and efficiently - global emissions must be cut by half in the next fifteen years in the view of the IPCC!

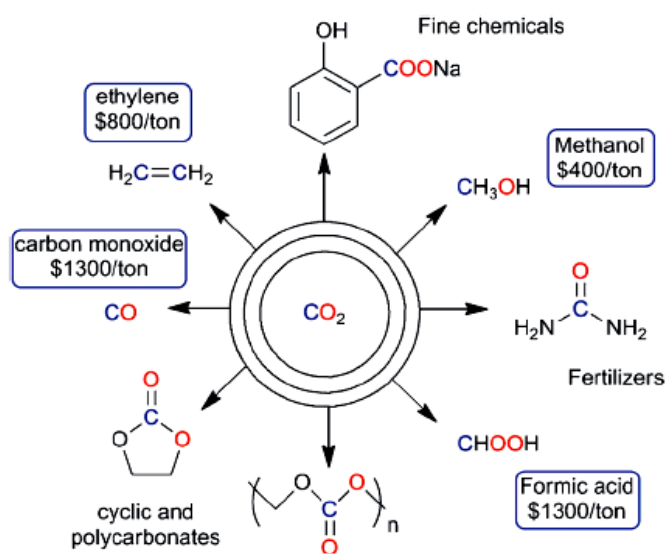
The big challenge for the global community is whether we have the scientific, technological, economic and political means and motivations for commercial implementations to agree upon an approach to accelerate the transition of fossil fuels to renewable forms of energy fast enough to avoid the ramifications of a CO<sub>2</sub> calamity?

At first sight this does seem like an almost impossible challenge if for example we look at the slow progress of carbon capture and storage worldwide with only one commercial plant on line

in Canada ([www.saskpower.com](http://www.saskpower.com)) While the storage element of this procedure is likely to be different if CO<sub>2</sub> is used as a feedstock, the time scale for carbon conversion seems an almost herculean task if a 2-5°C temperature rise is to be avoided.

The big problem in convincing all countries to work together to achieve a rapid decrease in global CO<sub>2</sub> emissions, is that the “have and have not” fossil fuel countries have starkly different perspectives on the benefits of curtailing emissions *versus* the detrimental effects it will have on their economies. In essence, capitalism and the climate are in conflict. It’s self-evident to see that, today, **life is at war with CO<sub>2</sub>**, Figure 1.

**At Peace Again with CO<sub>2</sub>** Perhaps the toughest challenge of ameliorating climate change and facilitating a sustainable energy future, in which life is at peace with CO<sub>2</sub>, is stopping ourselves from treating CO<sub>2</sub> as a waste product endangering life on Earth. Instead we need to utilize CO<sub>2</sub> as an abundant, non-toxic and low cost feed stock for making fuels and chemicals, enabling life to flourish indefinitely.



**Scheme** CO<sub>2</sub> is not a waste product to fear, it is an abundant, non-toxic, low cost C<sub>1</sub> chemical feed stock for making fuels and chemicals, Love, J.B. Chemical Communications, 2012, 48, 1392

This is a solvable chemical problem; if the rate of transformation of CO<sub>2</sub> to useful molecules and materials can be made to match its rate of production from the combustion of fossil fuels, then our greenhouse gas problem would be resolved and our war with CO<sub>2</sub> would be over.

In actualizing this possible reality, CO<sub>2</sub> is captured and converted in a carbon neutral cycle to provide fuels and chemicals forever, circumventing the specter of climate change. Essentially the goal is to short circuit the natural carbon cycle, basically doing what nature takes billions of years to do on a much shorter timescale. So now we just use the CO<sub>2</sub> we have in a synthetic carbon cycle, not dig up fossil fuels any more.

Sounds too good to be true, hardly, this is not a new problem. Large scale chemical processes have been known for more than a century for making fuels and chemicals using CO<sub>2</sub> as the feed

stock from direct air capture and fossil fuel burning electricity generating stations, steel, aluminum, cement and bio-ethanol industry sources.

Even though there has been a significant amount of research and development, considerably more effort and money needs to be spent to improve the performance of CO<sub>2</sub> conversion to technologically practical rates and efficiencies on an industrial scale and to integrate it into existing chemical and petrochemical industrial processes. Industry road maps show milestones and timelines as to why-how-when-where CO<sub>2</sub> conversion fits into their projected carbon fuels and chemicals pipeline.

Some examples of this paradigm are shown above in the **Scheme** that illustrates industry examples currently being practiced at the Megaton per year production scale for pharmaceuticals (Aspirin), liquid fuels (methanol), hydrogen storage and transportation (formic acid), polymers (ethylene, polycarbonates), fertilizers (urea) and carbon monoxide, which can be used as a feed stock for making myriad fuels and chemicals, such as gasoline, methanol and hydrogen. In principle, these kinds of industrial processes have the capacity to transform CO<sub>2</sub> to useful products around the world and could be scaled to produce Gigatons per year, thus making a pretty big dent in the CO<sub>2</sub> footprint.

The main contenders under active investigation for CO<sub>2</sub> conversion to fuels and chemicals include homogenous and heterogeneous catalysis, biomass, electrochemistry, photoelectrochemistry, solar thermal and photocatalysis. Although there are technical and economic pros and cons for each of these approaches, with continued research and development, there will likely emerge a creative mix of CO<sub>2</sub> conversion processes with the overall capacity of utilizing Gigaton amounts of CO<sub>2</sub> per annum for making fuels and chemicals. That sure beats storing it in the ground or emitting it into the atmosphere.

A real hurdle that must be overcome for any approach is that it must be cost effective. The cost of the production of fuels and chemicals must be cheaper than existing costs using fossil fuels. If cost effective conversion on an industrial scale can be demonstrated then the people that matter will start taking a real interest. It is noteworthy that CO<sub>2</sub> conversion to fuels



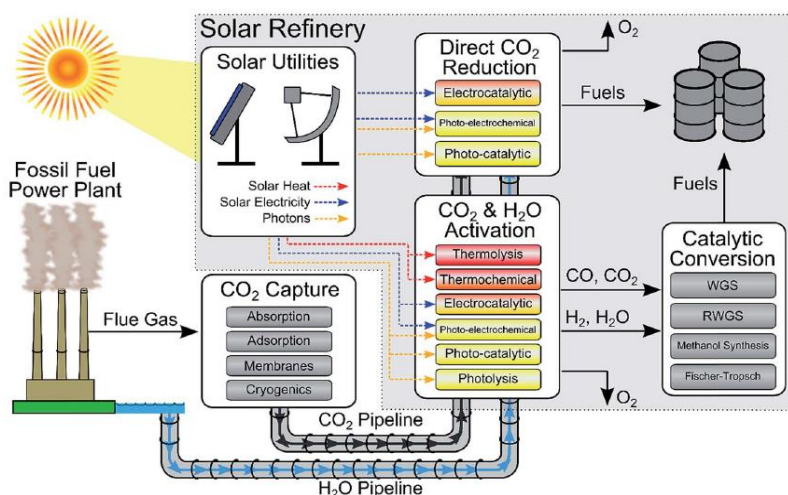
**Figure 2** Peace → War → Peace with CO<sub>2</sub> again enabled by the endeavors of chemists and chemical engineers; Courtesy of Chenxi Qian



and chemicals does not seem to be in the conversation at the moment for the IPCC, political leaders or the public.

Can we look forward to this “New CO<sub>2</sub> Economy” and a sustainable climate and energy future? With all the new solar fuels science and technology in the pipeline and poised to take off, could this “sleeping giant” emerge more quickly than industry, government, business stakeholders imagine? It seems possible, providing these processes are powered by renewable forms of energy (electricity and sunlight) and not fossil fuels. Any emissions of CO<sub>2</sub> into the atmosphere should be strongly regulated by a global CO<sub>2</sub> watchdog commission. In this way again, **life at peace with CO<sub>2</sub>**, will become an ‘ideal made real’, **Figure 2**.

## 38. Solar Refinery: Can we have our Carbon Cake and Eat It ?



There is a global effort underway to discover advanced engineering materials and processes to realize the 'solar refinery' of the future.

The purpose of the envisioned solar refinery is to enable an energy transition from today's unsustainable 'fossil fuel economy' with its associated risks of climate change caused by CO<sub>2</sub> emissions, to a new and sustainable 'carbon dioxide economy' that instead uses the CO<sub>2</sub> as a C1 feedstock,

**Scheme** Futuristic 'solar refinery' for making fuels and chemicals from CO<sub>2</sub>, H<sub>2</sub>O and sunlight, Energy and Environmental Science, 2014, DOI: 10.1039/c4ee01958j  
together with H<sub>2</sub>O and sunlight, for making solar fuels.

The structure and operation of the envisioned 'solar refinery' is illustrated in the **Scheme**. Key modules of the solar refinery, include materials and processes for (i) harvesting sunlight, (ii) capturing, purifying and releasing CO<sub>2</sub>, and (iii) converting CO<sub>2</sub> and H<sub>2</sub>O directly or indirectly to fuels. A flow diagram of how these modules are integrated to create a working solar refinery is illustrated in the **Scheme**.

There is actually nothing too surprising contained within each module of the solar refinery: (i) A solar utility harvests sunlight in the form of heat, light or electricity; (ii) A CO<sub>2</sub> facility uses absorption, adsorption, membrane or cryogenic techniques for capturing, purifying and releasing CO<sub>2</sub> on demand; and (iii) The CO<sub>2</sub> is piped with H<sub>2</sub>O and either *directly* transformed to fuels using electrochemical, photoelectrochemical or photocatalytic methods or *indirectly* converted to CO and H<sub>2</sub> by thermochemical, electrochemical or photoelectrochemical and photocatalytic means. The so formed CO and H<sub>2</sub> are subsequently made into fuels by well known industrial heterogeneous catalytic processes based on Fischer-Tropsch, methanol synthesis, water gas shift or reverse water gas shift chemistry.

What has been sorely missing in the open literature however, to assist teams of materials chemists, scientists and engineers around the world who are raring to contribute to the development of a solar refinery, is a life-cycle-assessment, a holistic technoeconomic analysis of the energy and economic costs of the alternative technologies contained within each module, including that required to build the solar collectors and chemical facilities. These teams of researchers also need to understand, how the ultimate price tag of fuels produced in the solar driven refinery compare with those generated in a fossil fuels powered refinery. With this information, they can improve the energy efficiency and economic burden of the materials and processes required for making fuels from the sun that can compete in the marketplace with those made from fossil fuels.

In a chemical engineering tour-de-force, Christos Maravelias and colleagues from the University of Wisconsin have recently modeled and analyzed the energy and economic cost of every step and each alternative technology contained in a solar refinery (Energy and Environmental Science, 2014, DOI: 10.1039/c4ee01958j). Their analysis encompasses all scales and all parameters that underpin the energy and economic costs of running a solar refinery. The result is a general framework that will allow scientists and engineers to evaluate how various improvements in materials manufacturing and processing technologies that enable carbon dioxide capture and conversion to fuels using solar, thermal and electrical energy inputs would accelerate the development, influence the cost and impact the vision of the solar refinery. It will also enable evaluation of which alternative technologies are the most economically feasible and should be targeted or highlight those that even if developed would still be hopelessly uneconomic and can therefore be ruled out immediately.

The view that emerges from this techno-economic evaluation of building and operating a solar refinery is one of guarded optimism. On the subject of energy efficiency, it is clear that solar powered  $\text{CO}_2$  reduction is currently lagging far behind that of solar driven  $\text{H}_2\text{O}$  splitting and more research is needed to improve the activity of photocatalysts and the efficacy of photoreactors. In the indirect process of transforming  $\text{CO}_2/\text{H}_2\text{O}$  to fuels, it is apparent that if the >10% currently achievable solar  $\text{H}_2\text{O}$ -to- $\text{H}_2$  conversion can be matched by solar  $\text{CO}_2/\text{H}_2$ -to-fuel conversion efficiencies, through creative catalyst design and reactor engineering, this would represent a promising step towards an energetically viable solar refinery. For the direct process of transforming  $\text{CO}_2/\text{H}_2\text{O}$  to fuels, improvements in conversion rates and product selectivity are key requirements for achieving energy efficiency in the solar refinery.

Economic efficiency is also a key to the success of the solar refinery of the future. For currently achievable  $\text{CO}_2$  reduction rates and efficiencies, the minimum selling price of methanol, a representative fuel, was evaluated by the techno-economic analysis and turned out to be more than three times greater than the industrial selling price analysis, as the cost of the  $\text{CO}_2$

reduction step, which is estimated to be quite costly, was not included in the estimates. Improvement in the activity of CO<sub>2</sub> reduction photocatalysts by several orders of magnitude would have a significant impact on the energy and economic costs of operating a solar refinery. It is anticipated that these developments are in the pipeline!

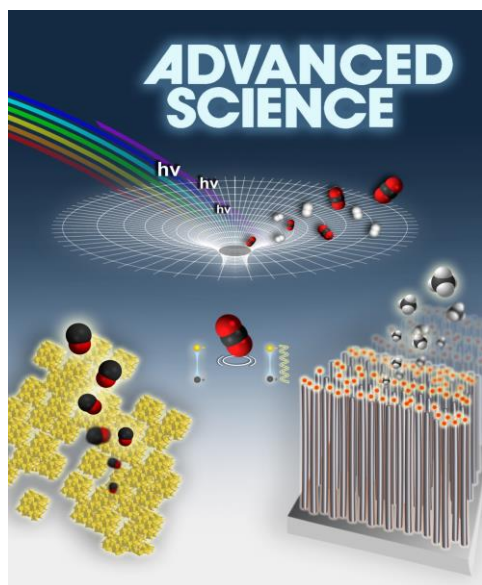
The paper by Christos Maravelias and his colleagues makes clear that the cost and energy efficiency of carbon capture and storage is an area where big improvements need to be made if the solar refinery is to be a success. Also, that absorption of CO<sub>2</sub> from the air was not going to be viable for some time and that carbon capture and storage from power stations and industrial plants would be concentrated on initially. In this context, there are encouraging developments underway at an emerging Swiss company [www.Climeworks.com](http://www.Climeworks.com) with commercially available equipment that enables an efficient two-step process involving (i) CO<sub>2</sub> capture and purification using specialized sorbents followed by (ii) CO<sub>2</sub> release using solar power. This positive development, together with advances in CO<sub>2</sub> photo-reduction rates and efficiencies, and product selectivity's, could enable 'net fuel energy generation' in a solar refinery, a prerequisite for successful commercialization.

One other point that is worth making is the question of the availability of water, which has not so far been referred to in the above discussion, although the Wisconsin paper touches on it and then decides not to discuss it further, as the transportation cost is a very small fraction of the overall process cost. However, in some parts of the world the availability of water could be a major factor. The whole question of water and solar availability could be the subject of another opinion editorial.

Returning to the question in the title of this article: can we have our carbon cake and eat it? One very important result of the dream of the solar refinery is that it will enable us to continue to have our carbon cake. We have become used to our carbon cake or carbon world and the movement to a sustainable 'carbon dioxide economy' will be a change which the world should be able to take in its stride. In the long term who knows what kind of cake will replace the carbon cake!

Multidisciplinary teams of materials chemists, materials scientists, and materials engineers across the globe believe in the dream of the solar refinery and a sustainable CO<sub>2</sub> based economy. It is abundantly clear from the analysis by Christos Maravelias and his colleagues that developing models to evaluate the energy efficiency and economic feasibility of the solar refinery, and at the same time identifying hurdles which have to be surmounted in order to realize the competitive processing of solar fuels, will continue to play a crucial role in the development of the required technologies. These analyses will serve to identify key aspects of materials properties and process design that are required to facilitate the transformation of ongoing solar fuels research and development into the

## 39. Advanced Science – The New Elite?



Front cover of the inaugural issue of Advanced Science, December 2014

In the world of scientific journals there is Nature and Science, the undisputed elite academic publishers, garnering the lion's share of the top papers in science, based upon the number of citations of the work published therein and the resulting citation impact of the journals.

Then there are all the other science publications, which according to the editors and peer reviewers of Nature and Science are unable to achieve the novelty, impact, timeliness and technological relevance figure-of-merit demanded by these elite journals and are thereby relegated to journals of lesser repute. I am sure that every reader of this article has at some time in their career, rightly or wrongly, experienced “the not novel enough” response from Nature and Science. It is a truism however that a vast body of amazing science published outside of Nature and Science journals still gets lots of attention and recognition.

Nature and Science have an illustrious history that began with the launch of Nature in 1869 and Science shortly thereafter in 1883. Some of the most important scientific discoveries of the last two centuries have appeared in these rival journals (<http://www.nature.com/news/the-top-100-papers-1.16224>; <http://news.sciencemag.org/scientific-community/2014/10/uprising-less-prestigious-journals-publishing-greater-share-high-impact>);). They continue to attract the largest portion of the most highly cited scientific papers from around the world, without too much competition from a myriad of journals who have tried, albeit with limited success, to achieve such privileged status.

I have been wondering for many years what miraculous feat it would take, for a new or existing journal to achieve the elite status that Nature and Science have earned since their inception. Clearly many journals have tried but have not yet managed to join the top ranks that Nature and Science enjoy and I must admit that I thought the chances of achieving this objective, by ‘a new journal on the block’, was looking increasingly bleak.

I could however be wrong as competition for elite status in scientific publishing might emerge in the form of the recently launched journal Advanced Science (<http://onlinelibrary.wiley.com/journal/10.1002/%28ISSN%292198-3844>), which is the new



premium open-access member of the VCH-Wiley family of science journals. Its publication history can be traced back to 1887 with the launch of *Zeitschrift für die Chemische Industrie* (Journal for the Chemical Industry). One year later this journal became *Zeitschrift für Angewandte Chemie* (Journal of Applied Chemistry) and eventually made its debut in the form of *Angewandte Chemie* (Applied Chemistry) in 1947. In 1988 *Advanced Materials* emerged first as a supplement to *Angewandte Chemie* and subsequently became an independent materials research journal eighteen months later. Without question *Advanced Materials* is amongst the most impressive materials research journals in the world today.

On a personal note, when I have had to make the crucial decision on where to publish what I perceived to be the most important work from my materials chemistry research group, I am embarrassed to confess that I tended to choose *Nature* or *Science* over *Advanced Materials*, on the grounds that the work would garner a larger readership, be cited more and have a greater impact. These considerations had ramifications, for example on my research funding as well as scholarships, awards and future careers of my coworkers.

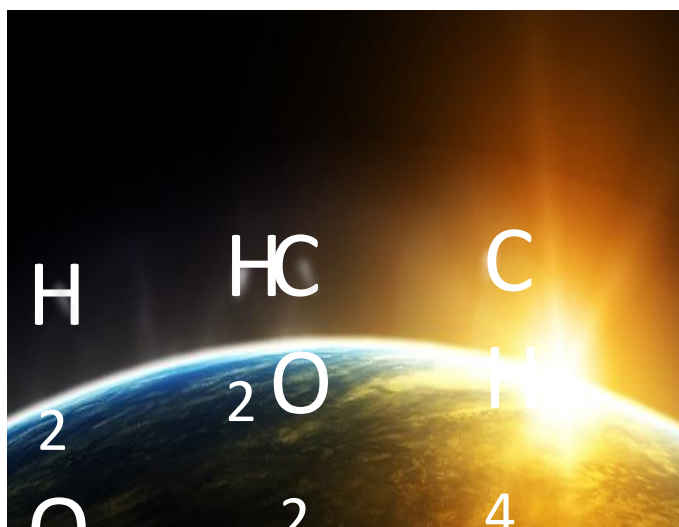
With the appearance of *Advanced Science* and its promise of achieving elite journal esteem, I now have a third and perhaps more appropriate option of where to submit the top materials papers that emerge from my research group.

The goal of the newly launched journal *Advanced Science*, like *Nature* and *Science*, is to publish the very best papers from all areas of science. The journal promises a high profile open-access platform for the rapid publication of the highest quality of peer-reviewed research, which I believe scientists around the world will embrace as a new and exciting home for their very best work, thereby facilitating its rise to elite status.

I should add that I enthusiastically support the emergence of open-access journals. It's pretty unfair that most research is funded by public money, yet all the work resulting from that research gets published in journals that are not accessible unless you pay for it. Open-access journals allow anyone to be able to read and engage with the scientific literature, regardless of whether they belong to an institution that is willing to foot the bill for premium journal access or not.

On a final note, I would like to take this opportunity to wholeheartedly congratulate Kirsten Severing, the lead editor of *Advanced Science*, and her able colleagues at VCH-Wiley, for coming up with a creative strategy for giving the scientific community a much needed alternative to the *Nature* and *Science* monopoly and I wish them the very best in their quest for achieving elite status of their new journal.

## 40. “Charge” of the “Sunlight” Brigade



**Figure 1** Concept of a sustainable solar fuels earth founded upon the light-assisted photo-conversion of  $\text{CO}_2$  and  $\text{H}_2\text{O}$  to solar fuels such as  $\text{CH}_4$ , adapted from [www.pinterest.com](http://www.pinterest.com)

Alfred, Lord Tennyson’s narrative poem, “Charge of the Light Brigade”, reminded me how humankind is now faced with a conflict between climate and capitalism and governments, business and society have to make the difficult choice between the nobleness and societal responsibility of transitioning to sustainable forms of energy versus the greed and communal irresponsibility of promulgating an unsustainable fossil fuel economy and its inconvenient consequences.

In this context, the “Sunlight” Brigade in the title of this article makes me think about a global army of heroic materials scientists and engineers who have dedicated their careers to help save humankind from the deleterious effects of

fossil fuel induced climate change. Their “Charge” into the climate change battle is motivated by the quest for solar powered technological solutions to the greenhouse gas problem through advanced materials energy research that can use carbon dioxide as a plentiful feed stock for making fuels and chemicals and thereby reduce its concentration in the earth’s atmosphere to pre-industrial levels.

Two promising approaches that offer the potential to ameliorate the adverse effects of anthropogenic carbon dioxide emissions on our climate are founded upon the use of sunlight to generate and manipulate charge in semiconductor materials. These are based upon: (i) the separation of electrons and holes to make solar electricity, and (ii) the reaction of electrons and holes with chemical compounds to make solar fuels. This two-pronged “Charge” of the “Sunlight” Brigade to generate solar electricity and solar fuels has the potential to greatly reduce the global energy demand currently supplied by non-renewable fossil fuels.

To amplify, molecule and materials chemistry has a pivotal role to play in the development of new and improved catalysts for the production of solar fuels from water, carbon dioxide and sunlight in order to meet the efficiency and scalability demands necessary to significantly impact the amount of carbon dioxide in the earth’s atmosphere. For example, in the ideal solar powered

regenerative energy system, using a tandem photo-reactor, water will be split by sunlight using an appropriately designed photo-catalyst and the hydrogen so produced will reduce carbon dioxide using sunlight and a second photo-catalyst, to produce a solar generated fuel such as carbon monoxide, methane, methanol, formic acid and dimethylether.

While these photo-chemical transformations are well known, photo-catalysts have not yet been discovered with the efficiency and stability required to deliver globally relevant quantities of molecular energy carriers that can meaningfully impact the levels of carbon dioxide greenhouse gas emitted into the earth's atmosphere.

Based upon exciting materials chemistry developments recently being reported for light-assisted, gas-phase photochemical conversion of carbon dioxide to fuels and chemicals, it seems like it is only a matter of time before globally significant efficiencies will be achieved, and the vision of the solar refinery of the future could be reduced to practice, Energy and Environmental Science, 2014, DOI: 10.1039/c4ee01958j.

In the context of the solar refinery, it is worth recalling a roughly one hundred year old quotation from a paper in Science by Giacomo Luigi Ciamician, considered by many to have pioneered the field of photochemistry, where he predicts that humans will one day master the ability to mimic photosynthesis (Ciamician, G. The Photochemistry of the Future, *Science*, 1912, 36, 385-394):

***“On the arid lands there will spring up industrial colonies without smoke and without smokestacks; forests of glass tubes will extend over the plains and glass buildings will rise everywhere; inside of these will take place the photochemical processes that hitherto have been the guarded secret of the plants, but that will have been mastered by human industry which will know how to make them bear even more abundant fruit than nature, for nature is not in a hurry and mankind is. And if in a distant future the supply of coal becomes completely exhausted, civilization will not be checked by that, for life and civilization will continue as long as the sun shines!”***

In his Science paper Giacomo Luigi Ciamician predicted that the photochemistry of the future should not be postponed to distant times and that industry would benefit by using all the energies nature puts at its disposal. He saw that human civilization was exploiting mainly legacy fossil solar energy and thought it would be much better to make use of radiant energy from the sun.

In a quote (<http://www.thomasedison.org/index.php/education/edison-quotes/>) about twenty years later Thomas Edison said:

***“I’d put my money on the sun and solar energy. What a source of power! I hope we don’t have to wait until oil and coal run out before we tackle that. I wish I had more years left.”***

Roughly thirty years later in his Accounts of Chemical Research paper, 1978, 11, 369-374, Nobel Laureate Melvin Calvin, said:

*"It is time to build an actual artificial photosynthetic system, to learn what works and what doesn't work, and thereby set the stage for making it work better".*

In view of the impending climate change and energy security challenges confronting the human race, the prescience of Giacomo Luigi Ciamician, Thomas Edison and Melvin Calvin is extraordinarily close to actuality today and the "Sunlight" Brigade is "Charged" with their mission to make the Utopian vision of a sustainable solar fuels earth, founded upon the light-assisted photo-conversion of  $\text{CO}_2$  and  $\text{H}_2\text{O}$  to solar fuels such as  $\text{CH}_4$ ,

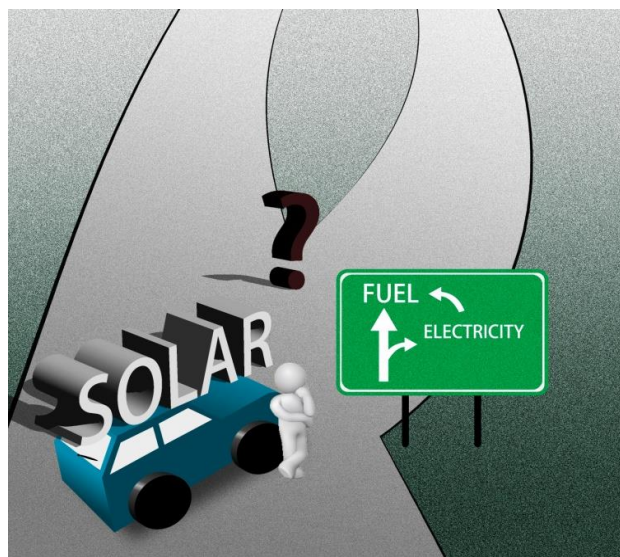
# 41 Big Picture Question: Solar-to-Electricity-to-Fuel or Solar-to-Fuel?

Materials researchers around the world, who are trying to discover materials and processes, abiological, biological or a hybrid of both, to enable solar powered conversion of  $\text{H}_2\text{O}$  and  $\text{CO}_2$  into chemicals and fuels, such as  $\text{H}_2$ ,  $\text{CO}$ ,  $\text{CH}_4$ ,  $\text{HCO}_2\text{H}$  or  $\text{CH}_3\text{OH}$ , if successful will ultimately be confronted with a “Big Picture Question”: is it “better” to go directly solar-to-fuel or indirectly solar-to-electricity-to-fuel or is there a place for both in different situations? And what do we mean by “better”, cost, energy efficiency, adoption, footprint?

This is a complex question without a simple answer but one that needs to be addressed every time a research proposal on advanced materials, devices and processes for innovative renewable energy solutions are submitted for funding. It is also one that the general public, mass media, industry stakeholders, business leaders and government officials need to understand in order to support informed policies.

The answer as discussed in this opinion editorial is direct solar-to-fuel conversion, where solar energy stored in solar fuels, made from  $\text{CO}_2$  function as a carbon-neutral renewable energy supply for making chemicals, powering transportation and running industrial infrastructure.

This question is addressed with estimates that compare, for illustrative purposes, the use of a two-step process that converts solar energy to produce electricity, which is then used to produce a fossil fuel substitute, with a one-step process that uses solar energy to produce the same fossil



The Big Picture Question confronted by the research community today is to decide which way to go scientifically, technologically and economically to produce solar fuels at a sufficiently high efficiency from  $\text{H}_2\text{O}$  and/or  $\text{CO}_2$  to have a meaningful impact on climate change, energy security and protection of the environment. Should solar fuels be made *directly* by solar-to-fuel *or indirectly* by converting solar-to-electricity-to-fuel? This important question is illustrated graphically with a thought provoking artwork courtesy of Chenxi Qian.



fuel substitute. The calculations take into account both the cost and the efficiencies of the one-stage *versus* the two-stage process.

How best to produce solar fuel is irrelevant if we don't need it. Solar electricity is already commercially viable in various jurisdictions, and applications and the costs are still falling. Can the production of solar electricity be increased and its applications expanded to the point that solar fuel is not needed? With appropriate storage, could solar electricity displace all fossil-fired generation to ultimately create a fully electrified world? And a complete transition to an electric vehicle mobility system can store large amounts of electricity and thereby reduce fossil fuel use for transportation.

Not exactly, due to their high energy density and transportability, liquid fuels are unlikely to be displaced by electricity in applications, such as aviation, shipping and trucks. Moreover, the production of most chemicals and petrochemicals for a diverse assortment of industries and consumer sectors of the economy are produced from oil and gas. The only way these can be substituted is by using solar fuels instead, electricity alone won't do. Furthermore, to address climate change net global anthropogenic emissions of greenhouse gases need to be reduced to zero. We need solar fuel to displace fossil fuels in those applications where electricity is not a feasible energy source.

So what is the best way to produce solar fuel: directly or indirectly using solar electricity? The indirect approach uses proven technologies. If we begin with 100 units of solar energy and convert them to electricity then we have about 20 units of energy in the form of electricity, using "standard" solar-to-electricity 20% efficiencies. By converting this electricity to chemicals using electrolysis, which is about 70% efficient, one obtains about 14 units of energy in the form of the heating value of  $H_2$ . One can then convert the gaseous  $H_2$  and  $CO_2$  to  $CH_4$ ,  $CH_3OH$  or  $(CH_3)_2O$  by conventional heterogeneous catalysis, which will involve some more losses. So the 100 units of solar energy yield about 8 units of energy in the form of fuel, which does not include the energy required to capture  $CO_2$ .

Direct production of solar fuel is still at the research stage. Recent advances in the discovery and development of new materials and processes to enable solar powered gas-phase photochemical and/or thermochemical reactions of  $H_2O/CO_2$  to form  $CO$  or  $CH_4$  in a solar refinery provide interesting and promising alternatives for generating solar fuels in a single step with an overall efficiency of about 12%. Therefore, 100 units of solar energy would yield about 12 units of energy in the form of liquid fuel. Note that high product selectivity is important to minimize separation losses on the overall efficiency.

The question also implicitly equates efficiency and cost. Solar radiation reaching the Earth is abundant and ubiquitous enough to meet the global energy demand even at very low conversion

efficiencies. However, because solar radiation is relatively diffuse - only 1 kW/m<sup>2</sup> - collecting and converting solar radiation into useful energy forms, such as electricity and fuels require large-area infrastructure. Higher energy conversion efficiencies imply smaller solar collecting areas for the same output, which in turn results in lower investment costs and, consequently, cheaper electricity and fuels. Thus, the “Big Picture Question” reduces to a question about energy conversion efficiency.

If the ultimate target is liquid hydrocarbon fuels for transportation, such as kerosene for aviation, then the direct  $\text{CO}_2 + \text{H}_2\text{O} \rightarrow \text{Fuels}$  process, with conversion-only efficiency of about 12%, outperforms the indirect  $\text{CO}_2 + \text{H}_2 \rightarrow \text{Fuels}$  solar-to-electricity-to-fuel pathway of about 8%. This is because it bypasses the inefficiencies and energy penalties arising from the water-gas-shift reactors and separations. Also, this comparison is limited to the solar energy used, so how differences in efficiency affect the cost have to be determined.

Calculating the “overall” efficiency of this kind of solar-to-fuels process is, to say the least, nontrivial. In addition to the solar-to-chemical efficiency “around” the reactor, one has to account, among others, for the energy to (1) capture and transport CO<sub>2</sub>, (2) separate CO<sub>2</sub> from the effluent of the reactor to recycle it, (3) separation of the product from reactants and byproducts. All of these separations require heat and electricity which should come from solar.

The cost of solar fuel will depend on the costs of the processes needed to produce it directly or indirectly. It seems like the direct approach offers the potential for lower costs because it involves fewer processes and more benign operating conditions. Something to percolate over in this context is that the cost of finding a solution to a problem is not always equated to efficiency. This is true only after lots of development and engineering. Often simplicity is equated to cost, dubbed “frugal innovation”. If one begins with a high cost engineered material, device or process, usually the cost decreases with increased efficiency. In the case of solar fuels this has yet to be determined.

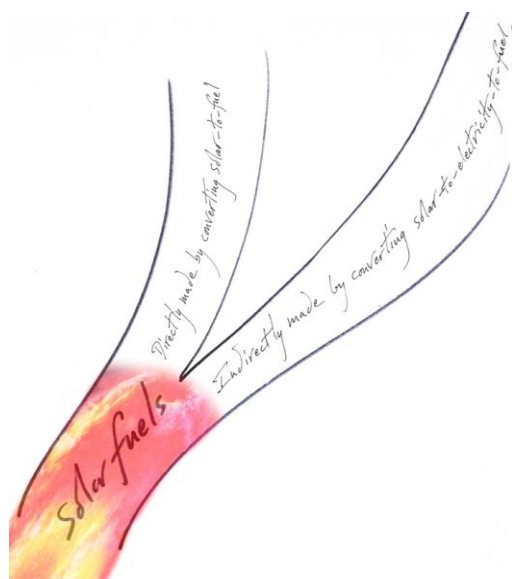
Hopefully materials researchers will find the insight derived from this type of brainstorming discussion, with energy engineering experts, to be helpful for placing basic-directed research aimed at the discovery and development of materials and processes for generating solar fuels directly from H<sub>2</sub>O and CO<sub>2</sub> into perspective, with respect to making solar fuels indirectly from solar electricity. In practice materials scientists and engineers will continue to explore both options simultaneously and competitively, to determine which technology would be most feasible, effective, efficient and economic. In choosing the right direction, the risk-and-rewards must be considered.

Clearly deciding which ways to go with the mix of renewable and non-renewable forms of energy are complex scientific, technological, environmental, societal, economic and political issues. While

there may not yet be a single or simple clear cut solution for the production of synthetic fuels from renewable sources of solar and/or electrical energy there is consensus it should be done in a neutral or negative carbon cycle using CO<sub>2</sub> as the chemical feed stock. Even without a definitive answer for the future production of sustainable fuels, framing the discussion for the benefit of materials researchers can be useful in its own right.

It is worth tempering the discussion by commenting that although there is great enthusiasm in the materials research community for making fuels from CO<sub>2</sub>, too large a communication gap exists between developments in the science and technology and awareness of these developments, and their implications for a sustainable future by the general public, industry stakeholders, business leaders and policy makers. This lack of understanding is slowing down the development of the industrial infrastructure needed for a new economy based on CO<sub>2</sub>.

An equally important and related societal and ethical question concerning the utilization of CO<sub>2</sub> as a source of renewable energy is: do we value economic cost more than environmental cost?



Metaphorming "The Big Picture Question" in the emerging field of Solar Fuels: Which Way to Go, Direct or Indirect? The drawing intimates that the shorter, simpler more "direct" path is, indeed (literally and figuratively speaking), the shorter, simpler and more direct way to go. Essentially, it reaffirms the upshot of the article. Art work, courtesy of Todd Siler.

What price are we willing to pay to keep our world inhabitable? If we spend so much money on things like military, space exploration, information technology, why should renewable energy have to be economically more profitable than fossil? Why is it acceptable to have high expenses on health and education, but impose economic impediments that an environmentally benign energy supply should cost no more than fossil fuels?

There is a strong focus on cost in the solar fuels community, which is unfortunate because mature technologies to avoid extra CO<sub>2</sub> emissions should be implemented as soon as possible, not when they are profitable. This point re-enforces the case for scientists and engineers to educate the public and politicians, make better use of mass media, and start an honest debate on what we as a society wish to do with our planet.

Hopefully conversations of the type presented in this opinion editorial, intended to inspire debate, will prove insightful and instructive for materials researchers trying to decide how to orchestrate their strategies, structure

their objectives and craft their promises in their quest to deliver clean, renewable and affordable

energy for humanity. For the time being, cutting-edge research in pursuit of long-term goals in the field of solar fuels is on the rise and until then all avenues of inquiry should be investigated as we do not know who the winners are going to be.

In closing this opinion editorial on a lighter note, it is only fitting to ponder an overarching question: how do we best educate the general public, mass-media, business leaders, industry stake-holders and government officials who need to understand or have some sense of the science and technology, to support informed policies? After all, the public (aka, consumers) enable this research to move forward in whatever directions materials researchers choose to go? Can we have educated policies without educating people?

One way to do this is through “Metaphorming” complex ideas in science and technology into art forms. This has been the lifelong practice of friend and colleague Todd Siler who applies the ArtScience process to envision viable solutions to real-world global challenges. He has a longstanding interest in exploring the potential of alternative energy systems that can help create a sustainable future, <http://www.toddsilerart.com/home>. I have recently joined Todd Siler in this endeavor using art to try to get the public to understand the science that underpins and interconnects climate change, energy security and protection of the environment, [www.artnanoinnovations.com](http://www.artnanoinnovations.com).

**Acknowledgments** In thinking about this question I have benefitted from discussions with Professor Christos Maravelias (Professor in the Department of Chemical and Biological Engineering at the University of Wisconsin–Madison), Dr. Erik Haites (Margaree Consultants in Toronto), Professor Jatin Nathwani (Ontario Research Chair in Public Policy for Sustainable Energy and Executive Director, at the Waterloo Institute for Sustainable Energy), Professor Aldo Steinfeld (Chair of Renewable Energy Carriers, at ETH Zurich) and Dr. Chris O’Neill (Manager, Emerging Technology at Enbridge, Alberta, Canada). Critical reading and insightful feedback on this article from Jan Rongé, Tom Mallouk, Dan Nocera, Mario Pagliari, Joseph Breu, Thomas Bein, and Avelino Corma is deeply appreciated.

## 42. You can't have an Energy Revolution without Materials, Chemistry and Catalysis

The central postulate of this article is that CO<sub>2</sub> is not to be regarded as a combustion waste product of fossil fuel but rather to be considered as a chemical resource to be harvested and recycled to a renewable fuel using the power of the sun and the assistance of a catalyst. This vision reminds one of a prescient quote in a Life Magazine interview by Richard Buckminster Fuller, American philosopher, systems theorist, architect and inventor, who said:

***"Pollution is nothing but resources we're not harvesting. We allow***

***them to disperse because we've been ignorant of their value. But if we got onto a planning basis, the government could trap pollutants in the stacks and spillages and get back more money than this would cost out of the stockpiled chemistries they'd be collecting"*** [1].



You can't have an Energy Revolution without Materials,  
Chemistry and Catalysis;  
Graphic image courtesy of Chenxi Qian.

In this context I have been pondering how the materials research community, being faced with the grand challenge of creating the science and technology to enable the transformation of CO<sub>2</sub>-to-fuel at a globally significant rate and efficiency, necessary to help solve what looks like an insolvable global problem, is related to policy and action?

Because CO<sub>2</sub> is the thermodynamic product of all fossil combustion processes, its efficient conversion back to an energy-rich fuel by thermochemical, electrochemical or photochemical means, requires the use of a catalyst. Synthesis of a champion CO<sub>2</sub>-to-fuels catalyst requires an in-depth understanding of the structure, properties and activity relations to make it work efficiently.

Catalysts are an essential piece of our modern society forming the bedrock for manufacturing a myriad of industrial chemicals and products. Catalyzed chemical reactions are also ubiquitous in nature driving many important biochemical processes and have been widely applied in the

chemical industry. By definition, a catalyst accelerates the rate of a chemical reaction by reducing its activation energy without being consumed in the process.

While catalysis can be traced to the rise of civilization with the fermentation of alcohol, it rose to prominence with the seminal work of Sabatier in 1890-1920 on hydrogenation catalysis, which set the ground-work for the evolution of both heterogeneous and homogeneous catalysis that we now depend on today.

A deeper understanding of the physical-chemical principles of catalysis began to take shape in the 20<sup>th</sup> century, emerging with the industrial scale production of bulk chemicals, notably ammonia for fertilizers and explosives, synthetic hydrocarbons for fuels, and methanol for the manufacture of a myriad of base chemicals. It was only when the need for explosives receded at the end of the First World War that industry turned its attention to the catalytic production of synthetic chemicals and fuels which powered the Second World War.

After the Second World War ended many new catalyst materials were being invented and catalytic processes developed, exemplified by the petrochemical industry for the high volume production of chemicals, fuels and polymers, by the pharmaceutical industry where catalysis was employed to make fine chemicals for medical applications, by the automobile industry for manufacturing exhaust gas catalysts for catalytic converters, and recently by the use of enzymatic bio-catalysis, for example in the bio-fuel, detergent, food, dairy, brewing and paper industries.

This brief backdrop on the history of chemistry and catalysis from ancient to modern times provides a preview to the next era of catalysis that marks the revolutionary vision for a sustainable-fuel future in the 21<sup>st</sup> century based on a CO<sub>2</sub> economy. We are now well aware of the deleterious effects of the continuous emission of CO<sub>2</sub> on our climate from burning fossil fuels to power our industries, energize our commercial sectors, run our transportation and heat our homes. Through catalysis of CO<sub>2</sub> reactions we can now envision an economically viable and secure energy supply, where CO<sub>2</sub> is treated not as a waste product, but rather as a valuable and bountiful chemical feedstock for making renewable fuels in a CO<sub>2</sub>-to-fuel carbon neutral catalytic cycle.

Ideas and practice on CO<sub>2</sub>-to-fuel catalysis have been published in detail earlier and will not be further elaborated upon in this article but rather the remaining discussion will be focused on the challenging transformation of the basic science of CO<sub>2</sub>-to-fuels to policy and industry implementation [2,3].

Seen in this new light, the CO<sub>2</sub> molecule is also, critically, the key driver of a clean-tech energy-innovation sector with goals that have been set out in renewed Science, Technology & Innovation Strategies of many countries. For fossil-rich countries this strategy stresses a gradual

shift away from dependency on its unsustainable fossil resource economy with its growing greenhouse gas emissions, which points to the validity and currency of developing a sustainable CO<sub>2</sub>-to-fuel conversion strategy as an alternative to continuing the current practice.

The leading scientists and institutions of many countries increasingly recognize that renewable-energy systems do not represent a single-pronged approach, depending solely, for example, on feeding renewable sources of electrical energy into the grid. Most importantly, they recognize the urgency of reducing greenhouse gases. However, they're uncertain about the most effective and efficient way to implement the reduction. These challenges are heightened by the fact that developing economic and environmental solutions are not confined to discrete countries but, rather, are the concerns of all countries.

These countries are seeking bold but pragmatic solutions with the greatest short-term and long-term impact, despite the complexity of this research concept.

The whole enterprise includes putting forward to politicians and governments this CO<sub>2</sub>-to-fuel conversion strategy and persuading them to adopt it as a goal. At the same time, the public should be informed and educated that this strategy is a viable economic and environmental solution to reduce greenhouse gases.

Many stakeholders have their sights on a "solar refinery" as one potential central energy strategy. This refinery system would offer "platform molecules" such as CH<sub>4</sub> and CH<sub>3</sub>OH, to produce energy in the form of chemical bonds, using a renewable like the sun and H<sub>2</sub> and CO<sub>2</sub> [4]. These ambitions are at the conceptual stage globally. Nevertheless they come with feasible strategic plans for implementing these CO<sub>2</sub> refineries, for example in the case of Germany [5], which aims to demonstrate this new refinery system.

