



Innovation

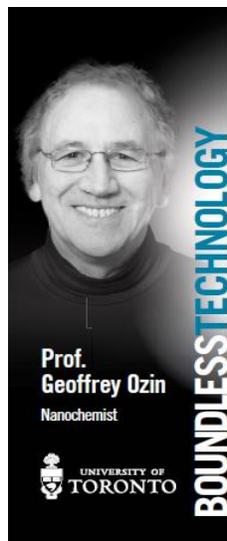
CO₂ Chemistry and Engineering Solutions to Climate Change

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Compendium of Opinion Editorials Published in Materials Views, VCH-Wiley Family
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CO₂ Chemistry and Engineering Solutions to Climate Change

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Motivation: After almost half a century of research in the field of nanochemistry, I was given the interesting opportunity to write invited monthly opinion editorials for the Materials Views section of the VCH-Wiley family of materials journals, Advanced Science, Advanced Materials, Advanced Functional Materials, Small, Particle, Advanced Energy Materials, Advanced Optical Materials, Advanced Materials Interfaces, Advanced Electronic Materials, and Advanced Healthcare Materials. This invitation from the editor of Advanced Materials Peter Gregory provided me with a superb vehicle to express opinionated and provocative views about hot button issues in nanochemistry. Dreaming up and composing these editorials has been a valuable lesson in how to write scientifically, technologically and politically correct critiques about controversial topics for a public forum, a pastime less risky for a senior scientist than a junior one. After having produced 55 of these opinion editorials on a variety of contemporary topics in nanochemistry, I thought it worthwhile to integrate them into a compendium of essays in the form of a monograph choosing those stories that focus on my obsession with CO₂. I hope the reader enjoys these stories as much as I had fun writing them and at the same time

learning much from knowledgeable colleagues who contributed insightful and important commentaries on my opinions, sometimes voicing heterodox views, many of which in anonymous form I included in much improved final drafts. I also received terrifically helpful editing on more-or-less every story from my talented and dynamic group of co-workers as well as much advice and excellent artistic renditions of the content of many of the stories from Wendong Wang, Chenxi Qian, Bob Davis, Dwight Seferos, Markus Antonietti, Hermanguildo Garcia and ArtScientist Todd Siler.

Brief Biography: Geoffrey Ozin studied at King's College London and Oriel College Oxford University, before completing an ICI Postdoctoral Fellowship at Southampton University. Currently he is the Tier 1 Canada Research Chair in Materials Chemistry and Nanochemistry and Distinguished University Professor at the University of Toronto, where he currently spearheads the activities of the Solar Fuels Cluster. Internationally he has been Global Chair at the University of Bath, Distinguished Research Professor at Karlsruhe Institute of Technology, Professorial Fellow at The Royal Institution Great Britain and University College London University, Alexander von Humboldt Fellow at the Max Planck Institute for Colloid and Surface Science, Sherman-Fairchild Scholar at Caltech and 3M Research Fellow, Minneapolis-St Paul. Recently he has been the recipient of the RSC Centenary Prize and the Albert Einstein Prize for his work in defining, enabling and popularising a chemical approach to nanomaterials for innovative nanotechnology in advanced materials, biomedical science and most recently CO₂ chemistry and engineering solutions to climate change.

Geoffrey A Ozin, Toronto July 2016

Materials Views: Opinion Editorial

A Burning Question: Anthropogenic CH₄!

The recent fervor over CO₂ capture and conversion technologies, inspired by the effort to control GHG emissions has often excluded CH₄, another major GHG contributor with a 100-year potency 30 times that of CO₂. In particular, vented, leaked and flared “fugitive” CH₄ 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 CH₄ and associated combustion product CO₂ building up in our atmosphere?



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A grand challenge for projects aimed at mitigating the two most potent greenhouse gas emissions CH₄ and CO₂, is to use

renewable forms of energy to simultaneously convert them in a single catalytic process

into value-added chemical energy carriers. 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, CH₄ and CO₂ that are rapidly accumulating in our atmosphere, can be simultaneously reduced, while creating a useable chemical feedstock, such as CO/H₂ synthesis gas. This synthon, known as syngas, can be transformed with known catalysts and processes, to methanol CH₃OH and dimethyl ether (CH₃)₂O, for applications as a feedstock for making a myriad of chemicals and a clean-burning replacement for polluting diesel fuel.

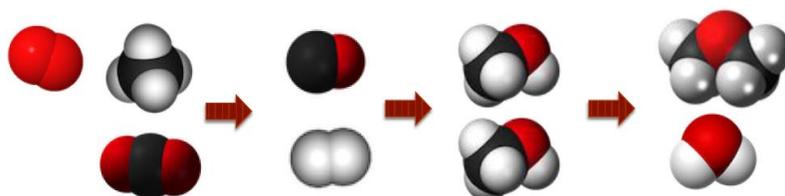


Illustration of the chemically catalyzed conversions, left to right, of CH₄/H₂/CO₂ to CO/H₂ to CH₃OH to (CH₃)₂O.

Using this approach, CH₄ flaring and leakage, a common occurrence at the natural gas well head, can be eliminated and fossil generated CO₂ 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 CO₂ emissions and seek alternatives that would ultimately end our dependence on fossil fuels. This year the concentration of CO₂ 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 CO₂ 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 CO₂ 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 conversion of CO₂ to CO, CH₄ and CH₃OH with high conversion rates, selectivity's and turnover frequencies. Industry is in the throes of figuring out where CO₂ utilization fits into its supply chain and how best to turn CO₂ into a profitable chemicals and fuels business that can compete with fossil resources.

As well as the CO₂ challenge we are also facing a growing anthropogenic CH₄ 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, CH₄ traps about 85 times the amount of solar heat than CO₂, meaning its global warming potential is 85. Taking into account that CH₄ in the atmosphere is gradually destroyed by solar radiation compared to CO₂ slowly dissolving into oceans and absorbing into soil and rock, the global warming potential of CH₄ is estimated at about 30 times that of CO₂.

All of this means the global warming equivalent of anthropogenic CH₄ in our atmosphere, compared to CO₂ is now roughly 60,000 ppb = 60 ppm and rising. At the current rate of increase, the effect of anthropogenic CH₄ on our climate, exacerbated by the recent boom in shale-gas production and exploration, will soon catch up and surpass today's unprecedented CO₂ concentrations of 404 ppm. So we have to face the reality of a growing CH₄ greenhouse gas climate change challenge as well as the CO₂ challenge.

To amplify, about 20% of the CH₄ 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 CH₄ comes from natural sources, which may be difficult to control, particularly if permafrost melts further releasing huge quantities trapped therein.

Every year, around 140 Billion cubic meters of natural gas is wastefully flared at thousands of oil fields globally. This results in more than 300 million tons of CO₂ 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 CH₄ emitted from a natural gas well it has been estimated that in CO₂ equivalents over a hundred year timeline, the CH₄ 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.

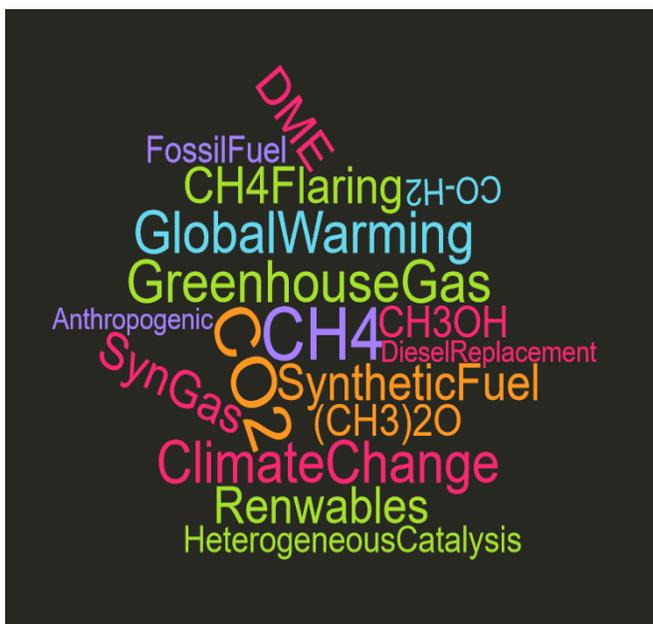
There have already been some notable successes in the discovery of earth-abundant and inexpensive nanomaterials, which enable the gas-phase heterogeneous catalytic conversion of CO₂ to CO and CH₄ with high conversion rates, selectivity and turnover frequencies. Today the materials chemistry and chemical 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 CH₄, CO₂ 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 CH₄ and CO₂ anthropogenic greenhouse gas emissions in “one fell swoop”. At the same time this breakthrough would create a useable chemical feedstock to make methanol CH₃OH and dimethyl ether (CH₃)₂O, both able to be used as value-added chemicals and fuels, the latter being favored these days by the automobile and transportation industries as a clean combustion replacement for highly polluting diesel fuel.

There are convincing arguments why (CH₃)₂O 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_x, 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/H₂ into (CH₃)₂O in a single step process rather than having to proceed through two-steps involving the production followed by the dehydration of CH₃OH.

It seems to me that if the increasing level of anthropogenic CH₄ being released into our atmosphere, exacerbated by the shale-gas boom, is neglected, we could win the battle against CO₂ emissions but end up losing the war on climate change!!!



Materials Views: Opinion Editorial

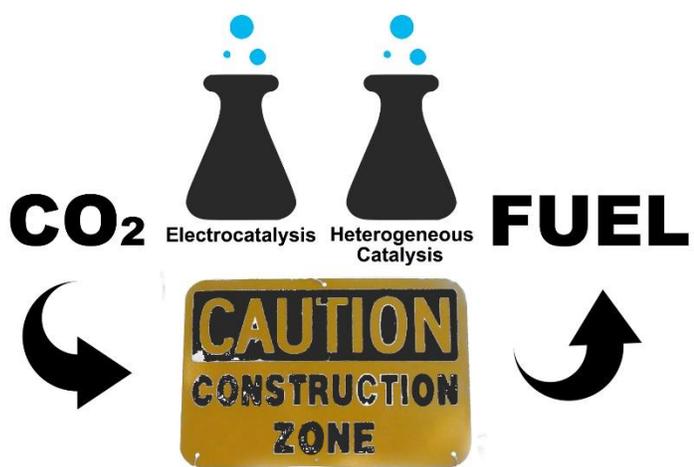
Weapons of Mass Construction in the War on Climate Change: Heterogeneous Catalysis and Electro-Catalysis

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.

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 like Quebec and Ontario in Canada, making use of electricity for the production of chemicals and fuels in the summer for use and consumption in the winter.

A contemporary view is that electrochemical storage of excess electricity by converting an aqueous solution of $\text{CO}_2/\text{H}_2\text{O}$ into chemicals and fuels by electro-catalytic methods is a good



In the war against climate change two promising approaches are being developed for catalytically converting CO_2 to value-added chemicals and fuels

strategy for fighting climate change. A parallel opinion is that the excess electricity can be used to drive thermochemical transformations of CO₂/H₂ 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.

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, however there will be a long-term 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 CO₂ 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 CO₂/H₂O and CO₂/H₂ 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 CO₂ 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 CO₂ and is being investigated extensively. The challenge for electrochemical synthesis using CO₂/H₂O 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 H₂/O₂ 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 CO₂ 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. In this way one can convert CO₂/H₂ 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 H₂ 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 CO₂ 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 CO₂. The same specious argument can be voiced against the use of captured CO₂ for enhanced oil recovery. On the other hand, renewable energy powered electro-catalytic and heterogeneous catalytic CO₂ 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 CO₂ 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 CO₂/H₂O and CO₂/H₂, 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 CO₂ 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 CO₂ may well play a part in this user sector.

In the case when CO₂ 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 CO₂ 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 CO₂ 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 CO₂, for example to CO, CO/H₂, CH₄, HCO₂H, C₂H₄, C₂H₄(OH)₂, CH₃OH, and (CH₃)₂O is of particular interest. Providing there is sufficient electricity from the grid, whether derived from fossil, nuclear, wind, solar, tidal, geothermal or hydroelectric sources, and these chemicals are not more costly to produce by CO₂ reduction than by current means, even with CO₂ 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.

In the case of heterogeneous catalysis, at the moment there is no technologically significant, commercialized working version of CO₂ + H₂O conversion to chemicals or fuels. In most of this research, the reductant is H₂, the majority of which comes from steam methane reformation and hydrocarbon sources. To make H₂ renewably and reduce CO₂ 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 H₂ generation have been commercialized where H₂ 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 CO₂ 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. Problematic also is the low solubility of CO₂ 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 CO₂, electro-catalyst and liquid electrolyte, thereby reducing mass transfer, charge transport, ohmic resistance and wettability restrictions in the electrochemical reduction of CO₂. 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, CO₂ 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 CO₂ 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 CO₂ into value-added chemicals and fuels. These include Liquid Light, Dioxide Solutions, Audi-Sunfire, Sandia National Laboratory, NewCO₂Fuels, Solar-Jet-Fuels, Syntrolysis Fuels, Doty Energy-WindFuels, Air-Fuel Synthesis, Green-Feed and E-Diesel.

Hopefully these CO₂ utilization ventures will be successful in their goal of converting CO₂ to profit and expanding their production facilities across the globe to a scale that can meaningfully impact greenhouse gas induced climate change.

Materials Views: Opinion Editorial

Can We Save the Planet with a Grain of Sand?

University of Toronto scientists solve the puzzle of converting CO₂ emissions to fuel, Nature Communications 23rd August 2016, DOI: 10.1038/ncomms12553

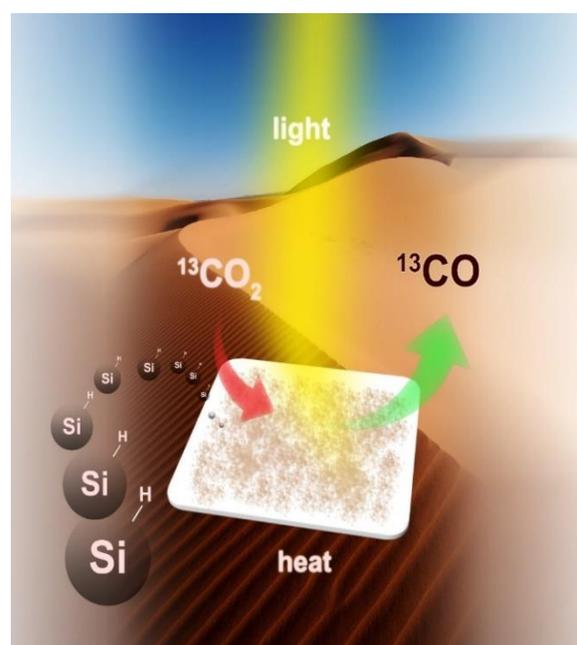
Geoffrey A. Ozin

In the war against climate change scientists and engineers are racing to try to find a fast and practical way of turning the 30,000,000,000 tons of CO₂ that we inject into our atmosphere every year, from the combustion of fossil fuels, into a valorized product, an asset rather than a hazardous waste and a liability.

There are many proposed solutions to this challenging problem but none have yet proven to be a panacea in the war against climate change.

A dream solution would be to convert the excess CO₂ in our atmosphere into synthetic fuels in a carbon-neutral carbon-cycle, to maintain the level of CO₂ constant and provide power for transportation, industry and buildings. This approach is akin to the way the photosynthetic cycle in Nature has been operating for millions of years to keep atmospheric concentrations of CO₂ constant and provide food to maintain life on earth.

To reduce this Utopian idea to practice one needs to discover a material and process that can accomplish this conversion efficiently, safely and economically, however because of the exceptionally high chemical stability of CO₂ one needs to provide large amounts of energy to make this transformation work. The most abundant and clean form of energy to enable this process is sunlight.



There is no shortage of sand in the world, it is industries source of elemental silicon. When fashioned as silicon nanocrystals with a coat of silicon-hydrogen bonds it functions as a powerful reducing agent for selectively converting CO₂ to CO with a little help from sunshine and proven by 13C isotope labeling. Graphic image courtesy of Chenxi Qian.

Because of the urgency of solving this CO₂ problem, there is a global effort to discover a material that can efficiently convert sunlight, CO₂ and H₂O to an energy rich fuel. The target material however, must be able to make synthetic fuels from CO₂ at a technologically significant rate and scale in order to have a meaningful impact on climate change. This will require the material to not only be highly active and selective for converting the CO₂ to fuel but it must also be made of elements that are earth abundant, low cost and non-toxic to make a scaled-up industrial process economically viable and environmentally acceptable.

The element of choice would be silicon, the main constituent of sand and this is the essence of the discovery recently reported by Professor Geoffrey Ozin and the solar fuels team in their Nature Communications paper. The material is a nanoscale form of silicon, which has the unique ability to harvest light from the sun and drive the conversion of CO₂ to carbon monoxide, CO, which is a well-known and highly prized feed-stock for making fuels using established industrial processes.

To amplify upon the breakthrough reported in the University of Toronto Nature Communications paper, silicon constitutes 28% of the earth's mass. Its high abundance, lack of toxicity and low cost, coupled with its distinctive electrical and optical properties, make silicon unique among the semiconductors for applications in microelectronics and photovoltaics. It is also proving to be a favored material for high capacity lithium ion batteries.

The big question, is could silicon also be the material of choice for converting gaseous CO₂ to an energy rich fuel?

It is significant that in the quest for materials that can make fuel from sunlight and CO₂, one is often confronted with what has been called the "materials dilemma", where the best performers are unfortunately composed of rare and expensive elements, like platinum, ruthenium, iridium, and gold. The University of Toronto solar fuels team show this is not necessarily true with their unprecedented observation that hydride-terminated silicon nanocrystals with an average diameter 3.5 nm, denoted ncSi:H, can function as a single component heterogeneous reducing agent for converting gaseous CO₂ selectively to CO, at an impressively high rate of hundreds of micromole per hour per gram of silicon.

The large surface area, broadband ultraviolet-to-visible-to-near infrared light harvesting properties, and high reducing power of active silicon-hydrogen bonds on the surface of ncSi:H, together play key roles enabling this CO₂ conversion process. Detailed studies of the wavelength, intensity and temperature dependence of the CO₂-to-CO conversion rate provide evidence that the reaction is driven by the heat and light from the sun.

The University of Toronto solar fuels team are working furiously to find ways and means to increase the scale and boost the throughput of the process, the goal being a laboratory demonstration unit and if successful a pilot solar refinery.

Making good use of the chemical reducing power of nanostructured silicon hydrides towards gaseous CO₂ is a conceptually distinct and technologically interesting strategy for making synthetic fuels directly from sunlight, with a little help from the second most abundant element on earth.

It can be seen that silicon continues to shine as the Samurai of semiconductors - the sweetheart for microelectronics, the favorite for solar cells, and the darling for lithium ion batteries, and perhaps with the University of Toronto advance, silicon could prove to be a new and powerful ally in the war against climate change.

Materials Views: Opinion Editorial

Grasping Our Growing Gigatonne CO₂ Challenge

Geoffrey A. Ozin

Our Growing Gigatonne Problem



We're all "Overlooking the Facts"

Graphic illustration courtesy of Todd Siler and Geoffrey Ozin, www.artnanoinnovations.com.

Materials Views: Opinion Editorial

Grasping Our Growing Gigatonne CO₂ Challenge

Geoffrey A. Ozin

To appreciate the magnitude of the roughly 30 Gigatonnes of anthropogenic CO₂ emissions that humans generate annually from the combustion of fossil fuels, it is useful to illustrate what 1 tonne of CO₂ 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 CO₂ Challenge”, rather than trying to visualize the magnitude of the number itself taken in isolation.



Figure 1 Your Annual CO₂ 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 CO₂, 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 CO₂ produced annually from the use of fossil fuels.

This image dramatically depicts what I call “Our Growing Gigatonne CO₂ 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 CO₂ problem, as this evocative image and others in this article intimate.

Just imagine 30B = 30,000,000,000 of these 1 tonne CO₂ 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 CO₂ 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 CO₂ Challenge” entails not only discovering and implementing different approaches for the mitigation and reduction of CO₂ emissions to meet greenhouse gas targets as defined in the Paris Climate Agreement. It also involves utilizing CO₂ 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 CO₂ in our atmosphere.