Fortunately, forward-looking teams of scientists and engineers internationally sense the importance of such a breakthrough that builds on technologically significant CO<sub>2</sub> conversion efficiencies. Their collective vision continues to inspire and forge essential global research collaborations committed to moving mutually beneficial discovery forward for a sustainable CO<sub>2</sub>-neutral renewable-fuels economy.

Further, in a recent study the Global Carbon Capture and Storage Institute concluded that once the economic and technical feasibility of producing hydrocarbon fuels from CO<sub>2</sub> is demonstrated, this could well accelerate the growth of carbon capture and sequestration and catalyze its mature commercial exploitation in the production of energy rich fuels [6].

Teams of academic and industry collaborators around the world are devoting considerable time and expertise to realize the dream of a CO<sub>2</sub> economy. They envision the intersection of materials, chemistry and catalysis with process engineering and systems research for these



large-scale types of projects. It is becoming increasingly apparent that the solar refinery of the future cannot be limited to the historical approach of aqueous-phase biomimetics, which is often characterized by low CO<sub>2</sub>-to-fuels conversion efficiencies [7]. A shift to gas-phase heterogeneous catalysis is occurring and looks promising in terms of its ability to deliver high CO<sub>2</sub>-to-fuel conversion efficiencies with the added advantage of being able to interface seamlessly with existing chemical and petrochemical industrial infrastructure [2,3].

In order to benefit from this necessary global enterprise, new working relationships between academic and industrial collaborators and competitors will need to be developed and implemented. This can be achieved through joint research projects, co-publication and knowledge dissemination, which involve elevating key international players' profiles in the paradigm shift. Through shared IP agreements with academic and, later, industrial collaborators and trustworthy licensees who share similar codes of ethics, all of this can be accomplished rapidly, further actualizing this paradigm shift.

Knowledge dissemination also includes making the global CO<sub>2</sub>-to-fuel paradigm known to politicians and the public. The most effective way to catch their attention would be by demonstrating a working pilot solar refinery that shows it has the potential to ultimately be economically viable.

This "pipeline" for CO<sub>2</sub>-to-fuels knowledge dissemination greatly increases the capacity to inform policy in individual countries, validated by basic and translational science across countries. As such, CO<sub>2</sub>-to-fuels teams around the world will become key players who enable a future strategic global economy in the new paradigm, both in research and development, and in the advanced training of a world-leading talent pool to enable a CO<sub>2</sub>-to-fuels economy.

Currently this "pipeline" seems to be extremely scattered in its aim and there needs to be more coordination. However, teams pursuing the "holy grail" of CO<sub>2</sub>-to-fuels conversion efficiency do not want to miss out on the prestige of being the one that succeeds and therefore at the moment no one really wants to coordinate in knowledge dissemination if that means another teams unfairly gets the glory.

This renewable energy revolution will not however be possible without chemistry, materials and catalysis research. These are the science and engineering disciplines that underpin the discovery of catalytically active materials and facilitate the chemical transformation of CO<sub>2</sub> to stored energy in the chemical bonds of CH<sub>4</sub> and CH<sub>3</sub>OH at rates, efficiencies and scales required for large volume production of fuel from CO<sub>2</sub>.

Consider a historical perspective on some energy related world-changing breakthroughs: the first practical solar cell is only a 60-year-old story; the first practical light-emitting diode (LED) is 50

years old; the past 40 years has seen aqueous-based photocatalysis to convert light and/or electricity into an energy-rich fuel.

None of these problems has been simple, and all of these breakthroughs have relied on the unique physical and chemical properties of semiconductors. In fact, nanostructured forms of semiconductors are precisely what a materials solution for the CO<sub>2</sub> economy will depend upon. It will likely be predicated upon a gas-phase conversion of a CO<sub>2</sub>-to-fuel system rooted in existing combustion driven, heterogeneous catalytic processes that, together with the renewable power of light and/or heat, will now outperform nature's leaf in accommodating the sheer volume of CO<sub>2</sub> available to be exploited.

Recently several promising candidate cost-effective materials and thermocatalytic, electrocatalytic and photocatalytic processes have been discovered for the move forward to the energy revolution that will identify the winning nanoscale materials and catalytic reactors as the key to CO<sub>2</sub> conversion efficiency success [2,3,8-11].

One overarching fact that can spur this revolution fast forward: the world is currently consuming about 400 Quads per year of energy from all fossil fuels sources (1 Quad =  $1.1 \times 10^6$  TJ = 0.033 TW-year =  $1 \times 10^9$  MBTU = 172MBOE). This is equivalent to about 70 billion barrels of oil which translates into about 20 billion ton equivalents of CO<sub>2</sub> emitted into the atmosphere per year.

The world's energy needs are projected to double by 2030. If one is to stabilize the expected level of CO<sub>2</sub> in our atmosphere in the next couple of decades then the sum total of all kinds of CO<sub>2</sub> refineries around the globe will have to cope with CO<sub>2</sub>-to-fuel conversion rates of 20-40 billions of tons per year.

The opportunity for a revolutionary change could be made to happen in practice however research efforts on converting CO<sub>2</sub>-to-fuel are currently scattered amongst isolated groups around the world, and not targeted at policy makers and the public in an effective way, which is unnecessarily delaying the transition. A global CO<sub>2</sub>-to-fuel initiative is needed to solve this global challenge. Clearly reducing this vision to practice would represent an energy revolution, which is not likely to occur without materials, chemistry and catalysis!

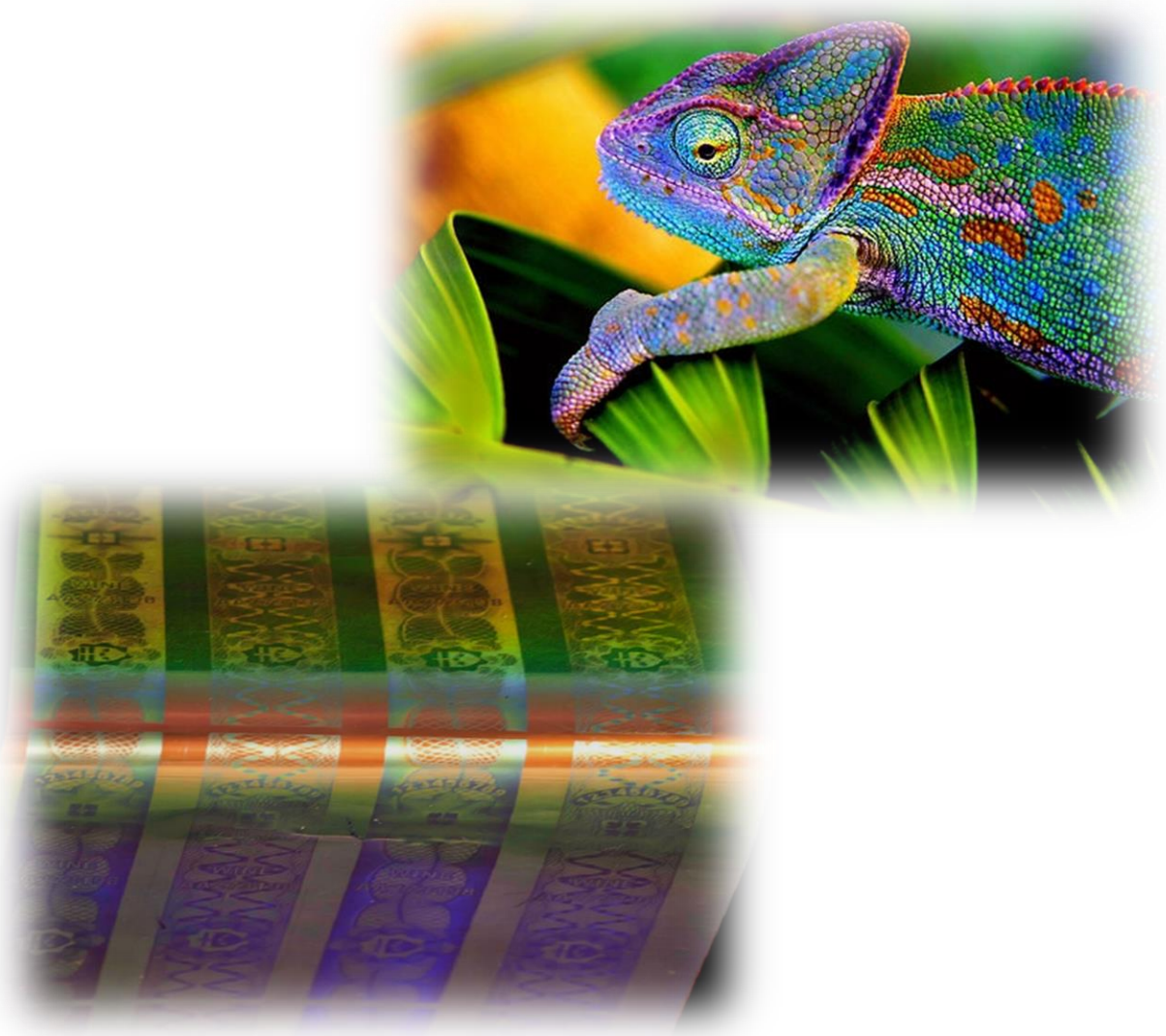
## **Acknowledgments**

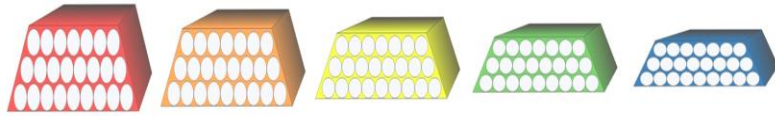
In percolating over the many competing forms of renewable energy and how they will emerge and impact the quality of life of future societies, I have benefitted enormously from the insight and writing skills of Ms. Lisa Boyes and Ms Laura Hoch.

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### 43. Keeping Good Company with the Chameleon





Photonic crystal chameleon – active photonic color from a tunable light-scale periodic structure - nature to laboratory to market

The ancient Greek philosopher Aristotle, more than two millennia ago, recognized and attempted an early explanation of the unique feature of chameleons to switch their color from one hue to another [1]. Like many vertebrae able to make these

impressive color changes to their skin for the purposes of communication, camouflage and thermoregulation, the origin of the color shift effect in the chameleon was generally thought to be through assembly-disassembly of organelle-containing pigments induced by neural or hormonal changes [2].

In a recent study [3] this picture of the variation of chameleon color has changed dramatically and has been traced as photonic rather than pigment color in origin, whereby the dimension of a photonic crystal comprised of a light-scale lattice of guanine nanocrystals is actively tuned to produce structural color variations. This bio-photonic color system is founded upon an upper dermal photonic crystal layer structured to reflect visible wavelengths of light, while a lower dermal layer is organized to reflect near infrared wavelengths, endowing the chameleon with predator protection, communication skills and body temperature control [3].

Roughly two decades before the phenomenon of color shifting in the chameleon was recognized as originating from photonic structure changes rather than pigment effects, color from structure was being developed in the materials chemistry laboratory in both passive and active synthetic forms [4]. Two classes of photonic color emerged in this early research. One involved “passive” structural color, derived from the reflection of light from a photonic crystal with a static lattice, which offered a single reflected color, by Bragg diffraction, the wavelength of which depended upon the dimension and refractive index of the lattice. The other, photonic crystals displaying “active” structural color, by contrast uniquely provided any reflected color from the near infrared to the visible to ultraviolet wavelengths, by Bragg diffraction from a dynamic lattice whose dimensions and refractive index could be continuously tuned for example by electrical, mechanical, thermal and chemical stimuli [4].

This was the first time that a single material could present an infinite number of colors in a continuous color-shift mode, a feat previously only achievable by mixing the complementary colors, red, green and blue. It represented a laboratory demonstration of color changes in the chameleon before it was known that the color shifting in the chameleon was photonic!

Since that time photonic crystals have moved into the realm of 1D, 2D and 3D light-scale photonic lattices and their practice, often stimulated by theory, has transitioned rapidly from mainstream photonic science to advanced photonic technology [4]. There is ample evidence from published research that the ability of photonic crystals to control photons can rival that of electronic crystals to manage electrons. This has proven to be especially true for high refractive index contrast 3D photonic crystals made of silicon whereby an omni-directional photonic band gap offers complete control over the movement of light in all three spatial dimensions.

Today it has been said that ‘photonic crystals have been the classic underachievers: full of promise, sound in theory but poor on implementation’. This criticism has mainly come from the optical physics community because of the difficulties experienced of adapting top-down semiconductor engineering techniques to fabricate photonic lattices with high enough structural and optical quality to enable the scale-up, manufacture, economics and delivery of photonic crystal components and modules into markets that include solar cells, light emitting diodes, lasers, displays, sensors and optical fibres.

Observing that top-down approaches to the fabrication of photonic crystals often require complex and expensive lithographic instrumentation, deposition equipment and clean-room facilities, materials researchers realized there could be an easier way to make photonic crystals using bottom-up building-block assembly methods. Using this approach, the choice of polymers and materials that could be employed for the building blocks was vast. The



OpalPrint roll-to-roll manufactured photonic color base material fabricated into product specific security features on banknotes, identification cards and passports – courtesy of Opalux Inc.

variety of compositions and structures available for the building blocks enabled a cornucopia of photonic crystal classes to be synthesized offering a range of electrical, optical, magnetic, thermal, chemical, electrochemical, photochemical and catalytic properties that could be tailored to a desired function and perceived utility [4].

This is more-or-less how the self-assembly approach to making tuneable photonic crystals began and has blossomed forth today into one of the most scientifically vibrant areas of research with a multidisciplinary footprint that is envisioned to deliver manufactured photonic crystal products to diverse markets. These include sensors for food and water quality control to anti-counterfeiting devices on banknotes and passports, security features on consumer goods to displays.

About a decade ago, active photonic color research was transferred from the laboratory to the marketplace to create a new dimension in authentication technology [5]. Keeping good company with the chameleon, a wide range of attractive, customizable, counterfeit-resistant security features have been developed by Opalux Inc., which command attention and provide straightforward verification. These features include interactive security features, individualized optically variable portraits, RFID-activated tags and chemical sensors. These security features, being photonic crystal in nature, are very hard to duplicate and are easy to integrate with a variety of standard security printing production methods and materials. These chameleon-like security features are bright, stable, durable, customizable and available in a wide variety of appearances and performance characteristics.

This class of tunable photonic crystal security features with bright unique chromatic appearances, like the chameleon have a precise nanostructure which makes them optically variable. Their appearance changes when viewed at different angles and under different lighting conditions. For example, transitions between bright reds, yellows, greens and blues, or even ultraviolet and infrared, are possible as lighting and viewing angles change. These colors are tunable, meaning that their appearance changes in response to a range of stimuli. Four photonic color technology platforms that provide powerful security features based on thermal, mechanical, electrical and chemical activation include OpalPrint, ElastInk, Photonic Ink and Photonic Nose [5].

OpalPrint is permanently patterned by the application of laser or heat. It can be used to provide fully customized and personalized optically variable devices, like optically variable passport holder portraits. OpalPrint technology combines personalization with optical variability in a single security feature to create personalized security. It provides attractive, optically variable document holder portraits for passports and identification cards. It can also provide other helpful authentication information, like signatures, control numbers and biometric information in a secure, easily read, optically variable feature. Personalization of OpalPrint film is

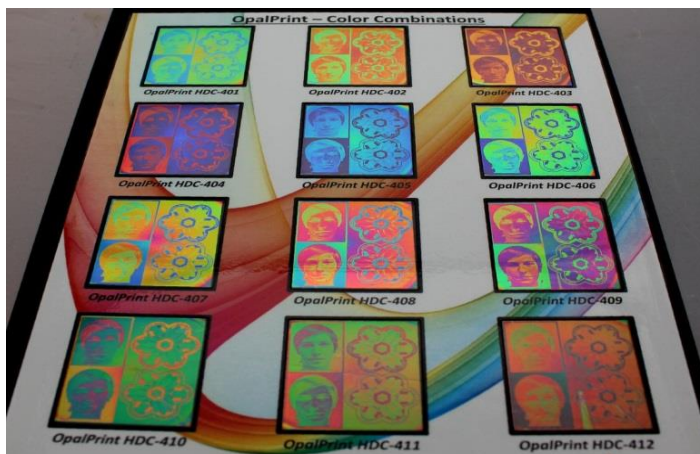


accomplished by laser tuning. Because OpalPrint is compatible with a range of security industry-standard laser personalization techniques it can be personalized both in centralized and decentralized production environments. OpalPrint can be used with a variety of security substrates, including paper, polymer and polycarbonate.

ElastInk is Opalux's interactive security feature. In addition to its inherent optical variability, ElastInk changes the information content in response to the application of finger pressure [6]. The pressure threshold, duration of activation and other aspects can all be customized. Elastink can be produced in a wide variety of form factors, including as a security thread for paper banknotes. This latter variant meets circulation hazard requirements for paper banknotes. Depending on security requirements, Elastink's appearance change can be either reversible or irreversible. For example, when used as a security thread in a banknote, a reversible variant is employed. However, for other applications such as tamper evidence, irreversible variants and variants that reverse in response to specific stimuli like heat may be employed. ElastInk is available in a range of initial colors, including red, yellow, green and blue, and a variety of pressure thresholds. Several variants of ElastInk are reserved for high security documents.

Photonic Ink is an RFID-activated security feature. Photonic Ink dramatically changes its appearance in response to the presence of an RFID field or other sources of electrical charge [7] and is optically variable. Photonic Ink operates at low voltages and current and can maintain static images with negligible energy. Photonic Ink can be deployed on rigid and flexible surfaces, is stable and not affected by harsh environments.

Photonic Nose authenticates products quickly, reliably and inexpensively by changing appearance in response to a variety of chemicals [8]. The human nose works by using a large array of olfactory neurons, each responsive to a different stimulus. By working in combination with each other, this array of olfactory neurons detects a wide range of substances, quickly, reliably and inexpensively. Inspired by the human nose, Photonic Nose uses an array of photonic crystal sensing units. These sensing units, in conjunction with a digital camera and image analysis software, permit the detection of a wide range of substances. Simpler versions, which change appearance in response to simple stimuli like water vapor, are also possible.



OpalPrint color combinations – courtesy of Opalux Inc

It is interesting how about two decades before it was known that the color shifting in the chameleon was photonic, the physical, chemical and biological principles that underpin the chameleon's skin color altering ability were being used in the materials chemistry laboratory to develop color from structure and have now been adapted and scaled in the advanced materials science and technology world in order to manufacture multi-color security devices that include banknotes, credit cards, passports, driving licenses, identification cards, tax stamps, color changing surfaces and graphics, automotive applications and smart windows [5].

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## 44. Race for a CO<sub>2</sub>-to-Fuel Technology



For the first time since the tracking of CO<sub>2</sub> in our global atmosphere began, concentrations have reached a new record of 400 parts per million:

<http://research.noaa.gov/News/NewsArchive/LatestNews/TabId/684/ArtMID/1768/ArticleID/11153/Greenhouse-gas-benchmark-reached.aspx>. In this article we imagine a world in which these anthropogenic CO<sub>2</sub> emissions could be recycled back to a synthetic transportable fuel using only H<sub>2</sub>O and renewable forms of energy such as solar, wind and hydro power, in a carbon-neutral CO<sub>2</sub>-to-Fuel sustainable carbon-cycle. The race is on amongst materials chemists, scientists and engineers around the world to discover materials and processes that can enable this Utopian dream in the most energy efficient, environmentally responsible and cost effective way; Graphic illustration courtesy of Chenxi Qian.

# Race for a CO<sub>2</sub>-to-Fuel Technology

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## Broader Context

It's ironical that after more than 40 years of globally competitive research on the conversion of CO<sub>2</sub>-to-Fuel, the first pilot demonstration to successfully take CO<sub>2</sub> from thin air to the petrol pump, turns out to be based on rather conventional materials and well established processing technology.



In this article we ask if this impressive advance towards a decarbonized energy economy using recycled CO<sub>2</sub> based fuels, could provide a panacea to a carbon-neutral, climate-friendly and environmentally-responsible global society, perhaps signaling the end of the road for unconventional rival approaches vying for a CO<sub>2</sub>-to-Fuel technology. For sure, the bold step of literally filling the tank of a car with fuel made from recycling the combustion product of fuel that can be produced at a price not too different to that obtained from legacy fossil resources is a monumental feat. It will definitely serve to catalyze materials science and engineering research aimed at improving the energy efficiency, expanding the scale and decreasing the cost of the process, thereby throwing down the gauntlet as the CO<sub>2</sub>-to-Fuel technology to beat.

# Race for a CO<sub>2</sub>-to-Fuel Technology

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The stakes have been raised in the quest for a commercially viable CO<sub>2</sub>-to-Fuel technology with the recent announcement, by the Audi-Sunfire-Climeworks consortium of companies, operating in Germany and Switzerland, of a pilot project for producing diesel fuel from CO<sub>2</sub> and H<sub>2</sub>O and

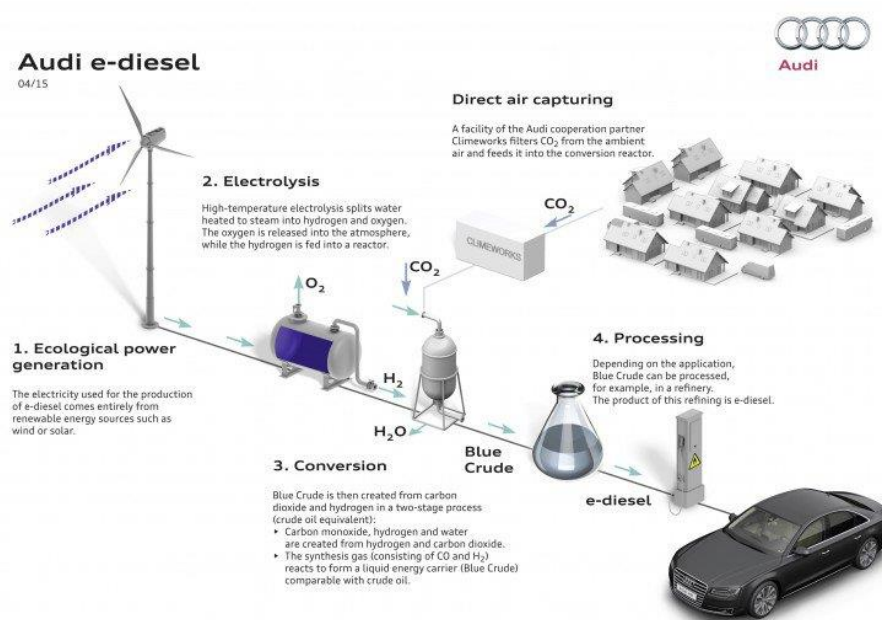


Figure 1: Audi process for producing diesel fuel from carbon dioxide and water, <http://www.sciencealert.com/audi-have-successfully-made-diesel-fuel-from-air-and-water>

renewable energy sources, such as wind or solar or hydro power. The CO<sub>2</sub> supply was obtained mainly from a biogas plant supplemented with some CO<sub>2</sub> captured directly from the air. The estimated price at the pump of 1-1.5 Euro/liter seems to make the future prospects for CO<sub>2</sub>-to-Diesel that is cost competitive with Fossil-to-Diesel a reality (see appraisal of this point below). A pilot plant in Dresden is destined in the months ahead to produce around 160 liters/day of the synthetic diesel, which they dubbed "blue crude" [1].

The process employed for making "blue crude" depicted in Figure 1 and for the purpose of this discussion, actually involves *five* main steps: the *first* requires capture of CO<sub>2</sub> from thin air; the

*second* involves electricity generation from renewable sources; the *third* uses electrical energy to electrochemically split water into a hydrogen (H<sub>2</sub>) and oxygen (O<sub>2</sub>) mixture from which the H<sub>2</sub> must be separated; the *fourth* uses this H<sub>2</sub> to reduce the CO<sub>2</sub> captured from the atmosphere, to form a mixture of carbon monoxide (CO) and water (H<sub>2</sub>O) in a high temperature and high pressure Reverse Water Gas Shift (RWGS) process, from which the H<sub>2</sub>O and unreacted CO<sub>2</sub> is separated; and the *fifth* mixes the CO with the H<sub>2</sub> to form synthesis gas (Syngas), which is subsequently converted in a high temperature and high pressure Fischer-Tropsch (F-T) catalytic procedure, to generate the long-chain hydrocarbons comprising the “blue crude”. To the best of our knowledge about 80% of the “blue crude” produced by the F-T process is suitable for synthetic diesel making is more analogous to crude oil where the other fraction is mainly lighter hydrocarbons which cannot be used in diesel fuel.

It appears that while the electrochemical, adsorption, separation and catalytic methods employed to make “blue crude” powered only by renewable energy sources are rather conventional in nature, the technology nevertheless works, can be scaled up and has set today’s benchmark standard for converting CO<sub>2</sub>-to-Fuel. For any technology to compete commercially with “blue crude” technology, it will have to be more straightforward in materials and process engineering with less steps involved and more energy efficient and attractive economically.

Let’s consider some back of the envelope calculations for making “blue crude”: 1 kilogram of diesel contains 43.4 MJ of energy, so 1 liter corresponds to 36 MJ or 10 kWh, assuming diesel has a density of 0.83 kg/L. In order to get an order of magnitude estimate of the cost to make a liter of “blue crude” let’s assume that producing this amount of chemical energy requires an equal amount of electricity. Assuming that renewable electricity costs 3 times more than conventional electricity [2], one determines that the electricity to produce 1 liter of gasoline would cost  $10 \text{ [kWh]} * 3 * 0.05 \text{ [$/kWh]} = \$1.50$  or 1.34 EUR.

Note that this is just the electricity for the electrolysis of H<sub>2</sub>O. It does not account for all remaining capital costs including CO<sub>2</sub> capture, conversion and separation nor for the additional required energy inputs, such as, the electricity to compress captured CO<sub>2</sub> for the RWGS and then the F-T reaction. This analysis suggests the cost estimate for a liter of “blue crude” is optimistic, if not unrealistic, at best.

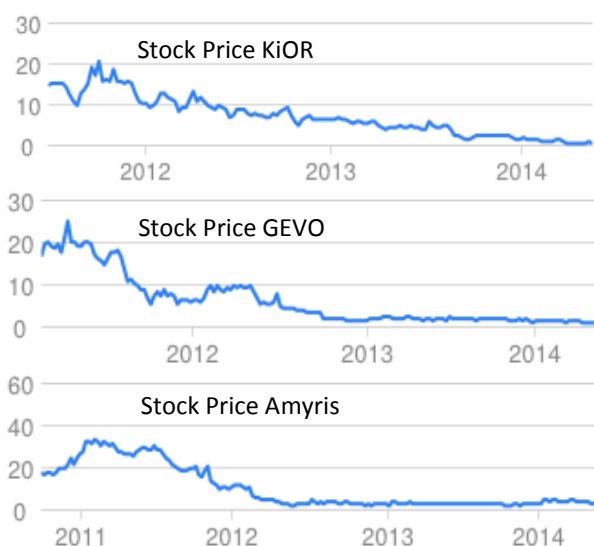


Figure 2: Boom and bust record of some biofuel spin-off companies <http://finance.yahoo.com/>



Concerning the most promising alternative CO<sub>2</sub>-to-Fuel methodologies being explored today, it is worth stating at the outset that an energy conversion efficiency of less than 1% for the typical photosynthetic biomass process is unlikely to be a viable route for CO<sub>2</sub>-to-biofuels as it cannot be obviously scaled to satisfy future global energy demands and is most likely unable to impact greenhouse gas induced climate change, even if all the unused cultivatable land on earth was utilized. It seems that life cycle analysis of the material and energy balances of CO<sub>2</sub>-to-Fuel processes upon which the commercial success of biofuels spin-off companies ultimately depend, has caused many of them to falter as can be seen in the fading stock value, Figure 2, of some once-big-startups [3]. In a world that produces ethanol from corn and starch and biodiesel from soybean oil it is rather important to develop and commercialize advanced materials and catalytic processes that use CO<sub>2</sub> and H<sub>2</sub>O as feedstock for making synthetic fuel.

That having been said, many people argue there will be no single renewable energy solution but a collection of solutions, each of which may be most viable to a specific location and environment. In this context, biofuels can play a role, especially in areas where crops such as sugar cane, which have photosynthetic conversion efficiencies up to ~6-8%, can be grown. Furthermore, even with low efficiencies the chemical energy can be regarded as free because nature has evolved to convert solar to chemical energy. So efficiency of biofuel production does not really impact capital cost as with other solar technologies where equipment has to be built to capture solar energy.

If not a biological approach for a viable CO<sub>2</sub>-to-Fuel technology, then what are the alternatives? Today, the main non-biological competitors are solar-powered photochemical, electrochemical, thermochemical and photothermal processes, the overall energy conversion efficiencies of which will determine the economics of the process [4,5,6].

In one route, akin to the “blue crude” process, CO<sub>2</sub> is reduced by hydrogen, which is renewably produced by splitting water. Notably, there has been significant progress in technologies for water splitting, [7-10]. Though, in order for the production of H<sub>2</sub> by the photochemical splitting of H<sub>2</sub>O using nanostructured catalysts to be cost competitive the materials and processes will require an improvement in efficiency by at least a factor of x100. Even if these efficiencies are achieved in practice it is not yet apparent that an aqueous phase solar powered water splitting process could be cost-effectively scaled up to handle globally significant quantities of H<sub>2</sub> for a viable CO<sub>2</sub>-to-Fuel economy that could impact greenhouse gas climate change.

The same efficiency, scalability and cost considerations apply to aqueous phase photochemical conversion of CO<sub>2</sub>-to-Fuel where efficiencies seem to be stalled around 1%. By contrast, if the efficiency of a “tandem” gas-phase light-assisted heterogeneous catalytic process involving the splitting of H<sub>2</sub>O to H<sub>2</sub> followed by the H<sub>2</sub> reduction of CO<sub>2</sub>, operated under ambient conditions



of temperature and pressure, could be improved by two orders of magnitude, it might become cost-competitive with “blue crude” technology.

In the case of H<sub>2</sub> generation using photovoltaic powered water electrolysis systems, PV-EC, solar-to-fuel conversion efficiencies are moving beyond the US DOE target of 10%. This remarkable feat is being achieved by coupling high-performance low-cost silicon and lead iodide perovskite solar cells with water splitting catalysts, [11-13]. The H<sub>2</sub> generated in this way can be transformed to electricity using fuel cells or converted to transportable liquid fuels by heterogeneous catalytic reduction CO<sub>2</sub> *via* RWGS and F-T processes, where an efficiency of at least 10% is necessary for technologies of this kind to be commercialized. It is envisioned that similar accomplishments may be achieved using lead iodide perovskite solar cells in PV-EC configurations to drive solar conversions CO<sub>2</sub>-to-Fuels. However, as mentioned above, the cost of scaling up an aqueous phase solar-powered CO<sub>2</sub>-to-Fuel process will likely become prohibitive.

In this context it is noteworthy that in the solar-thermal (heat), photo-thermal (heat and light) and photo-chemical (light) approaches to the catalytic conversion of CO<sub>2</sub>-to-Fuel, the overall process is simplified as the electricity generation and electrolysis requirements of H<sub>2</sub>O splitting are side-stepped. Hence, with further optimization of the photochemical and thermochemical activity, selectivity and stability of materials and improvement of process efficiencies, the overall performance of solar-thermal, photo-thermal and photo-catalysis methods could be improved so that these methods become economically competitive with the “blue crude” technology. Though, even if the U.S. Department of Energy’s target cost of 2-4 \$/kg of H<sub>2</sub> is met, the cost of the renewable hydrogen to produce synthetic diesel is already ~0.65-1.30 \$/L. A recent techno-economic analysis of photo-catalytic and photo-electrochemical water splitting systems calculated a price of 1.60-10.40 \$/kg of H<sub>2</sub>, though there are still considerable engineering challenges to overcome [14].

Here it is worth noting that the solar-thermal method utilizes concentrated solar power to enable a high temperature (1000-2000°C) two-step metal oxide based redox conversion of CO<sub>2</sub> + H<sub>2</sub>O into CO + H<sub>2</sub> Syngas, which is subsequently processed to hydrocarbon fuels via conventional F-T heterogeneous catalysis. The most efficient solar thermal system reported to date involves the production of H<sub>2</sub>-CO Syngas using a two-step H<sub>2</sub>O-CO<sub>2</sub> redox cycle. It is founded upon non-stoichiometric ceria and involves a high temperature reduction step operating around 1500°C,  $\text{CeO}_2 \rightarrow \text{CeO}_{2-x} + x/2\text{O}_2$  and low temperature re-oxidation steps occurring around 1000°C,  $\text{CeO}_{2-x} + x\text{H}_2\text{O} \rightarrow \text{CeO}_2 + x\text{H}_2$  and  $\text{CeO}_{2-x} + x\text{CO}_2 \rightarrow \text{CeO}_2 + x\text{CO}$ . This study utilized a 4-kW solar reactor converting CO<sub>2</sub> to CO with rates of 0.5 mL CO per min per g catalyst, yields of 4 mL of CO per g catalyst per redox cycle, and, most importantly, solar-to-fuel energy conversion efficiencies that approach 4%. This method for producing Syngas has recently been integrated with storage, compression and F-T processing to form liquid

hydrocarbons deemed suitable for commercial aviation. One only requires an improvement of 3-4 times for this  $\text{CO}_2 + \text{H}_2\text{O}$  to fuel process to become an economically competitive and industrially viable technology [15]. A major challenge however that still needs to be overcome with this approach is the thermal, chemical and mechanical stability of the metal oxide redox catalysts over many high temperature switching cycles.

It is possible that photo-thermal driven heterogeneous catalysis using both the heat and light of the sun could enable the conversion of  $\text{CO}_2 + \text{H}_2\text{O}$  or  $\text{H}_2$  to fuel under much milder conditions than currently employed in the solar-thermal method. Indeed, light-assistance of thermally allowed heterogeneous catalytic reactions is certainly an interesting opportunity and one that possibly could deliver a competitive  $\text{CO}_2$ -to-Fuel technology with continued improvements in efficiency. As a scientific goal, the study of how light gets involved in photo-thermal heterogeneous catalysis is important and may end up providing clues that will ultimately enable the dream of gas-phase light-assisted high-efficiency conversion process of  $\text{CO}_2 + \text{H}_2\text{O}$  to a fuel such as  $\text{CH}_4$  or  $\text{CH}_3\text{OH}$  to be realized in practice.

One way to transcend the complexity and efficiency of the multi-step Audi  $\text{CO}_2 + \text{H}_2\text{O}$  to fuel process is to discover a “dream” catalyst dubbed the “techno-leaf”, which is able to directly convert gaseous  $\text{CO}_2 + \text{H}_2\text{O}$  under mild conditions to a fuel, using just the energy contained in sunlight as the renewable power source. The gas-phase “techno-leaf”  $\text{CO}_2 + \text{H}_2\text{O}$  to fuel process, not to be confused with the aqueous phase “artificial leaf”, in essence combines steps 2 and 3 in the five step process described above with step 4 if we stop at  $\text{CO}$  and step 5 if we make fuels such as  $\text{CH}_3\text{OH}$ ,  $(\text{CH}_3)_2\text{O}$ ,  $\text{HCO}_2\text{H}$  or  $\text{CH}_4$ .

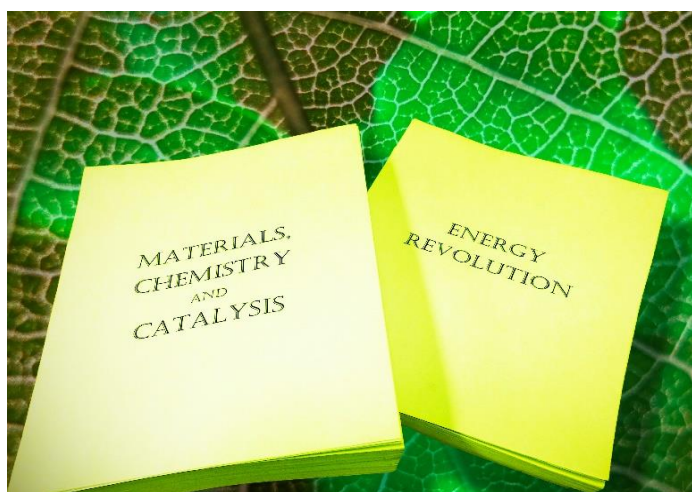


Figure 3: You can't have an energy revolution without materials, chemistry and catalysis; Graphic image courtesy of Chenxi Qian.

If the “techno-leaf” could also capture  $\text{CO}_2$  and  $\text{H}_2\text{O}$  from thin air and operate with low concentrations of  $\text{CO}_2$  in the presence of  $\text{O}_2$ , like the “real leaf”, it is a very serious “dream” to combine all 5 steps of the above mentioned process in one operation. With revolutionary advances in materials, chemistry and catalysis to enhance the  $\text{CO}_2$ -to-Fuel efficiency, this vision of the “techno-leaf” process could in principle be reduced to practice, Figure 3. This would be huge news, it would present serious competition to the leading Audi process

in the race to implement a CO<sub>2</sub>-to-Fuel technology to enable an energy revolution and resolve greenhouse gas climate change.

In the case of a light-assisted process that converts CO<sub>2</sub> and H<sub>2</sub>O to fuel, the water question is frequently asked. Conventional gasoline production requires roughly 3-7 liters of water per liter of fuel. Thus, the production of solar fuel is not expected to consume more water than the production of fossil fuel. One can argue that the required amounts of water can be provided by seawater desalination by reverse osmosis which is more energy efficient than extracting water from air by adsorption. The energy required for desalination is around 3-5 kWh per 1000 liters. The energy content of 1 liter of synthetic fuel is about 10 kWh. Thus, there are about three orders of magnitude between the energy required to desalinate water and the energy content of the fuel. This is entirely different to some biofuel paths, which require orders of magnitude more water to produce 1 liter of fuel. Then, water provision indeed becomes a problem, though this is, of course, dependent on the specific climate of the area.

Another pivotal concern is the carbon dioxide question, which relates to the most energy efficient and cost effective means of capturing and purifying CO<sub>2</sub> for processing with H<sub>2</sub>O to synthetic fuels by any of the aforementioned methods. In the Audi process, much of its CO<sub>2</sub> is captured from a concentrated stream from an industrial biogas plant, which is much more energy efficient than from the ambient air. In the short term, this makes practical and economic sense. Though for a long term sustainable solution, ideally, the co-extraction of CO<sub>2</sub> and H<sub>2</sub>O from ambient air by a champion adsorbent would provide attractive logistical benefits for the production of synthetic fuels, especially in regions with limited or no fresh H<sub>2</sub>O resources. In this context, amine-functionalized cellulose fashioned in nano-fiber form has recently been identified as a promising sorbent that is able to concurrently extract CO<sub>2</sub> and H<sub>2</sub>O vapor from ambient air with demonstrated potential for industrial scale applicability. The favorable adsorption and desorption capacities and energetics at low partial pressures, and tolerance to moisture in air bode well for the successful application of this CO<sub>2</sub> and H<sub>2</sub>O co-extraction process. By combining this process with the conversion of CO<sub>2</sub> and H<sub>2</sub>O to fuel, energy can be conserved and costs reduced because the need to transport CO<sub>2</sub> and consume fresh water resources are eliminated [16].

Some final thoughts. Clearly companies like Toyota and Tesla have confidence in the future of the electric car. It's true that renewable electricity with batteries is the simplest system, but batteries are costly, have limited range and take a long time to charge. But work is underway to address these limitations. Producing hydrogen and using it in a fuel cell is only a little more complex. But then you need a costly hydrogen infrastructure and good fuel cell performance. Despite millions spent by Ballard and other companies, fuel cells have not yet become competitive for vehicles. In this context, Audi's blue crude involves the most complex processing,

but produces a "drop in" diesel fuel replacement, requiring no new distribution infrastructure and no new vehicle design.

The outcome is not obvious. The good thing about the Audi process is that the companies Sunfire and Climeworks involved have taken the plunge and gone ahead with a pilot plant, which will stimulate lots of interest and no doubt some experience will be gained from this plus it will catalyze efforts by the materials researchers to work even harder to achieve the holy grail. However, we can't really believe that the fairly conventional Audi process is the path to go along for conversion of CO<sub>2</sub>-to-Fuel in the long term.

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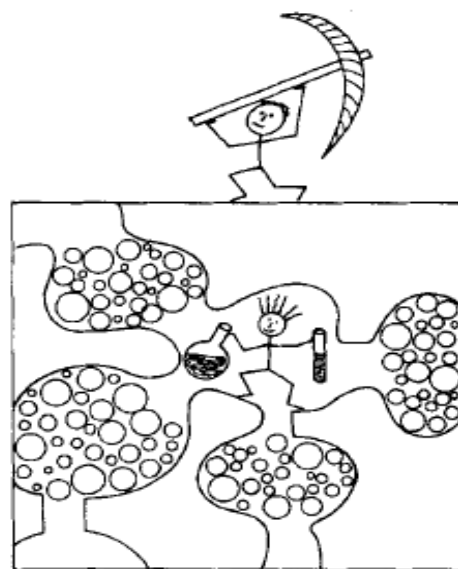
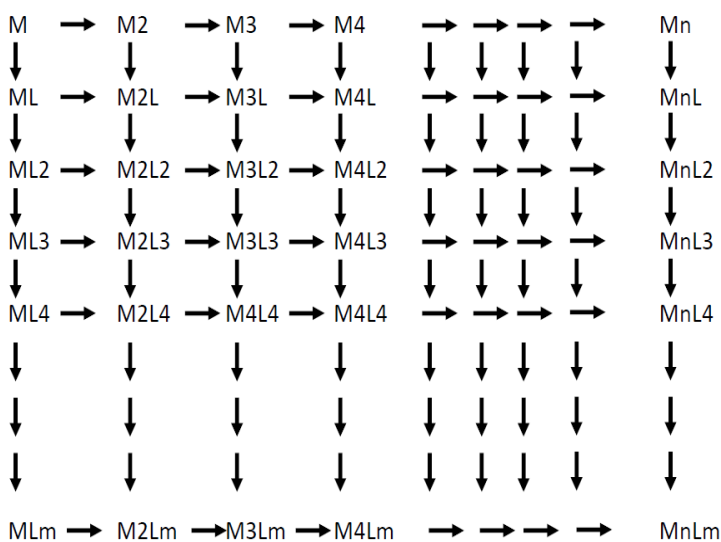
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# 45. Eureka Moments in Nanochemistry – 2015 Centenary Award

**Where did It All begin?** In this Perspective I will look back over my careers work and reminisce, with the help of a few graphical depictions, about the “eureka moments” that led me to imagine and help develop the field of Nanochemistry.

In the early seventies, the century-old field of colloid chemistry, pioneered by Thomas Graham (1805-1869), was undergoing its metamorphosis into today's Nanochemistry. Colloid science, propagated by Wolfgang Ostwald (1883-1943), was nucleating as today's Nanoscience. Graham had described the distinctive behavior of matter in the nanometer to micron size range, and Ostwald had enriched the subject in his book 'The World of Neglected Dimensions' (1914). This work inspired me as a new Assistant Professor arriving in the Chemistry Department at the University of Toronto in the summer of 1969, to address the challenge of



Ozin, G.A., Nanochemistry: Synthesis in Diminishing Dimensions *Advanced Materials* 1992

making materials with nanoscale dimensions using a bottom-up chemical approach. As a synthetic chemist, I was confronted at that time with an important unanswered question: How could chemistry be used to prepare nanoscale forms of well-known metals, semiconductors, and insulators having physical dimensions in the quantum size regime of around 1-100 nm with control over their size?

The dream was to study the size-tunable chemical and physical properties of these materials with an eye to elucidating function and ultimately to determine utility in a number of perceived applications that would benefit from the 'nano advantage'.

My first 'eureka' moment arose by performing chemistry with 'naked' metal atoms under cryogenic conditions, where chemical reactions could be 'stopped in their tracks' and reactive intermediates and products could be observed by various forms of spectroscopy. This revelation opened my mind to the tantalizing possibility that one could control nucleation and growth of metal atoms, one atom at a time, to form 'atom-precise' metal nanoclusters  $M_n$ , by allowing them to diffuse around, self-assemble and become immobilized in low-temperature inert and reactive solid matrices. This scientifically exciting feat had never been accomplished before. In this way, I was able to observe metal-atom-by-metal atom nucleation and growth reactions, and monitor and quantify the formation of  $M_n$  and define their aggregation kinetics. Furthermore, I established that it was possible to observe previously unforeseen  $M_nL_m$  compounds from reactions of these naked metal atoms and metal clusters with a wide range of small molecule ligands exemplified by  $L = CO, N_2$  and  $O_2$  (*Nature* 1972, *Nature* 1975).

One of my favorite early initiatives, undertaken while working as a Fairchild Fellow at Caltech in 1977 with William Goddard, was an experimental and theoretical study of  $Ni_n(C_2H_4)_m$ . This described for the first time the chemistry of 'naked' nickel atoms and nickel clusters with ethylene, envisioning them as a localized bonding model for ethylene chemisorbed on bulk nickel (*JACS* 1978). The ingenuity behind these 1970's experiments, summarized in *ACR* 1973 and *ACR* 1977, unveiled an unprecedented view of controlled size metal nanoclusters, the synthesis and study of which enabled the first explorations of the transition from molecular to quantum confined to bulk forms of metals (*JACS* 1980). They also provided a unique platform for investigating cluster-surface relations, chemisorption models and modelling them theoretically.

It is worth mentioning that I later expanded and enriched this work with the discovery of a collection of unprecedented metal atom and metal cluster photo-processes. These light induced processes included 'naked' metal atom photo-aggregation, 'naked' metal cluster photo-dissociation and 'naked' metal cluster photo-isomerization reactions as well as 'naked' metal atom-molecule photo-insertion reactions. The latter included the hydrogen-hydrogen bond of di-hydrogen and the carbon-hydrogen bonds of saturated hydrocarbons, such as methane to make binary  $MH_2$  and  $HMCH_3$  archetypes for many of the first transition series elements (*ACIE* 1983, 1986, *JACS* 1985). Together, these early experiments on the chemistry and photochemistry of 'naked' metal atoms and 'naked' metal clusters, were beginning to help lay the groundwork for the development of Nanochemistry as we know it today.



**Zeeing Zeolite** My desire to take the insights gained from this phase of my Nanochemistry work on ‘naked’ metal atom and ‘naked’ metal cluster cryochemistry, ‘out of the cold’, provided the link between my early work and the field of zeolite science. I envisioned making and stabilizing these tiny pieces of matter so that detailed studies of their structure, property, function and utility could be undertaken. In this context, it occurred to me that because these  $M_n$  and  $M_nL_m$  nanoclusters were inherently metastable with respect to further agglomeration to thermodynamically stable bulk materials, they had to be stabilized by some kind of surface protecting sheath. I performed the nucleation and growth reactions within the nanometer-sized voids of zeolites, ‘capping and trapping’ the nanoclusters in a ‘zeolate’ ligand cage (**AM** 2004). This work confirmed that zeolites could serve as nanoporous hosts for synthesizing and stabilizing metal and semiconductor nanomaterials.

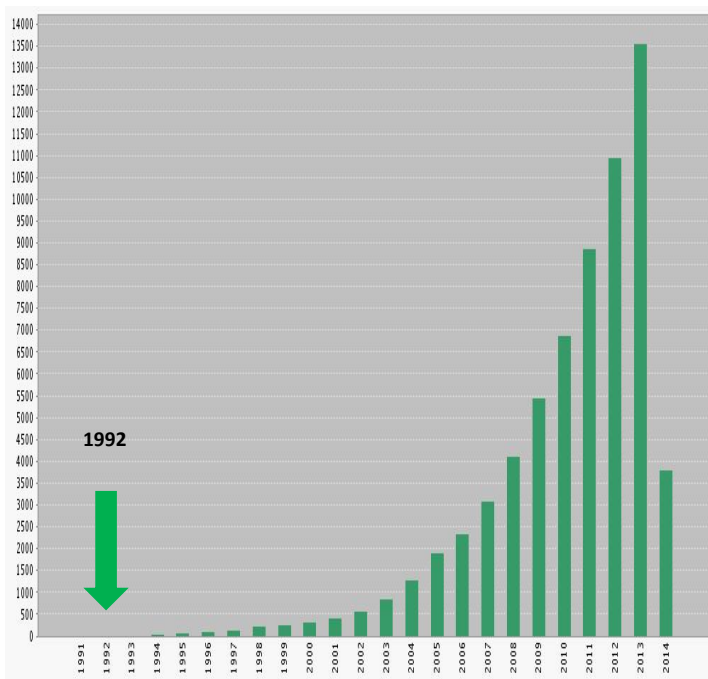
During this period, thinking within the zeolite community focused solely on the properties and applications of zeolites in catalysis and gas separation. However, I preferred to look at zeolites as solids filled with periodic arrays of nanoscale voids and wondered how they could perform and compete in the advanced materials research space. I saw their potential in areas such as information storage, photovoltaics, batteries, fuel cells, photo-catalysis, chemical sensors and drug delivery systems. Exploring this potential, I worked with Edith Flanigen at Union Carbide, Tarrytown New York for five years to bring some of these ideas to practice, ultimately describing a vision for the future direction of the field in my paper ‘Advanced Zeolite Materials Science’ (**ACIE** 1989).

Coincidentally, around this time the Union Carbide team made the extraordinary discovery that nanoporous materials could be made from elements across the periodic table, thus expanding the composition field of zeolites way beyond aluminosilicates and silicates. This advance inspired me to focus my attention on advanced materials applications of nanoporous metal chalcogenides, which I envisioned as semiconductors filled with nanometer holes (**Nature** 1997) with perceived utility in molecular size- and shape-discriminating sensing devices enabling the development of an early ‘electronic nose’, (**SC** 1995).

**Escape from the 1 nm prison** The 1 nm-size voids in zeolite hosts imposed on their imbibed guests presented an impediment to my quest to nucleate, grow, stabilize and study quantum-confined nanomaterials with physical dimensions in the 1-100 nm range. This length scale was defined by quantum physics, which necessitated larger voids than those offered by zeolites. It was Charles Kresge and co-workers 1989 discovery at Mobil Research, New Jersey of periodic mesoporous silica materials with nanometer tunable 2-100 nm voids that enabled me to break free from the 1 nm prison of zeolites.

**Birth of Nanochemistry** My ensuing research laid out the essence of a chemical approach to nanomaterials - a futuristic field that I called 'Nanochemistry', (**AM** 1992). This paper set the scene for a nanomaterials revolution that continues unabated today. In this paper I envisioned the novel world of Nanochemistry with its 0-D dots, 1-D wires, 2-D layers and 3-D open frames, configurations that surprised, shape- and size-dependent behaviors that startled. Here were the conceptual foundations, the description of a bottom-up paradigm for synthesizing nanoscale materials with nanometer-level command over their size, shape, surface and self-assembly. The potential I saw was breathtaking. It would be possible to produce nanoscale materials - perfect down to the last atom - from organic and inorganic components, with structure-property relations designed to yield new materials characterized by an array of novel behaviors and these materials would have real-world applications.

The field of Nanochemistry crystallized in 1992 and gave birth to an explosion of journals that publish Nanochemistry with citation impact-factors matching or exceeding those published in the flagship journal of their respective society. These include: *Nano Letters*, *ACS Nano*, *Nature Nanotechnology*, *Nanoscale*, *Small* and the list continues to grow. Chemistry and Nanotechnology were forever united through Nanochemistry, evidenced by the astronomical growth of Nano Chemistry ISI citations since 1992, more than 80M hits on Google, and the



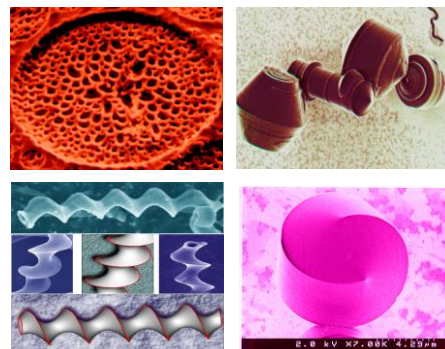
creation of numerous global initiatives in academic, industry, government, and defense institutions around research and education in Nanochemistry. It is likely that these initiatives would not have been possible without the key role that my research group played in developing the early phase of the field in the seventies - a contribution which subsequently inspired others to employ fundamental scientific principles and practices of Nanochemistry to solve challenging real world problems in Nanotechnology.

**Micro-, Meso-, Macro-Scale** This work mapped the foundation for much of my research on nanomaterials which underpinned my 'panoscopic' vision of materials self-assembly

over ‘all’ length scales (*ChemComm* 1999), a synopsis of which is described below with graphical illustrations.

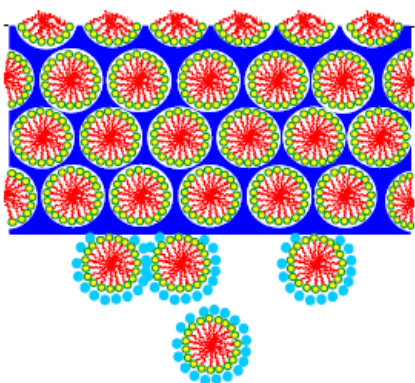
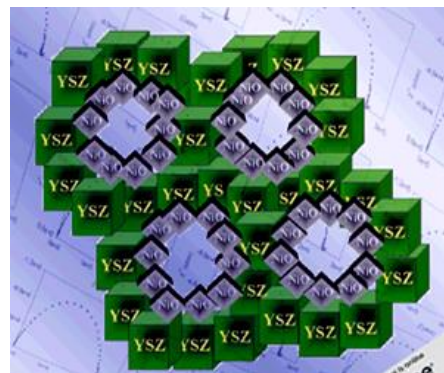
## 1. Biomimetic Nanochemistry

– The paradigm of learning how to transfer Nature’s best materials ideas into the Nanochemistry laboratory, inspired my discovery of ‘morphosynthesis’, a synthetic analogue of morphogenesis, the creation of shapes and patterns in the biological world. My work focused on controlling and understanding, from the nanometer to micron scale, the growth and form of inorganic materials with striking curved shapes and beautiful surface patterns that exhibited ‘natural form’. By natural form, I imply the visual perception of a class of materials with shapes and patterns recognized as being associated with the natural world. These amazing biomimetic constructs were made by template-directed hierarchical-assembly of organic and inorganic molecules and produced for the first time faux diatoms and radiolarian, exotic hollow helicoids and rounded figurines (*Nature* 1995, *Nature* 1996, *Nature* 1997, *Nature* 1997, *ACR* 1997).



## 2. Mesoscopic materials

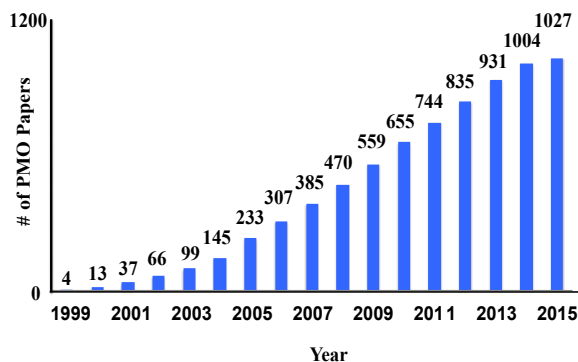
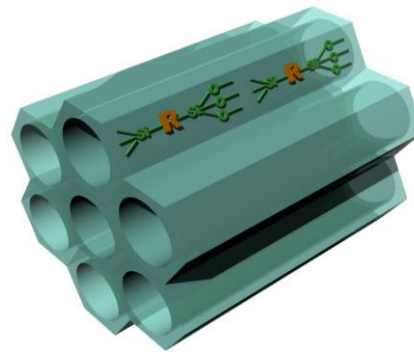
– This biomimetic way of thinking about template-directed co-assembly of materials led to my discovery of periodic mesoporous silica in the form of ‘oriented thin films’ formed at liquid-solid and air-solid interfaces (*Nature* 1995, *Nature* 1996). These seminal papers inspired a world-wide effort on finding utility for periodic mesoporous silica film in optics, fluidics, microelectronics and sensing, to name a few applications. I also advantageously used template directed co-assembly of



meso scale-inorganic materials with compositions beyond the archetype silica. These meso-materials included semiconducting germanium sulfide (*Nature* 1999), electrochromic nanocrystalline titania (*NL* 2004), transparent conducting indium tin oxide (*AM* 2009) and fast ion conducting yttria stabilized zirconia (*AFM* 2001), which displayed structural features intermediate between the nanoscopic and macroscopic length scales, and compositions that led to many meso-materials useful in today’s energy nanotechnologies

### 3. Hybrid nanomaterials chemistry

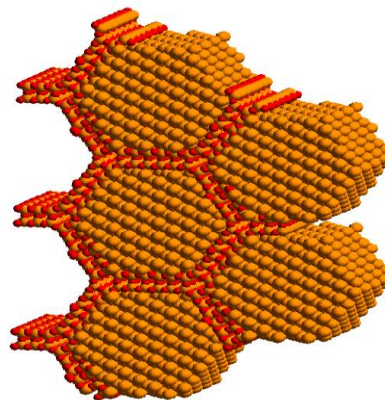
A new class of nanocomposite materials called periodic mesoporous organosilicas (PMOs), were also invented in this phase of my work (*Nature* 1999). These distinctive hybrid materials contain bridge-bonded organic molecules integrated into the silicate pore walls. The organic moieties include aliphatics, alkenes, aromatics, dendrimers, fullerenes and polyhedral oligomeric silsesquioxanes. Today, having undergone



extraordinary growth across the globe and across the borders of the science disciplines, PMOs deliver properties that transcend the sum of their inorganic and organic components and are finding widespread application as interlayer dielectrics in microelectronic packaging, chromatography stationary phases, chiral catalysis, dental implants and drug delivery vehicles (*Science* 2003, *Science* 2004, *ACR* 2005).

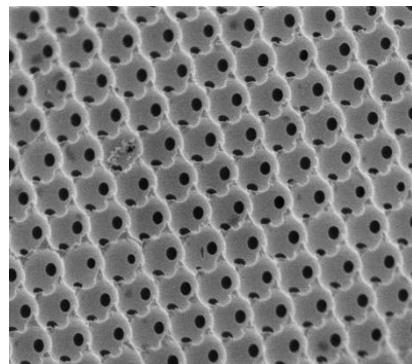
### 4. Host-guest inclusion chemistry

Using chemical vapor deposition and metal organic vapor deposition within the spatial confines of nanoporous hosts, I discovered how to control the nucleation and growth, stabilization and protection of size- and shape-controlled quantum-confined semiconductor nanomaterials, exemplified by nanometer dimension Si, Ge, Ag, AgCl, CdS, SnS<sub>2</sub>, MoO<sub>3</sub> and WO<sub>3</sub>, (*ACR* 1992) This genre of research inspired subsequent work on ligand-stabilized colloidal nanocrystals that underpin some of today's most promising nanotechnologies including solar cells and batteries, super-capacitors and fuel cells, medical diagnostics, imaging and theranostics.



### 5. Photonic crystal materials

I discovered how to employ self-assembly to synthesize the world's first 3D silicon photonic crystal with an omni-directional photonic bandgap operating at optical telecom wavelengths (*Nature* 2000). This genre of research inspired me to synthesize photonic crystals with a wide range of compositions that could display the full gamut of 'color from structure' as found in the natural world. I also discovered how the 'slow light' attributes of these



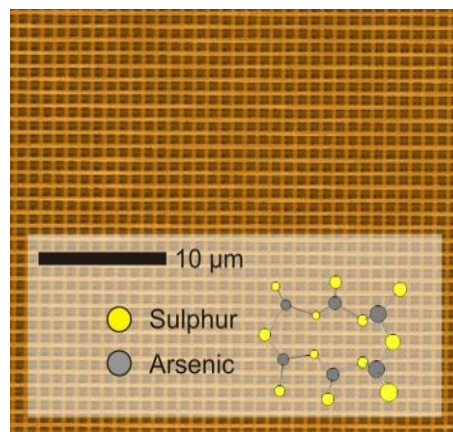
photonic crystals could be used to amplify light absorption, which inspired me to use them to enhance the efficiency of silicon and titania solar cells and titania photocatalysts (*NL* 2011, 2013, *AM* 2007, 2009). I also showed how to incorporate nanoscale planar defects into photonic crystals and how to implement them as a new class of chemical and biological color sensors (*AM* 2006).



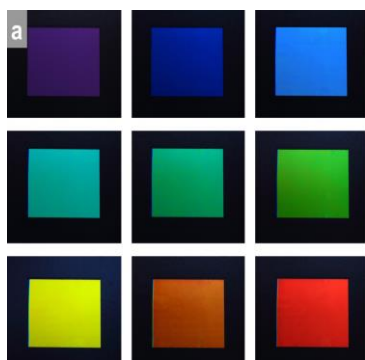
**6. Smart mirrors** – In a flurry of trendsetting papers I showed how to synthesize alternating composition multi-layers made from a wide range of nanomaterials comprised of main group and transition metal oxides, zeolites, mesoporous materials and clays. These self-assembled Bragg mirrors provided high porosity and large surface area, ion-exchange and molecule size discriminating properties to the constituent layers. This enabled active tuning of the structural color of reflected or transmitted light through chemically and physically induced changes in the thicknesses and/or refractive indices of the constituent layers and led to the development of a new class of colorimetric sensors and anti-bacteria patches with controlled release and detection capabilities. I also showed that Bragg mirrors made from transparent and conducting antimony and indium tin oxides, enabled the development of improved- performance organic light-emitting diodes, grey scale electrochromics and a new genre of solid state dye and polymer lasers (*CSR* 2013).

## 7. Multi-photon direct laser written (DLW) photonic bandgap nanomaterials

– In collaboration with colleagues at the Karlsruhe Institute of Technology, I used this nanofabrication method to invert a DLW polymer template in silica by atomic layer deposition. This enabled a subsequent inversion in silicon by disilane chemical vapor deposition, creating thereby a silicon replica of the original polymer template (*Nature Materials* 2006). Silicon photonic bandgap nanomaterials created by this inventive ‘double inversion’ method facilitate the development of silicon-based all-optical devices, circuits and chips with utility in optical telecommunication and computer systems. I spearheaded a creative extension of this work with single-step DLW in a high refractive index ‘inorganic’ photo-resist, arsenic sesquisulphide,  $\text{As}_2\text{S}_3$ . This opened the door to a large variety of new photonic bandgap materials and architectures that can be made by DLW without inversion of a sacrificial polymer template (*ChemMater* 2008).





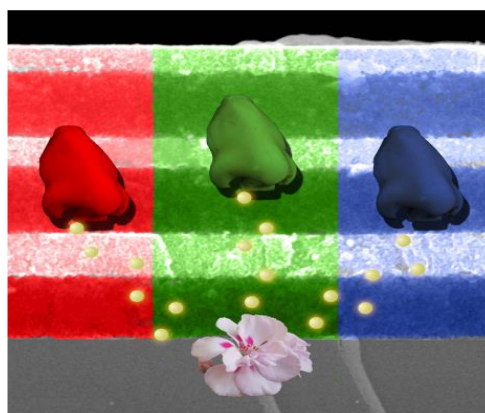


## 8. Photonic crystal Nanochemistry

– This research on photonic crystal nanomaterials enabled me to invent actively-tuned ‘photonic color’ systems (*Nature Materials* 2006, *Nature Photonics* 2007) now commercialized by Opalux, a spin-off company that I co-founded in 2006. These technology platforms include full color displays, authentication devices for anti-counterfeiting, color sensors for food and water quality control and pathogen detection ([www.opalux.com](http://www.opalux.com)).

## 9. Seeing the light

– One of the hallmarks of my research is the creative exploitation of the unique properties of regular arrangements of nanopores with dimensions that traverse nanometers to microns. For example, my research on periodic macroporous materials, which I aptly calls ‘light-scale’ materials, has been focused on electrically, thermally, mechanically, and chemically tuned ‘color from structure’.

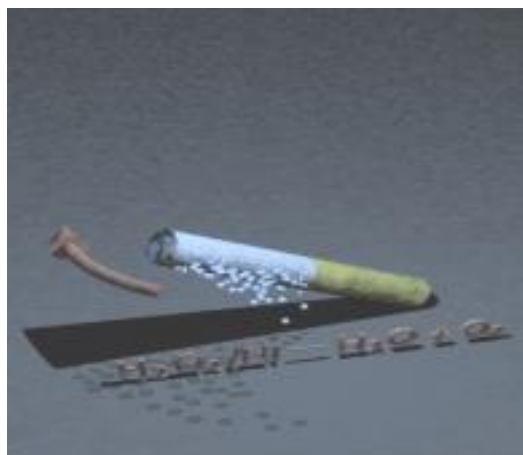


This revolutionary concept forms the basis of a new ‘photonic color’ nanotechnology being developed by Opalux who are introducing three unique manifestations of this nanotechnology to the market. **P-Ink** is a flexible, electronic paper-like material offering a full spectrum of electrically-tunable, reflective colors. Being bi-stable and power-efficient, it is one of three competitive technologies vying to add color to black-and-white electronic book readers such as Kindle and Kobo. **P-Nose** is an artificial nose comprised of a simple, cost-effective pixilated array of surface-functionalized nanoporous materials that enable discrimination of different analytes, such as molecules comprising the unique identifiers of different bacteria. Think of the possibilities for medical diagnostics, and food and water quality-control. **Elast-Ink** is a touch-sensitive material that responds to mechanical pressure while offering exceptional resolution and customizability. It is poised to answer global demand for effective authentication-technology, serving, for example, the pharmaceutical and banknote-printing industries.

It is worth pointing out that the **P-Ink** photonic color technology developed by Opalux was recognized by the Technical Development Materials Award in the USA in 2011, which identifies the most innovative and significant technical achievement in the field of materials development (<http://www.idtechex.com/printed-electronics-usa-11/awards.asp>). Opalux follows in the footsteps of many previous illustrious industry winners of this award in the US, Europe and Asia. In 2013, Opalux P-Ink Photonic Technology received the Global Innovation Award for its potential impact on the specialty colour displays industrial sector

([http://techconnectworld.com/World2013/participate/innovation/innovation\\_awards.html](http://techconnectworld.com/World2013/participate/innovation/innovation_awards.html)).

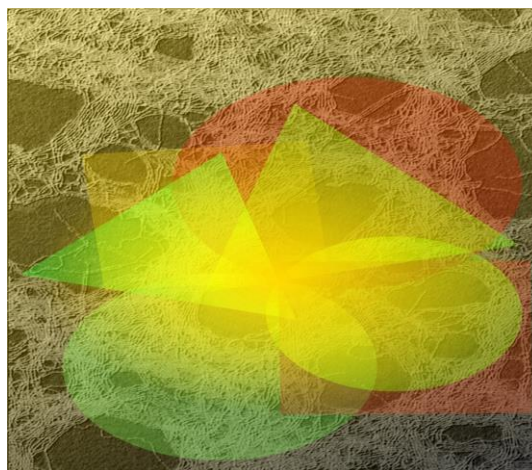
Opalux Opal-Print Technology was runner-up in the 2013 Excellence in Tax Stamps Awards for best new innovation in anti-counterfeiting, anti-diversion, document security, brand protection and holography technologies (<http://www.taxstampnews.com/awards>).



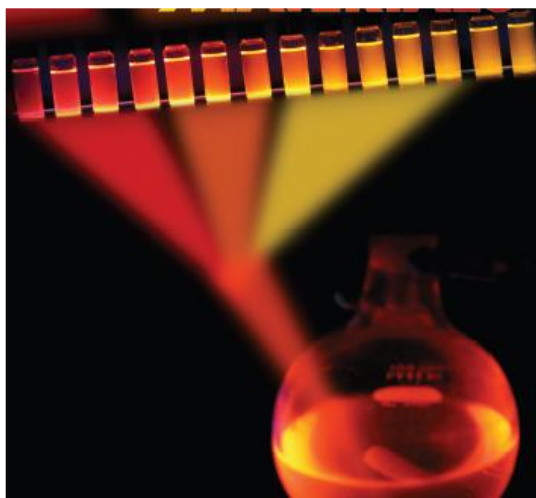
## 10. Clever new Nanochemistry twists

- I was amongst the first few scientists to demonstrate chemically-powered 'nano locomotion'. My work was based on chemical control of the motion of barcode nanorod motors, whose power is obtained from the decomposition of hydrogen peroxide into water and oxygen localized at the catalytic segment of the nanorod (*ChemComm* 2005, *AM* 2005). First experiments were aimed at nanorod rotors and

motors and understanding the origin and control of their motion and speed. Subsequently I was the first to show how to make them flexible by integrating polymer hinges between the segments of the nanorod (*Nature Nanotechnology* 2007). These papers have inspired a veritable 'nanomotor industry'. Activity in this field is now burgeoning around the world with envisioned nanomachine applications that include the removal of pollutants from water and as drug-carrying and drug delivery vehicles for targeted cancer therapy. Another innovation to emerge from my research involved the discovery of ultrathin inorganic nanowires (*ACIE* 2008), which are characterized by unprecedented small  $< 2$  nm diameters. These amazingly thin nanowires look, grow and behave like organic polymers (*JACS* 2012, 2010, *NL* 2009, *AM* 2009). This work inspired a flurry of activity around the globe to explore the composition space and structure, properties, and functionality of these uniquely-thin one-dimensional constructs. This work raised an important question about how to expand and enrich the myriad applications enjoyed by organic polymers into the completely uncharted territory of ultrathin inorganic nanowires. The opportunities appear to be boundless!





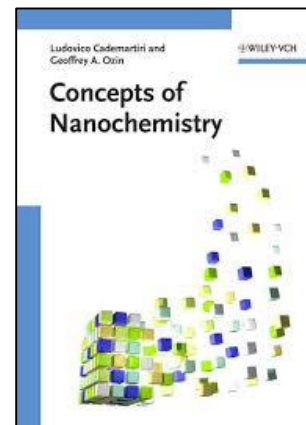
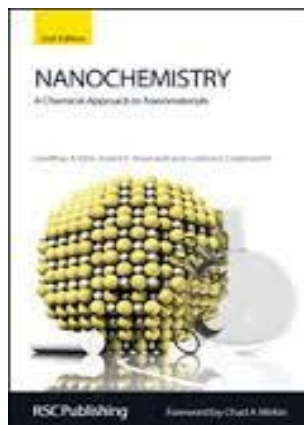


Lately, I have developed a passion for a greener kind of Nanochemistry and figured out how to separate poly-dispersions of quantum-confined silicon nanocrystals into mono-dispersed colloidally-stable fractions with tailored organic surfaces (*JACS* 2011). Incredibly, for the archetype semiconductor silicon, this feat was the first of its kind since the discovery of silicon nanocrystals more than thirty years ago. The brightly colored visible to near infrared photoluminescence of these size-separated silicon nanocrystals enabled

determination of their size-dependent absolute quantum yields, (*NL* 2012). These photoluminescence quantum yields were found to be surprisingly high and as a result are targeted for a range of 'green' nanotechnologies that include multi-color light-emitting diodes and biomedical diagnostics, and therapeutics and imaging for detecting and targeting tumors. I believe 'green Nanochemistry' founded on benign nanocrystalline silicon will help alleviate the fear of cytotoxicity that pervades the use of heavy metal chalcogenide and pnictide nanomaterials currently favored for advanced materials and biomedical nanotechnologies (*NL* 2011, 2012, 2013, *AM* 2012, *Small* 2012).

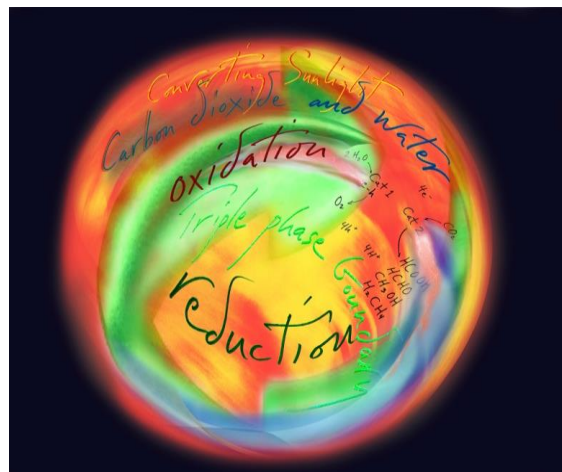
## 11. Nanochemistry education -

Another aspect of my work worth mentioning involves education. My textbooks '*Concepts in Nanochemistry*' and '*Nanochemistry: A Chemical Approach to Nanomaterials*', co-authored with former students Andre Arseault and Ludovico Cademartiri, are globally acclaimed as the gold standard reference works for teaching Nanochemistry to both undergraduate and graduate students.



My out-reach efforts through insightful and engaging lectures and monthly opinion editorials in Wiley materials journals (<http://www.materialsviews.com/author/gozin/>) aim to inform scientists and laypersons alike on pressing issues affecting the future of all of us. Hopefully, these inspiring, thought-provoking perspectives offer viable ways of improving the state of the world.

**12. ArtNanoInnovations** - In 2011 in collaboration with artist Todd Siler, I co-founded ArtNanoInnovations the mission being to explore the realization of nature-inspired innovations in nanoscience and nanotechnology, which aim to benefit humankind by meeting our global challenges. This work entails (connecting and transforming) the myriad forms of nanometer scale science through multimedia artworks and aesthetic experiences that connect us with Nature's creations, which we can build on in creating a sustainable future, [www.artnanoinnovations.com](http://www.artnanoinnovations.com).



**Nanochemistry what is next?** The genre of Nanochemistry research outlined above has provided the foundation for the most recent phase of my research on new nanomaterials for enabling a global energy revolution. The vision is based upon the discovery of nanostructured photo-catalysts capable of both capturing and converting gaseous  $\text{CO}_2$  into solar fuels that will replace their fossil fuel counterparts, ameliorate climate change and power our planet for the foreseeable future. It is clear that in order to address these crucial issues, new chemistry that enables advance energy materials and technologies must be developed (EES 2015, AM 2015).



This is where Nanochemistry research and very recent exciting developments in my group come into the picture. My group is a member of a University of Toronto multi-disciplinary solar fuels team of experimental and theoretical materials chemists and engineers, working together to build a materials technology

that can simultaneously harness abundant solar energy, capture and reduce gaseous carbon

dioxide into fuels and chemical feed stocks, simultaneously addressing issues of energy security and climate change.

The inventiveness and practicality of our early work in this field can be showcased with two of our recent discoveries. The first involves, the rational design of a single-component photocatalyst for the efficient gas-phase CO<sub>2</sub> reduction using both UV and visible light (AS 2014). The second concerns the efficient photomethanation of gaseous CO<sub>2</sub> on ultra-black silicon nanowire catalyst supports with visible and near-infrared photons, a step towards broadband solar fuels reactors (AS 2014). In this context it is noteworthy that even a modest target conversion rate of 10 mole CO<sub>2</sub> per hour per gram of photocatalyst would translate into a conversion rate of 1 Gt CO<sub>2</sub> per year per ton of photocatalyst, which configured as solar fuels panels could be incorporated into solar fuels chimneys built on land or floating on water to minimize usage of property. With an earth abundant, non-toxic, cost effective, scalable catalyst integrated with existing chemical and petrochemical industrial infrastructure, one can begin to appreciate that CO<sub>2</sub> conversion rates of this magnitude can provide a potentially practical, economical and sustainable alternative to burning and depleting fossil fuel reserves.

My vision for an energy transition from one based on unsustainable fossil fuels to a sustainable solar fuels energy technology founded on capturing and utilizing CO<sub>2</sub> – from both thin air and more concentrated localized sources – is compatible with existing CO<sub>2</sub> emitting industries around the world. To achieve this vision of a carbon-neutral air-to-fuel carbon-cycle technology my group is currently developing compact, tandem, concentrated solar powered photochemical reactors for efficiently splitting gaseous water first into H<sub>2</sub> and then using the H<sub>2</sub> to reduce gaseous CO<sub>2</sub> to fuels and chemicals. I believe the time it should take to convert solar fuels laboratory-scale science to a global technology could be short enough to circumvent the predicted adverse consequences of greenhouse gas climate change, enabling a timely energy transition from fossil fuels to solar fuels.

**Nanochemistry final thoughts** It is tremendously satisfying that my contributions to fundamental research laid out the essence of a chemical approach to nanomaterials, defining the conceptual foundations and securing credibility for a novel scientific discipline. I am thrilled by the way that this new discipline of Nanochemistry has developed and matured over the last 20 years and continues to serve as an integral driver of further developments in many tangential scientific undertakings which we now count upon to catalyze scientific, industrial and economic advancement. Of course none of my discoveries in the field of Nanochemistry would have been possible without the incredible contributions of a large cadre of highly creative coworkers many of which have gone on to academic positions in top notch universities, scientific positions in national laboratories and

chemical industries, and founded spin-off companies around the world. I am also indebted for the tremendous support and encouragement of a large number of University of Toronto colleagues, provincial and federal funding agencies, national and international collaborators, industrial partners and of course my wife and best friend, Linda Ozin. The RSC Centenary Award in recognition of my career's work in this exciting and developing discipline is deeply treasured.

## Acknowledgments

G.A.O. is Government of Canada Tier 1 Canada Research Chair in Materials Chemistry and Nanochemistry. Strong and sustained financial support from the Ontario Ministry of Research and Innovation (MRI), the Ontario Ministry of Economic Development and Innovation (MEDI), the Natural Sciences and Engineering Council of Canada (NSERC), the Connaught Innovation Fund and the University of Toronto is deeply appreciated. The creative contributions of the many faculty and students to the work described in this Perspective are deeply treasured.

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## 46. Utopia Electrified



Utopia Dystopia artwork, courtesy of Dylan Glynn,  
<http://www.dylanglynn.com/utopia-dystopia/>

artwork of Dylan Glynn, which dramatically represents the Utopian-Dystopian heterodox choices that humanity faces if we do not find sustainable solutions to the intertwined problems of energy, climate and environment.

With this setting to the story that follows, imagine a world roughly 30 years into the future, in which all fossil energy producing systems, to enable the operation of all transportation, heating and cooling systems, homes and industry, are powered by clean and renewable forms of electricity supplemented by some renewable hydrogen, generated electrochemically or photo-electrochemically, solely by wind, water and sunlight.

Naturally, the initial reaction to this Utopian vision of a clean and green electrified planet, safe from climate change and environmental pollution, is that it will be impossible to achieve such and energy transition in practice because of technological and economic hurdles, and social and political barriers that such a change will entail. The trauma of confronting this transition can however be realistically ameliorated by providing quantitative information on the feasibility of these changes and the benefits that will result if they are implemented.

While it is a truism that such change will be passionately resisted by those in, and who lobby for, the fossil and nuclear energy industries who stand to lose out financially, a recent detailed technical, economic and social analysis from a team of Stanford University Civil and Environmental Engineers, shows this is not necessarily true and the gains easily compensate for

Visionaries have often tried to imagine the future in terms of Utopian and Dystopian extremes, the former enabling balance and peace where all life is valued and sustained the latter permitting decay and destruction where life and nature are irresponsibly exploited and extinguished.

This is certainly true of the stark contrast envisioned for the future of humanity, namely one that is sustainable and safe using renewable forms of energy rather than unsustainable and insecure by continuing the use of fossil and nuclear energy sources.

These opposing views of our future are symbolically represented in the exquisite

the losses if such an energy transition can be reduced to practice in an efficient, effective and timely manner [1].

On the basis of a detailed and comprehensive all-energy sector roadmap for all 50 States of America, the claim is rather convincingly made that with currently existing technology it is possible to achieve a fully electrified world within a three-to-four decade time frame [1]. The analysis reveals profound and surprising economic advantages of transitioning a fossil and nuclear powered energy system into one founded on just wind, water and sunlight. The political challenge to reduce this Utopian vision to reality is how to implement the social and policy changes to replace combustible and nuclear fuels by clean and safe forms of renewable electricity by 2050 and thereby provide a safe and secure energy supply, stabilize climate change and protect the environment.

One can justly ask, how could this be possible, it seems too good to be true? To amplify on the details of the proposed pan-electrification roadmap, the analysis for each of the 50 States of America is based on a model of 80-85% conversion of existing energy systems by 2030 and by 2050 a replacement of 100% to wind, water and sunlight electrical systems. These energy technologies include wind, concentrated solar, geothermal, photovoltaics, tidal, wave, and hydroelectric power systems.

Here a few points are worth noting. Conspicuously absent from the pan-electrical roadmap are nuclear power, coal with carbon capture, natural gas and liquid or solid biofuels. Notably biofuels are excluded on the grounds that greenhouse gas emissions are on par with fossil fuels, the land and water requirements are much larger, and the photosynthetic efficiency for the same land use is about twenty times less than solar photovoltaics biofuels [1]. Second, a pan-electrical roadmap will have to include technologies for the large-scale grid-storage of electricity. This will be achieved using conventional forms of electricity storage that include compressed and liquefied air, pumped water and flywheels as well as advanced methods based on redox flow batteries, lithium and air batteries, supercapacitors, hydrogen and conversion of carbon dioxide using hydrogen to liquid hydrocarbon fuels, the bedrock of our current energy infrastructure. Third, there is no way around liquid hydrocarbon fuels in mobile applications where the energy density of electricity is too low and many forms of transportation will continue to rely on fuel of some kind and this is where solar thermochemical and photochemical catalytic conversion of CO<sub>2</sub>-to-fuel will have a role to play in utopia electrified. Fourth, today's benchmark to produce liquid fuels from H<sub>2</sub>O, CO<sub>2</sub>, and solar energy is based on the following process chain: 1) solar electricity; 2) H<sub>2</sub>O electrolysis; 3) reverse water-gas shift (RWGS) of H<sub>2</sub>+CO<sub>2</sub>, 4) syngas to liquid fuel, with an estimated overall efficiency of 8.2% (i.e., 19% for PV, 85% for water electrolysis, 80% for voltage mismatch, 90% for RWGS and 70% for Fischer-Tropsch synthesis). Significantly, the solar thermochemical approach has the potential of reaching higher efficiencies,



approaching 12%, because of thermodynamically favorable processes at high temperatures and because it bypasses the inefficiencies and energy penalties arising from the RWGS step. Higher efficiencies translate into economic competitiveness vis-à-vis the benchmark based on solar electricity. It remains to be seen whether the nascent solar photochemical approach can compete with the efficiencies achieved by solar thermochemical methods for producing liquid fuel from  $\text{CO}_2 + \text{H}_2\text{O}$  [2].

Returning to a pan-electrified Utopia, the efficiency advantages of an all-electrified energy system is estimated at roughly 39% based on the higher efficiency of electricity compared to combustion powered processes and end-use energy improvements. By the year 2050, the entire United States power demand would be provided by around 30.9% onshore wind, 19.1% offshore wind, 30.7% utility-scale photovoltaics (PV), 7.2% rooftop PV, 3% concentrated solar power (CSP) with storage, 1.25% geothermal power, 0.37% wave power, 0.14% tidal power, and 3.01% hydroelectric power.

The employment opportunities for all 50 States of America of such a massive energy replacement plan are extraordinarily interesting. Over a 40 year period construction and operation jobs for building and running the renewable energy facilities are estimated at 3.9M and 2.0M respectively. This opportunity more than adequately accommodates the 3.9M job redundancy in the conventional fossil and nuclear energy sectors.

The associated health and economic benefits of this energy transition are remarkable. Annual mortalities from air pollution in the United States would be reduced from today's 62,000 to 46,000 in 2050 saving \$600B per year in 2013 dollars in 2050. This amounts to an amazing 3.6% of the 2014 United States GNP!

The savings in the cost of the negative effects of global warming from climate change are even more impressive, \$3.3T per annum being eliminated just by reducing greenhouse gas emissions from the United States alone!

On a personal basis the economic benefits are significant, whereupon by 2015 roughly \$260 per person per year energy costs will be saved in 2013 dollars with an additional savings of \$1,500 and \$8,500 per person year related to health and global climate change problems, respectively.

Perhaps even more surprising are the estimated 0.42% of United States land requirements to enable this energy transition, which is rather miniscule and only grows slightly to 1.6% when the spacing area between wind turbines is taken into account.

It is to be noted that inevitable uncertainties in the aforementioned road maps, arising from unexpected technological, economic, social and political events, are captured in broad ranges of

energy, climate and health costs reported in the analysis. Therefore it is recommended that the road maps will need to be re-evaluated on a regular basis.

It is anticipated that the publication of this 50 States of America all-sector energy transition roadmap by the Stanford University researchers, will be quite an eye-opener to the global community of scientists and engineers, industry and business leaders, public and media, and policy makers and politicians. Hopefully this important report will inform and inspire politicians to implement the clean-energy policy changes required to enable 100% conversions of fossil and nuclear energy systems to clean and safe renewable electrically-based forms of energy. From the reported techno-socioeconomic analysis of the pan-electrification of all 50 States of America it seems that the conversion is technically and economically feasible by 2050 and the conclusions and recommendations of the report demonstrate plenty of advantages and few disadvantages.

Could this vision inspire and enable the transition of our fossil dystopia to an electrical utopia? While the numbers seem credible it is possible that for America and many other countries this vision will remain utopia! Take socially conscious Germany for instance, where it needed a 10-20% voting potential for the Green Party to gain momentum in the right direction and it is still not certain to what extent their Energiewende will succeed [3]. The lobby groups of many countries will insist on gaining access to the last drop of oil, coal and gas on the planet and shipping, transporting and piping it home oblivious of the dystopian consequences.