In the context of the larger perspective of 21st 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 CO₂ capture, storage and utilization, will further diminish the use of coal, oil and natural gas by increasing the conversion of CO₂ to value-added chemicals, materials and fuels. Together these approaches should enable control of atmospheric CO₂ 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 CO₂ utilization will most likely be based upon the use of biomass, electrocatalysis and heterogeneous catalysis for making chemicals and fuels from CO₂, which will be supplemented by mineralization of CO₂ to

inorganic carbonates, for permanent storage of CO₂ 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 H₂ from H₂O and using the H₂ for converting CO₂ 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 CO₂ footprint. It would not be smart to develop a biological or abiological CO₂ conversion process that ends up adding more CO₂ to the atmosphere somewhere else. For example, the use of grid electricity does not come for free in terms of CO₂. A trivial mass balance can be applied to describe the user-friendliness of a CO₂ conversion process: the amount of CO₂ emissions associated with the energy consumed is subtracted from the amount of CO₂ 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 CO₂ 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 CO₂ that constitutes the troposphere. Natural CO₂ is represented by the blue segment of the cube while the red segment is anthropogenic CO₂ created by the use of fossil fuels since the industrial revolution. The former is sufficient to maintain life on

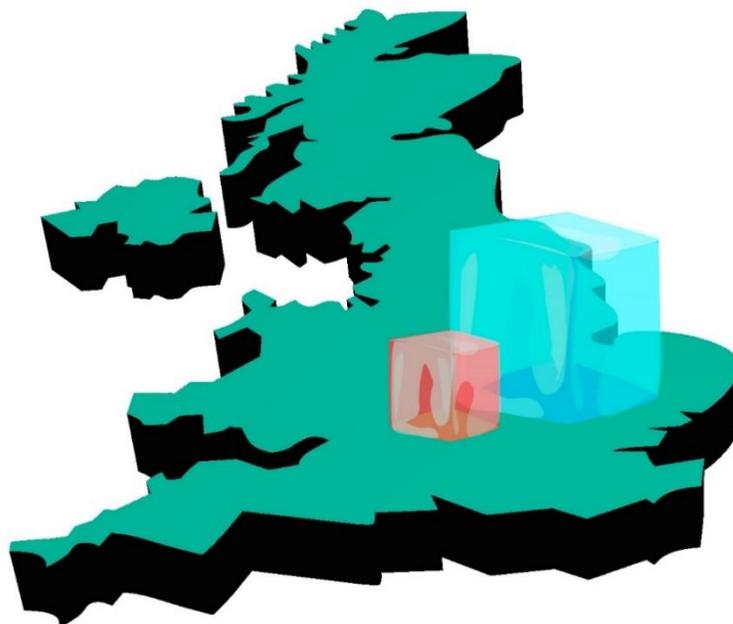


Figure 2 All the Earth’s CO₂, Natural (blue) and Anthropogenic (red) in a Box; Graphic illustration courtesy of Chenxi Qian.

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.

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 CO₂ 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) 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:

Our Growing Gigatonne Problem



"To answer your question as clearly as I can (re: 'what we are reflecting upon inside the

We're all "Overlooking the Facts". Graphic illustration courtesy of Todd Siler and Geoffrey Ozin, www.artnanoinnovations.com.

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 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 CO₂ 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 CO₂ 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

Materials Views: Opinion Editorial

CO₂ Conundrum

Geoffrey A. Ozin

The chemical industry are one of the largest manufacturing sectors in the world with global sales currently valued at around \$5B. 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 CO₂ as a feedstock for manufacturing chemicals, materials and fuels:

1. Scaling and Manufacture: what technological strategies for CO₂ utilization have the most promise for success in the short term?
2. Commercial Potential: what CO₂ derived products and uses offer the best opportunities?
3. CO₂ 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 CO₂ as a chemical feedstock?



Figure 1 Catalytic processes for converting CO₂ into value-added chemicals – which one would you bet on?

5. R&D Strategy: what areas of CO₂ enquiry should be invested in for the long-term?

To realise a technologically, economically and sociologically acceptable solution to the abatement of greenhouse gas emissions, five commandments for utilization of CO₂ as a chemical feedstock have been mandated, as a replacement for fossil based feedstocks and fuels in chemical industrial processes:

1. Reduces overall CO₂ 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 CO₂ 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 CO₂ emissions are expected to expand and that treating CO₂ as a non-traditional feedstock, viewed as an asset rather than a liability, will

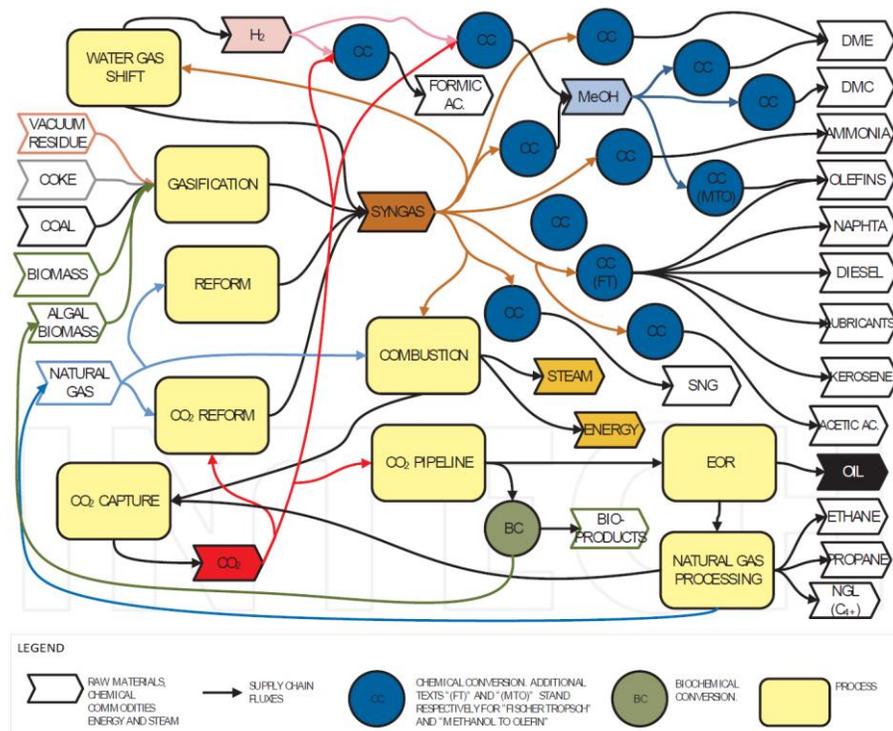


Figure 2 Chemical industry supply chain flow diagram depicting the coexistence of fossil and biomass feedstock uses and how CO₂ capture and utilization can be integrated into existing production infrastructure. CO₂ Utilization: A Process Systems Engineering Vision, Ofélia de Queiroz F. Araújo, José Luiz 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>.

help enable a transition to low-carbon processes based on existing infrastructure.

The opinion of the chemical industry seems to be that incorporation of CO₂ as a feedstock into their supply chain is most likely to be expected initially in mature technologies that focus on the 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 CO₂ 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 CO₂ to a value-added product.

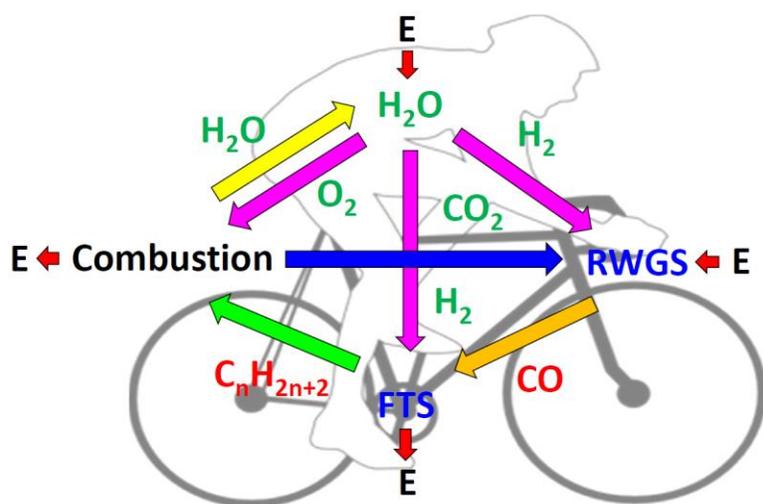


Figure 3 Carbon-neutral carbon cycle for making hydrocarbons from carbon dioxide and water.

In this light, there are six main catalytic CO₂ conversion processes currently under active investigation all vying for a stake in the race to utilize and valorize CO₂ 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 CO₂, 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 CO₂ 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 CO₂.

In this respect, an important initial target will involve the heterogeneous catalytic conversion of gaseous CO₂ into synthesis-gas CO/H₂, as it is an appealing feedstock for making key chemicals, such as NH₃, H₂, CO, CH₃OH and C_nH_{2n+2} 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 H₂O as a source of H₂ followed by use of the H₂ to reduce CO₂ 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 CO₂ one can draw the following conclusions:

1. CO₂ is a promising and sustainable feedstock for the chemical industry
2. CO₂ conversion to chemicals and fuels is at an early stage of development
3. CO₂ utilization is currently a very small fraction of greenhouse gas emissions
4. CO₂ 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 CO₂ 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 CO₂ 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 CO₂ emissions are monitored at local, regional and national levels, and legal and policy measures implemented to enforce compliance with CO₂ 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 CO₂ but is only a partial solution to climate change.

The solution proposed in your editorial will require governments to enact legislation that makes CO₂ generation too expensive to sustain without converting it to something valuable. This is because the technologies needed to convert CO₂ 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 CO₂ 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.