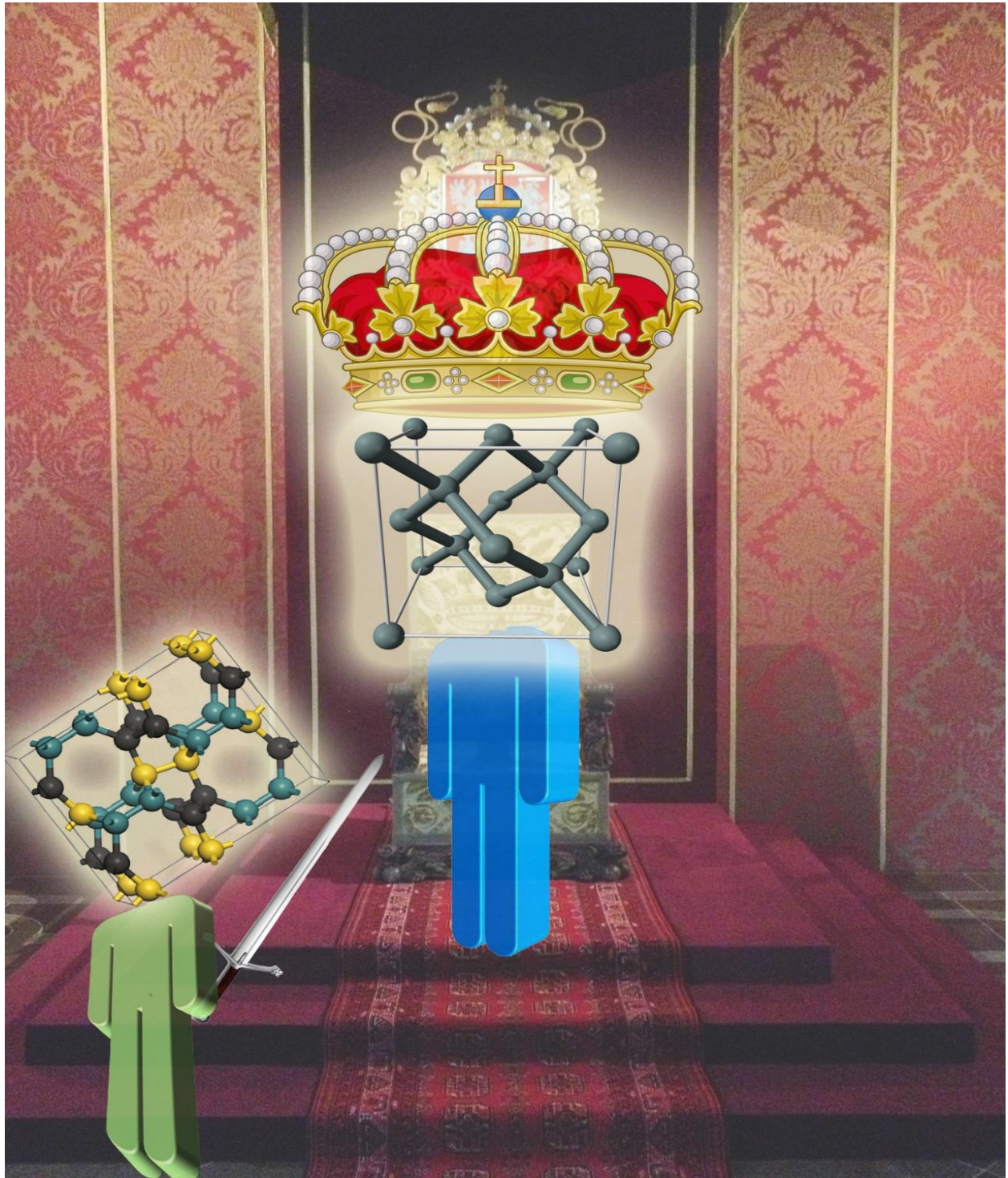
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# Threatening the Silicon Throne

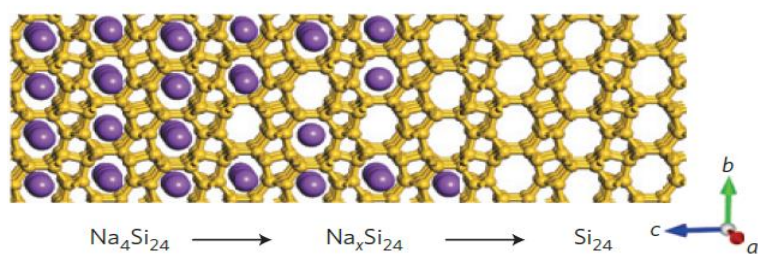


Graphic artwork courtesy of Chenxi Qian.

## 47. Silicon Does It Again!

**Silicon Dreams** Imagine inventing a new allotrope of silicon that still functioned equally well to the diamond form of silicon as a semiconductor making it suitable for microelectronics but also provided those much desired properties the diamond form of silicon has so far been unable to deliver to enable the development of improved performance solar cells, higher efficiency light emitting diodes and lithium ion batteries with better cycle-life and safety requirements.

Envisage in the case of silicon solar cells a new allotrope of silicon able to offer a direct bandgap of around 1.3eV. This would be the ideal value that optimizes the photon-to-electron conversion efficiency for a single p-n junction to meet the theoretical Shockley-Queisser limit of 33.7%. This new allotrope of silicon with its direct bandgap would also enable the required high efficiency electron-hole radiative recombination required to drive the next generation of light emitting diodes. Conceive also of anodes for lithium ion batteries made of this new allotrope of silicon that undergoes minimal volume changes and mechanical failure on electrochemical insertion and de-insertion of lithium. This property would help solve the charging-discharging cycle-life and safety problems that prevent the champion volumetric capacity of silicon from being realized in practical lithium ion batteries.



**Figure 1** Illustration of the structure and compositional change in the vacuum thermal transformation of  $\text{Na}_4\text{Si}_{24}$  (left) to  $\text{Si}_{24}$  (right) where sodium atoms are shown in purple and silicon atoms in yellow [1].

“non-existent” materials. Nowhere is this existential paradigm better seen than with a very recent report of a new allotrope of silicon, which is formulated as  $\text{Si}_{24}$  and that sure enough appears to provide all of the aforementioned desirable properties demanded of silicon in one structure. This breakthrough in materials synthesis points the way to a new era of advanced silicon devices that were never thought possible before [1].

To amplify, the synthesis of  $\text{Si}_{24}$  begins with the preparation of the known precursor  $\text{Na}_4\text{Si}_{24}$  by a high temperature high pressure reaction of elemental sodium and silicon in an anvil cell [1]. The

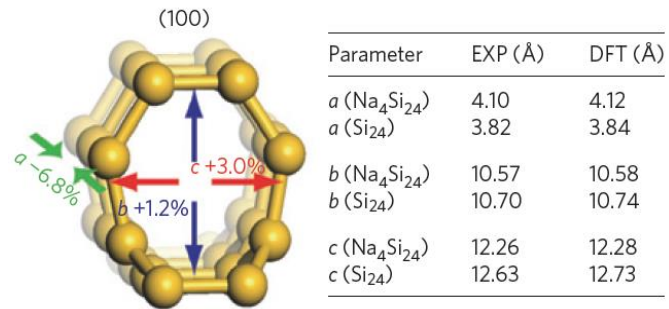
### Threat to the Silicon

**Throne** Materials researchers have long dreamed about this new allotrope of silicon but its discovery seemed just too much to expect. However, in my forty five years of practicing materials chemistry I have discovered to never-say-never about so-called

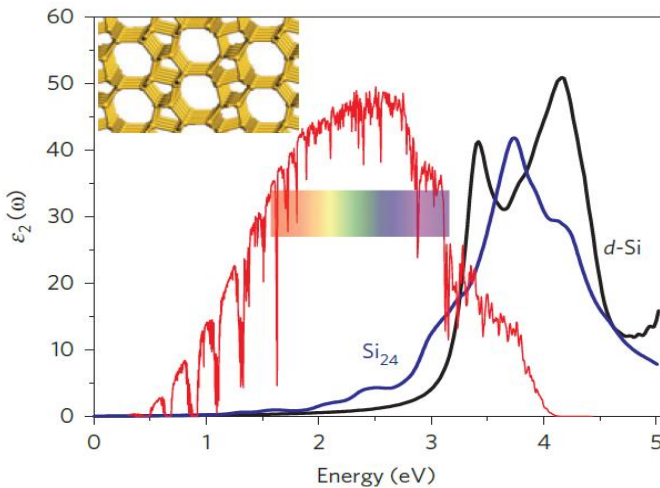


structure of  $\text{Na}_4\text{Si}_{24}$  is based upon an open-framework built of  $\text{sp}^3$ -bonded Si atoms forming 8-ring one-dimensional channels stuffed with linear chains of Na atoms. Of great significance is the observation that these intra-channel Na atoms can be completely removed by thermally induced diffusion and evaporation from the mouths of the channels at the rather low temperature of 400K and under dynamic vacuum conditions, as illustrated in **Figure 1**. This treatment causes a gradual reduction of the Na content in the channels to reach essentially zero after eight days as confirmed by XPS, PXRD and TEM-EDX analysis.

Significantly, the associated changes in the orthorhombic unit cell lattice parameters determined from Rietveld powder X-ray diffraction analysis of the transformation of  $\text{Na}_4\text{Si}_{24}$  to  $\text{Si}_{24}$  are only -6.8%, +1.2% and 3.0%, respectively. This corresponds to an increase in the diameter of the channels concomitant with a reduction in their length, **Figure 2**. This minimal volume swing of the unit cell dimensions on passing from stuffed  $\text{Na}_4\text{Si}_{24}$  to empty  $\text{Si}_{24}$  is unique in the context of other known allotropes of silicon and speaks well for the charging-discharging cycling stability of  $\text{Si}_{24}$  if used as the anode in a lithium ion battery. Noteworthy in this context is that theory and experiment indicate  $\text{Si}_{24}$  remains stable up to 750K and 10GPa [1].



**Figure 2** Illustration of how vacuum thermal removal of Na from  $\text{Na}_4\text{Si}_{24}$  to form  $\text{Si}_{24}$  has a minimal effect on the lattice parameters [1].



**Figure 3** Comparison of the calculated absorption spectra of  $\text{Si}_{24}$  (blue) and diamond Si (black) with the reference air mass (AM) 1.5 solar spectral irradiance (red) [1].

Density functional theory and optical reflectivity measurements and analysis of the absorption edge concur that  $\text{Si}_{24}$  has a quasi-direct electronic bandgap. This designation arises because in the  $\Gamma$ -Z direction of the Brillouin zone the energy of the highest valence and lowest conduction bands are essentially the same and very flat. This situation indicates that  $\text{Si}_{24}$  is best described as a quasi-direct bandgap material with very similar indirect and direct bandgap energies of 1.29eV and 1.39eV, respectively. Of related importance is the measured temperature

dependence of the electrical conductivity, which demonstrates that Si<sub>24</sub> behaves as a classical semiconductor with conductivity increasing with T according to the energy gap law,  $\sigma = \sigma_0 \exp(-E_g/2kT)$ . By contrast, Na<sub>4</sub>Si<sub>24</sub> displays metallic conductivity that as expected for a metal decreases with T. This behavior most likely originates from charge transfer of valence electrons associated with the intra-channel Na atoms to the conduction band of the Si<sub>24</sub> open-framework. Importantly, the optical absorption spectrum of Si<sub>24</sub> shows that its ability to absorb light compared to the diamond allotrope of silicon is significantly larger in the visible wavelength range where the intensity of the AM1.5 solar spectrum is at its maximum, **Figure 3**.

**Major Challenge** Together, the extraordinary properties of Si<sub>24</sub> outlined above, which can be enhanced and enriched by n-doping and p-doping and formation of native oxide, bode well for its future utilization in high capacity lithium ion batteries, enhanced efficiency photovoltaics and next generation light emitting diodes. A major challenge that confronts the implementation of Si<sub>24</sub> in next generation advanced silicon-based devices is the urgency of discovering ways of scaling the reported high P,T synthesis of the material to industrially relevant proportions or indeed finding an entirely different pathway for its large-scale preparation at a cost that is competitive with the diamond form of silicon.

In view of what is at stake in trying to dethrone the diamond form of silicon, the Samurai of semiconductors (<http://www.materialsviews.com/nano-silicon-samurai/>), I predict the materials community will diligently work to discover creative ways of making tons of the new Si<sub>24</sub> allotrope in the not too distant future.

1. Synthesis of an Open-Framework Allotrope of Silicon, Kim, D.Y., Stefanoski, S., Kurakevych, O.O., T.A. Strobel, *Nature Materials*, 2015, 14, 169-173, DOI: 10.1038/NMAT4140.

## 48. Photothermal Desalination

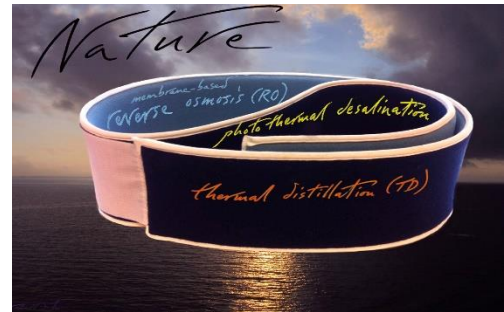
Water, water, every where,  
Nor any drop to drink

Rime of the Ancient Mariner  
Samuel Taylor Coleridge  
Lyrical Ballard's, 1798

Every continent is already experiencing freshwater shortages driven by population growth, global warming and environmental pollution. The number of people without access to a clean and secure freshwater supply is estimated to be about 1.8 billion, one quarter of the world's population. Another 1.6 billion people live in countries where the necessary infrastructure to take water from rivers and aquifers is lacking. Desalination of seawater and brackish water seems to be the only feasible way to increase the supply and solve these problems.

Today, the installed base of desalination plants around the world has a capacity of 19.8 billion US Gallons. The global market demand for water desalination products and services is estimated to be \$13.4B in 2015. Globally more than 17,000 desalination plants in 150 countries provide some freshwater to around 300 million people with capacity growing about 8 percent annually [1]. Out of necessity, countries in the Middle East have dominated the desalination market, however the specter of freshwater shortages are increasing around the world and many countries have opted to install desalination facilities [2]. These desalination processes are energy intensive and costly. They are powered mainly by electricity generated from fossil fuels with its associated adverse climate change and environmental consequences.

Desalination by membrane-based reverse osmosis RO and thermal distillation TD, are the two most practiced approaches for producing pure water from seawater and brackish water today. Solar and wind powered versions of these desalination methods avoid some of the problems inherent in the use of fossil fuels. Interestingly, the use of these intermittent renewable forms of generated electricity for powering RO or TD can be considered to be a means of electricity storage and reduction of peak demand. Direct absorption of heat from the sun can also be used



Metaphorming reverse osmosis RO, thermal desalination TD and photothermal desalination PD. Courtesy of Todd Siler and Geoffrey Ozin, [www.artnanoinnovations.com](http://www.artnanoinnovations.com).



for driving TD, however in this case bulk water is involved in the evaporative desalination process yet evaporation is a surface physicochemical phenomenon.

An thought-provoking means of reducing the energy, environmental and economic costs of solar powered TD would be to devise a means of locally concentrating light absorption and heat generation from the sun to just the interface between air and water, where the surface free energy and evaporation rate of the water is highest.

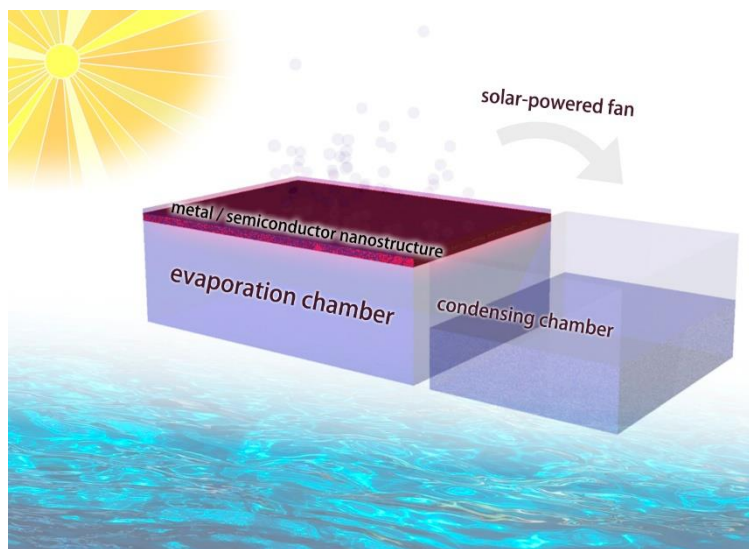


Illustration of an all-in-one solar distillation system for producing fresh water from salt water. Graphic courtesy of Chenxi Qian.

One way of achieving surface localized solar concentration to enable thermal evaporation of water and desalination is by exploiting the photothermal effect. This can be accomplished using a broad-band, highly absorbing, porous, thin hydrophobic membrane that floats on the surface of the water, as shown in the illustration. The conversion of solar photons to heat in the photothermal membrane causes local heating at the air-water interface. This in turn causes evaporation of the water through the pores of the membrane whereupon

it can be condensed in a cooler region of the desalination system. The challenge is the design of the photothermal material and architecture of the porous membrane and their integration, to optimize the light-to-heat-to-freshwater conversion efficiency as well as to maximize the long-term chemical, photochemical and mechanical stability of the composite membrane exposed to the harsh sunlight and salty water conditions.

It is interesting that solar thermal water heating systems utilized today for domestic and industry use have a long history that can be traced back to Archimedes in 214 BC, who used mirrors to heat water. Today black materials are used to absorb solar radiation, convert it to heat and transfer it to heat water in systems with different designs, architectures and uses. The absorbing materials in the solar collectors can be black paint, metal and semiconductor blacks that include copper, aluminum, steel and silicon, often with different kinds of textured surfaces to optimize the absorption of sunlight.

In the context of surface texturing and the photothermal effect, illumination of nanostructures at wavelengths corresponding to high optical absorption can turn them into nanoscale local sources of heat *via* the photothermal effect, whereby light through Joule resistive losses is transformed to heat. The most well studied systems are nanostructured metals that display conduction electron resonances at optical wavelengths, called plasmons, exemplified by Cu, Ag and Au. Optical excitation of these metal nanostructures at their plasmonic resonance provides a means of controlling temperature at the nanoscale, which can be controlled by the size, shape and organization of the nanostructures. Non-radiative relaxation of optically excited plasmons has enabled a number of photothermal nanotechnology applications that include cancer therapy and drug delivery, pollution control, photocatalysis, thermometry and surgery.

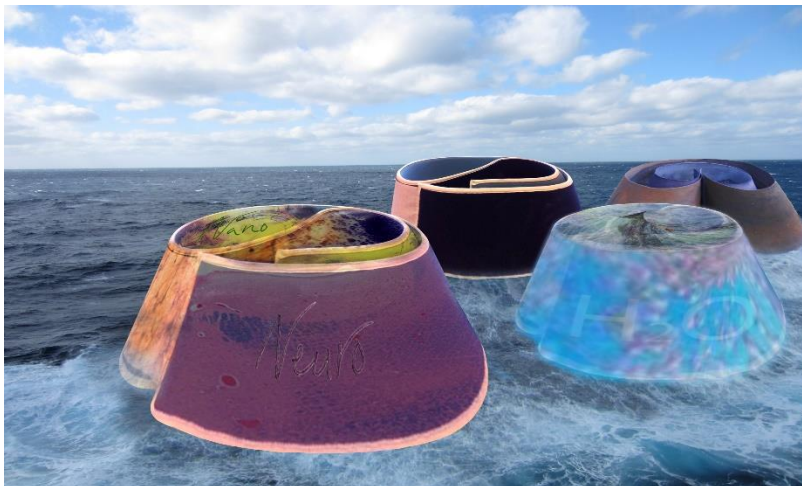
The photothermal effect can also operate through the non-radiative relaxation of phonons when organic or inorganic semiconductors are excited at energies above the electronic bandgap and when metals are excited at intra-band and inter-band energies. These excitations can result in localized heating of individual semiconductor and metal nanostructures in an array or delocalized heating of all the nanostructures in the array through collective thermal effects. The resulting temperature distribution in the array will depend on a host of nanostructure parameters that include, element composition, size, shape and geometrical arrangement, specific heat, mass density and absorption cross-section, thermal conductivity and dielectric constant of substrate and surrounding environment, light intensity, wavelength, polarization, continuous or pulsed illumination, monochromatic or polychromatic nature, and area of the illumination. Photothermal effects in semiconductor and metal nanostructures provide a means of controlling local temperatures enabling for example gas-phase light-assisted heterogeneous photocatalytic splitting of water and conversion of carbon dioxide into fuels such as carbon monoxide, methane and methanol.

Recently, an electro-polymerized black coating of poly-pyrrole grown on a stainless steel mesh, made hydrophobic by surface modification of the poly-pyrrole with a fluoroalkylsilane, was used as a photothermal membrane for local heating of interfacial water to enable water evaporation driven desalination. This solar absorbing membrane was employed in a proof-of-concept all-in-one solar distillation system for producing fresh water from salt water [3]. The evaporated water was transferred by a solar powered fan to a condensing chamber as depicted in the diagram to complete the photothermal desalination cycle.

Interestingly, little has been reported on photothermal desalination, whereby optically excited highly absorbing nanostructures have been integrated into porous membranes to selectively power surface evaporation of water using both the light and heat from the sun. Today there exist quite a large collection of black nanostructures and black nanocomposites based on various kinds of carbons, metals and semiconductors and combinations thereof that could be made

hydrophobic and stable in light and salty water. They could be used to coat the surface of different kinds of porous membranes providing them with the structural and physicochemical properties required for the development of an energy efficient and cost effective photothermal desalination system.

It will be interesting to see how the emerging field of photothermal materials applied to solar powered water desalination develops in the years ahead as the global demand for clean and secure freshwater supplies increases as a result of the combined effects of climate change and droughts, industrial expansion and environmental pollution, population growth, food demand and agricultural needs. In an increasingly thirsty and energy hungry world, maybe it makes more sense for large centralized RO and TD desalination plants to service the water demands of large cities while small decentralized TD ones that make use of photothermal desalination can serve small communities, industries and farms.

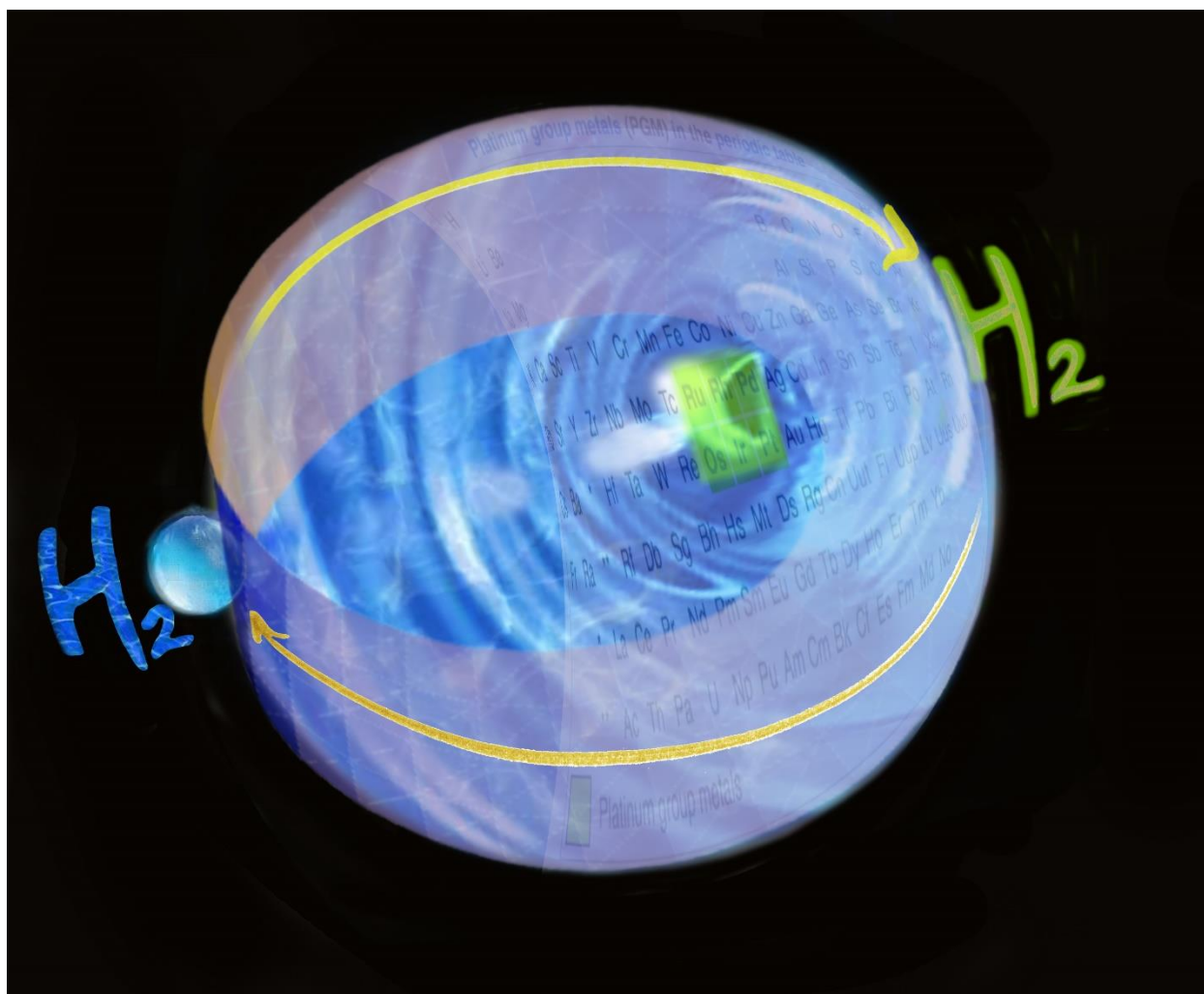


Metaphorming Nature's Desalination Plants. Courtesy of Todd Siler and Geoffrey Ozin, [www.artnanoinnovations.com](http://www.artnanoinnovations.com)

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[3] Zhang, L., Tang, B., Wu, J., Li, R., Adv. Mater., 2015, DOI: 10.1002/adma.201502362



H<sub>2</sub>O to H<sub>2</sub> to H<sub>2</sub>O cycle catalyzed by Pt nanocrystals. Metaphorming the Möbius strip suggesting how Pt can be produced on a large scale - like a common element – serving as the main catalytic metal for processing solar H<sub>2</sub> on a global scale for powering a worldwide hydrogen economy. Graphic courtesy of Todd Siler, [www.artnanoinnovations.com](http://www.artnanoinnovations.com).

## 49. Is it Possible to Produce Enough Pt to Run an Affordable Solar Powered Terawatt H<sub>2</sub> Economy?

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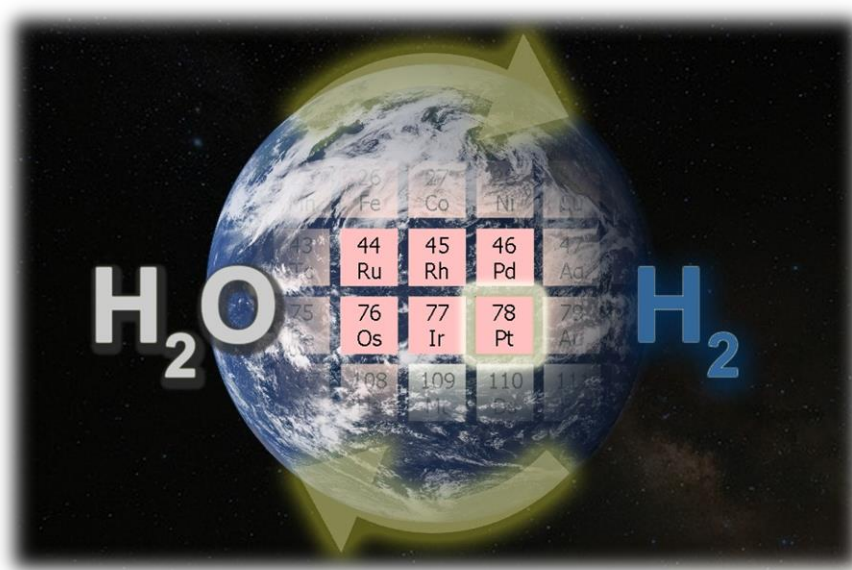
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Hydrogen as a clean energy source for fuel cells in the transportation and power generation sectors, as well as an effective reducing agent for transforming carbon dioxide to value-added chemicals and fuels, could solve some of the adverse consequences of burning fossil fuels that release greenhouse gas into the atmosphere and chemicals that pollute the environment [1, 2].

Today, hydrogen is produced by steam

reforming, gasification and electrolysis. Most of hydrogen is produced from fossil fuels (48% natural gas, 30% oil, 18% coal) while electrolysis of water accounts for only 4%. The electricity to enable water electrolysis has traditionally come from fossil and nuclear sources, which are increasingly being replaced by clean, renewable electrical energy from solar, hydro and wind.

The practical realization of the full environmental and security benefits of clean and renewable hydrogen for use in fuel cells and conversion of carbon dioxide to chemicals and fuels, will necessitate the development of large-scale, low-cost hydrogen generation methods from renewable resources with a minimal carbon footprint. Amongst the different options for



Let's not yet write off rare expensive Pt as the catalytic metal of choice for making solar H<sub>2</sub> on an industrially significant scale to power a global hydrogen economy. Graphic courtesy of Chenxi Qian.

generating hydrogen, the photo-electrochemical approach, which utilizes sunlight to directly split water is considered to be amongst the most promising technologically and economically. Nevertheless, efficiency, figures-of-merit and longevity issues, requiring basic-directed research to improve loss mechanisms and increase electrodes, materials and device performance and stability, ultimately to develop operationally safe systems, remain the most challenging and critically important issues to enable advances in the field [3].

Photo-electrochemistry is an electrochemical technique, which employs light harvesting catalysts most often based on specialized semiconductor and metal nanostructures and combinations thereof. It is a truism that many research scientists, who recognize the axiom of the 'materials dilemma', remain skeptical of finding a practical and efficient photo-catalyst that can enable the light-assisted electrochemical  $H_2$  evolution reaction from  $H_2O$  at a sufficiently large scale to facilitate a TW  $H_2$  economy.

This refers to the challenge often confronted by scientists, engineers, industry and manufacturers trying to discover champion materials for a large scale catalytic process, where the best performers are comprised of elemental compositions in short supply and too pricey while inferior performers consist of earth abundant low cost elemental compositions. This is certainly true for the catalytically active platinum group metals Ru, Os, Rh, Ir, Pd and Pt in nanostructured forms as well as the catalytic sites of diverse classes of molecules, clusters, polymers and materials.

In the case of the photo-electrochemical  $H_2$  evolution reaction from aqueous phase  $H_2O$ , the champion catalyst remains Pt despite much research devoted to find a more abundant cheaper alternative. This is simply because Pt as a  $H_2$  evolution catalyst still has the world-record exchange current density and low Tafel slope. Moreover, Pt is reported to be more durable in acidic environments, which is the common case in photo-electrochemical devices. This illustrates the difficult choice one has to make in translating solar fuels materials science to a technology that could be implemented on a large scale. Should one continue to focus attention on bringing down the cost of rare and expensive superior performance materials like Pt or devote time and effort to improving the poorer performance of common cheap materials?

It turns out not surprisingly that the efficiency of the  $H_2$  evolution reaction sensitively depends on the loading and size of the nanostructured Pt catalyst integrated with the photon harvesting, electron transporting photocathode. In this context, it is pertinent that a recent study has quantified how much Pt is actually required to optimise the  $H_2$  evolution rate in a photo-electrochemistry experiment using an exceptionally well-defined Pt-TiO<sub>2</sub>-Ti-pn<sup>+</sup>Si composite photocathode [4].

In this experiment, the size and loading of Pt nanoparticles were controlled using a sophisticated supersonic molecular beam source that was able to deposit mass-selected Pt

nanoparticles from the gas-phase, with retention of their size, onto the photocathode. From detailed materials characterization measurements and in depth photo-electrochemistry experiments, it was found that the size of the most active Pt nanoparticles for the H<sub>2</sub> evolution reaction was 5 nm at a loading level of 100 ng/cm<sup>2</sup> on the photocathode. For a state-of-the-art over-potential of 50 mV this translated to about 54 tons of Pt in order to create a TW scale photo-electrochemical H<sub>2</sub> generation infrastructure. How often this 54 tons have to be replaced is a crucial question. The issue of a well-designed Pt recycling system is clearly advisable. This tonnage amounts to around 30% of the current global annual production of Pt most of which is currently used in automobile catalytic converters and jewellery.

In terms of known Pt mineral resources (earth abundance  $3.7 \times 10^{-6}$  %) this does not seem like an insurmountable obstacle if it was decided by policy makers, the renewable energy industry and process engineers to establish an economically and environmentally viable TW H<sub>2</sub> clean and green global technology founded upon the photo-electrochemical splitting of H<sub>2</sub>O using Pt as the metal of choice.

It is pertinent to note that it may prove possible to reduce this amount of Pt by many orders of magnitude if the size of the Pt nanoparticles could be reduced from 5 nm to the atomically dispersed state and the catalytic activity for the H<sub>2</sub> evolution reaction maintained if not improved [5]. Encouragingly in this context, a recent report revealed that the readily accessible, nanoporous layered material carbon nitride (C<sub>3</sub>N<sub>4</sub>), can anchor individual Pd atoms at the N sites and is able to function as a thermally stable hydrogenation catalyst for the production of many organic substances [6]. If this breakthrough can be extended to Pt atoms on C<sub>3</sub>N<sub>4</sub>-based photocathodes, this has the potential to reduce the Pt catalyst tonnage requirement by orders of magnitude.

For photo-electrochemical hydrogen generating systems, besides the availability and cost of Pt, techno-economic challenges will also be encountered by constraining the area for water splitting to that of the light harvesting units and the area and cost of required land. The overall cost analysis of this kind of integrated photo-electrochemistry system will have to be compared with the cost efficiency of competing hydrogen producing technologies that employ Pt electro-catalysts based upon electrically integrated photovoltaic-electrolysis systems and grid integration of decoupled photovoltaics and electrolysis systems [7].

It is worth noting that the production of Pt since the early 2000s has varied between just over 150 tons to about 220 tons. Obviously there is scope for further production if necessary. The price has been volatile. It was stable from 1992 to 2000 and then steadily rose until it touched about \$2,252 per ounce in 2008. It then fell off a cliff later in 2008 falling to \$774 per ounce. It has since gone up and down, as high as \$1,900 per ounce and today stands at about \$950 per ounce [8]. The price of Pt seems to be related to the fortunes of the economy, when the economy is good and growing so does the price of Pt. A big question is, do we want to base a H<sub>2</sub>



economy on a rare element like Pt, where countries could be held to ransom on either the price or supply rather like the current situation with oil?

Perhaps, when more research scientists challenge the doctrine of the 'materials dilemma' by using new value propositions with economic models for producing Pt, they may entice business and industry leaders to produce Pt as if it were a 'common element', one that was absolutely essential for creating a sustainable future.

Currently, fossil fuel industry methods remain economically advantageous, despite the adverse consequences on our environment and climate. A transition to clean energy technologies will take time, nevertheless many companies have already realized the benefits of this ground-breaking change. An impressive example of the conversion from fossil to H<sub>2</sub> fuel is seen with Toyota. After more than twenty years of rigorous research and development they have manufactured automobiles with H<sub>2</sub> fuel-cell powered engines to become commercially available later this year [9]. To enable this transition, H<sub>2</sub> fuel stations as well as H<sub>2</sub> generators integrated into automobiles will have to be rapidly developed.

It seems that we should not yet write off rare expensive Pt as the catalytic metal of choice for making solar H<sub>2</sub> on an industrially significant scale to power a global hydrogen economy. If Pt is selected as the catalyst of choice, there should as well be alternative choices of cheap and abundant elemental compositions, which can quickly take the place of Pt as a photo-catalyst. We shouldn't stop looking for cheaper alternatives as there's a whole bunch of interesting alternative materials out there.

To invoke the wisdom of the American novelist, Mark Twain: "It ain't what you don't know that gets you into trouble. It's what you're sure you know that does."

If we're *so sure* that Pt is too rare and expensive to process on a global industrial scale, we may be adding to our troubles, rather than resolving them with this nano solution.

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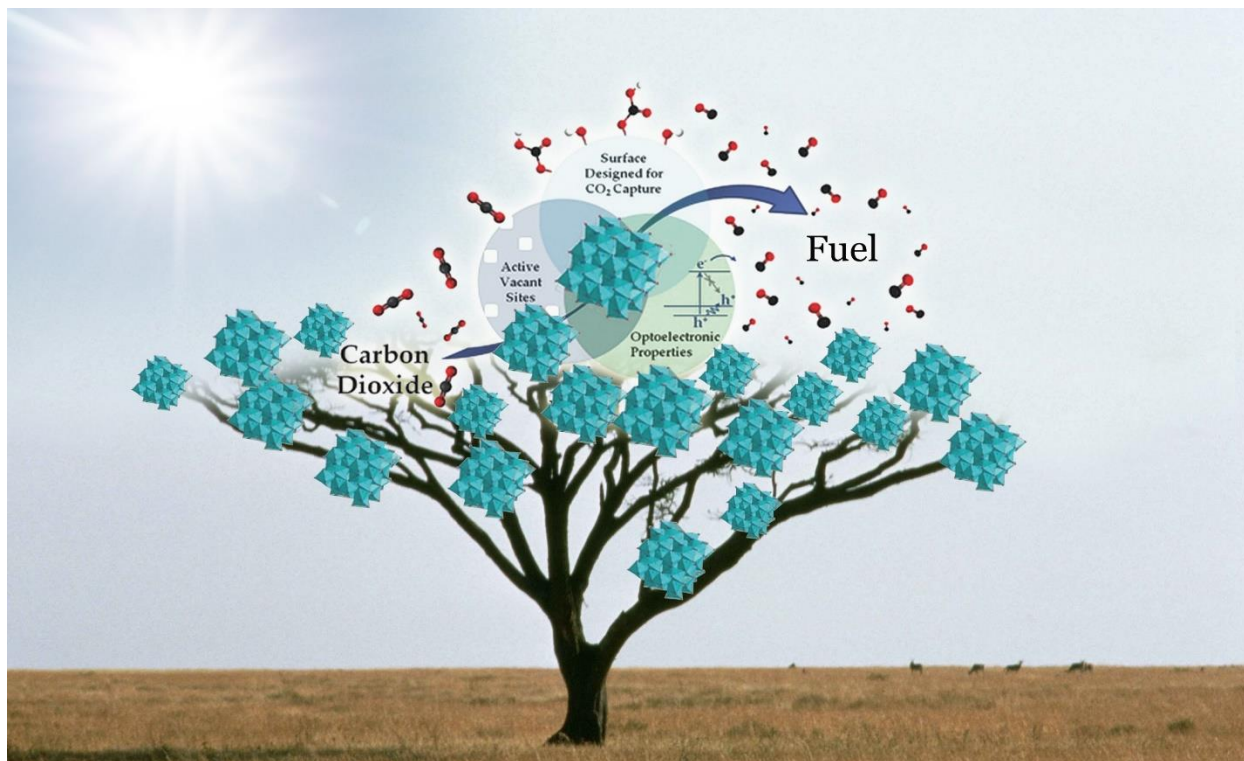
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## 50. Solar Fuels Cluster University of Toronto

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Solar fuels tree – graphic courtesy of Chenxi Qian

# Solar Fuels Cluster University of Toronto

Geoffrey A. Ozin

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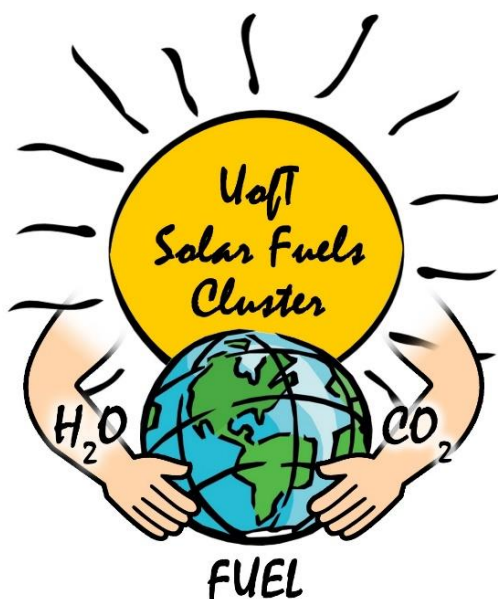
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## Golden Opportunity

After more than 45 years of research in the field of materials chemistry I was given the interesting opportunity in 2012 to write invited monthly opinion editorials for the Materials Views section of the VCH-Wiley family of materials journals. This invitation from the editor of Advanced Materials, Peter Gregory, provided me with a superb and irresistible vehicle to express opinionated and provocative views about hot button issues in materials chemistry, my major field of interest.

I must confess that dreaming up and composing these editorials has been a valuable lesson in how to write scientific and technological critiques about timely and controversial topics for a public forum, a pastime less risky for a senior scientist, such as myself, than a junior one. I hope the readers have enjoyed these editorials as much as I had fun writing them.

After having produced 49 of these opinion editorials on a variety of contemporary topics, the collection of which can be found at <http://www.materialsviews.com/category/opinion/>, I thought it worthwhile and exciting for my 50<sup>th</sup> to compose a Golden Anniversary editorial about my current all-consuming passion - the creation, mission and activities of the University of Toronto Solar Fuels Cluster that I have had the good fortune to be able to spearhead over the past three years.



University of Toronto Solar Fuels Cluster – Solar Fuels from the Sun Not Fossil Fuels from the Earth. Graphic courtesy of Chenxi Qian.

## An Important Historical

**Note** The discovery of insulin by Banting and Best at the University of Toronto as a cure for diabetes in 1921, is hailed as one of the biggest discoveries in medicine, saving the lives of millions of people around the world suffering from this life threatening disease. This miracle breakthrough was recognized by the Nobel Prize in Physiology or Medicine in 1923 for its UofT inventors



1923 Nobel Prize for the discovery of insulin, Banting and Best, University of Toronto

<http://www.nobelprize.org/educational/medicine/insulin/discovery-insulin.html>. Income from the manufacture and commercialisation of insulin has been used by the UofT to fund leading-edge research under the auspices of the Connaught Fund, which rewards research that meets society's challenges, <http://connaught.research.utoronto.ca/>.

Recently they created a \$1M Connaught Global Challenge Award to expand and enrich research directed at grand challenges of global importance to humanity, <http://www.research.utoronto.ca/research-funding-opportunities/connaught-global-challenge-award/>. The UofT Solar Fuels Cluster are the 2015 recipient of this prestigious award for their project, The New CO<sub>2</sub> Economy – Solar Energy Enabled Closed Carbon Cycle, [www.solarfuels.utoronto.ca](http://www.solarfuels.utoronto.ca), [www.news.utoronto.ca/could-carbon-dioxide-be-solution-climate-change](http://www.news.utoronto.ca/could-carbon-dioxide-be-solution-climate-change).

The parallels between these seemingly different scientific challenges are rather poetic. Insulin enables the body to convert and store blood sugar as a fuel to provide energy on demand; while the natural process of photosynthesis converts and stores sunlight energy in the form of sugars produced from CO<sub>2</sub> and H<sub>2</sub>O, which energize plants and ultimately produce the fossil energy our global society currently depends on. Our mission is to convert and store



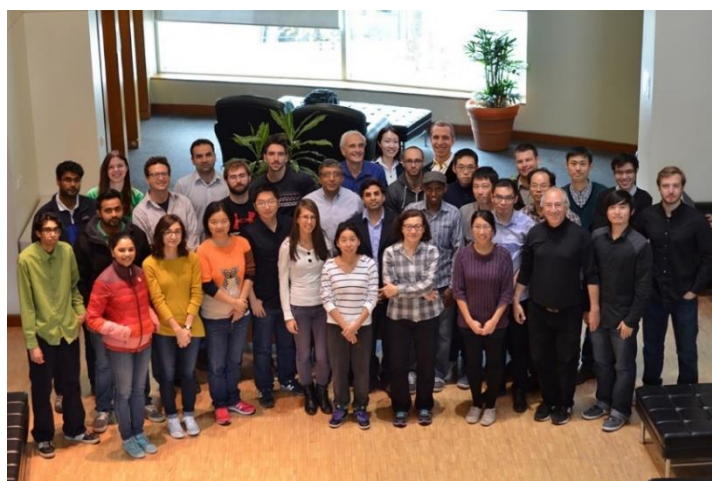
Illustrations on the utilization of CO<sub>2</sub>: the illustration depicts the grand challenge that the global community must confront in the face of CO<sub>2</sub> induced climate change in order to achieve a sustainable environment, a renewable energy supply and a carbon neutral economy. Graphic courtesy of Chenxi Qian.

sunlight energy in synthetic Solar Fuels produced from  $\text{CO}_2$  and  $\text{H}_2\text{O}$ , which could help end our dependence on fossil energy and solve the intertwined climate, energy and environment problems confronting humanity today. Just imagine how sweet it is!

**Challenge** While the stored chemical energy in coal, oil and natural gas has enabled the rapid rise of modern civilization, the burning of these legacy fossil fuels with its accompanying anthropogenic  $\text{CO}_2$  emissions is occurring at a rate that is outpacing nature's carbon cycle. The effect of these emissions is now considered by the Intergovernmental Panel on Climate Change [1] to be high to very high risk and could lead to a rapid and massive upheaval of human society unless a global scale solution to the intertwined effects of fossil fuels, energy security, environmental protection and climate change is found. In this context, a recent modeling research study concluded that most of the world's fossil fuel reserves need to stay in the ground over the period 2010-2050 to not exceed the  $2^\circ\text{C}$  warming limit and avoid the risk of dangerous global warming [2]. Clearly, climate change is a complex technological, environmental, societal, economic and political issue without a simple solution.

To address this challenge, the UofT Solar Fuels Cluster, as well as many other talented researchers and top rank groups around the world, are targeting innovative technological solutions that focus on the capture and conversion of  $\text{CO}_2$  into renewable fuels using sunlight as the energy source,  $\text{H}_2\text{O}$  and/or  $\text{H}_2$  as the co-reactant. This transformative research paradigm treats  $\text{CO}_2$  as a renewable resource rather than a waste product, turning  $\text{CO}_2$  from a liability to an asset, thereby providing a chemical platform for developing a carbon-neutral  $\text{CO}_2$  economy that can enable a sustainable future for humankind. Progress of research in this area is gathering momentum and will probably continue to do so for the foreseeable future.

It is worth commenting that in this endeavor there exist two schools of thought: (i) an aqueous process, which is likened to artificial photosynthesis practiced by the leaf, with more than four decades of research activity aimed at developing laboratory scale mimics and ultimately scale-up and (ii) a gas-phase process, which is more akin to heterogeneous photocatalysis, of a more recent vintage that more closely resembles heterogeneous catalysis practiced by industry. The latter approach is the main focus of attention of the UofT Solar Fuels Cluster.



University of Toronto Solar Fuels Cluster,  
[www.solarfuels.utoronto.ca](http://www.solarfuels.utoronto.ca)

**UofT Solar Fuels Cluster** This multidisciplinary team of accomplished academic researchers and budding young scientists have collectively risen to the grand challenge of discovering new materials and processes that can enable solar powered heterogeneous catalytic conversion of gaseous CO<sub>2</sub> to value-added chemicals and fuels. The team comprises the full spectrum of materials chemists, materials scientists and engineers, chemical engineers, and electrical and optical engineers. Between them they have the combined experimental and theoretical expertise to achieve the following:

- (i) synthesize photoactive nanostructured materials;
- (ii) determine their structures and measure their properties;
- (iii) computationally model and guide experiments on light-assisted heterogeneous catalytic conversion of CO<sub>2</sub>-to-Fuel; and
- (iv) design and build photoreactors to evaluate the catalytic performance of photoactive materials for the conversion of gaseous CO<sub>2</sub> to chemicals and fuels using sunlight as the source of power.

**Talent Pool** Another important target for the UofT Solar Fuels Cluster is the recruitment and training of highly qualified personnel, who will not only contribute actively to the solar fuels research program, but who will consequently begin to grow a unique solar fuels renewable energy talent pool, as the cornerstone of a new global cleantech subsector in conversion of CO<sub>2</sub> to chemicals and fuels.

**The Cluster and Industry Partners** The long term objective of the research of UofT Solar Fuels Cluster is to function as a hub for a global network of solar fuels scientists, engineers and industry partners. The network we have built encompasses nationally and internationally renowned scientists, engineers and economists, working in fields that include:

- (i) photochemistry and photoelectrochemistry of nanoscale inorganic materials directed towards the generation of solar fuels;
- (ii) design of solar fuel materials tailored to catalyze specific reactions by combining high-performance computation with precise synthetic chemistry;
- (iii) development of theory, models and algorithms for the solution of fundamental and practical problems in the area of solar fuels process development, assessment and production; and
- (iv) environmental economics and emissions trading aspects of climate change and renewable energy.

The UofT Solar Fuels Cluster will deepen collaborations with national and international industry partners, the ultimate goal being to facilitate the transition of laboratory-scale solar fuels



experiments to a prototype pilot demonstration unit that will be instrumental for the development of an efficient and scalable technology to provide future generations with sustainable solar chemicals fuels using CO<sub>2</sub> as feed stock.

As the collaboration with Industry Partners progresses, the UofT Solar Fuels Cluster and our Industrial Partners will also need to communicate to politicians and governments the viability of this CO<sub>2</sub>-to-fuel conversion strategy and to persuade them to adopt it as a goal. At the same time, the public should be informed and educated that this strategy is a viable economic and environmental solution to reduce greenhouse gases.

**Advances and the Future** During the first three years of their solar powered CO<sub>2</sub>-to-Fuels research, the “evolutionary” phase, the UofT Solar Fuels Cluster have identified a promising series of nanostructured solar fuel materials, and developed appropriate research methodologies and established the instrumental facilities for their structure characterization, property measurements and catalytic testing [3-7].

Today, champion rates for light-assisted conversion of gaseous CO<sub>2</sub> to hydrocarbon fuel molecules achieved by the UofT Solar Fuels Cluster are within an order of magnitude of the mol/h·g<sub>cat</sub> target rate. Based on these advances it is envisioned that with continued research and development, fuels made in a solar refinery could gradually replace those produced in a refinery powered by fossil fuels [8].

The UofT Solar Fuels Cluster and their collaborators will now be involved in major activities aimed at expanding upon and enriching the accrued knowledge of published and patented work gained by the cluster during the evolutionary phase to transition it to the revolutionary phase, aimed at a solar fuels technology [3-7]. In this “revolutionary” phase of the research, the goal is to build upon the basic materials science and engineering experiences they have gained for solar powered conversion of gaseous CO<sub>2</sub> to fuels, to combine materials and processes that can achieve technologically significant conversion rates of mol/h·g<sub>cat</sub>. The target is the discovery and development of earth-abundant, low-cost materials able to effectively harvest sunlight, capture CO<sub>2</sub> and efficiently drive a cost-effective gas-phase heterogeneous photo-catalytic CO<sub>2</sub> conversion process in a solar refinery to form a transportable fuel at a technologically significant rate.

To this end, the focus of their continuing research will be on the discovery of next generation solar fuel materials, through both experimental and theoretical methods, and development of new and improved photo-reactors and processes. This continuing research will comprise:

- (i) discovery, structure determination and property measurements of nanostructured materials active for light-assisted, gas-phase CO<sub>2</sub> photoreduction;
- (ii) evaluation of conversion rates and efficiencies for production of solar fuels, such as CO, CH<sub>4</sub>, CH<sub>3</sub>OH by light-assisted, gas-phase heterogeneous catalytic reduction of CO<sub>2</sub>; and

- (iii) experimental and computational studies of surface chemistry, energetic, kinetics and mechanisms pertinent to these photoreactions.

These studies will be complemented by:

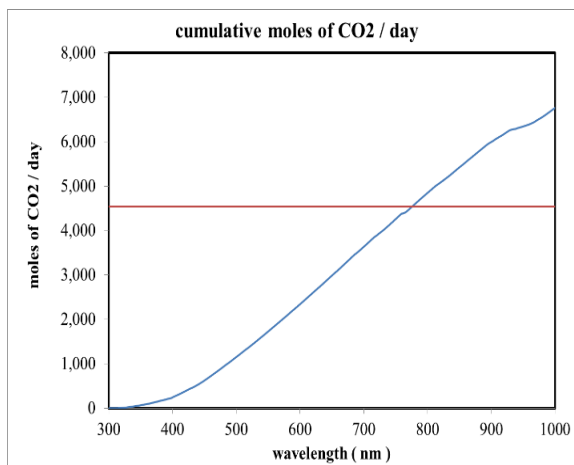
- (iv) optimization of materials catalytic performance;
- (v) developing material fabrication technologies for scaling;
- (vi) development and testing of prototype pilot photoreactors;
- (vii) evaluation of solar concentration on CO<sub>2</sub>-to-Fuel conversion rates, efficiencies, mass and energy balance; and
- (viii) life cycle process modeling to assess material, energy and economic flows and hence the feasibility of making a solar fuels production facility from CO<sub>2</sub> for the most active materials.

**CCEMC Grand Challenge – Innovative Carbon Uses** In 2009 the Alberta based Climate Change and Emissions Management Corporation (CCEMC) was established to reduce greenhouse gas emissions and help Alberta adapt to climate change through the discovery development and deployment of clean technology. CCEMC was created as a key part of Alberta's Climate Change Strategy and movement toward a stronger and more diverse lower-carbon economy. CCEMC have issued a Grand Challenge to the science and engineering research community around the world to devise innovative materials and processes that can enable the conversion of CO<sub>2</sub> emissions into value-added products and markets [www.ccemc.ca/grand-challenge](http://www.ccemc.ca/grand-challenge). Funding of \$35M has been committed by CCEMC in a three stage competition to achieve this goal. Round 1 attracted 347 submissions from 37 countries and seed funding of \$500,000 was awarded to 24 projects based on their chances of success in achieving this objective. Round 2 has recently been announced (closes January 2016) and a second world wide intake on technologies is being considered along with advancements of the original 24. Five development grants each of \$3M will be awarded for projects that can demonstrate annual net reductions of greenhouse gas emissions of 1 net Megatonne together with a viable business plan for implementing and deploying the technology in Alberta. In the final Round 3, an award of \$10M will be made to a demonstrated technology able to yield products that result in a net reduction of greenhouse gas, and is judged to be scalable and economically viable and is best positioned for commercial deployment. .

**Carbon XPRIZE - Reimagining CO<sub>2</sub>** A \$20 Million carbon XPRIZE sponsored by NRG COSIA is a global competition challenging scientists and engineers to develop disruptive technologies that will convert CO<sub>2</sub> emissions from power plants and industrial facilities into valuable products like building materials, alternative fuels and other items that we use every day [www.carbon.xprize.org](http://www.carbon.xprize.org).

Teams will compete in three rounds for \$20 million. The competition has two technology tracks one involving the development of a test platform at a coal power plant and the other at a natural gas power plant. Each will operate as a separate competition on the same timeline. Teams in Round 1 will be appraised on technical and business information concerning the technology, process, products, and implementation to achieve the practical requirements and defined goals of the competition. Up to 15 teams in each track will move onto Round 2 with a focus on technologies that meets minimum CO<sub>2</sub> conversion requirements in a laboratory demonstration. Five teams selected for Round 3 will share a \$2.5M milestone achievement purse. The grand challenge is to scale and demonstrate the effectiveness of technologies working with real-world flue gas emitted by operating power plants. The technology that wins the \$7.5M grand prize will have to achieve performance metrics based on a minimum CO<sub>2</sub> conversion rate of 200 kg/day (4,600 moles/day) using a maximum land area of 2,300 m<sup>2</sup>.

**Challenge Perspective** Let's imagine targeting solar powered conversion of CO<sub>2</sub>-to-CH<sub>3</sub>OH, a reaction which consumes 6 e<sup>-</sup> for each molecule of CO<sub>2</sub> converted assuming a conversion efficiency of 10% and 8 hours of operation each day. The analysis involves determination of the number of photons per m<sup>2</sup> to provide the number of CO<sub>2</sub> molecules converted per m<sup>2</sup> which provides the daily conversion of CO<sub>2</sub>. One arrives at the conclusion that to win the carbon XPRIZE, one would need to make use of harvested light up to 780 nm as seen in the plot of cumulative moles of CO<sub>2</sub> converted per day as a function of wavelength.



The carbon XPRIZE challenge for solar powered conversion of CO<sub>2</sub>-to-CH<sub>3</sub>OH, courtesy of Tom Wood.

Imagine the bounty of new materials we can create by optimally harvesting light in the same effective and efficient way nature does to sustain its world of energy systems. We already have the key knowledge and applied know-how we need to make continuous breakthroughs that can advance everything from solar electricity to fuel cells to battery power. Virtually everything we need for creating a sustainable future is within our minds and fingertips that control our most ingenious technology to this end. We now simply need to work together in grasping the CCEMC Grand Challenge and Carbon XPRIZE and realizing the potential of the NanoAdvantage!

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by the Ontario Ministry of Research Innovation (MRI); Ministry of Economic Development, Employment and Infrastructure (MEDI); Ministry of the Environment and Climate Change; Connaught Innovation Fund; Connaught Global Challenge Fund; Natural Sciences and Engineering Research Council of Canada (NSERC).

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# 51. A Global CO<sub>2</sub> Utilization Strategy that Benefits Everyone and Earth

Geoffrey A. Ozin

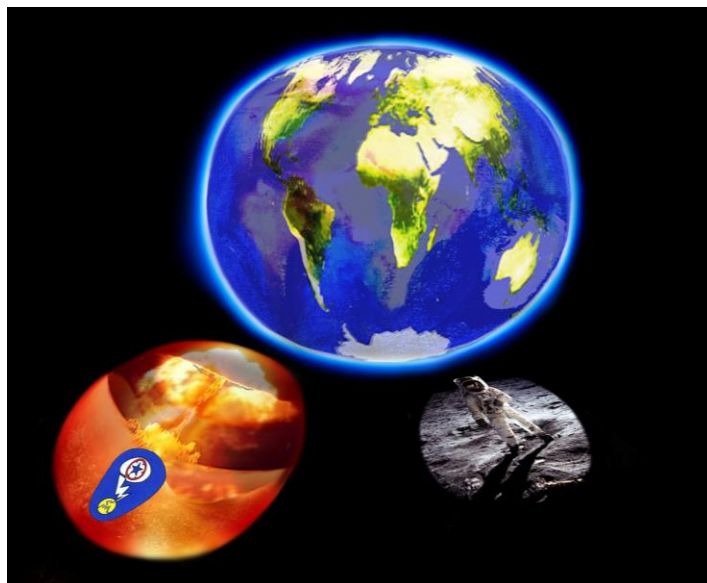
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Solving the looming climate change problem caused by anthropogenic greenhouse gas emissions differs from other unprecedented, large-scale collaborations that have changed our world dramatically.

It “sharply” differs because it’s a global challenge driven by compassionate intentions and understanding expressed by many nations that now recognize the science substantiating the foreseeable peril. Failure to find an answer in a timely manner could have inconvenient consequences for the whole world.

The photomontage depicts contrasting examples of urgent yet seemingly impossible problems and challenges that brought together groups of the brightest scientists and engineers working towards a common goal. The most prominent 20th century examples include The Manhattan Project and NASA’s Apollo 11 lunar landing. These projects, different in scale and scope, are unmistakably distinguished by the common associations invoked by man’s most destructive and constructive potential.



This composite image, courtesy of Todd Siler and Geoffrey Ozin [www.artnanoinnovations.com](http://www.artnanoinnovations.com), visually implies that from two past unprecedented large-scale collaborations, a contrast of two destructive and constructive events, a new and benevolent enterprise, “a global CO<sub>2</sub> utilization strategy”, can leverage the collective knowledge and wisdom gained from these earlier works to change the world in an entirely compassionate and environmentally responsible way. The “visual weights” of these images emphasizes the Earth and everything we’re doing now to preserve it while acknowledging the ever present reality of nuclear war, which is symbolic of all kinds of “disruptive” technologies we choose to create for defensive reasons. Also, implicit in the images is the visceral feeling that if our world leaders do not choose wisely now, we can end up inadvertently and irreversibly upsetting our planet.

They express our deep conviction: “anything is possible” when we’re willing and able to work collaboratively in solving major problems and meeting our most pressing challenges by focusing our full attention on them.

The climate change problem is however, very different from the other two problems. The first two had a definite end and they agreed what they wanted to achieve. There is scientific agreement that net global anthropogenic emissions need to be reduced to zero, although disagreement on the schedule due to different views on the temperature increase target (1.5 or 2 °C) and the probability of achieving the target (66%, 50% or less).

The Global CO<sub>2</sub> Utilization Project is a new and benevolent endeavor with a message of hope and higher awareness. It is founded on the premise that CO<sub>2</sub> emissions can be employed as a feedstock for the synthesis of chemicals and production of fuels. The capture, storage and utilization of CO<sub>2</sub> emissions for chemical synthesis achieve three desirable goals: (i) less CO<sub>2</sub> is emitted into the atmosphere, (ii) a safe supply of chemicals is provided and (iii) the demand for secure energy is satisfied. This paradigm makes CO<sub>2</sub> capture, storage and utilization potentially a “partial solution”, treating it as a commodity chemical to be used as a valuable reserve instead of a waste, an asset rather than a liability.

Resolving the problem will necessitate a global alliance of universities, industries and governments working together to find the best solution for a common and generous cause that can leverage the collective knowledge and wisdom gained from these earlier collaborations.

The climate change problem is on much too large a scale to be solved by a single country. For the first time in the history of humankind we are faced with the existential challenge of having to reduce CO<sub>2</sub> emissions produced by our fossil based resources, an inconvenient necessity considering



This photomontage unites the vision of a global CO<sub>2</sub> utilization strategy with a fuel synthesis plant that enables closing the carbon cycle. Images courtesy of Todd Siler and Geoffrey Ozin, [www.artnanoinnovations.com](http://www.artnanoinnovations.com), and Matthias Gommel and Peter Weibel, “GLOBALE: Exo-Evolution” exhibition at the ZKM Center for Art and Media in Karlsruhe, Germany, 31.10.2015 to 28.02.2016.

they have miraculously created and energized our global economy since the industrial revolution. But paradoxically, fossil fuels that empower our globalized society now threaten its future.

Fortunately, a partial solution does exist. It is founded upon the vision of a global CO<sub>2</sub> utilization strategy. We already have the technology in place to realize this vision. There are currently many emerging companies and established industries around the world that use CO<sub>2</sub> from different sources to produce megatons of chemicals, materials and fuels. These industrial processes and products are changing our way of thinking about CO<sub>2</sub>, not as a waste product to fear, nor as a costly liability but instead as a valuable asset.

All we need to do is put the policies and institutions, and public and private investment in place to increase production of these commodities by CO<sub>2</sub> utilization at industrial facilities around the world. A key question however, is how much capacity and market demand is there for CO<sub>2</sub> utilization products? Estimates from different sources of current market demands for products seem to favor around 5% conversion of global CO<sub>2</sub> emissions into synthetic chemicals and about 10% into synthetic fuels, [www.co2chem.co.uk/carbon-capture-and-utilisation-in-the-green-economy](http://www.co2chem.co.uk/carbon-capture-and-utilisation-in-the-green-economy). With continued research and development it is expected that the market potential for manufactured CO<sub>2</sub> built products will grow.

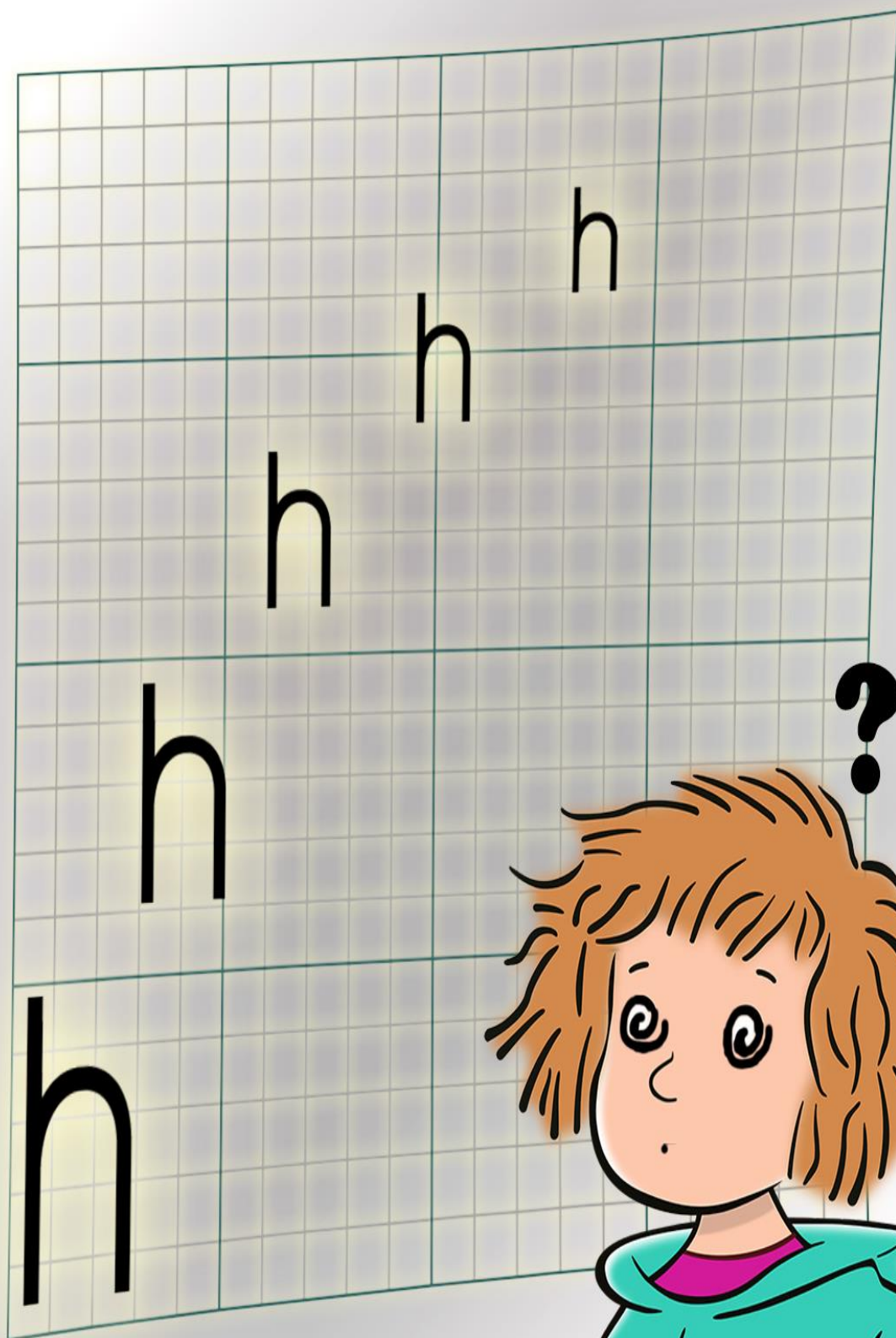
For illustrative purposes, in a scenario where 100% urea, 30% minerals, 20% chemicals and polymers, 10% methanol, and 5% diesel and aviation fuels are made from CO<sub>2</sub>, this would be equivalent to 83% of the IPCC 2030 global emission reduction target (Armstrong, K. & Styring, P., *Frontiers in Energy Research*, 3, 8, 2015; Lim, X., *Nature* 526, 628, 2015; Scott, A., *Chemical and Engineering News*, 93, 10, 2015). While carbon capture and utilization today may not be a complete solution it is complementary to carbon capture and storage and together they can play an important role in helping to close the carbon cycle.

The consensus in these reports is that CO<sub>2</sub> utilization can be commercially viable with short turnaround times for profits on investment. Even with a tax on carbon and government subsidies, this seems like a small price to pay to help commodities made from re-cycled CO<sub>2</sub> establish a firm footing in the global economy to ensure that they stay competitive with those made from finite fossil resources.

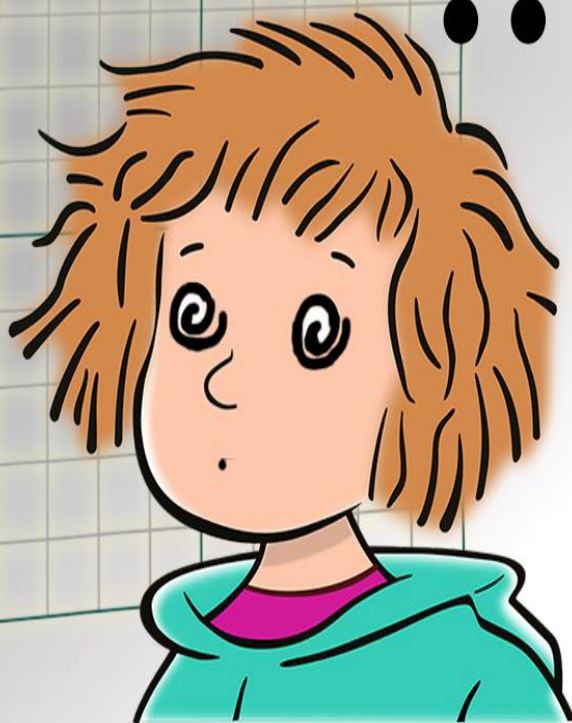
This new and benevolent collaborative endeavor can change the world, but only with a world of global citizens cooperating and committed to change. Science-technology-industry-government working in a concerted manner are “not” enough. People must champion and sustain these efforts to make it work. We know what we need to do, we know how fast we need to do it, and we know the energy and economic balances to enable a carbon neutral sustainable world. The



question is do we have the will to work together and do it in a timely manner before an irreversible and deleterious climate event occurs and changes our way of life?



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## 52. h

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*“When a measure becomes a target, it ceases to be a good measure”*

Goodhart’s law

It is probably safe to say that the research enterprise, especially in academia, will see profound changes in the next decade. As outlined in the commentary by Whitesides and Deutsch,<sup>1</sup> part of the reason will be the changing accountability towards tax payers. As life is becoming tougher for the average citizen of the western world, the research enterprise represents a uniquely vulnerable target



(in certain countries more than others) for the increased thirst for accountability. Ultimately, different people have different angles on this, but the trend appears robust and enabled by the lack of complexities that accompany any aggression to the ivory tower. The repercussions of cutting science budgets are less politically complex to manage than cutting other types of inefficiencies that have, in many cases, “political immune systems”. Our community of scientists is (or act as if we would be) oblivious to these dynamics and is usually contented to claim that we ought to be supported due to the very simple and self-evident (to us scientists at least...) fact

that research and development, in one form or another, are the reason why we are not living in caves anymore. This unwillingness to engage with all the complexities of science's place in society, makes most of us blind to the long term repercussions of our *modus operandi*. Ironically, the class of people that most prides itself for having a long term vision, is, in my view, becoming victim of a shortsightedness that, as I will try to postulate here, will bring havoc to our most valuable asset: credibility.

A trend that hasn't been discussed sufficiently in my view, is our society's shift towards transparency. For better or for worse, because of technological developments, what we do and what we say are becoming increasingly easier to monitor and observe and frighteningly easier to broadcast for the world to see. This has, of course, led to an increasing volume of information to which our society has become addicted. As all addicts could testify, what gave you a high a year ago is not sufficient anymore. In the same manner our society has become more and more receptive to scandals, negativity and buzz. The increasingly excitable nature of society is driving viral patterns. The way in which science is covered in the news is an example of this. The facility with which information is broadcast makes "news" extremely easy to produce to the voracious public.

How does this connect to science and to what we do?

We are exposing science by *de facto* embracing a model of accountability that we should be (at least from an historical and philosophical perspective) concerned with, the model of "publish or perish". This has been replaced by an even less sophisticated incarnation represented by the h-index which is defined in the following way: "an author-level metric that attempts to measure both the productivity and citation impact of the publications of a scientist or scholar. The index is based on the set of the scientist's most cited papers and the number of citations that they have received in other publications".<sup>2</sup> Some however believe that publication numbers are just as important as h. Proponents of the h-index would say that the h-index is the antidote to our obsession with publication numbers without realizing that it didn't work this way. While "publish or perish" could have been interpreted constructively (as Faraday did) to mean that finished work must find its way to the public or it might as well not exist, the current model leaves no room for interpretation: here is the handle and here is how to crank it. Now crank it!

With the globalization of science and technology, explosion of research scientists and research institutes, proliferation of new journals and easy access to the internet, we find ourselves exposed to a system that produces too many papers too fast. We are all suffering from information overload, 'infobesity', making it impossible to keep abreast of developments within and around ones chosen field, let alone tangential interests. To compete successfully in this system, where your evidence of esteem is measured by the number h and the publication numbers, there is a rush to publish in the elite journals from a rapidly growing pool of scientists being fed by the emerging economies. Inevitably, this has resulted in increasing rates of

submission of papers to these journals forcing very low acceptance rates with the majority being relegated to lower impact journals. Faced with an excess of information, there is a tendency for researchers to read and cite mainly those papers that make it into the elite journals. This creates a system of citations that is rigged to mainly enhance the impact of papers that make it into the elite journals at the expense of many excellent papers that are demoted to second and third tier journals - the need to publish in elite journals only truly affects a small proportion of the scientists who actually have a shot at it. It's a self-perpetuating system that skews the impact of science.

Unfortunately, we are showing poor vision by not realizing that these numbers, if held to any value, become metrics that are now extensively used by policy-makers to calculate return-on-investment on research, quantify opportunity costs and applying economics to science in an effort to improve efficiency (however that is calculated) through the principles of capitalism. How does one assess return on investment on time scales where the research outcomes are still in the process of being digested, appreciated and understood by the community? The cycle where a politician is in office is 3-7 years whereas the time for a scientific topic to mature is 1-1.5 decades. While I am not an economist I am concerned that the principles of capitalism might not hold water when value cannot be quantified precisely (as it is the case of knowledge creation as well as education). Even if we decide to embrace a business approach to scientific research, we should probably remember Goodhart's law in economics<sup>3</sup> that "when a measure becomes a target, it ceases to be a good measure" or Campbell's law in sociology<sup>4</sup> that "the more any quantitative [social indicator](#) (or even some qualitative indicator) is used for social decision-making, the more subject it will be to corruption pressures and the more apt it will be to distort and corrupt the social processes it is intended to monitor."

Yet, this is not what I am most concerned about. The backbone of science is trust. There is nothing else, really. The entire system is based on it, starting from the scientific method and the concept of reproducibility. Reproducibility, brought up by Robert Boyle as a concept in the 1660s, set a gold standard for scientific experimentation, i.e., all the empirical findings, arising from observing nature and drawing conclusions, must be verified by independent replications. In this sense, researchers could trust the scientific publications providing sufficient detail regarding protocols, procedure, equipment and observations. This is the narrow sense. On the other hand, and more generally speaking, trust is also a fundamental part of the leverage that we still have on the public. Many are willing to pay for accurate information about what to do and what not to do. Anybody who dealt with extension services of universities, and the role universities have in advising the population can appreciate this. In a world like ours subject to an overdose of information, I expect trustworthiness to become an increasingly valuable currency, and one that could, if protected, help sustain funding to science.

But in our search for fairness and feelings of accomplishment we have got ourselves in a pit from which it will be hard to get out. The pressure that used to be exerted among us to publish more and in better journals has become now a pressure from the outside. And as the basic tenets of competition dictates, the bar on whatever metric you have chosen constantly moves upward. But as we all know, the bar for productivity and quality cannot keep rising infinitely. The system is rigged, unsustainable, and most of us have the nagging feeling that the quality of publications is not being maintained or even going down. At the same time, this has increased the pressure on the youngest members of our community to the point that it is becoming almost common for assistant professors in high intensity research-driven universities to divorce due to stress during the time they are striving to achieve tenure.

Most troubling is the fact that, in a search for the quick publication (and anyone who has tried to tackle real scientific problems know how ludicrous this notion really is) and the high impact factors, I have started noticing, beside the well-known drastic increases in the reported cases of scientific fraud, an increase in what we would probably consider (in a very academically appropriate way) “misrepresentation”. I am not alone with this observation.<sup>5</sup> Deceptive citations, suggestive writing and other dubious strategies, are becoming increasingly common (at least in my recent experience) in the literature to ignore, deemphasize, mislead, slant or obfuscate prior work in order to claim more impact for the publication at hand. Of course, these cases are never going to be indicted as fraud because they are not frauds. The data is real, the work is real, and the necessary citations are somewhere in the references. But the devil is in the details, isn't it?

I have been around long enough to know that this type of behavior is as old as the world. I know many of my colleagues would argue one of four things: i) this has always happened and it has never compromised science, ii) that science will eventually self-correct and that the really important claims will be double checked (everything else will not be checked because it doesn't matter), iii) that I should not be talking about this and disturb the peace, and (this for the more feisty ones) iv) that I might be bringing this up because I must be concerned about my h-index and making sure I can always find someone whose impact is lower than mine.

Furthermore, the situation will get worse with the changes in teaching methods to ones which are more internet-based. There be less personal contact and less chance to assess a student through day-to-day contact. There was also recently a disconcerting story about an epidemic of student cheating in British Universities which made the front page of The Times: "Almost 50,000 students at British universities have been caught cheating in the past three years amid fears of a plagiarism “epidemic” fueled disproportionately by foreign students.”<sup>5</sup> While this number only represents about 2% of the British student population and probably underestimates the actual amount of cheating, it gives concern that the problems faced at the research level in universities is not going to go away, but only get worse, unless tough action is taken. Universities often turn a blind eye to this type behavior because of the fear that fees or funding will be lost.

My take on this is that these arguments fail to consider the changing landscape of science in society. The increased transparency that is happening will make these type of behaviors increasingly evident and increasingly known to the public. Peter GöThe chief editor of *Angewandte Chemie International Edition* has echoed these concerns. His view is that unacceptable practices, admittedly amongst “black sheep”, are leading to a general suspicion of scientists that is spreading through the offices of journals and funding organizations<sup>6</sup>. The cost in terms of lost trust will be, I fear, horrific with very serious repercussions for our ability to provide our best and brightest with the resources we have been given and entrusted with to do research.

Here is what I think we could do, as a community, to help buck this trend. I take inspiration from previous comments by Whitesides and Deutsch<sup>1</sup> and Heller<sup>7</sup> who have written about some of these issues with greater clarity and diplomacy than I ever could.

1. Shift the focus from “how much” and “where” to “what”. At my age, I find frustrating how difficult it is for our community to focus on the hard questions. And one of those hard questions is “what have you discovered?” Few of us ever like to be asked that. You’ll not find this question in any grant application, and you’ll hardly ever hear it uttered in conferences, if not with ill intent. It should not be so. Shifting the focus towards the problems and how our work is targeting its solution will do, I believe, wonders in reprioritizing how research funding is being spent, what projects are being funded, and what scientists we should follow. This should prompt all scientists, old and young, to pursue the hard problems. It would prompt them to answer the What? question with *what* they are trying to achieve. It would make them more sensitive about the quality of the problem they are trying to solve rather than whether the problem can lead to fast publications. Research, if one really scrutinizes it carefully, is not even incremental, but it is still publishable. If we compare a research problem to climbing Everest, transformative research will be the one that finds new routes to the top. Incremental research, almost as noble, in its genuine incarnation, uses an understood route and puts one foot after the next for those who will follow. The “still publishable” type of research runs in circles around the base camp, claiming that their scouting will somehow help others make it to the top.
2. Debate rather than appease. Conferences used to be places where research findings and data were discussed and fleshed out. Quantum mechanics was discovered and proposed by Planck at a conference. Regardless of how ridiculous the idea of quantized energy levels would have sounded to many. There is immense value to creating environments such as those. But to do that we have to promote a culture in which asking a challenging question at a conference should be the norm rather than the exception. And that when this happens the questioner should not be viewed as a disturber of the peace. Questioning an interpretation is not a measure of disrespect. Failing to question a dubious interpretation or claim should be. Questioning a result or interpretation and disrespecting its author are mutually



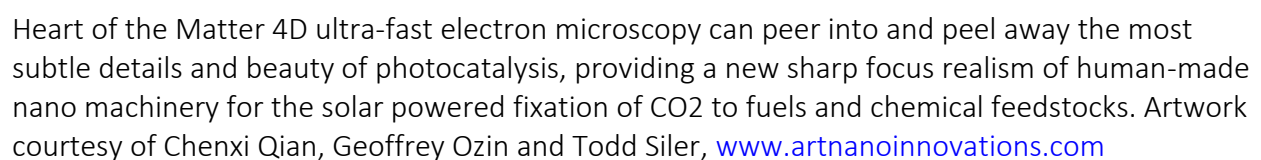
exclusive. I can't stress how important this attitude should be for our duties in educating the young scientists of tomorrow. On the other hand, I do not believe that blogs, twitters, and internet forums qualify as suitable venues for such discussions. Even with moderation, these formats are especially subject to disruption, manipulation, and the relentless force of consensus.

3. While society's shift towards transparency can be used by researchers in a positive way to promote the benefits of the research enterprise, I think that too much talk *via* internet avenues can be counter-productive. Actions speak better than words. It is better to go out and "do it" and then you can talk about the successful solutions which have helped to promote a better society to live in. For young scientists who have not yet had chance to do anything on their own, they need to talk about *what* they are trying to achieve. In both cases, a funds provider is faced with the question whether the researchers have the ability to solve the problem and must also take into account, as part of its decision-making process, whether the researchers have those subjective factors such as trust, integrity and drive to achieve a solution. Those attributes will always be a vital asset which must be protected and nurtured on both sides.

In closing, as it is becoming customary these days, I should now offer some measure of apology for the opinions expressed. But I won't do so, as these opinions originate from a concern for the state of science and the future of our best and brightest. I will apologize, however, that the manner in which these opinions have been laid out might not be the clearest or the most savory.

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Geoffrey A. Ozin



# Peering into the Heart of Photocatalysis

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## If the Samurai of semiconductor electronics is silicon then the Titan of semiconductor photocatalysis is titania.

The most photoactive form of titania is the Anatase polymorph of  $\text{TiO}_2$ . Its structure is based upon a three-dimensional interconnected network of six-coordinate  $\text{TiO}_6$  octahedra. In its intrinsic form it has a wide band gap and only absorbs the ultraviolet wavelength range of the solar spectrum. Visible light absorption can be induced for example by isomorphous replacement at the Ti(IV) site with transition metal dopants like V(V) and Cr(VI) and at the O(-II) site by N(-III), the creation of oxygen vacancies, and dye and plasmonic sensitization.

The high oxidation potential of photogenerated holes makes  $\text{TiO}_2$  a powerful oxidant for water and organics. This functionality has spawned wide-ranging utility, such as anti-bacterial paints, self-cleaning windows, tiles and cements, and water purification. Photogenerated electrons in  $\text{TiO}_2$  similarly exhibit a high reduction potential enabling the production of solar fuels, such as  $\text{H}_2$  from  $\text{H}_2\text{O}$  and  $\text{CH}_4$ ,  $\text{CH}_3\text{OH}$  and  $\text{CO}$  from  $\text{CO}_2$ .

There are other wide band gap photoactive Ti(IV) based oxides, such as the Rutile and Brookite polymorphs of  $\text{TiO}_2$ , the Perovskite form of strontium titanate  $\text{SrTiO}_3$ , and in the context of this editorial, the nanoporous open-framework titanosilicate,  $\text{Na}_4\text{Ti}_2\text{Si}_8\text{O}_{22} \cdot 4\text{H}_2\text{O}$ .

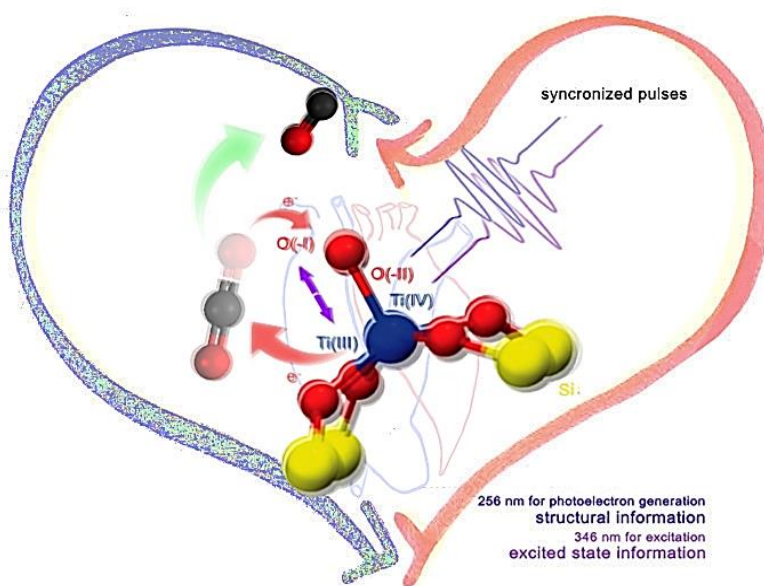
What distinguishes the titanosilicate from the other mentioned Ti(IV) based oxides is that the Ti(IV) is five-coordinate with a square pyramidal geometry, having one short 1.70 Å axial Ti=O double bond with four longer 1.96 Å equatorial Ti-O single bonds, as illustrated in the scheme.

This five-coordinate  $\text{TiO}_5$  site is photoactive and sterically accessible to molecules with the right size and shape, able to enter the voids of the open-framework titanosilicate. As a result of these properties, nanoporous titanosilicates have enjoyed wide-ranging applications in chemo-, regio-, and shape-selective oxidations of organic compounds.

It is interesting to note that while the photoactivity of the aforementioned titanosilicate has been known for many years, the precise description of the photoexcited state has never been observed directly in real time and has only been conjectured to involve the electronic-structural change

$\text{Ti(IV)O(-II)} + h\nu \rightarrow \text{Ti(III)O(-I)}$ . It has been imagined that ultraviolet band gap excitation causes an oxide-like valence band electron to be promoted to a titanium-like conduction band to create initially an electron-hole pair, which then undergoes trapping in formally mid-gap states that are distinct from recombination centres. The structure of these transient states is unknown but has been likened to an oxygen-to-titanium, ligand-to-metal charge-transfer excitation. Based on this idea, one would have speculated the Ti-O bond length in the excited state would be longer than in the ground state.

Now we have a new tool to answer these questions. Recent work using 4D ultrafast diffraction has come to the rescue with a femtosecond resolved dynamical study of the nature of the photoactive  $\text{TiO}_5$  site in the titanosilicate photocatalyst [1]. We now have new evidence that the electronically induced  $\text{Ti(IV)O(-II)} + h\nu \rightarrow \text{Ti(III)O(-I)}$  structural transformation occurs because an analysis of the time-dependent changes in the intensity of 2 Bragg diffraction orders was found to be consistent with a model in which there is an increase in the apical bond length in the excited state of the  $\text{TiO}_5$  square pyramidal site, by as much as  $0.8\text{\AA}$  on the sub-picosecond



Heart of the Matter 4D ultra-fast diffraction methods can peer into and peel away the subtlest details and beauty of photocatalysis, providing a new sharp focus realism of human-made nano machinery for the solar powered fixation of  $\text{CO}_2$  to fuels and chemical feedstocks. Artwork courtesy of Chenxi Qian, Geoffrey Ozin and Todd Siler, [www.artnanoinnovations.com](http://www.artnanoinnovations.com).

timescale. This relatively large change in bond length by itself is quite unusual, especially given the low excitation and few sites contributing to the signal. It could even be bigger.

This 4D ultra-fast electron diffraction experiment was performed on an electron microscope that employs two synchronized pulses of 259 nm and 346 nm light to respectively produce the photoelectron electron beam for diffraction and generate the photoexcited state of the titanosilicate single crystal. By controlling the time delay between the two laser pulses the spatiotemporal dynamics of excitation and relaxation of the photoactive site could be determined.

This experiment provides a model for the spatiotemporal transformation of the ground state apical  $\text{Ti(IV)=O(-II)}$  double bond of the  $\text{TiO}_5$  site to the excited state apical  $\text{Ti(III)-O(-I)}$  single bond. In this model, the structural change occurs by simple displacement of the titanium and oxygen double bond electrons and atomic positions with respect to one another. There seems to be however, insufficient experimental evidence to directly resolve this structure change as there were only two diffraction orders apparently undergoing significant changes. A more complete sampling of reciprocal space is needed to put this suggested mechanism on firm ground but the picture given is intriguing.