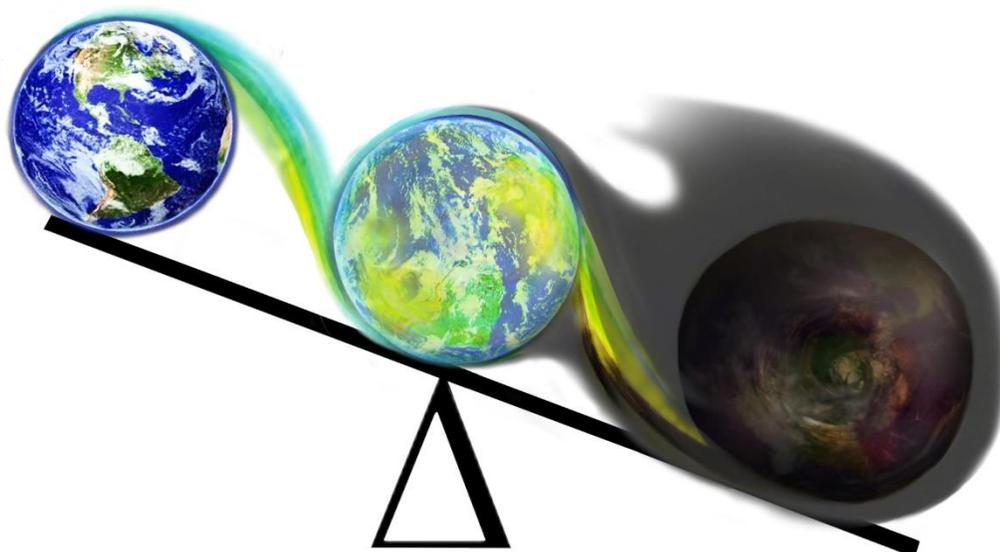
This is probably not what you wanted to hear, but most people, including voters, look into their pocketbooks and their lives and vote and spend accordingly. Solving the climate change crisis will require nothing less than global lifestyle changes, rather than most inhabitants of every developing country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

Materials Views: Opinion Editorial

Tipping the Balance between Sustainability and Extinction

Geoffrey A. Ozin



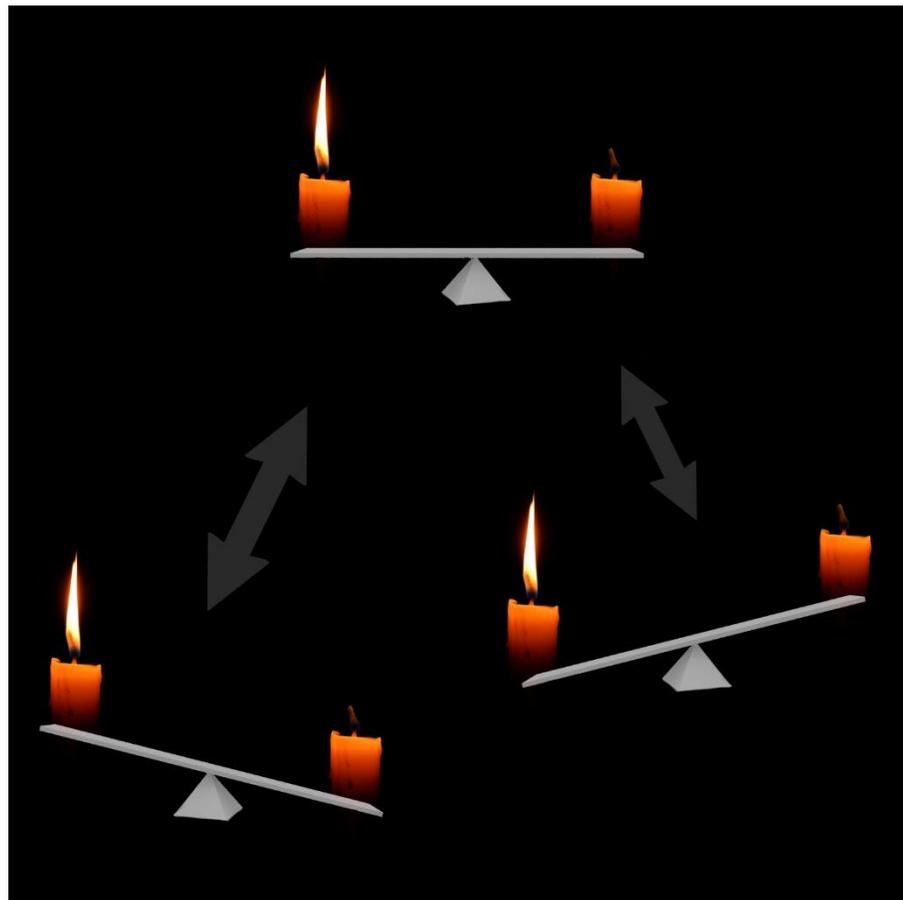
Wait to Weight? How long must we weigh in on our Energy Transition before Extinction? Artwork by Todd Siler and Geoffrey Ozin, www.artnanoinnovations.com.

Materials Views: Opinion Editorial

Tipping the Balance between Sustainability and Extinction

Geoffrey A. Ozin

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



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

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

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 CO₂ 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).

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). 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 CO₂ 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.

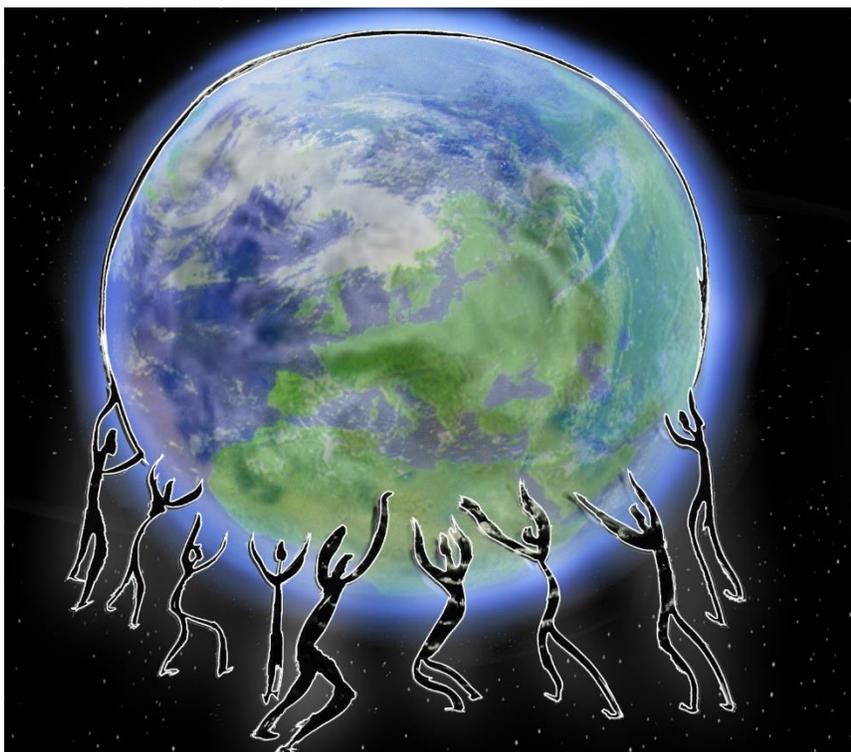
It is disquieting however that there does not appear to be much public discussion on the possibility that increases in the concentration of CO₂ from "business as usual", could cause the sixth mass extinction. This time the collapse of our entire ecosystem would be unnatural in origin, caused by *Homo 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). 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 CO₂ 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 CH₄, trapped as methane 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

Global Climate Change will not Change without You! In the war against CO₂-CH₄ 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.

CH₄ supersaturation in surface water. We know that CH₄ is a much more potent greenhouse gas than CO₂. And we know that the amount of trapped CH₄ in the Arctic is around 4-5 times greater than the trillions of tons of CO₂ 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 CO₂ threat to our civilization - but more devastatingly, a CO₂-CH₄ crisis. The potentially "Perfect Storm" CO₂-CH₄ 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 CH₄ as the permafrost melts.

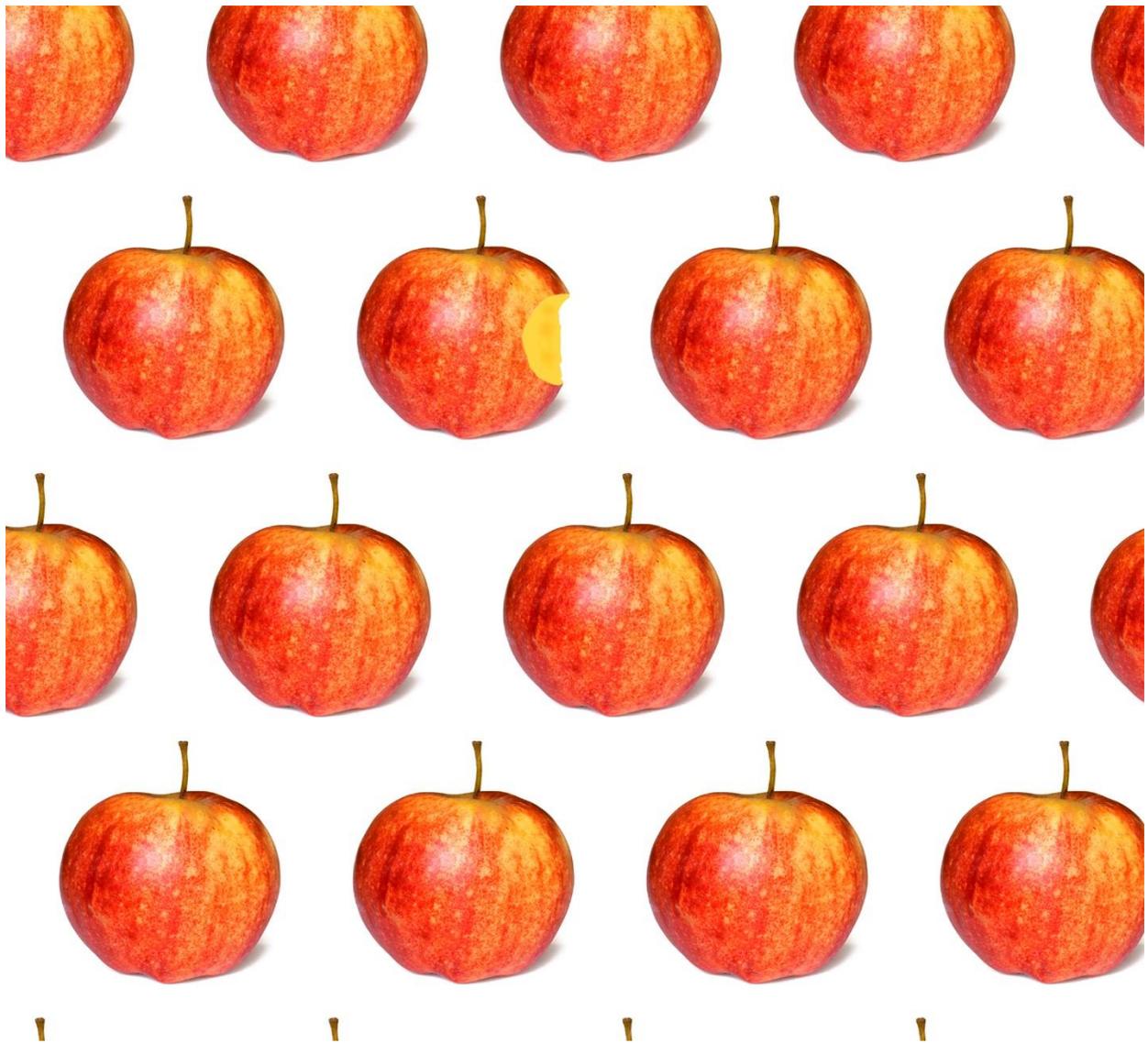
So we're all in a phenomenal war against CO₂-CH₄ driven climate change. To tip the balance in favor of sustainability rather than extinction, we must all now shoulder the responsibility of caring for our Earth with the same degree of concern as we care for ourselves and our collective future.