In the context of photocatalysis, the observed femtosecond dilation of the apical double bond induced by photogeneration of the electron-hole pair occurs on a much shorter time scale than electron-hole pair recombination and accompanying structural relaxation. It is important to note that the short photogeneration and slow recombination dynamics of the suggested trapped electron-hole pair provides sufficient time for catalytic reactions to occur at the photoactive  $\text{Ti(III)-O(-I)}$  site.

The ramifications of these observations in photocatalysis could be significant. In this archetypal study of an open-framework titanosilica, ultraviolet light is proposed to transform a ground state  $\text{Ti(IV)O(-II)}$  site into an excited state  $\text{Ti(III)O(-I)}$  site. The latter is both a highly oxidizing and reducing site and is imagined to play a pivotal role in many light-assisted reactions of titania based catalysts.

Within this proposed model, there is also a time-scale placed on the dynamics of the photoactive state in relation to competing chemical processes, such as reduction of  $\text{CO}_2$ ,  $\text{CO}$  and  $\text{H}_2\text{O}$  and physical effects, such as radiative and non-radiative recombination that can ensue following photogeneration of the electron-hole pair.

In the emerging and exciting field of gas-phase, light-assisted heterogeneous catalysis, I envision ultra-fast electron diffraction determination of the spatiotemporal structure and dynamics of the photoactive state, will prove indispensable in the synthesis of nanostructured photocatalytic semiconductors by design rather than by chance. Imagine being able to observe at the atomic level a chemical reaction in real time. This feat has recently been demonstrated with sufficient

sampling of reciprocal space for metal to metal electron transfer to invert to real space. This work is the first full atom resolved chemical reaction where the enormous number of atomic motions can be seen by eye to reduce to a few key modes [2]. Catalysis is next.

This new and powerful ultra-fast structural tool will greatly empower materials scientists and engineers racing to discover champion photocatalytic nanostructures that can enable the reduction of CO<sub>2</sub> to fuels and chemical feedstocks. To be technologically meaningful and economically sensible, solar powered CO<sub>2</sub> fixation will have to function at an efficiency and scale high enough to significantly impact greenhouse gas driven climate change, clean enough to ameliorate environmental pollution, and secure and safe enough to provide a renewable and sustainable energy resource to ensure the future health of humankind (for example, <http://solarfuelshub.org/>, <http://solarfuels.utoronto.ca/>, <http://www.solar-fuels.org/>).

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## 54. Fixing CO<sub>2</sub>

### Doing Something Fast and Economically Sensible with CO<sub>2</sub>

Geoffrey A. Ozin

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Graphic illustrating “Fixing CO<sub>2</sub>” showing the sphere or circle of interconnected influences and influencers that need to help realize this global challenge. Courtesy of Todd Siler and Geoffrey Ozin, [www.artnanoinnovations.com](http://www.artnanoinnovations.com).



# Fixing CO<sub>2</sub>

## Doing Something Fast and Economically Sensible with CO<sub>2</sub>

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*There's no end in sight for abating global greenhouse emissions. We need fresh insights into how we can rapidly and realistically fix the problem once and for all, using viable methods for stabilizing the amount of CO<sub>2</sub> in the atmosphere. This should be our primary global goal and task, which we've already agreed to act on to achieve the 2015 Paris Agreement <http://mission-innovation.net/>.*

Now is the time for a massive influx of patient and flexible government funding and private investment from visionary countries, to create new tools that can power the world without the accompanying production of CO<sub>2</sub>.

Two basic strategies exist in principle for putting a safe cap on atmospheric CO<sub>2</sub> in the next 20-30 years. One uses CO<sub>2</sub> capture and storage the other utilizes the captured CO<sub>2</sub> for making value-added chemicals and fuels.

In the wake of the Paris conference a great deal of hope has been placed on the large number of CO<sub>2</sub> capture and storage, and biomass projects underway. *Unfortunately, their economic viability and ability to meaningfully decrease our greenhouse gas emissions and solve our energy issues in the foreseeable future are in serious doubt.*

It is touted that captured CO<sub>2</sub> rather than being stored can be used as a carbon-negative solution for the enhanced recovery of oil. *While technically feasible, it is not a permanent solution as it does not account for CO<sub>2</sub> leakage and*

*the liberation of CO<sub>2</sub> by dissolution of carbonates. Moreover, it is enormously expensive, not to mention the fact that it's very difficult to justify using CO<sub>2</sub> to get more fossil fuels out of the ground. I mean, the public raises its eyebrow and grimaces: Is this really a climate-friendly solution?*

Advocates of biomass and bioenergy technologies also claim that biological CO<sub>2</sub> fixation is key to sustainability being carbon-negative. If the US was to replace gasoline with biodiesel they would need seven times the area of the USA to plant corn. *Yet, do the energy and economic flows account for the massive loss of food productive land and justify the overall gain in CO<sub>2</sub> from growing, harvesting, processing, storing and transporting the biological feedstock and products?*

Sources of renewable solar and wind energy are expanding at an ever increasing pace around the world. *The question is how long will we have to live with the adverse effects of climate change caused by the continuous rise of anthropogenic CO<sub>2</sub> from our continued reliance on the use of fossil energy?*

In the urgent search for the innovation solution to fix CO<sub>2</sub>, there does however appear to be agreement that the economic viability of CO<sub>2</sub> capture and storage can be improved by working hand-in-hand with utilization of the CO<sub>2</sub> for producing value-added chemicals and fuels. This strategy is under development in a range of established and emerging industries around the world that productively fix CO<sub>2</sub> in the form of fertilizers, cement, chemicals and polymers, and aviation and diesel fuels, at the mega ton scale. *If we already have commercialized technologies that utilize CO<sub>2</sub> at the mega ton scale what's stopping us from expanding the capacity of these industries to a globally-significant, climate-friendly scale?*

It is important to keep in mind that any utilization process based upon hydrogenation of CO<sub>2</sub> will necessitate a large-scale source of inexpensive H<sub>2</sub> other than fossil-based steam reforming of

methane, coal gasification or partial oxidation of oil. Ultimately, this will likely have to come from H<sub>2</sub>O electrolysis powered by renewable forms of electricity or photoelectrolysis using sunlight.

With a world “drowning” in CO<sub>2</sub> and H<sub>2</sub>O, this all seems like a no-brainer! Clearly, there is an urgent need for a large and rapid injection of public and private funds into research and development aimed at ironing out the scientific and technological challenges of bringing CO<sub>2</sub> utilization industries on stream. *Isn't the key to economical, sociological and political success, to prove that it is possible to scale CO<sub>2</sub> utilization processes to proportions that can make a difference to climate change?*

Success-breeds-success. Demonstration of technologically and economically sensible ways of fixing CO<sub>2</sub> to value-added chemicals and fuels, in a reasonable time frame, will breed confidence in further private and public investment that will facilitate globally significant quantities of CO<sub>2</sub> to be converted from a liability to an asset.

Transformative ideas are emerging from academic, industry and government research institutions aimed at discovering molecules, materials and processes that can transition our energy future to a near zero emissions world. *The question is how do we get the most innovative and promising research ideas from the lab-to-market to protect us from the adverse effects of climate change?*

It is exciting that Bill Gates and an impressive list of billionaire private investors, with collective holdings of \$350B, have founded “The Breakthrough Energy Coalition”, <http://www.breakthroughenergycoalition.com/en/index.html>. Their mandate is to work with a growing list of visionary countries who collectively agree that a solution to climate change will require faster action than the energy sector has ever mustered before. They have committed to double government spending on basic and applied energy research in the next five years to fix climate change.



Graphic illustrating “Fixing CO<sub>2</sub>” showing the sphere or circle of interconnected influences and influencers that need to help realize this global challenge.

Courtesy of Todd Siler and Geoffrey Ozin, [www.artnanoinnovations.com](http://www.artnanoinnovations.com).

This is because transitions in energy generation historically take more than fifty years to implement and he warned “the climate threat is too serious to allow technology to evolve at the usual slow pace”. *It is exciting that on their list of “cool” energy innovations includes, solar-chemical technology, which converts the sun’s energy into hydrocarbons that can be stored and used as fuel,* <https://www.washingtonpost.com/news/energy-environment/wp/2015/11/30/bill-gates-on-climate-change-we-need-to-move-faster/>.

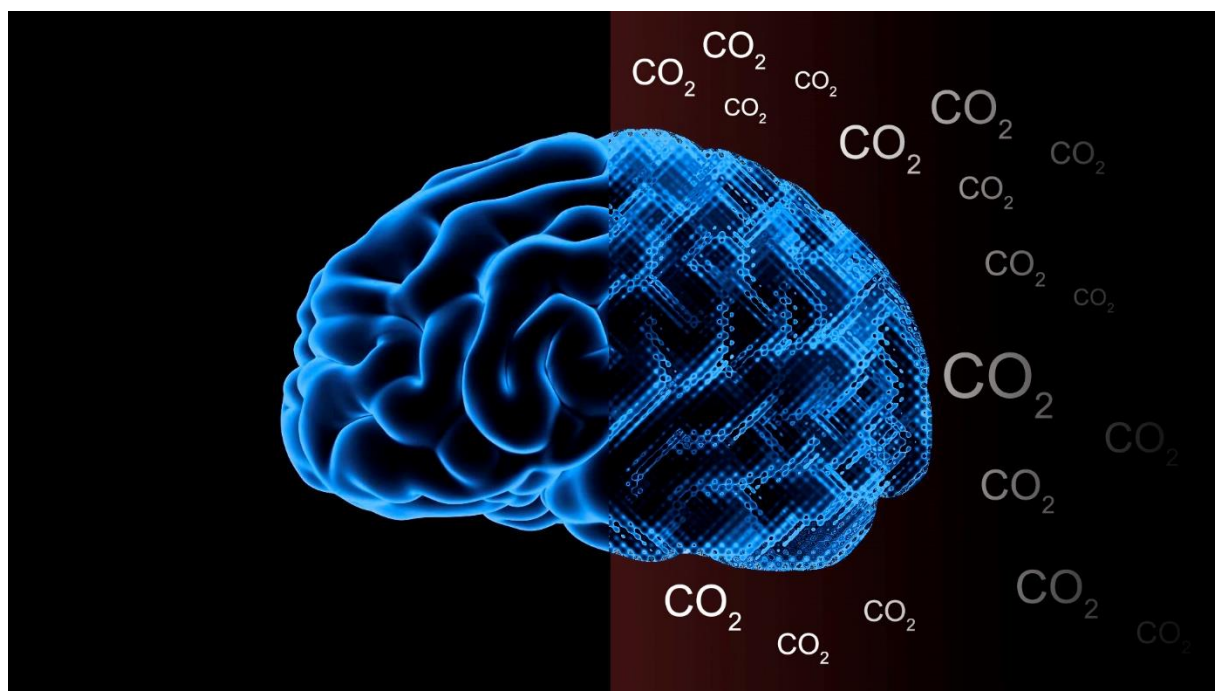
The return on investment to fund a “fast-track” global energy transition that treats CO<sub>2</sub> as a chemical resource rather than a waste product is beyond profit making. *It’s a moral imperative. Implementing this energy transition will advance the common good by improving the quality of life for all of humankind.*

***We all love CO<sub>2</sub> - let’s do it, let’s fix CO<sub>2</sub> fixation!***

## 55. CO<sub>2</sub> on the Brain and the Brain on CO<sub>2</sub>

Geoffrey A. Ozin

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# CO<sub>2</sub> on the Brain and the Brain on CO<sub>2</sub>

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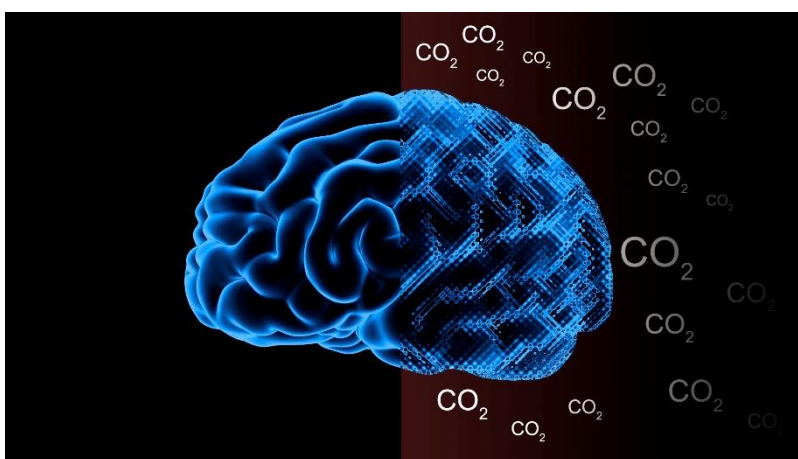
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Do you think we have a serious greenhouse gas climate change problem caused by anthropogenic CO<sub>2</sub> emissions in our atmosphere, which is threatening the future health and well-being of our civilization?

Well if you think that isn't bad enough it seems that we also have to be seriously concerned about the impact of CO<sub>2</sub> on the brain, which in a direct and negative way is impacting the cognitive and decision-making functions of humans at home and in our classrooms and

workplaces. We are not talking here about the cause-and-effect of extraordinarily high levels of CO<sub>2</sub> but rather concentrations that most of us would experience in closed poorly ventilated spaces on a day-to-day basis, when living, working and traveling respectively in our homes, classrooms, offices, planes, trains and cars.

I came across this information in a 2012 public health study from Lawrence Berkeley National Laboratory investigation [1] and a more recent 2015 public health study published by the Harvard T. H. Chan School of Public Health [2]. These two independent studies concur that statistically significant and meaningful reductions in decision-making performance, which could significantly affect productivity, learning and safety, are observable with increases in CO<sub>2</sub> levels from 600 to 1000 to 2500 ppm. While these levels seem high in comparison to the 405 ppm CO<sub>2</sub>



Save our brains from the destruction of cognitive functionality by excessive levels of CO<sub>2</sub> in our living, working and travelling environments so we have enough brain power left to solve the climate problem driven by increasing concentrations of CO<sub>2</sub> in our atmosphere. Graphic artwork courtesy of Chenxi Qian.

currently recorded in our atmosphere, they are commonplace in poorly ventilated spaces of the kind mentioned above, where we spend large proportions of our time.

By inspecting results displayed in Figure 1, for nine double blind tests, for the dependence of cognitive function on the concentration of CO<sub>2</sub>, one is amazed to discover that average cognitive scores of typical participants, decreased by 21% with respect to 400 ppm increases in CO<sub>2</sub> levels [2].

The adverse effects of high levels of CO<sub>2</sub> are of course well-documented in for example, space travel, scuba-diving and submarines, aeroplanes and fire-fighting situations. However, the impact of greenhouse gas emissions on human health from living, working, playing and traveling in tightly sealed environments, is a disquieting surprise to many of us already worrying about the negative effects of greenhouse gas on our climate. While it is a truism that throughout our lives we make and exhale CO<sub>2</sub> it is now apparent that we were not created to live in an atmosphere with increasingly high levels of CO<sub>2</sub>.

Isn't it ironic that in our earnestness to create more energy efficient buildings with sustainable green designs to reduce levels of CO<sub>2</sub> in our atmosphere and thereby ameliorate climate change, we have made more tightly sealed indoor environments, which increases the level of CO<sub>2</sub> we

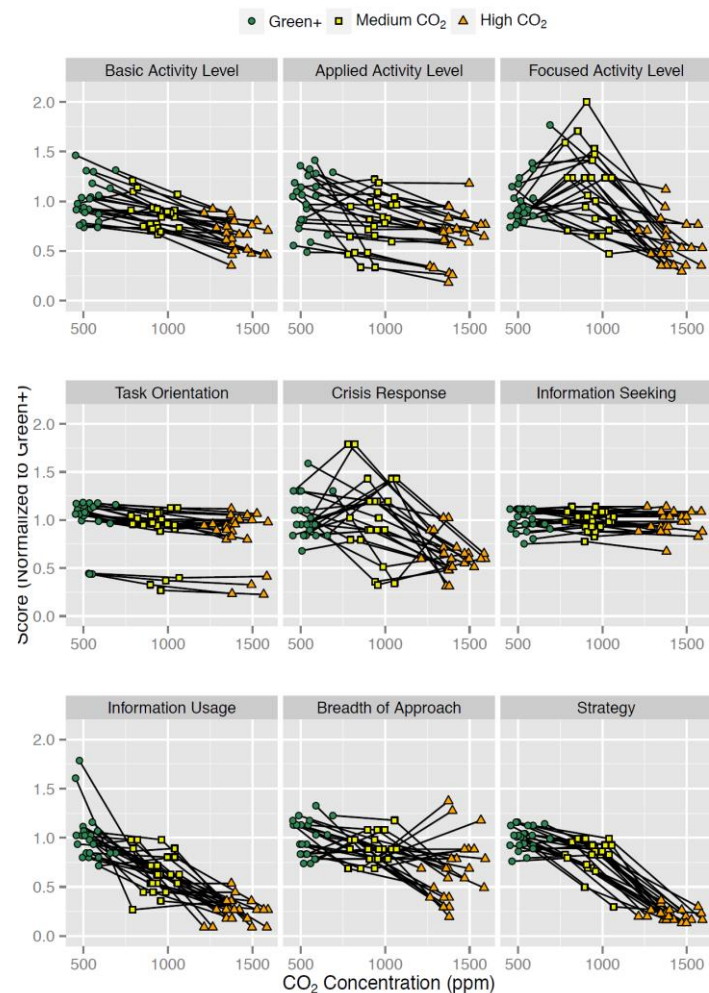


Figure 1 Cognitive function scores by domain and participant, and corresponding carbon dioxide concentration in their cubicle. Each line represents the change in an individual's CO<sub>2</sub> exposure and cognitive scores from one condition to the next, normalized by the average CO<sub>2</sub> exposure across all participants during the Green+ conditions [2]. Reproduced with permission from Environmental Health Perspectives.



breathe and can negatively affect our overall well-being. Building and ventilation codes that optimize conditions for human health and productivity are hopefully being vigorously evaluated.

How high can indoor levels of CO<sub>2</sub> go? In a reported study, it was found that in a substantial number of poorly ventilated classrooms and workplaces, CO<sub>2</sub> levels can average 1000 ppm, a significant proportion of these exceeded 2000 ppm and some even reached 3000 ppm. Keep in mind we are all currently living in an outdoor environment of 405 ppm with no sign that these levels will be abated for decades. In fact they are significantly higher in our cities. These levels are increasing at a rate of 2 ppm annually and the rate is accelerating. At some threshold yet to be defined but thought to be around a 1000 ppm, human cognition will begin to be negatively impacted. Latest research indicates we could attain this threshold outdoors in the next century, and the dissipation of CO<sub>2</sub> in our atmosphere takes centuries.

So we have two looming health and safety problems to fret about, the negative effect of CO<sub>2</sub> on our climate and also on our brains. In this context, two public health recommendations have emerged from these studies: (i) build better ventilation systems that use outside air in our buildings and transportation systems and (ii) decrease the use of fossil fuels to keep atmospheric levels below 600 ppm.

In this context I would anticipate that next generation aeroplanes will likely be employing CO<sub>2</sub> sorbents, with standards established for spaceships and submarines, to solve this problem and soon these sorbents will be employed increasingly to control safe CO<sub>2</sub> levels within a host of indoor environments. This is a task for the science and engineering of porous materials. Continued research and development to improve their CO<sub>2</sub> sorption selectivity, capacity and stability, scalability and cost, provides new economic opportunities for clean-tech industries, wherever control of CO<sub>2</sub> levels is deemed necessary for health and safety reasons.

It certainly seems that the risk of not doing anything is that “bad things” will begin to happen to the intellect, health and well-being of our entire civilization, if we let CO<sub>2</sub> go beyond the 600 ppm threshold in our indoor and outdoor environments.

If we ever get into this dire circumstance, we may not have sufficient brain power left to solve the greenhouse gas problem which is beginning to play havoc with our climate.

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<http://dx.doi.org/10.1289/ehp.1510037>

We can't have a clean-energy revolution without molecules, polymers and materials. But what have we really done to help win the war against climate change?



We must all now shoulder the Herculean responsibilities of caring for our Earth with the same degree of concern as we care for ourselves and our collective future.

56. We can't have a clean-energy revolution without molecules, polymers and materials. But what have we really done to help win the war against climate change?

Geoffrey A. Ozin

The chemistry research community is largely responsible for inventing many key molecules, polymers and materials, which are and can be deployed in technologies that will enable the transition of our civilization from non-renewable to renewable forms of energy.

Indeed, we all should be very proud of these practical scientific and technological innovations that will most definitely shape the future of renewable energy systems when fully implemented. The question remains: What is our research community doing collaboratively to ensure that these essential innovations are actually implemented as we originally envisioned?

Given the fact that the public, news media and governments rely on our expertise, know-how and applied imagination to curtail climate change quickly and sensibly, I'm wondering whether



What's the use of having developed a science well enough to make predictions if, in the end, all we're willing to do is stand around and wait for them to come true? Noble Laureate Sherwood Rowland 1995.

The vessel of evidence-based science isn't just "half-full". It's overflowing now! Todd Siler Art-Scientist 2016. Artwork courtesy of Todd Siler and Geoffrey Ozin, [www.artnanoinnovations.com](http://www.artnanoinnovations.com).

we have been too passive on guiding everyone on what needs to be done immediately and the implications if governments fail to act quickly. I believe we can do much more to make our collective voices heard, and to hasten change by fast-tracking the mobilization of the public, media and governments about the urgency of this crucial transition from a non-renewable to a renewable energy economy.

We know that if global warming, induced by increasing levels of carbon dioxide in our atmosphere, reaches its tipping point, with less than two degrees considered to be a safe limit, it can induce sudden local alterations in the sea ice, oceans, snow cover, terrestrial biosphere and permafrost. In the case of the latter, a local temperature change in the Arctic or Antarctica could cause melting of the ice caps and concomitant release of trillions of tons of methane trapped as ice clathrates. This methane greenhouse gas effect has a good chance of causing the collapse of our entire ecosystem and totally devastating our civilization. But we seem to be content just to go on doing our research while watching it happen.

We remain largely quiet while climate scientists work to inform and mobilize the public, news media and governments about the urgency of fast-tracking the transition from a non-renewable to a renewable energy economy. One could argue that the chemistry research community needs to educate and inform the climate scientists better about the wonderful chemistry solutions to climate change they have developed so that the climate scientists can inform and mobilize governments and businesses better and get them to act faster by implementing our solutions in renewable energy systems.

We often say in the introductions and conclusions of our papers that our work is motivated by our desire to help win the battle against climate change. But too often we do little more than publish the results of our research in scientific journals – leaving up to others the equally important task of actually fighting the climate change war by ensuring these results are implemented in renewable energy systems.

We know that climate science and economics provide the foundation for climate change regulation, legislation and policy. Nonetheless, we are the ones that create the chemistry that will enable the transition from fossil energy to clean energy. I believe we can do more to make our collective voices heard, and to hasten change.

Every paper I read in the burgeoning field of advanced energy molecules, polymers and materials, devices and processes, pays lip-service to greenhouse gas induced climate change. We all claim the raison d'être for our research is to help solve the climate crisis, but truthfully, what real actions are we taking as a research community to advance the speed of the transition from the dirty-energy to the clean-energy solutions we have envisioned, modeled, verified and stand behind scientifically?

Duty calls us all to be proactive as world citizens. We must now work together synergistically to meet the most challenging and urgent goal of all, doing everything in our power to help halt global warming through socio-economic and political means. However, there does not seem to be a concerted attempt to do this on a worldwide basis. It is very piecemeal and uncoordinated. There should be say a 5 year plan of action and experts in lobbying or public relations should be involved to assist in this process. One needs a leader who is prepared to devote most of his or her time to ensuring the message is got across. In addition to education I think the chemistry research community needs to study why its developments are not coming to fruition as quickly as they would like – where is the bottleneck and what actions have been most successful in bringing new developments to the attention of the public. I think a pilot plant project using the new developments is worth a thousand words. Something like the pilot plant that transforms  $\text{CO}_2/\text{H}_2$  to diesel fuel, sponsored by VW/Audi in Germany seems to have gained lots of publicity. The talents of the chemistry research community may be better deployed in this direction rather than as lobbyists. The question is how does one persuade investors/governments to put up the money for these developments - maybe a tax on each barrel of fossil fuel? The problem at the moment is that no one is going to back these new technologies because the price of oil is low and the price of gas and liquefied natural gas is even lower. The price of the latter in Asia has fallen to almost 20% of what it was 2 years ago and the price is not expected to improve until the next decade. In Europe prices have fallen by a third and in America they have halved.

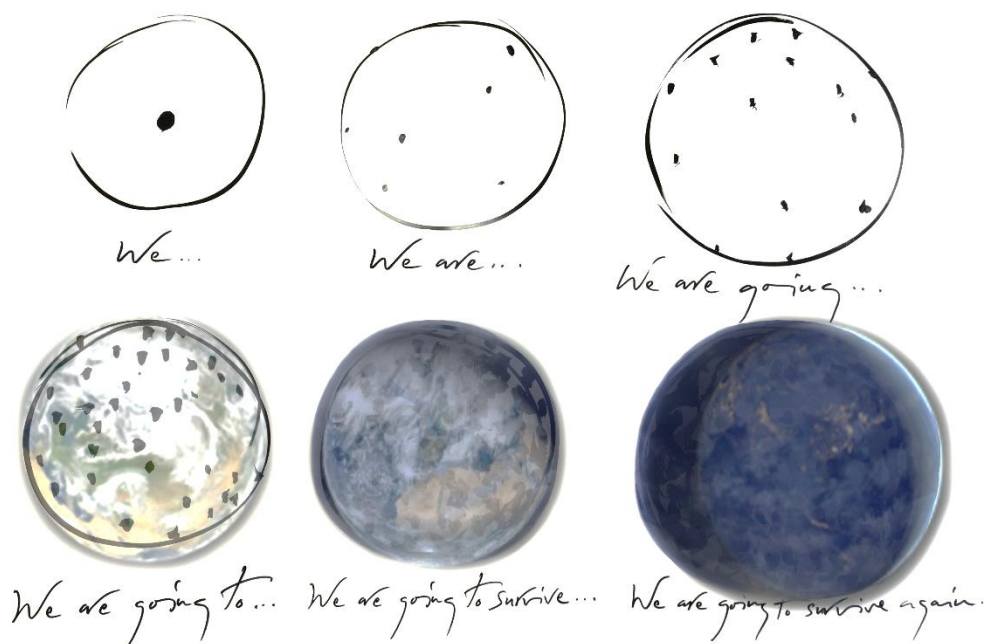
Despite all of these challenges, I am excited by the growing momentum to curb climate change, particularly in light of the recommendations and agreements that have emerged from the United Nations conference in Paris. I am encouraged by the commitments of all of the dominant fossil economies to get their greenhouse gas emissions in order. I am amazed at the amount and rate at which solar, wind, tidal, geothermal and hydroelectric electricity is being created and impressed by how the parallel growing capacity to store this renewable electricity in batteries is being deployed.

Now is the time to show how ‘game-changing’ chemistry has the potential to drive this energy revolution. It’s not enough to entrust government lobby groups to do our work for us. We can show the impact of our work through world-wide outreach, high school and public education projects and by demonstrating the practicality of our innovations by demonstration units and pilot plants. But this can only happen with the ongoing support of the public, news media, industry and governments. It’s a commitment to our collective future we all must make, to make it real.

The key to informed social activism and involvement is to tap every possible public medium in highlighting how these accomplishments, born in chemistry, will enable the transition from non-renewable to renewable forms of energy. These science communications must be highly visible and accessible to the public. Otherwise these pivotal contributions by the news corps will remain slow and sluggish, rather than fast-tracking our civilization to a sustainable future.

We should be much more visible in publicising the myriad of exquisite materials which are playing a major role in many emerging advanced energy technologies. The physical dimensions of these materials are often smaller than the wavelength of light, electrons, holes or excitons. As a result the beneficial effects of quantum confinement on electrical, optical, thermal and mechanical properties emerge and are now put to good work in the fabrication of photovoltaic, fuel cell, lithium ion battery, supercapacitor, piezoelectric and thermoelectric energy devices.

The small size and high surface area of these materials are also exploited to advantage in water splitting and carbon dioxide utilization systems. At these tiny scales, enhancing the absorption, diffusion and scattering lengths and strengths of photons, electrons, holes and ions which contribute to energy generation, storage and



Are we all clear about this “certainty”? Are we all willing to bet on our survival? Artwork courtesy of Todd Siler and Geoffrey Ozin, [www.artnanoinnovations.com](http://www.artnanoinnovations.com).

transport processes, are of paramount importance in the design and discovery of efficient energy materials and their implementation in energy devices.

We urgently need to highlight these technological innovations through every possible public medium - showing how these accomplishments can facilitate the transition from non-renewables to renewables. Highly visible communication of these pivotal contributions through the media and arts will help fast-track our civilization to a sustainable future. Demonstration units and pilot plants will certainly help to capture the imagination of the public, government and industry.

Perhaps, the most difficult obstacle or challenge the public struggles to embrace is the reality of perception: We look outside our windows and see a beautiful spring day, or we walk in open



fields under fresh blue summer skies, and can hardly believe there's anything wrong with our atmosphere that needs immediate care. A problem however, is that the current state of the world economy has come at completely the wrong time for the transition from a non-renewable to a renewable energy economy. If we had a high price for fossil fuels this would encourage investment in the technologies that are being developed by the chemistry research community. It is difficult to find investors or governments prepared to invest in these technologies in the present financial climate. Plus of course you have the sceptics who in some cases are in sufficiently powerful positions to make it difficult for agreement to be reached by governments to fast-track the transition to a renewable energy economy.

Little wonder why public surveys and polls reveal a growing skepticism and criticism of "alarmists", and a general distrust in even the most reliable data we've gathered and shared to date. There's a natural disconnect between the "reality of our perceptions and our perceptions of reality". This disconnection produces what the legendary English chemist and physicist, Michael Faraday, called "mental inertia". As Faraday reminds us to this day: **"Nature, our kindest friend and best critic in experimental science, if we only allow her intimations to fall unbiased on our minds"**.

I would like to end this article with a few philosophical points beginning with the Herculean task of solving the greenhouse gas climate change crisis that our civilization has to confront in order to ensure our survival.

Recall Einstein knew best when he said: "If at first an idea is not absurd, there's no hope for it", and Bob Noyce, co-inventor of the microchip and co-founder of Intel Corporation said: "Optimism is an essential ingredient for innovation. How else can the individual welcome change over security, adventure over staying in safe places?".

Our whole world needs to embrace that same optimism and sense of hope. That's what will enable us to survive the next 100 Years and beyond – by realizing the power of human ingenuity. We've already invented the viable science and technology solutions to ensure a sustainable future. Now we need everyone's help implementing them, including ourselves, the "discoverers and inventors" of the chemistry that can be purposed to this end.

Those of us who passionately toil away in the chemistry trenches daily and who have generously contributed to climate change solutions, must now join the work of world-wide activists who are determined to make a difference. Common sense and rationality have jolted even the most practical-minded among us into action. There is no more time to delay and debate to death the urgency of climate change. Our chemistry solutions cannot be implemented without us all working together to make them real, and effective. By choosing to work together, collaboratively and synergistically, we can meet this most urgent global challenge: climate change!

There is no “Atlas” or “Hercules” shouldering the burden of Earth to ensure our survival! We only have ourselves to rely on, doing everything in our power, to fulfill the potential of our climate saving chemical inventions and technological innovations. They work! But they require everyone to do the work, too!

As a chemistry research community, we have created some of the most important tools for fighting climate change, and we have a responsibility to see to it that those tools are put to good use. How would you suggest we do this? What “simple”, yet specific, goal would you recommend that our community do as a concerted effort to catalyze change? What Call to Action would be significant enough to gain everyone’s attention and support?

No matter how believable the “envisionists” at Marvel Comics make their most benevolent Action Heroes succeed at doing the impossible, we only have us mortals - nothing more, nothing less - to do what must be done by all of us without further delay.



We have no Hercules, or Herculean men and women, to shoulder the Earth and protect its wellbeing. We only have ourselves to help ourselves. That fact fills the core of this Reality! We only have Human

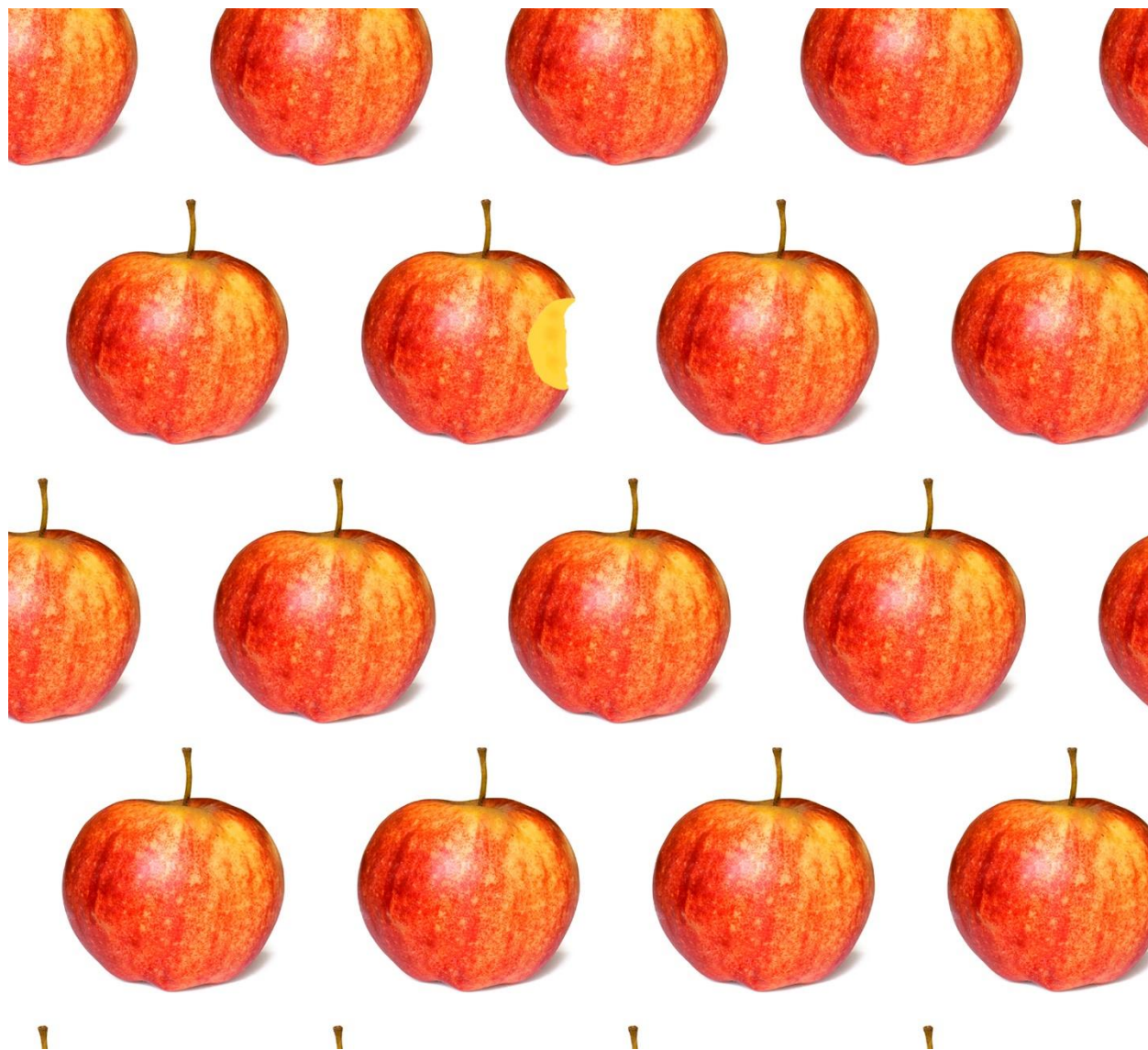
Ingenuity to rely on to tap our full creative potential in unprecedented ways. Artwork courtesy of Todd Siler and Geoffrey

Ozin, [www.artnanoinnovations.com](http://www.artnanoinnovations.com).

## 57. Perfectly Imperfect: Tailoring Chemically and Physically Functional Defects for Utility

Geoffrey A. Ozin

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# Perfectly Imperfect: Tailoring Chemically and Physically Functional Defects

Geoffrey A. Ozin

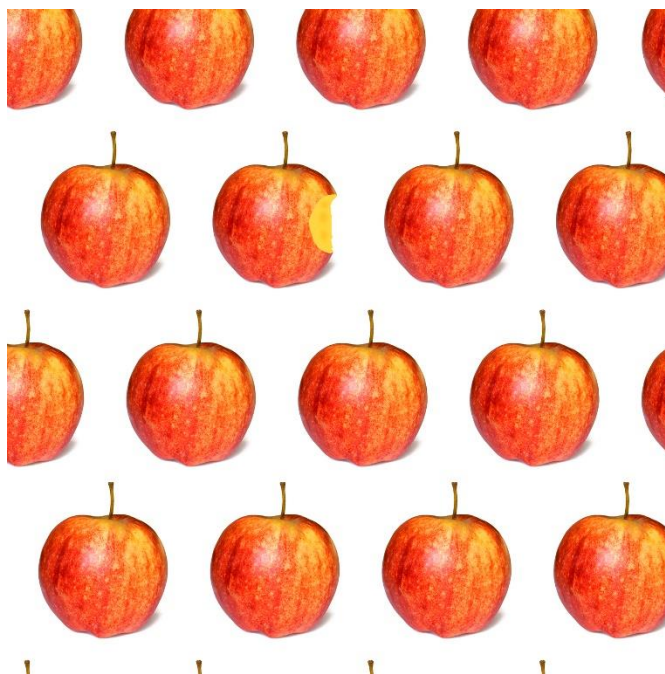
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I often say to undergraduate and graduate students who attend my courses in materials chemistry and nanochemistry: defects, defects, defects, you can't live with them and you can't live without them. Everything in life and nature alike is chockfull of obvious and subtle imperfections, without exception.

My students are often surprised at the beginning of their studies, to discover that there is no such thing as a perfect material and if it did exist, its functionality and utility would be limited. Defects are also pervasive in biology, where for example damage or mutation in DNA determines evolution, aging and disease. Students soon realize how common this phenomenon is even in our daily life. A

classic example is that the purest man-made materials on earth is semiconducting grade silicon, in which impurities can be reduced to less than parts per billion. However, we don't use pure silicon as the circuit element in electronics - it has to contain boron or phosphorous functional defects to endow it with utility. A more recent example is the utilization of nitrogen to create defects in diamonds to realize qubits for quantum computing applications.

The idea is to convey the reality to students that it is the defects in solids that create functionality. Moreover, it is the ability to actually build on this kind of imperfection that enables utility in diverse kinds of advanced materials and biomedical technologies, from high speed magnetically levitated trains to dental implants. Look around you. Everything in your office, home, or immediate environment is riddled with countless examples of imperfections, structurally and functionally speaking, that makes things work.



Perfecting Imperfection in the Materials World.  
Graphic illustration courtesy of Chenxi Qian.

Students learn about the different classes of point defects in solids that include: (i) n-doping and p-doping with elements that produce excess electrons or holes, (ii) Schottky charge-balancing substitutional cation-anion vacancy pairs and Frenkel substitutional cation vacancy-interstitial cation pairs, (iii) substitution of lattice sites with elements of the same oxidation state to create stoichiometric phases or different oxidation states to make non-stoichiometric phases and (iv) electron-proton insertion to create lattice hydroxyls and reduced metal oxidation states.

They also discover that at higher concentrations, randomly distributed point defects of the aforementioned kind can self-assemble and interact to create new classes of defects with higher levels of complexity and novel properties. These defects include local reconstructions into defect clusters, organized into isolated or self-assembled line and planar defect phases, and formation of defect super-lattice structures. Beyond these defect classes, students learn about other degrees of complexity that include edge and screw dislocations, line disclinations, stacking faults, twin boundaries and grain boundaries. For example, perfecting grain boundaries in materials is a key strategy for controlling their mechanical properties.

Through their experimental studies and improvisations they also come to realize that in nanomaterials with large surface-to-volume ratios, exposed surface defects that are distinct to the bulk become prevalent. This class of defects include coordinately unsaturated metal sites, anion and cation vacancies, reduced and oxidized metal sites.

On passing from atomic scale crystal lattices that diffract X-rays to the light scale photonic lattices that diffract photons, students learn about the colorful world of photonic crystals. At this length scale, point, line and planar defects can be tailored to localize, guide, reflect and amplify light, for applications that range from optical telecommunications to security features on banknotes.

Finally students discover that not all materials are perfectly crystalline and new kinds of defects can arise in partially disordered and completely amorphous phases that are distinct to the crystalline phases of the same material. This is also true for quasi-crystals, renowned for their ability to display five-fold symmetry. This unique class of crystals have ordered lattices which diffract X-rays. While not strictly periodic they are still found to have many of the defects in common with ordinary crystals.

The central message that emerges from these teachings is that to design purposeful materials one requires a profound knowledge of the different classes of defects. The key to success is how to make and tailor them in a rational and systematic way, to create specific structure-property relations that enable desired functionality and utility, for different applications.

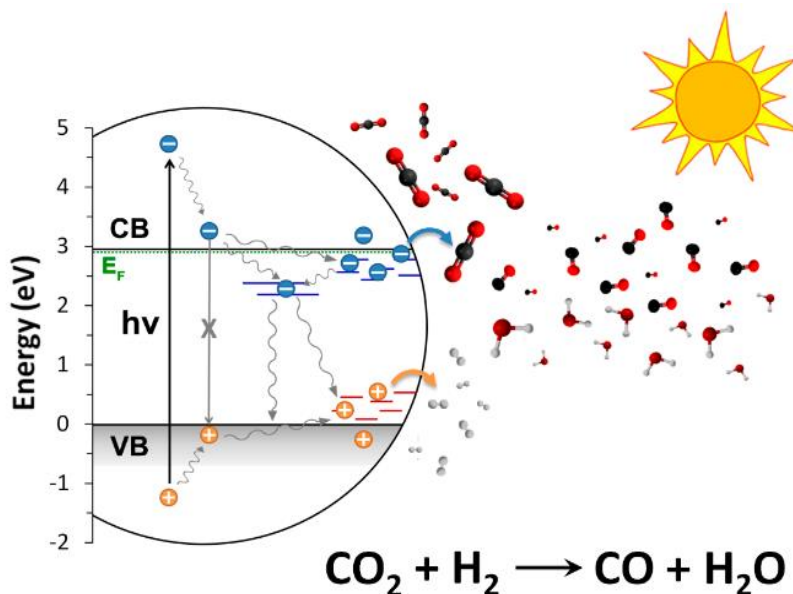
Often one finds that it is the physical properties of defects that determines their functionality and provides opportunities for developing useful technologies. Defect enabled physical properties include electronic and ionic conductivity, optical absorption, reflection, scattering and

emission, different kinds of magnetic, mechanical and dynamical effects. It is perfecting the imperfection inherent in physical defects that has enabled development of transistors and diodes, lithium batteries, silicon solar cells, hydrogen fuel cells, light-emitting diodes and lasers, ceramic superconductors, spintronic, quantum optic, thermoelectric, pyroelectric and piezoelectric devices.

These days I've pondered the kinds of defects in nanostructured materials that enable chemical functionality and utility. The possibilities are inexhaustible. By changing the way of thinking – shifting the focus from physical to chemical properties – one discovers that defects are capable of doing much more, especially in surface chemistry and catalysis, an intriguing possibility which arouses one's curiosity.