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

Materials Views: Opinion Editorial

Perfectly Imperfect: Tailoring Chemically and Physically Functional Defects for Utility

Geoffrey A. Ozin



Materials Views: Opinion Editorial

Perfectly Imperfect: Tailoring Chemically and Physically Functional Defects

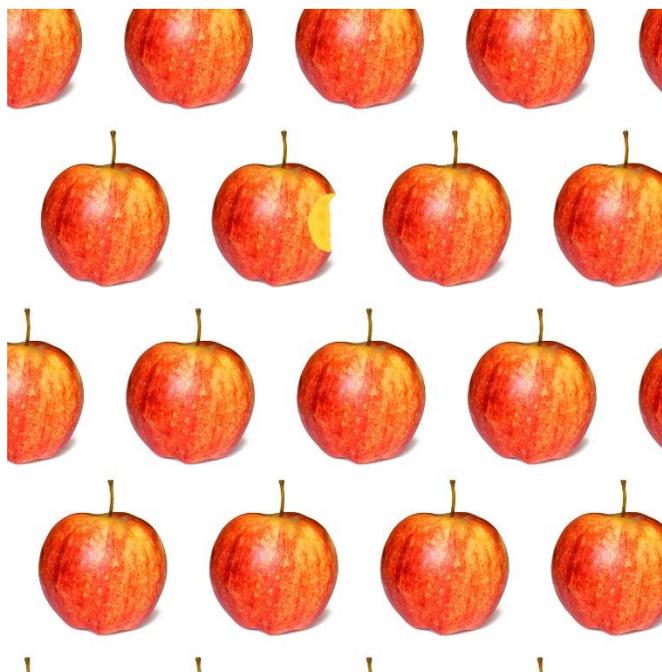
Geoffrey A. Ozin

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



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

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.

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.

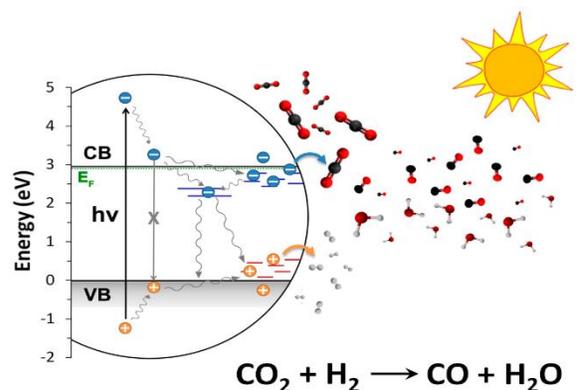
Often one finds that it is the physical properties of defects that determines their functionality and provides opportunities for developing useful technologies. Defect enabled physical properties include electronic and ionic conductivity, optical absorption, reflection, scattering and emission, different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

Especially interesting are those classes of defects that have recently been shown to participate in light-assisted heterogeneous catalytic reduction of gaseous CO₂ 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 CO₂ 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.

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 CO₂ by H₂ or H₂O to products, such as CO, CH₃OH and C_xH_y.



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

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 CO₂ and H₂ or H₂O. 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 CO₂.

Current research in the field of CO₂ 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 CO₂ 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.

Materials Views: Opinion Editorial

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.

Materials Views: Opinion Editorial

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?



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.artnoinnovations.com.

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 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 CO_2/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.

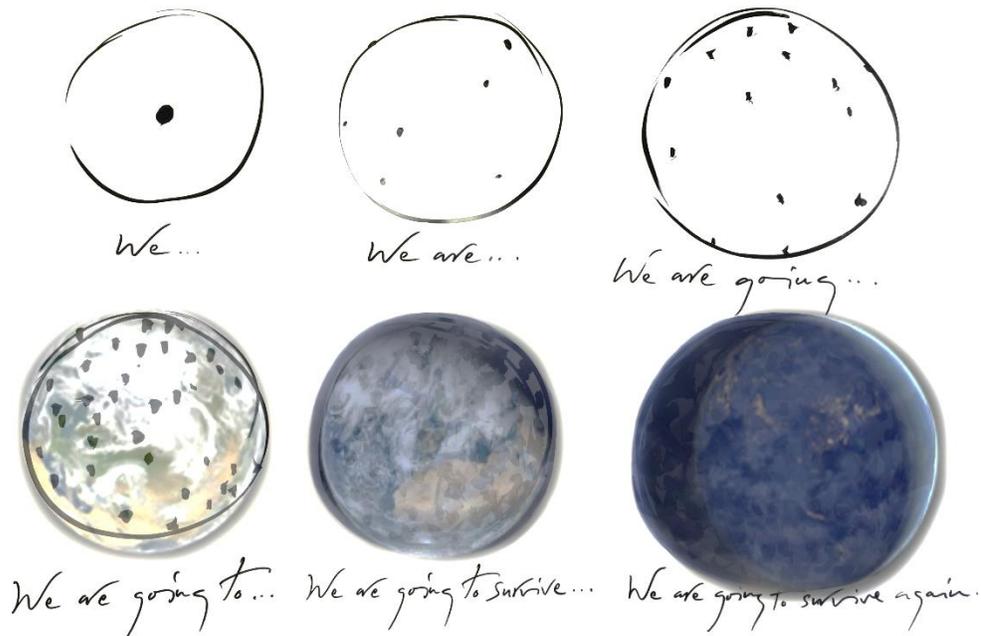
Now is the time to show how 'game-changing' chemistry has the potential to drive this energy revolution. It's not enough to entrust government lobby groups to do our work for us. We can show the impact of our work through world-wide outreach, high school and public education projects and by demonstrating 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



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.

energy generation, storage and 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.



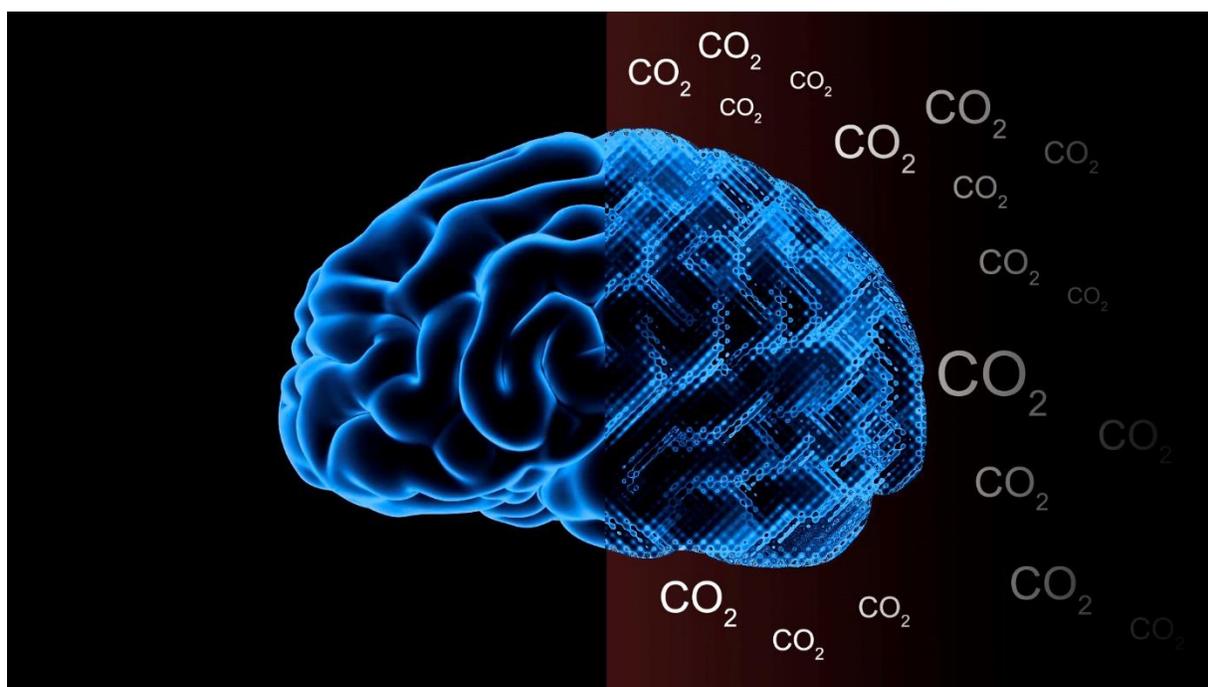
We have no Hercules, or Herculean men and women, to shoulder the Earth and protect its wellbeing. We only have ourselves to help ourselves. That fact fills the core of this Reality! We only have Human Ingenuity to rely on to tap our full creative potential in unprecedented ways. Artwork courtesy of Todd Siler and Geoffrey Ozin, www.artnanoinnovations.com.