Especially interesting are those classes of defects that have recently been shown to participate in light-assisted heterogeneous catalytic reduction of gaseous CO<sub>2</sub> to chemicals and fuels. These have included the introduction of dopants or substituents into the crystal lattices of catalytic nanostructures designed to modify their electrical and optical properties. They are usually tailored to (i) shift ultraviolet absorption into the visible to enhance the harvesting of solar photons to (ii) enhance the population and mobility of photo-generated electrons and holes and to (iii) facilitate the adsorption and charge-transfer to reactants.

The objective of both of these approaches is to improve CO<sub>2</sub> conversion rates and efficiencies. While sound in their intentions, the opposite outcome has often been observed whereby these lattice defects, which often exist as localized mid-gap states, instead enhance recombination of photo-generated charge carriers, which defeats the desired intention of improving light harvesting, charge mobility and charge transfer efficiency.



Defects, Defects, Defects – Can't Live with Them Can't Live Without Them! Graphic illustration courtesy of Laura Hoch.

A way around this problem has been recently discovered in nanostructured metal oxides/hydroxides, with surfaces chemically tailored to support large populations of oxygen



vacancies, hydroxide groups and coordinately unsaturated metal sites. These kinds of defects have been viewed as Surface Frustrated Lewis Pairs, which exist as localized electronic states at energies between the valence and conduction bands. They serve multiple functions that favor the light-assisted reduction of gaseous CO<sub>2</sub> by H<sub>2</sub> or H<sub>2</sub>O to products, such as CO, CH<sub>3</sub>OH and C<sub>x</sub>H<sub>y</sub>. This photo-activity appears to originate in the synergistic (i) trapping of photo-generated electrons in oxygen vacancies and holes in hydroxide groups, (ii) reduction of electron-hole recombination rates, and (iii) adsorption, activation and reaction of CO<sub>2</sub> and H<sub>2</sub> or H<sub>2</sub>O. The long-lived electrons and holes located in these mid-gap defect states can function as the reducing and oxidizing agents, and/or the basic and acidic sites, responsible for the surface chemistry that facilitates the reduction of CO<sub>2</sub>.

Current research in the field of CO<sub>2</sub> fixation by gas-phase heterogeneous (photo)catalysis is focused on the characterization of functional defects in nanostructured materials and how to tailor and exploit them in the quest to achieve technologically relevant conversion rates and efficiencies.

The take home message of this editorial is that defects in materials and nanomaterials are not all bad. By understanding the physical and chemical properties of different classes of defects their inherent imperfection can be tailored to perfection and exploited to advantage not only in advanced materials electronic, optical and magnetic devices but also in the field of surface chemistry and catalysis. Especially exciting in this regard is their ability to enable challenging chemical reactions, exemplified by CO<sub>2</sub> conversion to value-added chemicals and fuels, an emerging approach for engineering solutions to climate change.

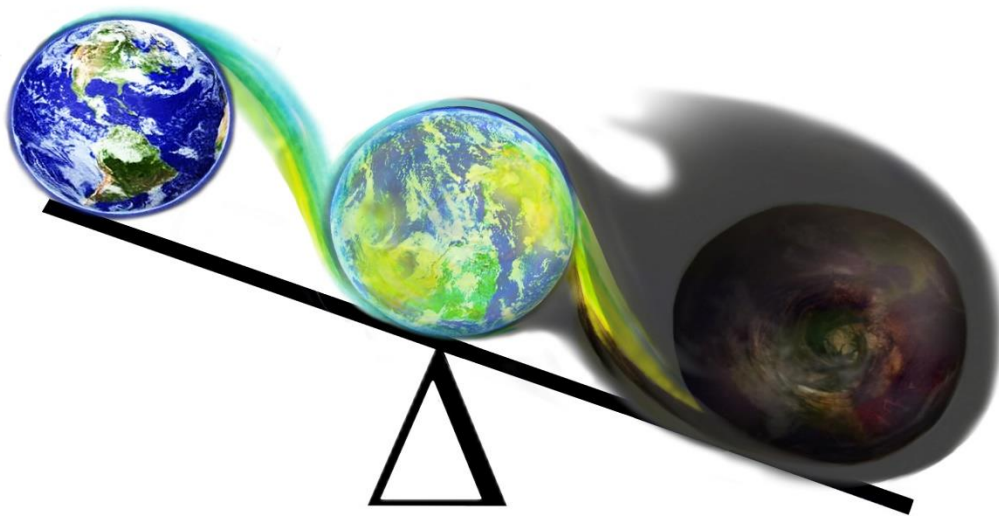
The broader takeaway here is that although creative inquiry can be as messy as the defect state, its pursuit often yields surprising insights that can catalyze scientific discoveries—adding true value to the whole discovery process.



# Tipping the Balance between Sustainability and Extinction

Geoffrey A. Ozin

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**Wait to Weight?** How long must we weigh in on our Energy Transition before Extinction? Artwork by Todd Siler and Geoffrey Ozin, [www.artnanoinnovations.com](http://www.artnanoinnovations.com).

## 58. Tipping the Balance between Sustainability and Extinction

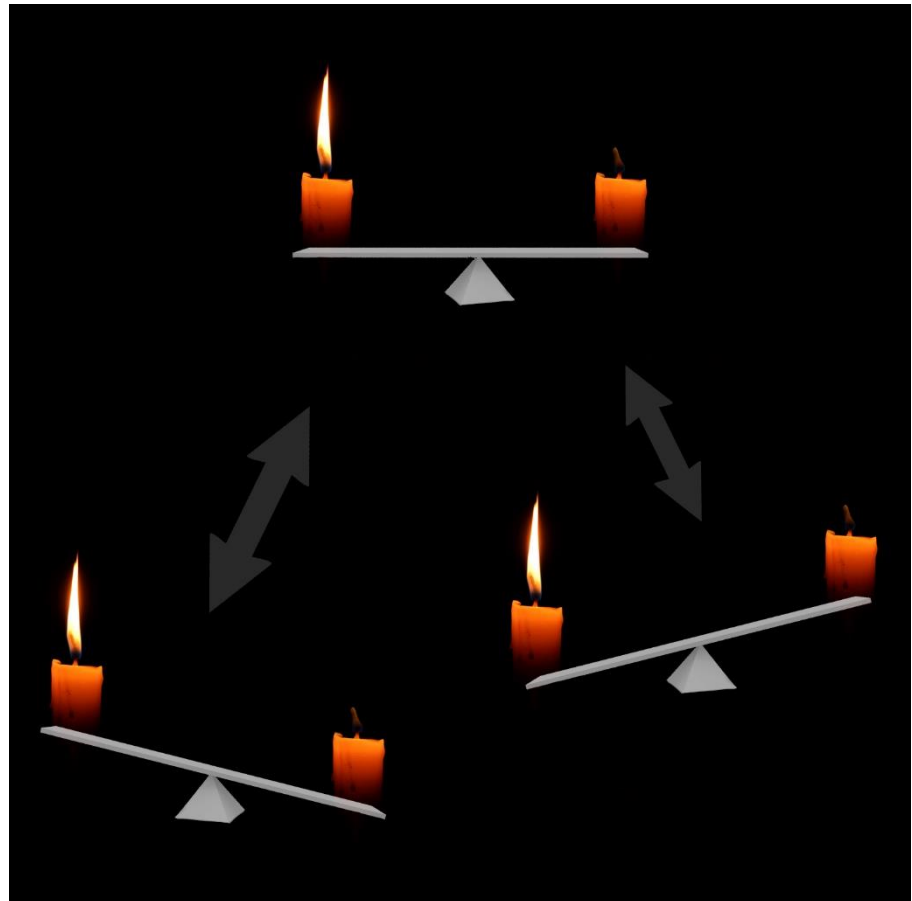
Geoffrey A. Ozin

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Homo sapiens, anatomically modern humans, evolved from archaic humans in the Middle Paleolithic Period, about 200,000 years ago. We cohabit a planetary ecosystem in which a biological network of animals, plants and microbes interact with an abiological system of water, air, soil and minerals. Surely we are ever so wise and powerful that we could never be the architects of the collapse of our own ecosystem and drive all living organisms, including ourselves, to a mass

extinction? While we are all living with the looming threat of global warming and climate change caused by greenhouse gas emissions, and beginning to accept life in a much warmer world, the gloomier possibility of a self-inflicted mass extinction is not on our radar screen of “unthinkable” events.

This apocalyptic scenario of mass extinction of all or much of life on earth is not unprecedented. In fact, it may be a way of life. It has a history of five main occurrences that began 400 million



The seesaw of life and extinction. Graphic illustration courtesy of Geoffrey Ozin and Chenxi Qian.

years ago at the end of the Ordovician Period. The first extinction occurred at the end of the Devonian Period about 370 million years ago followed by the second extinction at the end of the Permian Period around 245 million years ago. Notably, this extinction was caused by a temperature increase beyond 6°C from lava flow in Siberia and concomitant methane release from the permafrost. That particular natural catastrophe took around 50 million years for the earth's complex organisms to recover. The fourth extinction occurred some 210 million years ago, at the end of the Triassic Period. This was after the evolution of mammals and dinosaurs, when an increase in atmospheric CO<sub>2</sub> from volcanic activity, caused global warming, ocean acidification and extinction of life on earth. Finally, the fifth extinction, during the Cretaceous Period around 65 million years ago ended the era of the dinosaur and many other life forms. While the causes of the “big five” mass extinctions were complex in origin, ultimately the annihilation of life could be related to climate change ([https://en.wikipedia.org/wiki/Extinction\\_event](https://en.wikipedia.org/wiki/Extinction_event)).

Some 2.6 million years ago, during the Quaternary Period, glaciation events and associated climatic and environmental changes caused the extinction of many species. During the Holocene Period of the past 12,000 years, human activity began to have a noticeable effect on the rate of species extinctions. With the advent of the industrial revolution we now find ourselves in a new era called the Anthropocene Period. It is marked by the increasing use of fossil fuels to provide the day-to-day needs of a growing global population. Climate science and environmental studies have determined that humans are, indeed, causing global warming, which raises considerable concern about the future of life on earth.

In response to these concerns, scientists have recommended and governments have agreed, at the 2015 Paris **Climate** Change Conference, to implement challenging measures to keep the global temperature rise to less than 1.5°C ([https://en.wikipedia.org/wiki/Paris\\_Agreement](https://en.wikipedia.org/wiki/Paris_Agreement)). These measures include mitigation of greenhouse gas emissions and reduction in the use of fossil fuels. The goal is to minimize the risk of a “business as usual” scenario from the continuing use of fossil fuels with its accompanying CO<sub>2</sub> atmospheric emissions, which are now recognized to result in increases in extreme weather conditions that lead to more severe droughts, heat waves, water and food shortage, and the rise of sea levels.

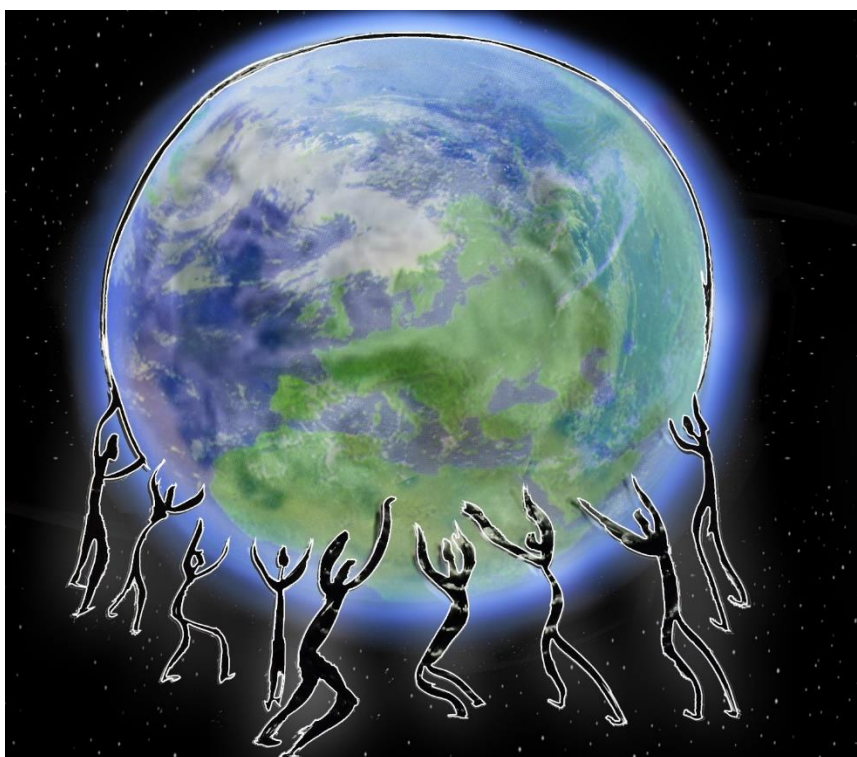
It is disquieting however that there does not appear to be much public discussion on the possibility that increases in the concentration of CO<sub>2</sub> from “business as usual”, could cause the sixth mass extinction. This time the collapse of our entire ecosystem would be unnatural in origin, caused by Homo sapiens, instead of being triggered by natural events that were responsible for the previous five mass extinctions.

It's ironic that since 1947, with the creation of the Doomsday Clock that measures the time to a possible global catastrophe, we have always thought that the demise of the human race would

likely be self-inflicted through nuclear war ([https://en.wikipedia.org/wiki/Doomsday\\_Clock](https://en.wikipedia.org/wiki/Doomsday_Clock)). Instead, we find ourselves in a war against climate change caused by our dependence on fossil fuels. A war that could lead to the sixth mass extinction, unless we gradually transition from non-renewable to renewable forms of energy by the end of this century.

This raises the debate on what have been termed “thresholds” and “tipping points”. These relate to non-negotiable planetary preconditions that as a globalized society we have to respect in order to avoid an abrupt state-change, which could induce a catastrophic adjustment in our environment at a global scale, and mass extinction. There is well documented evidence from studies of local and regional ecosystems such as, coral reefs, forests and lakes, that abrupt changes in state can occur when critical thresholds in nutrient supply, fresh water, biodiversity and harvesting are crossed. However, there is less information available about state changes at the global scale if we allow our planet to cross a temperature threshold that could result in collapse of the entire ecosystem of the earth. Scientists and politicians have now come to the realization that the temperature threshold condition to avoid abrupt changes of our ecosystem is well below 4°C and to play it safe, has been recommended to be no more 1.5°C.

It turns out that the scenario of a sixth mass extinction driven by a global temperature rise and state change, will most likely not come directly from increasing levels of CO<sub>2</sub> in the atmosphere. Instead, it will come indirectly from the amplifying feedback, exacerbating the temperature rise expected to accompany the release of trillions of tons of CH<sub>4</sub>, trapped as methane



Global Climate Change will not Change without You! In the war against CO<sub>2</sub>-CH<sub>4</sub> driven climate change we must all now act together responsibly and shoulder the burden of caring for our Earth with the same degree of concern as we care for ourselves and our collective future. Graphic illustration courtesy of Todd Siler and Geoffrey Ozin, [www.artnanoinnovations.com](http://www.artnanoinnovations.com).

clathrates, caused by thawing of Arctic and Antarctic ice.

We now know this mass release is caused by thawing of Arctic and Antarctic ice. We know that the rate of temperature rise of Arctic ice is about the same as the Antarctic, which is approximately double that of the rest of the Earth. We know that the thawing of the permafrost is already occurring with reports by Arctic and Antarctic specialists of extreme CH<sub>4</sub> supersaturation in surface water. We know that CH<sub>4</sub> is a much more potent greenhouse gas than CO<sub>2</sub>. And we know that the amount of trapped CH<sub>4</sub> in the Arctic is around 4-5 times greater than the trillions of tons of CO<sub>2</sub> that we have already released into the atmosphere, mainly from the use of fossil fuels since the industrial revolution.

In spite of all this considerable scientific knowledge, we're still maintaining a status quo fossil fuel global society. With this inevitable greenhouse gas induced temperature rise, we will not just be facing a CO<sub>2</sub> threat to our civilization - but more devastatingly, a CO<sub>2</sub>-CH<sub>4</sub> crisis. The potentially "Perfect Storm" CO<sub>2</sub>-CH<sub>4</sub> crisis will likely be intensified by the self-amplifying behavior of the permafrost thawing, which is creating a positive feedback cycle, runaway global warming, and maybe the sixth extinction.

Clearly but slowly, we are realizing that the survival of our civilization and world as we know it is in our hands. And our hands, literally and figuratively speaking can trigger the sixth extinction with the catastrophic release of CH<sub>4</sub> as the permafrost melts.

So we're all in a phenomenal war against CO<sub>2</sub>-CH<sub>4</sub> driven climate change. To tip the balance in favor of sustainability rather than extinction, we must all now shoulder the responsibility of caring for our Earth with the same degree of concern as we care for ourselves and our collective future.

This is only possible to do, if we believe we can do *the impossible*: Work together to create a truly sustainable future!

# 59 CO<sub>2</sub> Conundrum

Geoffrey A. Ozin

The chemical industry are one of the largest manufacturing sectors in the world with global sales currently valued at around a staggering \$5 Trillion. Many of the chemical feedstocks are fossil based and most chemical processes are powered by fossil fuels. They are also one of the largest producers of greenhouse gas and like most of us are concerned about the effect of greenhouse gas emissions on global warming and how they will affect our climate.

In the war now being waged against climate change, there are five big questions being asked by concerned citizens in university, industry, business and government who are motivated by fast, pragmatic and economically sensible solutions to the urgent problem of how best to abate greenhouse gas emissions by utilizing CO<sub>2</sub> as a feedstock for manufacturing chemicals, materials and fuels:

1. Scaling and Manufacture: what technological strategies for CO<sub>2</sub> utilization have the most promise for success in the short term?
2. Commercial Potential: what CO<sub>2</sub> derived products and uses offer the best opportunities?
3. CO<sub>2</sub> Footprint: what products and uses can achieve a carbon-neutral carbon-life-cycle?
4. Policy Making: what procedures are required to speed the adoption of products and uses based on CO<sub>2</sub> as a chemical feedstock?
5. R&D Strategy: what areas of CO<sub>2</sub> enquiry should be invested in for the long-term?



Figure 1 Catalytic processes for converting CO<sub>2</sub> into value-added chemicals – which one would you bet on?

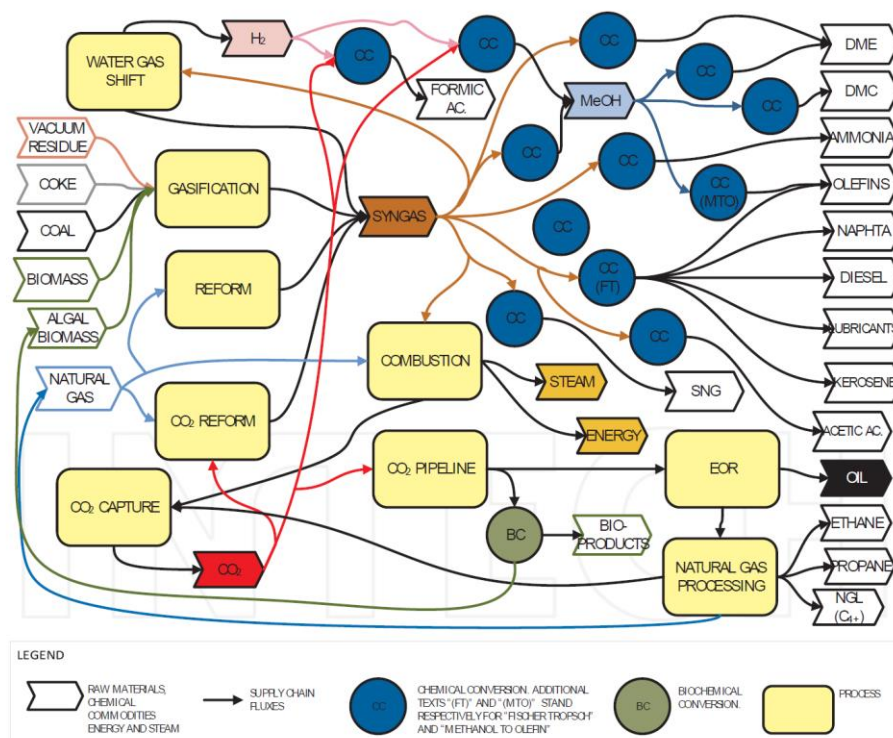
To realise a technologically, economically and sociologically acceptable solution to the abatement of greenhouse gas emissions, five commandments for utilization of CO<sub>2</sub> as a chemical feedstock have been mandated, as a replacement for fossil based feedstocks and fuels in chemical industrial processes:

1. Reduces overall CO<sub>2</sub> emissions
2. Lowers materials and energy intensity
3. Employs safer conditions
4. Operates on a commercial scale
5. Demonstrates economic viability

In this context, the chemical industry have been asking how CO<sub>2</sub> capture, utilization and valorization fits into the current supply chain, which comprises about 40,000 chemicals produced from the four

traditional feedstocks: oil, gas, coal and biomass. The perception of the chemical industry is that their CO<sub>2</sub> emissions are expected to expand and that treating CO<sub>2</sub> as a non-traditional feedstock, viewed as an asset rather than a liability, will help enable a transition to low-carbon processes based on existing infrastructure.

The opinion of the chemical industry seems to be that incorporation of CO<sub>2</sub> as a feedstock into their supply chain is most likely to be expected initially in mature technologies that focus on the



**Figure 2** Chemical industry supply chain flow diagram depicting the coexistence of fossil and biomass feedstock uses and how CO<sub>2</sub> capture and utilization can be integrated into existing production infrastructure. CO2 Utilization: A Process Systems Engineering Vision, Ofélia de Queiroz F. Araújo, José Luiz de Medeiros and Rita Maria B. Alves, <http://dx.doi.org/10.5772/57560>, © 2014 The Author(s). Licensee InTech. This work is distributed under the terms of the Creative Commons Attribution License <http://creativecommons.org/licenses/by/3.0>.



production of the key chemicals carbon monoxide, hydrogen, olefins, aromatics, ammonia, methanol and hydrocarbon fuel, see **Figure 2**. Notably, this change will require the rapid development of enhanced activity and selectivity catalysts that will facilitate advances in chemical process performance, intensification and optimization.

The chemistry challenge to achieve these goals relates to how to overcome the exceptional stability of the  $\text{CO}_2$  molecule, measured by its high free energy of formation of 394 kJ/mole. Its high thermodynamic stability means that high input of electrical, thermal or solar energy together with very active catalysts are required for any chemical conversion of  $\text{CO}_2$  to a value-added product.

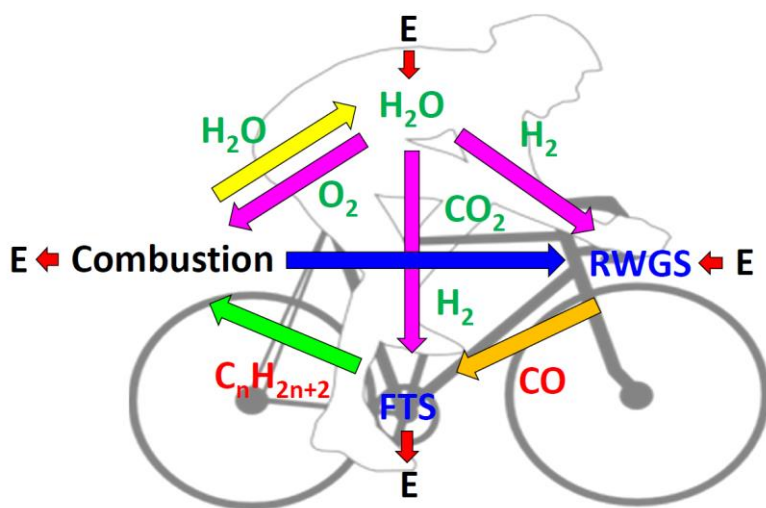


Figure 3 Carbon-neutral carbon cycle for making hydrocarbons from carbon dioxide and water.

In this light, there are six main catalytic  $\text{CO}_2$  conversion processes currently under active investigation all vying for a stake in the race to utilize and valorize  $\text{CO}_2$  as a supply chain feedstock for producing chemicals and fuels, **Figure 1**. Recall that the role of catalysts is to lower the activation energy barrier for chemical reactions in order to accelerate their rates and allow them to occur under much milder conditions.

Specifically, in the case of large volume production of chemicals from  $\text{CO}_2$ , which has to be accomplished at the megaton level to meaningfully impact climate change, the discovery of high performance catalysts is especially important to achieve processes with a low carbon footprint, high energy efficiency and economies of scale.

The goal of every catalytic  $\text{CO}_2$  conversion method illustrated in **Figure 3** for the case of hydrocarbons, is to provide carbon neutral alternative and sustainable sources of chemicals, polymers, pharmaceuticals and fuels. A big question however, concerns which are the preferred methods for innovative game-changing research to drive future technology development and commercialization? The answer to this question will enable decisions on which methods are ready to be accelerated through to pilot scale demonstration units, in order to facilitate the

replacement of existing processes based on traditional oil, gas, coal and biomass chemical feedstocks, with sustainable processes founded on CO<sub>2</sub>.

In this respect, an important initial target will involve the heterogeneous catalytic conversion of gaseous CO<sub>2</sub> into synthesis-gas CO/H<sub>2</sub>, as it is an appealing feedstock for making key chemicals, such as NH<sub>3</sub>, H<sub>2</sub>, CO, CH<sub>3</sub>OH and C<sub>n</sub>H<sub>2n+2</sub> and moreover makes use of existing tried-and-true chemical industry infrastructure.

To amplify, in the case of hydrocarbon fuels, this can be achieved in a carbon-neutral carbon-cycle of the kind shown in **Figure 2**. The cycle begins with H<sub>2</sub>O as a source of H<sub>2</sub> followed by use of the H<sub>2</sub> to reduce CO<sub>2</sub> in a reverse water gas shift process to form CO, which is then used to make hydrocarbons in a Fischer-Tropsche process. A similar cycle can be devised for making important chemicals and fuels exemplified by methanol, dimethylether, dimethylcarbonate, olefins, naphtha, diesel, lubricants, acetic and formic acid.

In terms of the short term industrialization of CO<sub>2</sub> one can draw the following conclusions:

1. CO<sub>2</sub> is a promising and sustainable feedstock for the chemical industry
2. CO<sub>2</sub> conversion to chemicals and fuels is at an early stage of development
3. CO<sub>2</sub> utilization is currently a very small fraction of greenhouse gas emissions
4. CO<sub>2</sub> most likely will integrate into the chemical industry supply chain and processing infrastructure as synthesis gas derived products, hydrogen, carbon monoxide, methanol, ammonia, and synthetic fuels.

These indicators imply that the future looks bright for the exploration and development of innovative CO<sub>2</sub> chemistry solutions to enable a sustainable chemical industry that will help mitigate climate change, reduce our dependency on fossil fuels, and enhance our protection of the environment. The development of these solutions is essential if the chemical industry are to reduce their carbon emissions and achieve the emission reduction targets imposed on the chemical industry in the next few years. They cannot achieve these targets by carbon efficiency measures alone.

In order to achieve these innovative CO<sub>2</sub> chemistry solutions, it is also essential that there be cooperation between the research community, the chemical industry and governments so that the necessary investment is available for pilot scale demonstration units and ultimately the scaling up of the winning units to a megaton commercial level. The expertise of the chemical industry will also be important with regard to the latter. It may be that there should be incentives for those chemical companies who are proactive in supporting and financing the pilot scale demonstration units required and ultimately the scaling up of units to a megaton commercial level.

In closing, it is worth noting that whichever greenhouse gas mitigation, reduction and utilization action plans are adopted to hold global temperature rise below 2°C, a successful outcome can only be assured if CO<sub>2</sub> emissions are monitored at local, regional and national levels, and legal and policy measures implemented to enforce compliance with CO<sub>2</sub> emission targets.

## Postscript from Industry

I will end this article with a postscript on some sobering words of wisdom from a friend and colleague in the chemical industry, who read this opinion editorial and offered the following remarks:

There is a lot going on in the chemical industry. They are continuously working on lowering the energy footprint of every one of their products and processes. The impact of implementing energy saving technologies in the chemical industry would reduce energy usage throughout the world significantly, which amounts to a lot of CO<sub>2</sub> but is only a partial solution to climate change.

The solution proposed in your editorial will require governments to enact legislation that makes CO<sub>2</sub> generation too expensive to sustain without converting it to something valuable. This is because the technologies needed to convert CO<sub>2</sub> to something of value have to pay off and ultimately be self-sustaining mid to long term for major corporations to get involved. If the senior management of corporations tried to altruistically invest in CO<sub>2</sub> conversion without a compelling business case, they would be replaced before they got very far!

The solution to this problem is a difficult balancing act that will likely involve legislation, start-ups who see the \$\$\$ that eventually will come with saving the world, VC's who are willing to gamble and wait, and finally major corporations getting into the act when they can see past the risk to a business.

This is probably not what you wanted to hear, but most people, including voters, look into their pocketbooks and their lives and vote and spend accordingly. Solving the climate change crisis will require nothing less than global lifestyle changes, rather than most inhabitants of every developing country wanting to live like American's, European's or Britain's.

It's interesting that what is needed is a sort of "conversion experience", where people suddenly look past their own needs to those of their grandchildren. It likely means that most of us will have to live more like those in the developing world. This "conversion experience" may be brought about by scientific proselytizing, but will enough of the public be converted to result in change? I can see the challenge here; people mostly don't change when they see the light, but when they feel the heat - perhaps literally in this case.

# Grasping Our Growing Gigatonne CO<sub>2</sub> Challenge

Geoffrey A. Ozin

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## *Our Growing Gigatonne Problem*



We're all “Overlooking the Facts”

Graphic illustration courtesy of Todd Siler and Geoffrey Ozin, [www.artnanoinnovations.com](http://www.artnanoinnovations.com).

## 60. Grasping Our Growing Gigatonne CO<sub>2</sub> Challenge

Geoffrey A. Ozin

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To appreciate the magnitude of the roughly 30 Gigatonnes of anthropogenic CO<sub>2</sub> emissions that humans generate annually from the combustion of fossil fuels, it is useful to illustrate what 1 tonne of CO<sub>2</sub> actually looks like physically, in relation to a well-known object. The idea is to obtain a more realistic and striking sense of scale of “Our Gigatonne CO<sub>2</sub> Challenge”, rather than trying to visualize the magnitude of the number itself taken in isolation.



Figure 1 Your Annual CO<sub>2</sub> Footprint – Roughly Twenty Times Bigger Volume than a London Double-Decker Bus. Graphic illustration courtesy of Chenxi Qian.

To help grasp this reality, **Figure 1** shows a picture of a 10 meter diameter sphere of CO<sub>2</sub>, which weighs 1 tonne in relation to a London double-decker bus. This graphic illustration gives meaning to mass in the form of volume. By relating the problem to familiar objects, a more meaningful and comprehensive picture forms, which gives us a better feel for the masses of CO<sub>2</sub> produced annually from the use of fossil fuels.

This image dramatically depicts what I call “Our Growing Gigatonne CO<sub>2</sub> Challenge” that we must now work together to solve forever. This urgent collaborative work is a key part of this challenge to radically reduce greenhouse gas-induced climate change. More to the point: a disturbing picture emerges that may prompt people to realize that we’re all contributing to the growth of this Gigatonne CO<sub>2</sub> problem, as this evocative image and others in this article intimate.

Just imagine 30B = 30,000,000,000 of these 1 tonne CO<sub>2</sub> spheres being injected into our atmosphere every year from the combustion of fossil fuel. With the current population of the

world at 7.4B, this today amounts to around 4 tonnes per person annually. I find it disquieting that currently there is no obvious technology-policy evidence we know how to reduce the global CO<sub>2</sub> emission rate and solve the looming global warming and climate change problems fast enough. Yet, it is now a global priority that we find ways and means to cut these emissions in half to avoid the inconvenient consequences of global warming.

Tackling together “Our Growing Gigatonne CO<sub>2</sub> Challenge” entails not only discovering and implementing different approaches for the mitigation and reduction of CO<sub>2</sub> emissions to meet greenhouse gas targets as defined in the Paris Climate Agreement. It also involves utilizing CO<sub>2</sub> as a feedstock for making value-added chemicals, materials and fuels as fast as possible and at a scale, efficiency and cost that can stabilize the concentration of CO<sub>2</sub> in our atmosphere.

In the context of the larger perspective of 21<sup>st</sup> century solutions to the global energy and environment challenges that we face, one has to breakdown the problem into short (2030), medium (2050) and long term (2100) approaches to enable the transition from a non-sustainable fossil energy system to a sustainable renewable one.

Remember that today’s fossil intensive global energy infrastructure and globalized economy required trillions of dollars and over a century to create from scratch. An energy transition to a carbon neutral sustainable world will take time and will be expensive with challenging trade-offs with economic growth. This transition will only be possible if the political and business leaders of the major greenhouse gas emitting nations believe in climate change and are prepared to invest in renewable energy technologies.

Thinking about the near term strategy to enable this energy transition, the consensus is that improvements in energy efficiency for industrial processes, building construction, land, sea and air transportation, information technology, use of natural gas and conversion to electric powered vehicles, together will serve to gradually replace coal and reduce the use of oil and natural gas.

In the mid-term, the increased implementation of solar and wind power, fuels cells, biomass, biofuels and biogas, waste heat recovery and smart grids, together with CO<sub>2</sub> capture, storage and utilization, will further diminish the use of coal, oil and natural gas by increasing the conversion of CO<sub>2</sub> to value-added chemicals, materials and fuels. Together these approaches should enable control of atmospheric CO<sub>2</sub> emissions at a level that maintains average global temperatures below the Paris Agreement target of 1.5-2.0°C by 2030.

Fast, practical, large-scale and economically sensible mid-term approaches to CO<sub>2</sub> utilization will most likely be based upon the use of biomass, electrocatalysis and heterogeneous catalysis for making chemicals and fuels from CO<sub>2</sub>, which will be supplemented by mineralization of CO<sub>2</sub> to

inorganic carbonates, for permanent storage of CO<sub>2</sub> and manufacture of construction materials, like concrete and cement.

Long term solutions to our energy and environment challenges will include the use of solar power for generating H<sub>2</sub> from H<sub>2</sub>O and using the H<sub>2</sub> for converting CO<sub>2</sub> into chemicals and fuels, grid-scale battery storage of renewable electricity, superconducting electricity transmission and maybe even the long-awaited “holy-grail” breakthrough of nuclear fusion energy.

A measure of the success of all of these processes will be the CO<sub>2</sub> footprint. It would not be smart to develop a biological or abiological CO<sub>2</sub> conversion process that ends up adding more CO<sub>2</sub> to the atmosphere somewhere else. For example, the use of grid electricity does not come for free in terms of CO<sub>2</sub>. A trivial mass balance can be applied to describe the user-friendliness of a CO<sub>2</sub> conversion process: the amount of CO<sub>2</sub> emissions associated with the energy consumed is subtracted from the amount of CO<sub>2</sub> converted in the process and should be neutral or negative.

Along the lines of **Figure 1** is another powerful image shown in **Figure 2** that depicts in strikingly visual scientific and artistic form, a cube that contains all the CO<sub>2</sub> in the earth’s atmosphere lumped into two domains. This cube is about 120 km on an edge and at a pressure and temperature equivalent to that at sea-level contains roughly 3 trillion tonnes of CO<sub>2</sub> that constitutes the troposphere. Natural CO<sub>2</sub> is represented by the blue segment of the cube while the red segment is anthropogenic CO<sub>2</sub> created by the use of fossil fuels since the industrial revolution. The former is sufficient to maintain life on

Earth. Continuing to increase the latter, by business as usual consumption of fossil fuels, has the potential to tip the balance between life and extinction on Earth.



Figure 2 All the Earth’s CO<sub>2</sub>, Natural (blue) and Anthropogenic (red) in a Box; Graphic illustration courtesy of Chenxi Qian.



I have always been an optimistic scientist in my approach to problem solving but to be quite honest I am not sure whether we really know how to solve our Gigatonne CO<sub>2</sub> problem fast enough to prevent average global temperatures rising above the perceived threshold value of 1.5-2.0°C. Climate change is certainly the greatest challenge that our global family has had to face in the history of humanity.

Perhaps it will be climate economics that comes to our rescue as climate change gains momentum as a global investment enterprise because of the impact transitioning from non-renewable to renewable forms of energy will have on investors' portfolios.

Clearly, we must all now shoulder the Herculean responsibilities of caring for our Earth with the same degree of concern as we care for ourselves and our collective future. The big question is, can "We" rise to this Herculean challenge and can "We" do it in time?

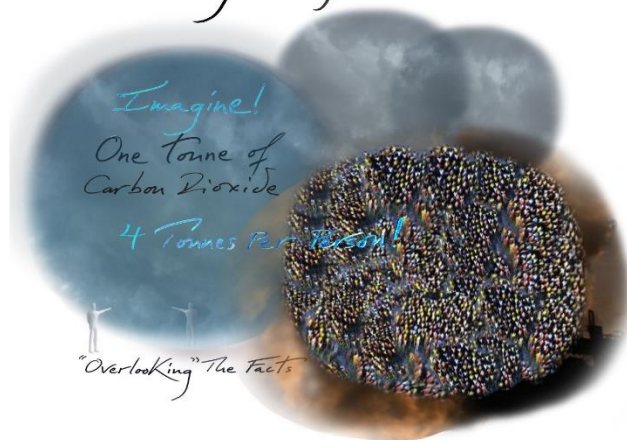
## Post Script

I commented to my artist colleague and friend Todd Siler ([www.toddsilerart.com](http://www.toddsilerart.com)) who created his signature style Metaphorm of the message conveyed in this opinion editorial that it was not clear to me what we are reflecting upon inside the grey spheres. His insightful response to my comment is presented verbatim below:

"To answer your question as clearly as I can (re: 'what we are reflecting upon inside the grey spheres'), allows me to share this true story: When astronaut Neil Armstrong took his first step on the Moon, shortly after he and Buzz Aldrin landed in Apollo 11 on July 20, 1969, at 20:18 UTC, one wide eyed journalist asked Bucky Fuller excitedly: "What do you think it would be like to be in space?" To which Fuller replied incredulously, "We are in space!"

Even the most educated, inquisitive, concerned world citizens reading your wise opinion editorials may not see themselves as being one of those 7.4 billion people who are standing "inside" (alongside everyone else on our planet) those overlapping grey spheres that symbolize our polluted biosphere. In fact, nobody's standing "Outside The Problem" omnisciently looking

### *Our Growing Gigatonne Problem*



We're all "Overlooking the Facts". Graphic illustration courtesy of Todd Siler and Geoffrey Ozin, [www.artnanoinnovations.com](http://www.artnanoinnovations.com).

over The Problem who isn't directly affected by it. So, we all need to try our best to be actively conscious of Our Growing Gigatonne CO<sub>2</sub> Problem.

That's what's implied by this double-entendre, "Overlooking The Facts." In trying to "look over" the facts on climate change - in trying to evaluate the potential impact of The Problem - most people don't see ourselves contributing to it by releasing 4 tonnes of CO<sub>2</sub> every year. That number is massive when you consider the mass of humankind doing that collectively!

To press this point and "hyperbolize" it (create a visual hyperbole), I've overcrowded one of the spheres. That Metaphorm may strike you as a Malthusian image invoking Thomas Malthus's "Essay on the Principle of Population" (1798), but it's not. I'm suggesting that our global environment may "**feel**" like this image looks! Especially, when you consider it in the context of what you've described in an earlier opinion editorial concerning the trillion tons of methane that will be released from permafrost if we don't make our numbers noted in the Paris Agreement.

As you know so well, our perceptions define reality. If we perceive ourselves as not being part of "The **Problem**" or overlooking it rather than constantly looking over it and responding to it then we won't "Grasp It" or do anything to significantly change what needs to be changed now.

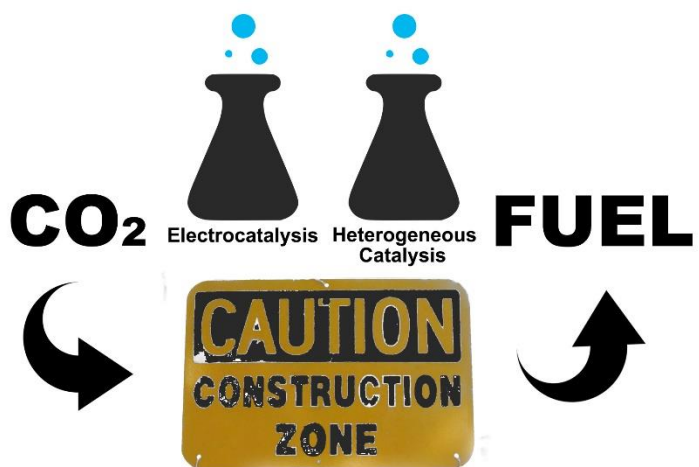
Each of us is "that person" who's reflected in the mirror-like sphere. That's not just a human measure to help us understand the magnitude of The Problem. It's a critical "Human Detail" that will determine our future."

Todd Siler

## 61. Weapons of Mass Construction in the War on Climate Change: Heterogeneous Catalysis and Electro-Catalysis

Geoffrey A. Ozin

In some countries the most energy-efficient and cost-effective way of storing excess electricity, whether fossil or renewable on a large scale, greater than Megawatts, is in the form of potential energy by pumping water up to mountain lakes, as thermal and mechanical energy by adiabatically compressing air, and as rotational energy in spinning flywheels. In many countries, all of these electricity storage methods combined represent only a few percent of actual total electricity generation.



In the war against climate change two promising approaches are being developed for catalytically converting CO<sub>2</sub> to value-added chemicals and fuels

There are many opinions on this subject and until grid-scale storage of electricity, in for example flow batteries, is part of the electricity infrastructure the jury is still out on what to do with excess electricity, especially as renewable electricity becomes abundant, the essence of our envisioned sustainable future. An important point here is that flow batteries are good for diurnal storage or at best short term storage of electricity. This is due to limited capacity and temporal discharge. Chemical storage of electricity on the other hand using electro-catalysis or heterogeneous catalysis methods allows seasonal storage, which can offer advantages for example, in electricity rich provinces, making use of electricity for the production of chemicals and fuels. Depending on location chemical storage may be best in the summer for use and consumption in the winter or vice versa.

A contemporary view is that electrochemical storage of excess electricity by converting an aqueous solution of CO<sub>2</sub>/H<sub>2</sub>O into chemicals and fuels by electro-catalytic methods is a good strategy for fighting climate change. A parallel opinion is that the excess electricity can be used to drive thermochemical transformations of CO<sub>2</sub>/H<sub>2</sub> by heterogeneous catalytic approaches to chemicals and fuels. The idea in both cases is that grid-scale electrical-to-chemical energy

storage can be employed to control load leveling of power and demand of the electrical grid as well as the production of value-added chemicals and fuels. A counterargument to this approach centers on the thesis that currently there is not enough excess electricity to have any significant impact on climate change and instead the surplus is more wisely used in charging stations to power up the rapidly growing number of electric vehicles. Some believe that charging stations directly powered by solar electricity may be the way of the future.

Others believe in a much grander plan - an international effort to provide renewable electricity to 139 nations around the globe by 2050 with about 37% wind, 58% solar, 4% hydropower, and 1% geothermal, wave, and tidal power. This would essentially eliminate the need for stationary storage batteries, biomass, nuclear power, carbon capture, or natural gas.

While all of this may be good for urban transportation, it is not feasible for long-haul road and aviation mobility, where high energy density fuels are needed. This may change with time, imagine short flight electric and long haul fuel cell planes, however there will be a pretty long dependence on hydrocarbon transport fuels. Electricity to chemicals and fuels technologies by electro-catalysis and heterogeneous catalysis offers a potential solution. While at first glance this appears to be contrary to mitigation strategies as the CO<sub>2</sub> is released on combustion, an often neglected fact is that using this approach it is possible to avoid more fossil oil derived fuels entering the supply chain.