Materials Views: Opinion Editorial

CO₂ on the Brain and the Brain on CO₂

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Materials Views: Opinion Editorial

CO₂ on the Brain and the Brain on CO₂

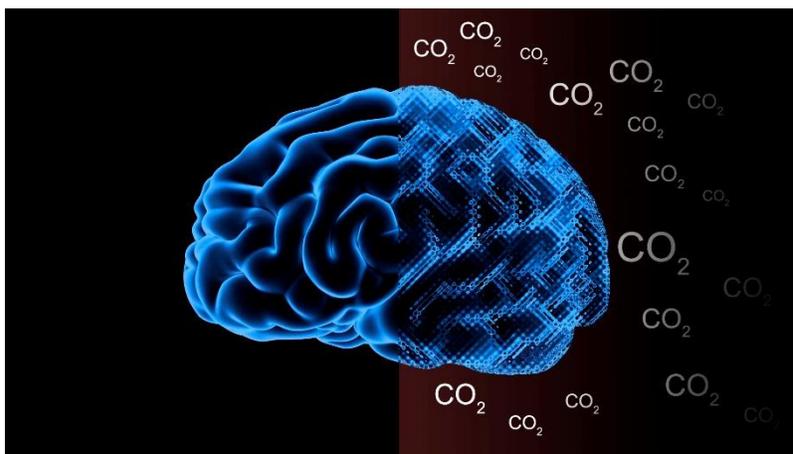
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Do you think we have a serious greenhouse gas climate change problem caused by anthropogenic CO₂ emissions in our atmosphere, which is threatening the future health and well-being of our civilization?

Well if you think that isn't bad enough it seems that we also have to be seriously concerned about the impact of CO₂ 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 CO₂ 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



Save our brains from the destruction of cognitive functionality by excessive levels of CO₂ in our living, working and travelling environments so we have enough brain power left to solve the climate problem driven by increasing concentrations of CO₂ in our atmosphere. Graphic artwork courtesy of Chenxi Qian.

statistically significant and meaningful reductions in decision-making performance, which could significantly affect productivity, learning and safety, are observable with increases in CO₂ levels from 600 to 1000 to 2500 ppm. While these levels seem high in comparison to the 405 ppm CO₂ 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 CO₂, one is amazed to discover that average cognitive scores of typical participants, decreased by 21% with respect to 400 ppm increases in CO₂ levels [2].

The adverse effects of high levels of CO₂ 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 CO₂ it is now apparent that we were not created to live in an atmosphere with increasingly high levels of CO₂.

Isn't it ironic that in our earnestness to create more energy efficient buildings with sustainable green designs to reduce levels of CO₂ in our atmosphere and thereby ameliorate climate change, we have made more tightly sealed indoor environments, which increases the level of CO₂ we

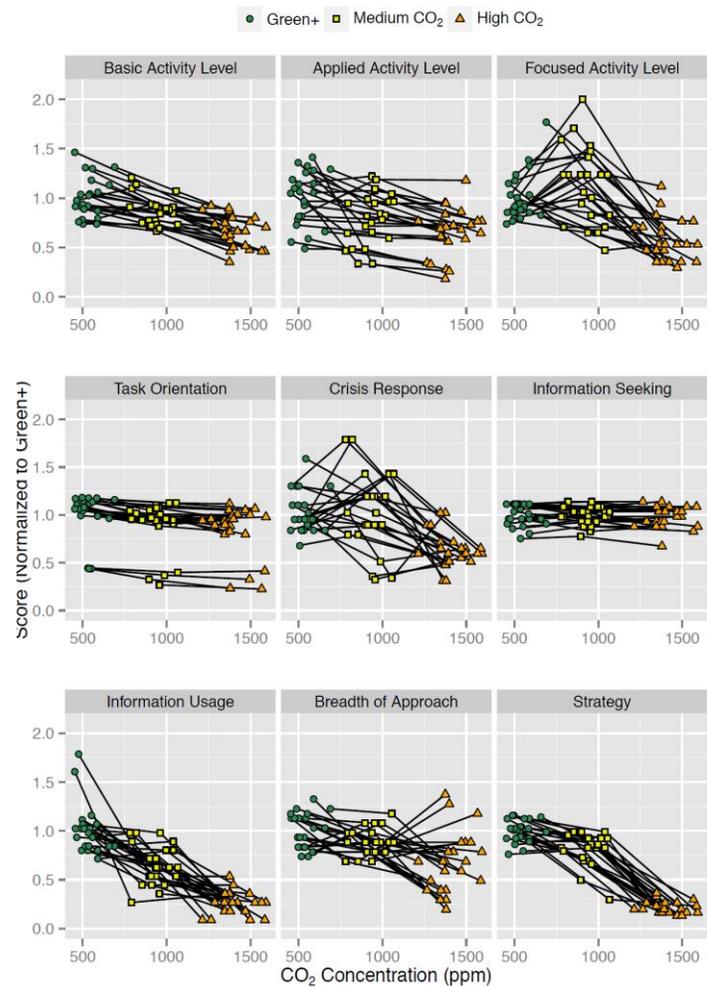


Figure 1 Cognitive function scores by domain and participant, and corresponding carbon dioxide concentration in their cubicle. Each line represents the change in an individual's CO₂ exposure and cognitive scores from one condition to the next, normalized by the average CO₂ exposure across all participants 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 CO₂ go? In a reported study, it was found that in a substantial number of poorly ventilated classrooms and workplaces, CO₂ 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 CO₂ in our atmosphere takes centuries.

So we have two looming health and safety problems to fret about, the negative effect of CO₂ 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 CO₂ sorbents, with standards established for spaceships and submarines, to solve this problem and soon these sorbents will be employed increasingly to control safe CO₂ 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 CO₂ sorption selectivity, capacity and stability, scalability and cost, provides new economic opportunities for clean-tech industries, wherever control of CO₂ 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 CO₂ 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.

1. Usha Satish, Mark J. Mendell, Krishnamurthy Shekhar, Toshifumi Hotchi, Douglas Sullivan, Siegfried Streufert, and William J. Fisk, Is CO₂ an Indoor Pollutant? Direct Effects of Low-to-Moderate CO₂ Concentrations on Human Decision-Making Performance, *Environmental Health Perspectives*, 2012, 120, 1671-1677.

2. Joseph G. Allen, Piers MacNaughton, Usha Satish, Suresh Santanam, Jose Vallarino, and John D. Spengler, Associations of Cognitive Function Scores with Carbon Dioxide, Ventilation, and Volatile Organic Compound Exposures in Office Workers: A Controlled Exposure Study of Green and Conventional Office Environments, *Environmental Health Perspectives*, <http://dx.doi.org/10.1289/ehp.1510037>

Materials Views: Opinion Editorial

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 TiO_2 . Its structure is based upon a three-dimensional interconnected network of six-coordinate 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 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 TiO_2 similarly exhibit a high reduction potential enabling the production of solar fuels, such as H_2 from H_2O and CH_4 , CH_3OH and CO from CO_2 .

There are other wide band gap photoactive Ti(IV) based oxides, such as the Rutile and Brookite polymorphs of TiO_2 , the Perovskite form of strontium titanate SrTiO_3 , and in the context of this editorial, the nanoporous open-framework titanasilicate, $\text{Na}_4\text{Ti}_2\text{Si}_8\text{O}_{22}\cdot 4\text{H}_2\text{O}$.

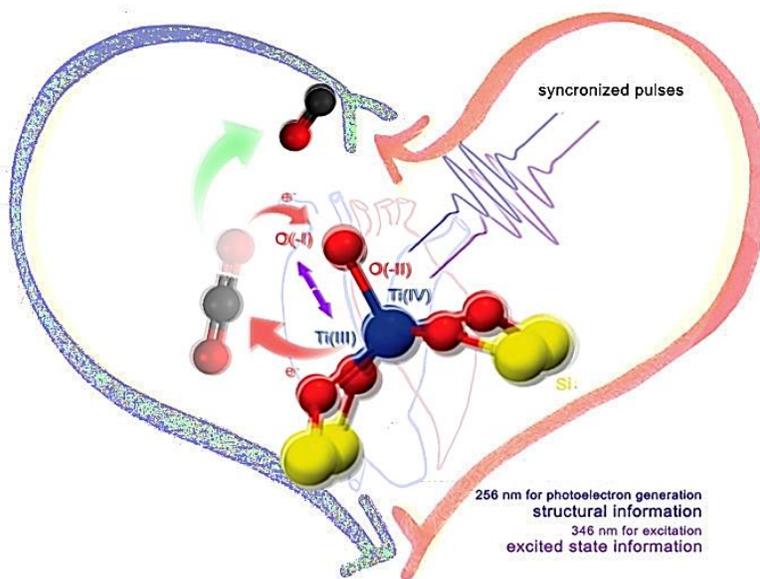
What distinguishes the titanasilicate from the other mentioned Ti(IV) based oxides is that the Ti(IV) is five-coordinate with a square pyramidal geometry, having one short 1.70 Å axial Ti=O double bond with four longer 1.96 Å equatorial Ti-O single bonds, as illustrated in the scheme.

This five-coordinate 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 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 TiO_5 square pyramidal site, by as much as 0.8\AA on the sub-picosecond 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.



Heart of the Matter 4D ultra-fast diffraction methods can peer into and peel away the most subtle details and beauty of photocatalysis, providing a new sharp focus realism of human-made nano machinery for the solar powered fixation of CO_2 to fuels and chemical feedstocks. Artwork courtesy of Chenxi Qian, Geoffrey Ozin and Todd Siler, www.artnanoinnovations.com.

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 Ti(IV)=O(-II) double bond of the TiO₅ site to the excited state apical 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 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 Ti(IV)O(-II) site into an excited state 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 CO₂, CO and H₂O 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 CO₂ to fuels and chemical feedstocks. To be technologically meaningful and economically sensible, solar powered CO₂ 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/>).

1. Yoo, B-K., Su, Z., Thomas, J.M., Zewail, A.H., On the Dynamical Nature of the Active Center in a Single-Site Photocatalyst Visualized by 4D Ultrafast Electron Microscopy, PNAS, 2016, 113 (3), 503-508; published ahead of print January 4, 2016, doi:10.1073/pnas.1522869113.
2. Ishikawa, T., Hayes, S.A., Keskin. S., Corthey, G., Miller, R.J.D., et al, Direct Observation of Collective Modes Coupled to Molecular Orbital Driven Charge Transfer, Science 2015, 350 (6267), 1501–1505.

Materials Views: Opinion Editorial

Fixing CO₂

Doing Something Fast and Economically Sensible with CO₂

Geoffrey A. Ozin

University of Toronto Solar Fuels Cluster, www.solarfuels.utoronto.ca



Graphic illustrating "Fixing CO₂" 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.

Materials Views: Opinion Editorial

Fixing CO₂

Doing Something Fast and Economically Sensible with CO₂

Geoffrey A. Ozin

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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 CO₂ 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 CO₂.

Two basic strategies exist in principle for putting a safe cap on atmospheric CO₂ in the next 20-30 years. One uses CO₂ capture and storage the other utilizes the captured CO₂ 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 CO₂ 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 CO₂ 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 CO₂ leakage and the liberation of CO₂ by dissolution of carbonates. Moreover, it is enormously expensive, not to mention the fact that it's very difficult to justify using CO₂ 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 CO₂ 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 CO₂ 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 CO₂ from our continued reliance on the use of fossil energy?*

In the urgent search for the innovation solution to fix CO₂, there does however appear to be agreement that the economic viability of CO₂ capture and storage can be improved by working hand-in-hand with utilization of the CO₂ 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 CO₂ 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 CO₂ 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 CO₂ will necessitate a large-scale source of inexpensive H₂ other than fossil-based steam reforming of methane, coal gasification or partial oxidation of oil. Ultimately, this will likely have to come from H₂O electrolysis powered by renewable forms of electricity or photoelectrolysis using sunlight.

With a world “drowning” in CO₂ and H₂O, 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 CO₂ utilization industries on stream. *Isn't the key to economical, sociological and political success, to prove that it is possible to scale CO₂ utilization processes to proportions that can make a difference to climate change?*

Success-breeds-success. Demonstration of technologically and economically sensible ways of fixing CO₂ 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 CO₂ 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.

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,



Graphic illustrating “Fixing CO₂” 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.

<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 CO₂ 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.*

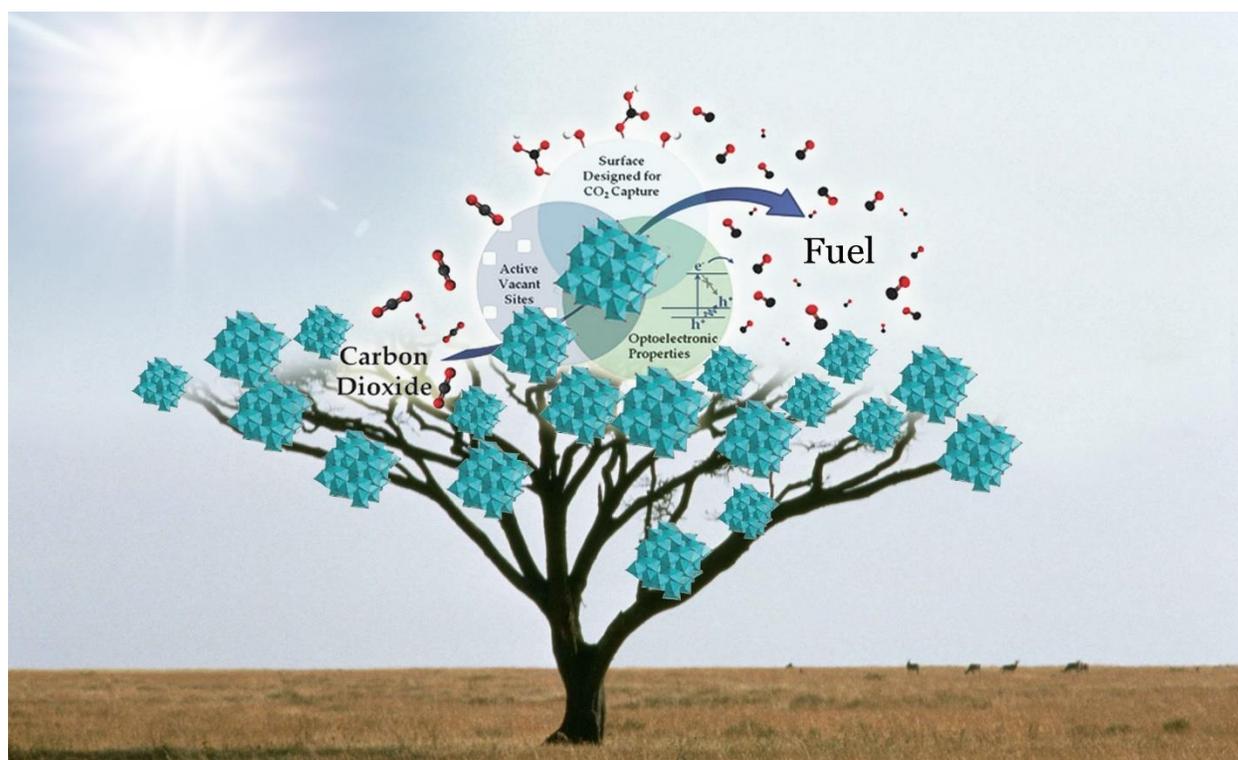
We all love CO₂ - let’s do it, let’s fix CO₂ fixation!

Materials Views: Opinion Editorial

Solar Fuels Cluster University of Toronto

Geoffrey A. Ozin

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Solar fuels tree – graphic courtesy of Chenxi Qian

Materials Views: Opinion Editorial

Solar Fuels Cluster University of Toronto

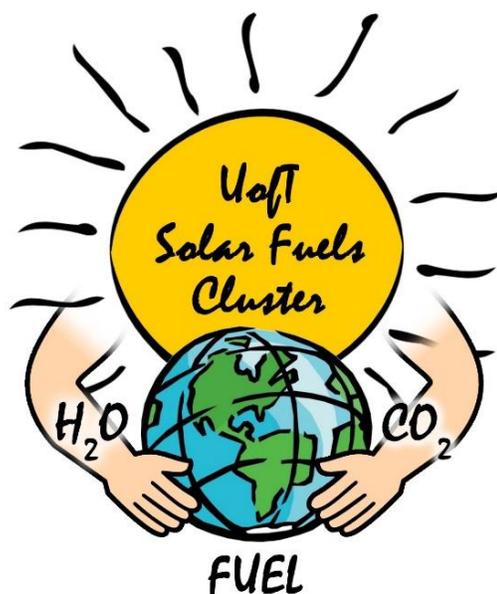
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Golden Opportunity After more than 45 years of research in the field of materials chemistry I was given the interesting opportunity in 2012 to write invited monthly opinion editorials for the Materials Views section of the VCH-Wiley family of materials 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 50th 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 CO₂ Economy – Solar Energy Enabled Closed Carbon Cycle,

www.solarfuels.utoronto.ca,
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 CO₂ and H₂O, which energize plants and ultimately produce the fossil energy our global society currently depends on. Our mission is to convert and store



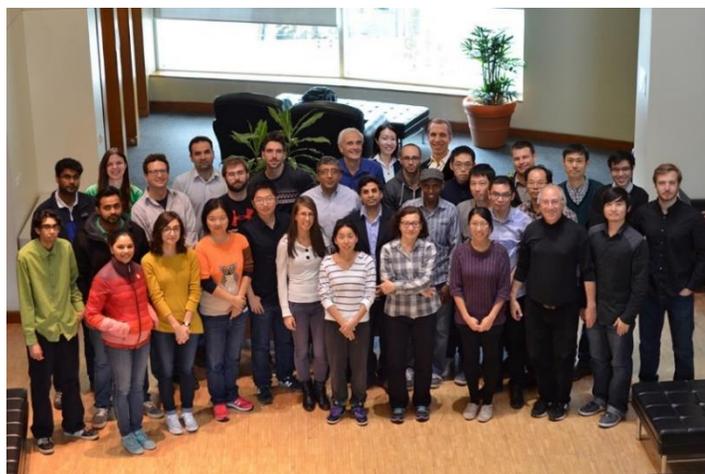
Illuminations on the utilization of CO₂: the illustration depicts the grand challenge that the global community must confront in the face of CO₂ induced climate change in order to achieve a sustainable environment, a renewable energy supply and a carbon neutral economy. Graphic courtesy of Chenxi Qian.

sunlight energy in synthetic Solar Fuels produced from CO₂ and H₂O, 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 CO₂ 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°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 CO₂ into renewable fuels using sunlight as the energy source, H₂O and/or H₂ as the co-reactant. This transformative research paradigm treats CO₂ as a renewable resource rather than a waste product, turning CO₂ from a liability to an asset, thereby providing a chemical platform for developing a carbon-neutral CO₂ 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



University of Toronto Solar Fuels Cluster,
www.solarfuels.utoronto.ca

attention of the UofT Solar Fuels Cluster.

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 CO₂ 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 CO₂-to-Fuel; and
- (iv) design and build photoreactors to evaluate the catalytic performance of photoactive materials for the conversion of gaseous CO₂ 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 CO₂ 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 CO₂ 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 CO₂-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 CO₂-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 CO₂ to hydrocarbon fuel molecules achieved by the UofT Solar Fuels Cluster are within an order of magnitude of the mol/h·g_{cat} 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 CO₂ to fuels, to combine materials and processes that can achieve technologically significant conversion rates of mol/h·g_{cat}. The target is the discovery and development of earth-abundant, low-cost materials able to effectively harvest sunlight, capture CO₂ and efficiently drive a cost-effective gas-phase heterogeneous photo-catalytic CO₂ 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 CO₂ photoreduction;

- (ii) evaluation of conversion rates and efficiencies for production of solar fuels, such as CO, CH₄, CH₃OH by light-assisted, gas-phase heterogeneous catalytic reduction of CO₂; 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 CO₂-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 CO₂ 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 CO₂ emissions into value-added products and markets 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. .

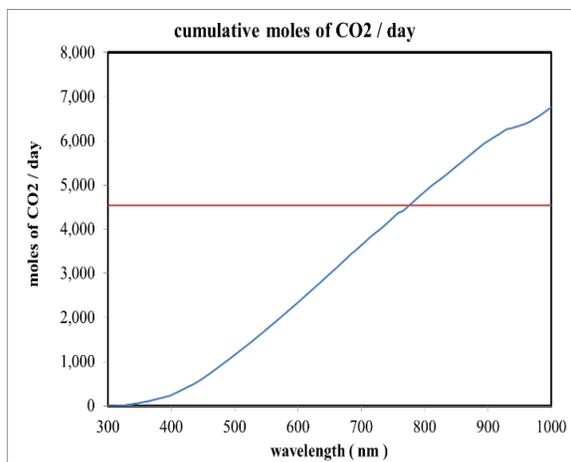
Carbon XPRIZE - Reimagining CO₂ A \$20 Million carbon XPRIZE sponsored by NRG COSIA is a global competition challenging scientists and engineers to develop disruptive technologies that will convert CO₂ emissions from power plants and industrial facilities into valuable products like building materials, alternative fuels and other items that we use every day www.carbon.xprize.org.