Another concern is the question of the cost of electricity, which is the most expensive 'reagent' for converting CO<sub>2</sub>/H<sub>2</sub>O and CO<sub>2</sub>/H<sub>2</sub> into stored chemical energy using aqueous phase electro-catalysis or gas phase heterogeneous catalysis, respectively. If one could do this using sunlight directly, it becomes a non-issue but neither of these solar powered CO<sub>2</sub> to chemicals and fuels processes is efficient enough process to be commercially viable.

So, the cost of electricity is a key parameter in any business model for making a profit from CO<sub>2</sub> and is being investigated extensively. The challenge for electrochemical synthesis using CO<sub>2</sub>/H<sub>2</sub>O as the feedstock, at today's industrial electricity rates, is to make the product at a competitive cost. Therefore, to achieve commercially acceptable energy and economic flows together with an overall carbon neutral footprint, one needs to pick a product carefully with respect to the lowest possible electricity load and highest value-added product, as well as choosing ones energy source carefully in terms of cost. The jury is still out on the product of choice for a commercially successful business. It could be formic or oxalic acid as a safe hydrogen storage source for use in H<sub>2</sub>/O<sub>2</sub> fuels cells, carbon monoxide as a feedstock for the synthesis of hydrocarbons and methanol, ethylene glycol for making polyester fibers and antifreeze or ethylene as a basic building block for polymers and copolymers.

This is potentially good news for renewable electricity from wind and hydro during off-hour periods where the cost of the electricity is not too high. Solar electricity can work too if the

chemical product is considered as a stored energy source for dark usage, but it is not commercially competitive with wind and hydro-electricity at this point for chemical synthesis using CO<sub>2</sub> as the feedstock.

Here one must question whether the development of new electrochemical technologies for the transformation of excess electrical energy to stored chemical energy could really have an impact on greenhouse gas climate change? This is an argument for integrating electricity powered, thermally driven heterogeneous catalytic reactor technology into the existing chemical and petrochemical industrial infrastructure. An alternative approach would be to integrate a small chemical plant next to a power plant. Capturing and transporting/storing CO<sub>2</sub> can be expensive. A detailed techno-economic analysis is needed of course to decide which is better

In this way one can convert CO<sub>2</sub>/H<sub>2</sub> to chemicals and fuels, at a sufficiently large scale, high efficiency and low cost that it could meaningfully impact climate change. Now the question of the source of H<sub>2</sub> and its cost becomes a discussion point, just as one appraises the supply, demand and sources of electricity in different countries, the insolation that reaches the earth's surface in different parts of the globe, and the availability of sufficient quantities of water of the right quality. Think about the surfeit of hydroelectricity in Quebec and Iceland and plethora of sunlight in the Middle East and North Africa.

In the context of countries rich in coal and natural gas that decide to keep on using them as an energy source, for example in electricity generating stations, an argument forwarded for their continued use, is that the heat of combustion can be usefully employed to drive gas-phase heterogeneous catalytic processes for converting the associated CO<sub>2</sub> emissions to value-added chemicals and fuels. While this can be considered a short term solution, it wouldn't work in the long term of achieving carbon-neutrality as the mined coal and natural gas will have to end up somewhere, which is likely the atmosphere in the form of CO<sub>2</sub>. The same specious argument can be voiced against the use of captured CO<sub>2</sub> for enhanced oil recovery. On the other hand, renewable energy powered electro-catalytic and heterogeneous catalytic CO<sub>2</sub> utilization processes can create a complete carbon-neutral cycle and hence a better long-term solution to climate change.

Perhaps a more important consideration would be the efficiency of multiple processes in the CO<sub>2</sub> to chemicals and fuels supply chain. While storing grid electricity in batteries and charging units is probably more efficient than converting the electricity into chemicals and fuels using CO<sub>2</sub>/H<sub>2</sub>O and CO<sub>2</sub>/H<sub>2</sub>, and then using them later, there are all the other considerations that have to be taken into account. Both positive and negative, these considerations include the efficiency and scale of the conversion process, being able to store the chemicals and fuels for longer time frames and transport them across longer distances, and energy density in chemicals and fuels compared to batteries.

Since batteries are a well-developed and mature technology, while electro-catalysis and heterogeneous catalysis for CO<sub>2</sub> conversion are still in their infancy, with none or very few commercial examples, one can understand the argument of storing excess electricity in electric cars. However, batteries cannot be used for large scale transportation such as tankers and cruise ships, planes and large trucks, which accounts for 40% of the transportation industry. So chemicals and fuels from CO<sub>2</sub> may well play a part in this user sector.

In the case when CO<sub>2</sub> derived chemicals and fuels are needed, whether electro-catalysis or heterogeneous catalysis is the better approach for their production is currently a very difficult question to answer, because there are so many factors that need consideration. For the case of electro-catalysis, one needs electricity to drive the kinetics and thermodynamics of the reaction. An economically viable aqueous phase electrochemical CO<sub>2</sub> utilization technology will require a large current density to enable a high rate of conversion, a high Faradaic efficiency to favor a desired product, low over-potential to facilitate a high energy efficiency, and optimum electro-catalyst stability to permit a long electrode lifetime. Similarly, a practical gas phase heterogeneous catalytic CO<sub>2</sub> conversion process driven by electrical energy should achieve high reaction rates, turnover frequencies and efficiencies under as mild conditions of temperature and pressure as possible. In both approaches, selective conversion of CO<sub>2</sub>, for example to CO, CO/H<sub>2</sub>, CH<sub>4</sub>, HCO<sub>2</sub>H, C<sub>2</sub>H<sub>4</sub>, C<sub>2</sub>H<sub>4</sub>(OH)<sub>2</sub>, CH<sub>3</sub>OH, and (CH<sub>3</sub>)<sub>2</sub>O is of particular interest. Providing there is sufficient electricity from the grid, whether derived from nuclear, wind, solar, tidal, geothermal or hydroelectric sources, and these chemicals are not more costly to produce by CO<sub>2</sub> reduction than by current means, even with CO<sub>2</sub> at \$50/ton, this may be feasible.

Something to consider here is that industries requiring large amounts of energy tend not to be reliant on the grid. Instead they have their own cogeneration facilities, a combined heat and power system that provides both electric power and heat from a single fuel source. It may be that these industries will install wind turbines and solar arrays dedicated to the processes, offsetting the capital expenditure costs against buying in power. A problem here, is that these industries rely on a “steady” supply of energy because they tend to employ continuous “steady-state” units. So, they can use renewable technologies but they will still need to have “traditional” on-site production or be connected to the grid.

In the case of heterogeneous catalysis, at the moment there is no technologically significant, commercialized working version of CO<sub>2</sub> + H<sub>2</sub>O conversion to chemicals or fuels. In most of this research, the reductant is H<sub>2</sub>, the majority of which comes from steam methane reformation and hydrocarbon sources. To make H<sub>2</sub> renewably and reduce CO<sub>2</sub> through heterogeneous catalysis in a carbon neutral carbon cycle, the best source would be through water electrolysis, which would need electricity anyway. So if both heterogeneous catalysis and electro-catalysis processes need electricity, is there really an advantage to one or the other? In this context, it is

noteworthy that proton exchange membrane electrolyzers for H<sub>2</sub> generation have been commercialized where H<sub>2</sub> is generated at the point of need.

The other considerations are infrastructural in nature. Where would electrochemical cells be located - in line with factories or refineries, downstream from various industrial processes, and how would CO<sub>2</sub> be delivered to them? One advantage of electro-catalysis is being able to separate the electrodes and hence the products into different compartments. However, the aqueous-phase electrochemical systems are likely not as versatile and easy to implement as gas-phase heterogeneous catalytic systems, which are pervasive at the Megaton scale in the chemical and petrochemical industries. They can also be implemented as micro-structured heterogeneous catalytic reactors, modules of which can be assembled at different scales on-demand. Micro-heterogeneous catalytic reactors have the advantages of high energy efficiency, conversion rates and yields and provide scalable on-site demand and production with impressive process control. The analogue in electrochemistry would be microfluidic electrochemical cells, assembled to the scale required for a particular application and geographic location.

Electrochemical cells need a lot of infrastructure, including cells, electrodes, membranes and electrolytes. Problematical also is the low solubility of CO<sub>2</sub> in water that can limit conversion rates to products and which have to be purified by separation from the aqueous phase. To overcome solubility challenges, specially designed porous electrodes are needed to enhance the interaction between the gaseous CO<sub>2</sub>, electro-catalyst and liquid electrolyte, thereby reducing mass transfer, charge transport, ohmic resistance and wettability restrictions in the electrochemical reduction of CO<sub>2</sub>. By comparison, gas-phase heterogeneous catalysis would need flow reactors, high pressures and high temperatures, and if solar powered, light harvesting.

So to really compare and decide which is preferred over the other, one needs a full energy, scalability and stability CO<sub>2</sub> foot-print, and economic analysis, to meaningfully assess all of the aforementioned considerations. In this context, a number of life cycle and techno-economic analyses have been carried out in recent years. These show that the processes are currently not economically viable, however, this is mostly due to geographical location and economies of scale.

The reality today is that carbon capture and utilization technologies are small in comparison to global total carbon dioxide emissions and it is still two orders of magnitude greater than carbon capture and storage. Carbon avoidance is probably a better target at this time than focusing exclusively on mitigation.

My view is that collaborative research and development projects between university and industry that focus attention on both approaches for converting CO<sub>2</sub> to chemicals and fuels should be greatly intensified so that we have as many weapons of mass construction to support our war against climate change. The element of competition in research and development



between the two approaches must be considered a good thing assuming there are enough teams involved in each approach.

It is interesting to speculate what drives the research and development for each approach. Is it the commercial, technical and infrastructural considerations of the industrial companies which would adopt one of these approaches? There have been many inventions where there have been two competitive options but even though one was clearly technically superior to the other, the inferior one was adopted as the one throughout the industry.

At this stage, research and development for both approaches should be intensified if that is at all possible. Also it should be remembered that research and development does not move in a straight line and that if one of the processes is discounted at some point, there is a possibility that exciting developments for that approach could be lost.

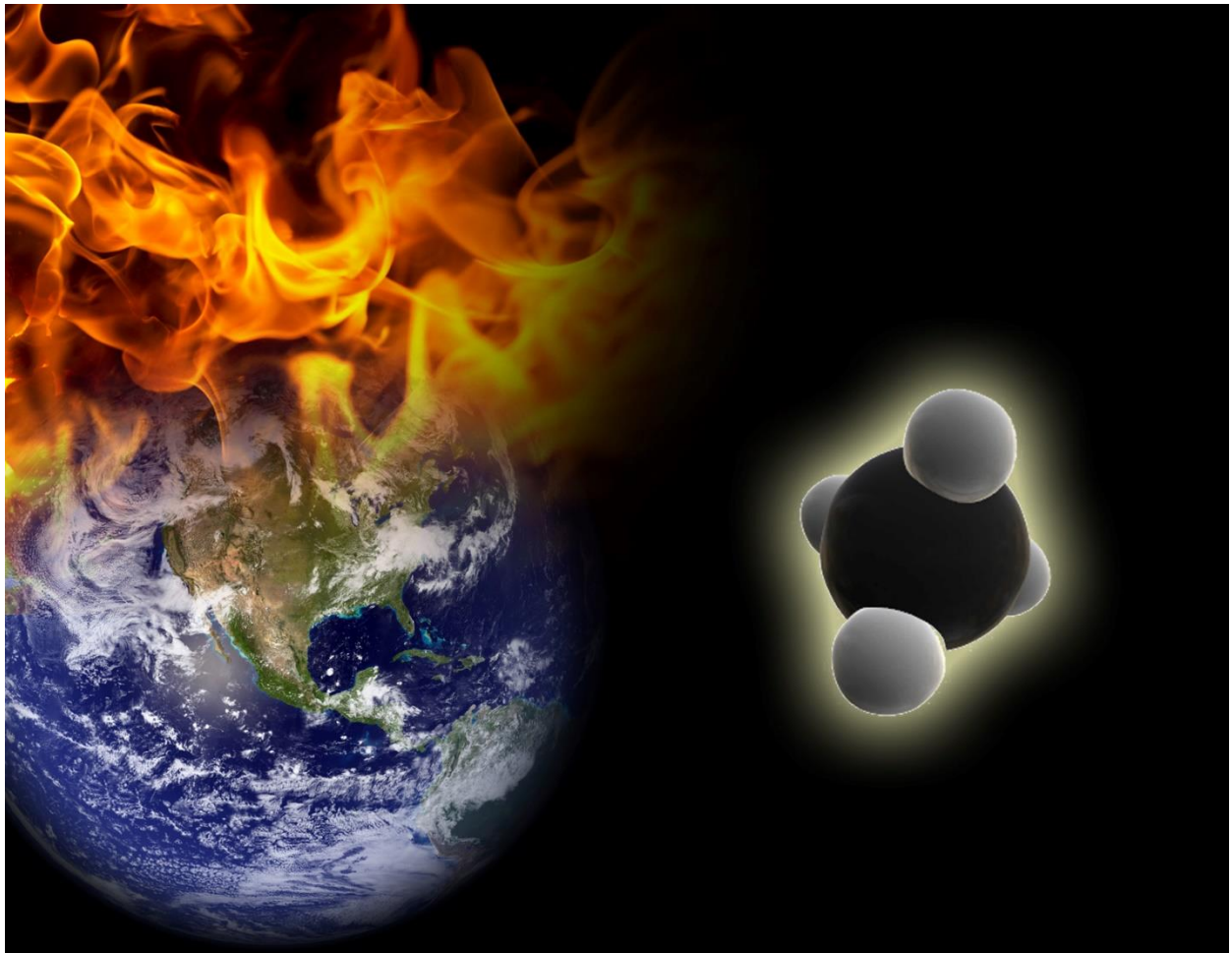
In this context I am encouraged to see a number of heroic scientists, engineers and investors creating spin-off companies dedicated to the development of high efficiency and cost effective electro-catalytic and heterogeneous catalytic processes for converting CO<sub>2</sub> into value-added chemicals and fuels. These include Liquid Light, Dioxide Solutions, Audi-Sunfire, Sandia National Laboratory, NewCO<sub>2</sub>Fuels, Solar-Jet-Fuels, Syntrolysis Fuels, Doty Energy-WindFuels, Air-Fuel Synthesis, Green-Feed, Opus 12, Enerkem, Quantiam, LanzaTech, Catalytic Innovations and E-Diesel.

Hopefully these CO<sub>2</sub> utilization ventures will be successful in their goal of converting CO<sub>2</sub> to profit and expanding their production facilities across the globe to a scale that can meaningfully impact greenhouse gas induced climate change.

On this Utopian vision, a knowledgeable colleague commented that to make a profit out of CO<sub>2</sub>, one has to find the right products. The end game most likely is not going to be the vector sum of many smaller commercialization vectors. Each one might point in slightly different directions, but together they will bring technologies that are massive and competitive enough to move the needle on CO<sub>2</sub> emissions and climate change. Nobody currently knows what these paths will look like definitively, but I'm guessing the people who created the Apple App store and Google Play also did not predict Uber/Lyft and the many other billion dollar companies at the time.

In closing, maybe it is worth commenting that making a profit out of CO<sub>2</sub> will always be difficult, as almost everything that can be made from CO<sub>2</sub> can also be made from CO. Since syngas CO/H<sub>2</sub> can be obtained from natural gas, it will be very difficult to compete. So maybe a better case can be made on societal need to address environmental challenges without too large a cost.

# A Burning Question: Anthropogenic CH<sub>4</sub>!



## 62. A Burning Question: Anthropogenic CH<sub>4</sub>!

*The recent fervor over CO<sub>2</sub> capture and conversion technologies, inspired by the effort to control GHG emissions has often excluded CH<sub>4</sub>, another major GHG contributor with a 100-year potency 30 times that of CO<sub>2</sub>. In particular, vented, leaked and flared “fugitive” CH<sub>4</sub> emissions from shale-gas wells is shaping up to be a major contributor to climate change. The big question is, what are we going to do with the rapidly increasing concentrations of CH<sub>4</sub> and associated combustion product CO<sub>2</sub> building up in our atmosphere?*



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### The Other Greenhouse Gas

A grand challenge for projects aimed at mitigating the two most potent greenhouse gas emissions CH<sub>4</sub> and CO<sub>2</sub>, is to use renewable forms of energy to simultaneously convert them, using a small number of catalytic steps, into value-

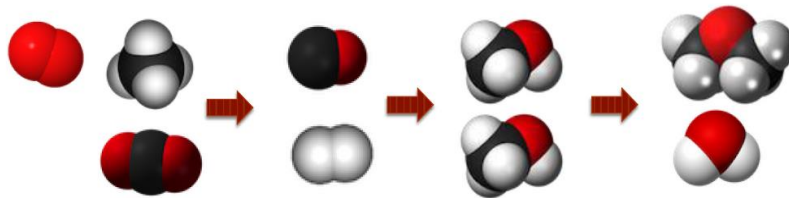


Illustration of the chemically catalyzed conversions, left to right, of CH<sub>4</sub>/H<sub>2</sub>/CO<sub>2</sub> to CO/H<sub>2</sub> to CH<sub>3</sub>OH to (CH<sub>3</sub>)<sub>2</sub>O.

added chemical energy carriers. Ideally, this process could be executed in a single stage. Success in this endeavor would provide an effective way of transforming renewable electrical, solar or thermal energy into stored chemical energy, which can be used for load-leveiling on the electrical grid or as a synthetic fuel replacement for fossil fuels.

With this strategy of “killing two birds with one stone”, the two most potent anthropogenic greenhouse gases, CH<sub>4</sub> and CO<sub>2</sub> that are rapidly accumulating in our atmosphere, can be simultaneously reduced, while creating a useable chemical feedstock, such as CO/H<sub>2</sub> synthesis gas. This synthon, known as syngas, can be transformed with known catalysts and processes, to methanol CH<sub>3</sub>OH and dimethyl ether (CH<sub>3</sub>)<sub>2</sub>O, for applications as a feedstock for making a myriad of chemicals and a clean-burning replacement for polluting diesel fuel.

Using this approach, CH<sub>4</sub> flaring, venting and leakage, a common occurrence at the natural gas well head, can be eliminated and fossil generated CO<sub>2</sub> can be reduced and valorized, both contributing positively to the reduction of greenhouse gas emissions in the war against climate change.

To expand upon this vision, in the light of climate change and the world's growing energy demands, it has become imperative to reduce global CO<sub>2</sub> emissions and seek alternatives that would ultimately end our dependence on fossil fuels. This year the concentration of CO<sub>2</sub> in our atmosphere reached the unprecedented level of 404 ppm to be compared to the 297 ppm pre-industrial revolution levels. To meet the Paris Cop 21 global warming targets this rate of increase in CO<sub>2</sub> emissions must be curtailed by 2030.

In this spirit, research groups around the world have been actively pursuing the discovery and evaluation of novel catalytic nanomaterials capable of producing sustainable chemicals and fuels, from the plethoric quantities of anthropogenic gaseous CO<sub>2</sub> present in our atmosphere. They have already been quite successful in the discovery of novel, scalable and inexpensive metal oxide based nanomaterials, which enable the thermochemical, photochemical or photothermal conversion of CO<sub>2</sub> to CO, CH<sub>4</sub> and CH<sub>3</sub>OH with high conversion rates, selectivity's and turnover frequencies. Industry is in the throes of figuring out where CO<sub>2</sub> utilization fits into its supply chain and how best to turn CO<sub>2</sub> into a profitable chemicals and fuels business that can compete with fossil resources.

## **The CO<sub>2</sub> Scylla is Here, Now Enter Charybdis**

As well as the CO<sub>2</sub> challenge, we are also facing a dangerous anthropogenic CH<sub>4</sub> problem, with atmospheric concentrations having reached around 2000 ppb, compared to pre-industrial revolution levels of about 700 ppb, with no sign of abatement. Note that, pound-for-pound, CH<sub>4</sub> traps about 85 times the amount of solar heat than CO<sub>2</sub>, meaning its global warming potential is 85. Taking into account that CH<sub>4</sub> in the atmosphere is gradually destroyed by solar radiation compared to CO<sub>2</sub> slowly dissolving into oceans and absorbing into soil and rock, the 100 year global warming potential of CH<sub>4</sub> is estimated at about 28-36 times that of CO<sub>2</sub>.

All of this means the global warming equivalent of anthropogenic CH<sub>4</sub> in our atmosphere, compared to CO<sub>2</sub> is now roughly 60,000 ppb = 60 ppm and rising. At the current rate of increase, the effect of anthropogenic CH<sub>4</sub> on our climate, exacerbated by the recent boom in shale-gas production and exploration, will soon catch up and surpass today's unprecedented CO<sub>2</sub> concentrations of 404 ppm. So we have to face the reality of a growing CH<sub>4</sub> greenhouse gas climate change challenge as well as the CO<sub>2</sub> challenge.

To amplify, about 20% of the CH<sub>4</sub> concentration in our atmosphere stems from the production of coal, oil and natural gas, another 50% comes from other anthropogenic sources, such as

fermentation, cultivation, biomass burning, animal waste, sewage treatment and landfills, while the remainder emanates from natural sources that include permafrost, ocean and termites.

Therefore about 30% of CH<sub>4</sub> comes from natural sources, which may be difficult to control, particularly if permafrost melts further releasing huge quantities trapped therein.

Every year, around 150 Billion cubic meters of natural gas equivalent to 5.3 Trillion cubic feet, is wastefully flared at thousands of oil fields globally. The total burned is equivalent to around one quarter of the annual gas consumption of the US. This results in more than 300 million tons of CO<sub>2</sub> being emitted to the atmosphere, equivalent to emissions from approximately 77 Million cars. If this amount of gas were used for power generation, it could provide more electricity (750 Billion kW-hr) than the annual consumption of Africa. Currently, natural gas is flared for a variety of technical, regulatory and economic reasons because capture is not given high priority.

In the US, fueled largely by technological advances and the associated boom in shale-gas extraction, the production of natural gas has increased by more than 20 percent in the last five years. Currently there exist around half a million natural gas wells and thousands of miles of pipelines, with no sign of the shale-gas explosion slowing down. While there is some uncertainty in the exact amount of fugitive CH<sub>4</sub> emitted from a natural gas well it has been estimated that in CO<sub>2</sub> equivalents over a hundred year timeline, the CH<sub>4</sub> GHG effect in the US will supersede the sum total of GHG emissions from all US iron, steel, aluminum and cement manufacturing facilities combined.

North American governments are clamping down on the practice of flaring, but oil producers are often left without economic options for dealing with this gas. The “Zero Routine Flaring by 2030” initiative is endorsed by 9 countries, 10 oil companies and 6 development institutions was launched in April 2015 by UN Secretary-General Ban Ki Moon and World Bank President Jim Yong Kim. The endorsers collectively represent more than 40 percent of global gas flaring, with Canada and the United States within the top 10 grouping.

In oil-rich regions across the globe, many of which are located in remote areas of the country, surely it makes sense to catalytically convert fugitive CH<sub>4</sub>, directly at the well-head, into a storable and transportable liquid energy carrier, such as methanol, rather than continuing the current practice of venting and flaring the CH<sub>4</sub> with its associated greenhouse gas problems.

## **The Fight Begins with the Catalyst**

Dry reforming of methane with CO<sub>2</sub> (CO<sub>2</sub> and CH<sub>4</sub> to CO and H<sub>2</sub>) has been undertaken using noble metals (Rh, Pd, Pt, Ru) for years. Commercially, firms have used nickel (Ni) based catalysts, but have created problems with coking via the Boudouard reaction. Without the appropriate catalyst, the dry reforming reaction requires temperatures above 1475 K. Recent work on “Super Dry-Reforming” uses a nickel based catalyst while supplying oxygen using a sacrificial iron oxide

(Fe<sub>2</sub>O<sub>3</sub>) combined with MgAl<sub>2</sub>O<sub>4</sub> operating at 1023 K. Since many sources of fugitive methane come from decentralized sources (1,000-10,000 Nm<sup>3</sup>/day), any conversion process will require even lower temperature catalysts operating at near atmospheric pressures, creating a low parasitic load, while possibly using renewable energy (solar, wind, run-of-the river hydro, geothermal, etc.) to run and energize a dry-reforming system that yields an easy to store and a low-cost liquid fuel intermediary.

There have already been some notable successes in the discovery of earth-abundant and inexpensive nanomaterials, which enable the gas-phase heterogeneous catalytic conversion of CO<sub>2</sub> to CO and CH<sub>4</sub> with high conversion rates, selectivity and turnover frequencies, energized by sources of heat and/or light. Today the materials chemistry and chemical engineering community are faced with the task of developing energy efficient and economically viable gas-phase heterogeneous catalysis processes, using renewable forms of energy, able to convert CH<sub>4</sub>, CO<sub>2</sub> and CO into readily storable, transportable and usable value-added chemicals and fuels.

If such an advance can be transformed into a scalable, commercially viable and globally significant technology, the result would be the reduction of both CH<sub>4</sub> and CO<sub>2</sub> anthropogenic greenhouse gas emissions in “one fell swoop”. At the same time this breakthrough would create a useable chemical feedstock to make methanol CH<sub>3</sub>OH and dimethyl ether (CH<sub>3</sub>)<sub>2</sub>O, both able to be used as value-added chemicals and fuels, the latter being favored these days by the trucking and power generator industries as a clean combustion replacement in compression ignition engines, eliminating highly polluting petroleum diesel.

Currently, Chinese and European automotive companies have developed methanol (M15, M85 and M100) automobiles that effectively utilize wood alcohol mixtures in spark-ignition engines. Unlike electric cars using lithium based batteries, vehicles using methanol and dimethyl ether can be fuelled in few minutes, last for 10's of years and can be almost completely recycled. More importantly, methanol and dimethyl ether vehicles can be built for under \$15,000 in North America, making clean vehicles available for most citizens. Today's electric car is a “nice to have” for wealthy buyers in industrialized nations with extensive grids. The global transportation emissions problem requires a low cost global solutions that uses locally produced, easy to store, renewable fuels for a vehicle that can be recycled easily.

## Enter the Methanol Economy

There are convincing arguments why (CH<sub>3</sub>)<sub>2</sub>O is regarded as a clean energy source for the next generation of fuels. It can be handled like propane fuel; it generates fewer exhaust pollutants such as NO<sub>x</sub>, hydrocarbons, carbon monoxide and soot, the latter as there are no C-C bonds; its global warming potential is considerably lower than diesel; and it has the highest well-to-wheel efficiencies next to natural gas. A challenge for the catalyst materials and chemical process engineering community is to discover a way to directly convert syngas CO/H<sub>2</sub> into (CH<sub>3</sub>)<sub>2</sub>O in a

single step process rather than having to proceed through two-steps involving the production followed by the dehydration of  $\text{CH}_3\text{OH}$ .

Ideally, a low temperature, low pressure photo-catalytic process chain powered by renewable energy could be developed to convert  $\text{CH}_4$  and  $\text{CO}_2$  to  $\text{CH}_3\text{OH}$  and/or  $(\text{CH}_3)_2\text{O}$ . Ideally, this systems parasitic load would be powered by solar power. Since a photo-catalytic process would operate in a semi-continuous mode, the separation columns could also operate semi-continuously, yielding reduced energy consumption during the separation and purification stages.

Methanol is a global chemical sold into a global market, 66 Million tonnes being produced yearly with a current value of over \$21 Billion. The methanol market is supported by a global logistic chain stretching from Cape Horn to Inner Mongolia to the Baltic Sea. Converting methanol to  $(\text{CH}_3)_2\text{O}$  is an easy process. Moreover, since  $(\text{CH}_3)_2\text{O}$  is handled like propane,  $(\text{CH}_3)_2\text{O}$  can also leverage the global propane infrastructure. In the methanol economy, there is no need for cryogenic storage and high pressure carbon fibre tanks. Moreover, unlike CNG and LNG, there is no change for  $\text{CH}_4$  venting within the logistic chain.

Global  $(\text{CH}_3)_2\text{O}$  capacity is currently about 10 Million tonnes. China Energy Limited is the largest producer of dimethyl ether in the world, delivering nearly 880,000 tonnes per year. The company uses liquid phase dehydration technology to produce DME. The company sells  $(\text{CH}_3)_2\text{O}$  to LPG distributors who blend it into propane and the result is a product with improved combustion. China Energy also produces  $\text{CH}_3\text{OH}$ . Current non-Asian  $(\text{CH}_3)_2\text{O}$  producers include Oberon, Mitsubishi, Shell, Grippo and Akzo Nobel. Non-Asian producers typical use a two-step process, dehydrating methanol after methanol synthesis.

## Living with the New Natural Gas

Although oil prices are in decline, global diesel and natural gas prices are diverging. Natural gas prices will continue to remain low due to horizontal drilling and hydraulic fracturing. On an energy equivalent basis, diesel and heating oil prices (10 \$/GJ) will likely remain significantly higher than shale produced natural gas prices (3\$/GJ) in the future.

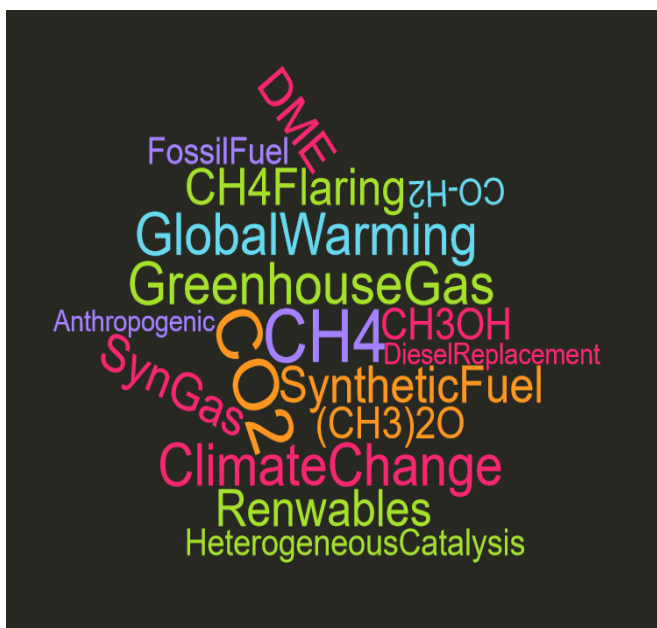
Canada is the world's fifth-largest natural gas producer and has enough natural gas reserves to meet current national energy demand for 300 years. The continuing price spread between refined oil products and natural gas will provide an ongoing competitive advantage for power sources using natural gas as feedstock. Currently, coal generation is being phased out and replaced by natural gas and some renewable sources for baseload operation. Under the shadow of Fukushima and a self-induced moratorium on North America hydro, natural gas is the baseload power leader.



Canadian federal and provincial governments will continue penalizing carbon dioxide emissions. With abundant, low cost natural gas feedstock, Canada can deploy thermally integrated poly-generation units, producing power and fuels, while capturing CO<sub>2</sub> and supported by renewable energy sources. Facilities that reduce and recycle CO<sub>2</sub> emissions, using additional renewable energy, will emerge as an important component of governmental energy policy and will receive preferential treatment from national and local authorities.

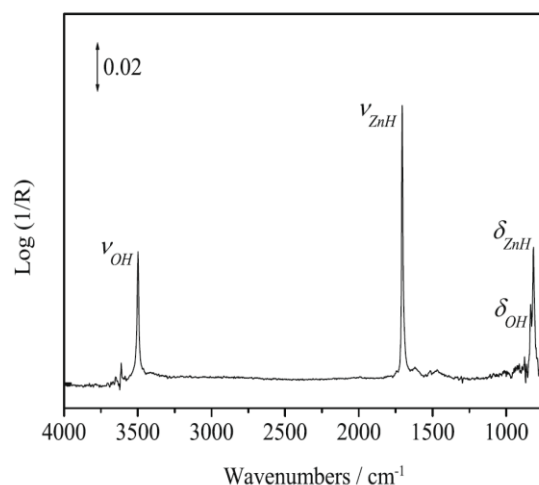
Low natural gas prices have supported a weak North American economy for the last decade, supplying inexpensive power and heat to households and industry.

It seems to me that if the increasing level of anthropogenic CH<sub>4</sub> being released into our atmosphere, exacerbated by the shale-gas boom, is neglected, we could win the battle against CO<sub>2</sub> emissions but end up losing the war on climate change!!!



## 63. The Articulation and Exploitation of Frustrated Lewis Pairs – Rediscovery in Science

More than half a century ago Eischens, Pliskin and Low discovered that  $\text{H}_2$  dissociates on crystalline ZnO [1]. The observation of diagnostic infrared active ZnH and OH stretching and bending modes, implied that the  $\text{H}_2$  splits heterolytically into a surface zinc hydride and a hydroxyl group on a geometrically and electronically anisotropic  $\text{Zn}\bullet\bullet\bullet\text{O}$  surface site, to form a proximal hydride and a proton, denoted  $\text{ZnH}\bullet\bullet\bullet\text{OH}$ , **Figure 1**.



**Figure 1** Diffuse reflectance infrared Fourier transform spectrum (DRIFT) of  $\text{H}_2$  adsorbed on nanocrystalline ZnO at 323K [5].

At that stage, before the rise of nanochemistry [2], Eischens, Pliskin and Low could not imagine that their pioneering work would inspire the design and construction of surface frustrated Lewis pairs (SFLPs) in a range of solid state materials for a myriad of surface chemistry and catalytic reactions [3,4].

Fifty years hence, a great deal more is known about the chemical and physical surface and bulk properties of ZnO, in single crystal and nanocrystal forms that are deemed responsible for the heterolytic dissociation of  $\text{H}_2$  on ZnO [5].

With the accrued structure and properties knowledge that is available today for the thermodynamically stable hexagonal polymorphic würtzite crystalline form of ZnO, obtained using a battery of diffraction, microscopy, spectroscopy, adsorption and thermal analytical techniques in combination with density functional theory, it is now understood that the energetics and dynamics of the  $\text{H}_2$  dissociation reaction on the surface of ZnO are crystal face specific and depend sensitively on the type and population of surface defects, in particular the chemical and physical properties of oxygen vacancies [5].

In addition, because ZnO alone or in combination with a co-catalyst such as Cu, is an active ingredient for enabling the (reverse) water gas shift reaction and formic acid and methanol synthesis, it has been important to understand how ZnO interacts with the small molecules, CO,  $\text{CO}_2$ ,  $\text{H}_2$ ,  $\text{H}_2\text{O}$ ,  $\text{CH}_2\text{O}$ ,  $\text{HCO}_2\text{H}$  and  $\text{CH}_3\text{OH}$ , known to participate as reactants, intermediates and products in these catalytic transformations [5].

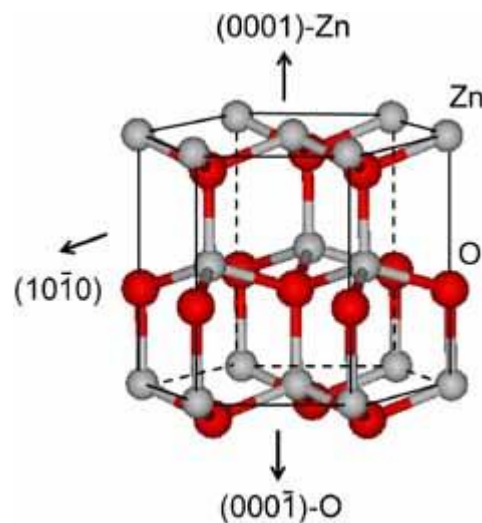
Furthermore, obtaining an in-depth appreciation of the reactivity of different exposed crystal facets and the role of oxygen vacancies in ZnO has proven invaluable in the design, implementation and optimisation of not only ZnO but also other metal oxides and an expanding variety of materials, as high efficiency heterogeneous catalysts for the above reactions.

To understand the face specificity of the surface chemistry of ZnO, it is important to examine the anisotropic crystal structure of the stable wurtzite polymorphic form, and to look at the different surface sites that exist on the dominant non-polar  $(10\bar{1}0)$  and polar zinc  $(0001)$  and oxygen  $(000\bar{1})$  terminated crystal faces, illustrated in **Figure 2**, [6].

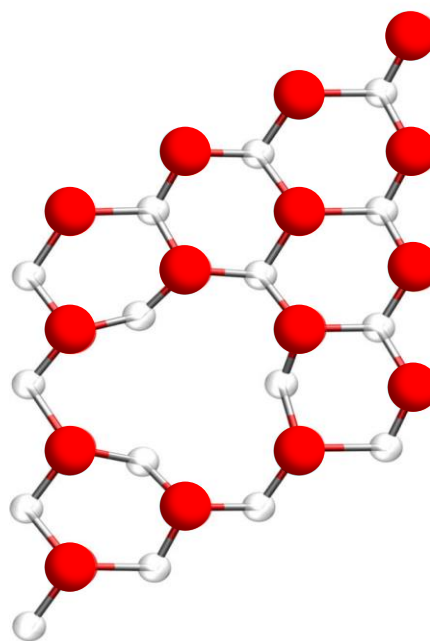
The non-polar surface contains equal numbers of close-packed Zn(II) and O(-II) regularly arranged in rows of Zn-O dimers. This surface is electrically neutral and devoid of a surface dipole, to be contrasted with the polar Zn(II) and O(-II) surfaces, which present positive and negative surface charges respectively, with associated surface dipoles. Because the non-polar surface is more stable than the polar ones, different chemical reactivity is anticipated and observed in practice with the above mentioned small molecules. This insight emphasizes the importance of synthetic control of crystal morphology in the design of nanostructured forms of ZnO with optimum catalytic activity and the extension of these ideas to other metal oxides [5].

An equally important consideration is the formation of oxygen vacancies obtained by removing an oxygen atom from the crystal lattice of stoichiometric ZnO to form non-stoichiometric  $\text{ZnO}_x$  and the resulting effect these vacancies have on the stability and reactivity of the non-polar and polar surfaces of ZnO [5].

These vacancies can be created through loss of lattice oxygen by either vacuum thermal treatment or removal as water by thermal reaction with hydrogen. Depending on the number of electrons removed with the lattice oxygen the vacancies can be in a neutral ( $V_O^0$ ), singly ionized ( $V_O^+$ ) or



**Figure 2** Crystal structure of the wurtzite hexagonal polymorphic form of ZnO showing the dominant crystal faces [6].



**Figure 3** Structure of an oxygen vacancy in a Zn  $(0001)$  surface, red O, white Zn, adapted from [5].

doubly ionised ( $V_O^{++}$ ) state, energetically located in the mid-bandgap and induce either semiconducting or metallic character in the non-stoichiometric oxygen deficient  $ZnO_x$  [5].

The structure of an oxygen vacancy formed in a Zn (0001) surface, is illustrated in **Figure 3**. Compared to a vacancy-free ZnO surface, the Zn(II) sites in  $ZnO_x$  can be seen to have a higher degree of coordinate unsaturation making it a stronger Lewis acid. Its proximity to Lewis base O(-II) sites provides it with the structure, property and reactivity attributes demanded of what is considered to represent a surface frustrated Lewis pair (SFLP) [3,4]. Today the SFLP is considered the heterogeneous analogue of the homogeneous frustrated Lewis pair (FLP), the latter also considered to be a story of articulation and exploitation in synthetic molecular chemistry [9-11].

To amplify on the history of the FLP before it assumed this descriptor, Halpern in 1958 foresaw the catalytic action for the heterolytic dissociation of  $H_2$  on proximal LA-LB pairs, exemplified by Cu(I) or Ag(I) complexes in solution, in particular when the Lewis acidic metal ion is surrounded by Lewis basic ligands or solvent molecules, [9]. He raised awareness that catalytic activity seemed to require a metal complex with the Lewis acidic metal site in the right valence state and correct surrounding environment. He anticipated the need for “bi-functionality”, in which electron-accepting and proton-accepting sites are simultaneously present - what prescience for today’s FLP. In addition, he realized that some aspects of heterolytic dissociation of  $H_2$  on heterogeneous catalysts could also be interpreted with a similar LA-LB model for homogeneous catalytic  $H_2$  activation.

In this context, Dayton even earlier in 1953 had solution phase kinetic isotope based mechanistic evidence that forecast the current thinking about FLPs, an insight obtained from the observation of H-D exchange enabled by exposure of  $D_2$  to strong alkali metal bases. This exchange chemistry was exemplified by the interaction of  $D_2$  with KOH in water and  $KNH_2$  in liquid ammonia, both of which have strong Lewis acid  $K^+$  sites located in the proximity of strong Lewis base  $OH^-$  and  $NH_2^-$  sites [10,11].

While the origin and the language of the SFLP in materials and the FLP in molecules is different [3,4,8], their chemistry clearly has demonstrated inherent similarities, such as the ability to heterolytically dissociate  $H_2$  into a proton and a hydride, respectively bound to the Lewis base LB and Lewis acid LA sites, namely  $LBH^+ \cdots LAH^-$ . This reaction is proving to be a key step in the homogeneous and heterogeneous reduction of gaseous  $CO_2$  to energy carrier’s that include CO,  $CH_3OH$ ,  $HCO_2H$ ,  $(CH_3)_2O$  and  $CH_4$  [3,4,10].

Activation of  $H_2$  by the acceptor-donor interactions of the surface Lewis acid Lewis base proximal pair with the sigma bonding and sigma anti-bonding orbitals of  $H_2$  serve to weaken and thereby facilitate the heterolytic dissociation of the H-H bond to form  $ZnH^- \cdots OH^+$ . The hydride and proton can be transferred to the electrophilic carbon and nucleophilic oxygen of gaseous (Eley-

Rideal) or adsorbed (Langmuir-Hinshelwood) CO<sub>2</sub> to form reduced products, such as methanol or formic acid [3,4].

Clearly, the FLP is a new direction in synthetic molecular chemistry and homogeneous catalysis that has a long and recently recognised foundational history in the work of Halpern and Dayton, [9-11]. Similarly, the SFLP has a long and recently recognized history in surface chemistry and heterogeneous catalysis, which can be traced to pioneering work by Eischens, Pliskin and Low concerning the heterolytic dissociation of H<sub>2</sub> on crystalline ZnO [1], the mechanism of which, in the language of today, involves the activation of H<sub>2</sub> by a Zn•••O SFLP [3,4]

Appreciation of this early pioneering work inspires the design and construction of SFLPs in a range of materials for a myriad of surface chemistry and catalytic reactions based on metal oxides, boron and phosphorous doped silicon nanoparticles, carbon nanotubes, as well as the anchoring of molecular FLPs to the surface of silica nanoparticles, zeolites and metal organic frameworks.

With the wisdom of hindsight, the revelations presented above can be considered an instance of anticipation of FLPs and SFLPs and envisioning their consequences in different classes of molecules and materials. Today with the wisdom of foresight, the attributes of FLPs and SFLPs can now be exploited to advantage in an expanding range of chemical problems involving homogeneous, heterogeneous and enzymatic hydrogenations.

In closing, it is worth mentioning an insightful comment from a colleague who read this opinion editorial, who remarked that this story shows how important it is to revisit or rediscover old work, which because of subsequent developments means that the old discovery or ideas can be used as a springboard for further discoveries or developments. It also begs the question whether enough time is spent on rediscovery or revisiting. Also does the amount of work and papers produced over the last 50 years make it more difficult now to ensure that old work is rediscovered to the benefit of current work? Are there modern tools being developed to assist researchers in rediscovery? Has anyone tried to harness AI to assist in this regard? This whole subject probably could be the subject of a separate article.

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