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 CO₂ 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 CO₂ conversion rate of 200 kg/day (4,600 moles/day) using a maximum land area of 2,300 m².

Challenge Perspective Let's imagine targeting solar powered conversion of CO₂-to-CH₃OH, a reaction which consumes 6 e⁻ for each molecule of CO₂ converted assuming a conversion efficiency of 10% and 8 hours of operation each day. The analysis involves

determination of the number of photons per m² to provide the number of CO₂ molecules converted per m² which provides the daily conversion of CO₂. 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 CO₂ converted per day as a function of wavelength.

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!



The carbon XPRIZE challenge for solar powered conversion of CO₂-to-CH₃OH, courtesy of Tom Wood.

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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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Materials Views: Opinion Editorial

A Global CO₂ Utilization Strategy that Benefits Everyone and Earth

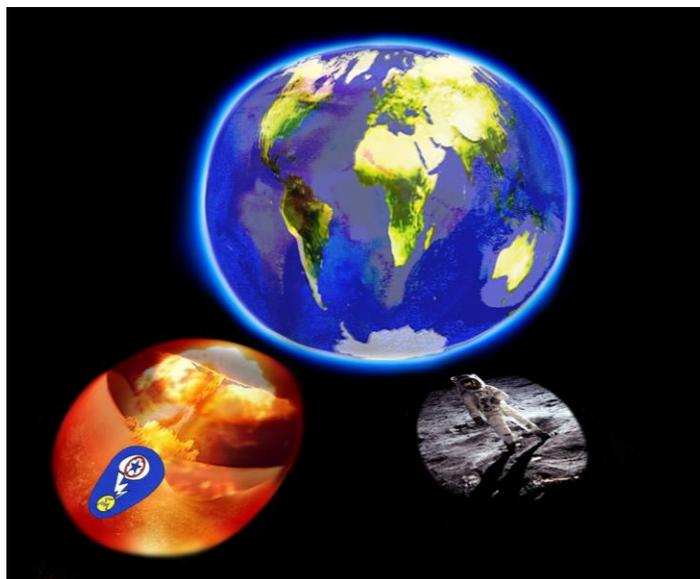
Geoffrey A. Ozin

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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. They express our deep conviction: “anything is possible”



This composite image, courtesy of Todd Siler and Geoffrey Ozin 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 CO₂ 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

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 CO₂ Utilization Project is a new and benevolent endeavor with a message of hope and higher awareness. It is founded on the premise that CO₂ emissions can be employed as a feedstock for the synthesis of chemicals and production of fuels. The capture, storage and utilization of CO₂ emissions for chemical synthesis achieve three desirable goals: (i) less CO₂ 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 CO₂ 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 CO₂ emissions produced by our fossil based resources, an inconvenient necessity considering



This photomontage unites the vision of a global CO₂ utilization strategy with a fuel synthesis plant that enables closing the carbon cycle. Images courtesy of Todd Siler and Geoffrey Ozin, 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 CO₂ 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 CO₂ from different sources to produce megatons of chemicals, materials and fuels. These industrial processes and products are changing our way of thinking about CO₂, 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 CO₂ utilization at industrial facilities around the world. A key question however, is how much capacity and market demand is there for CO₂ utilization products? Estimates from different sources of current market demands for products seem to favor around 5% conversion of global CO₂ emissions into synthetic chemicals and about 10% into synthetic fuels, 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 CO₂ 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 CO₂, 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 CO₂ 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 CO₂ establish a firm footing in the global economy to ensure that they stay competitive with those made from finite fossil resources.

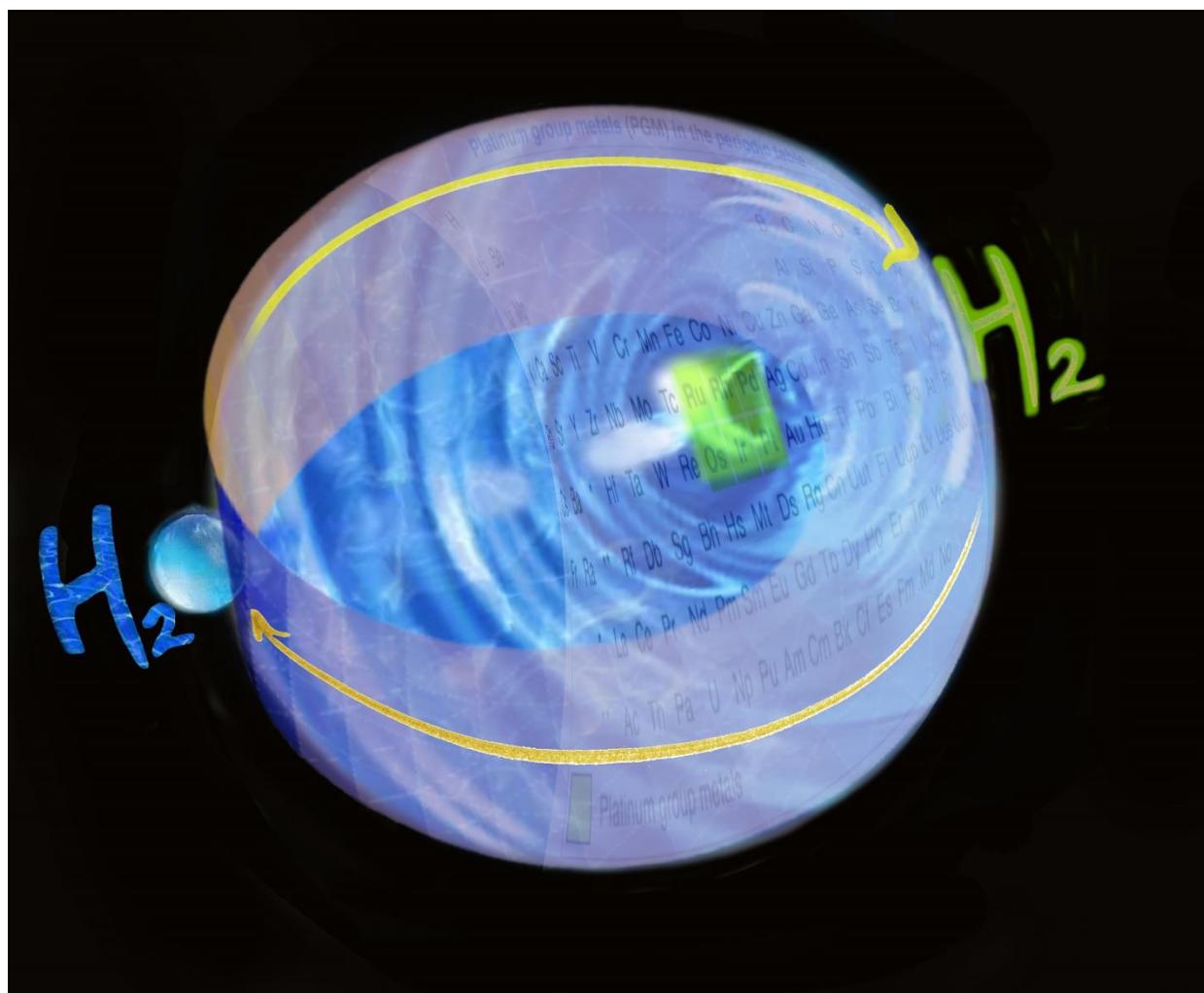
This new and benevolent collaborative endeavor can change the world, but only with a world of global citizens cooperating and committed to change. Science-technology-industry-government working in a concerted manner are “not” enough. People must champion and sustain these efforts to make it work. We 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?

Materials Views: Opinion Editorial

Is it Possible to Produce Enough Pt to Run an Affordable Solar Powered Terawatt H₂ Economy?

Geoffrey A. Ozin



H₂O to H₂ to H₂O 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 H₂ on a global scale for powering a worldwide hydrogen economy. Graphic courtesy of Todd Siler, www.artnanoinnovations.com.

Materials Views: Opinion Editorial

Is it Possible to Produce Enough Pt to Run an Affordable Solar Powered Terawatt H₂ Economy?

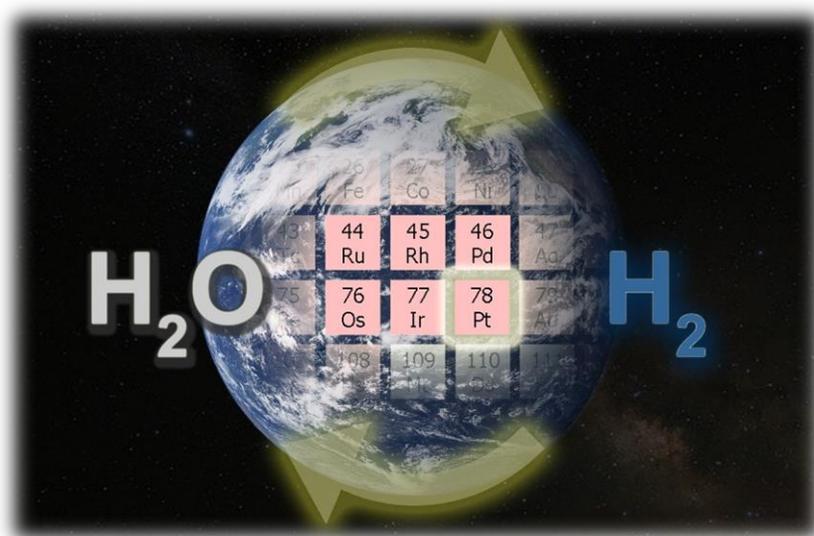
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Hydrogen as a clean energy source for fuel cells in the transportation and power generation sectors, as well as an effective reducing agent for transforming carbon dioxide to value-added chemicals and fuels, could solve some of the adverse consequences 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.



Let's not yet write off rare expensive Pt as the catalytic metal of choice for making solar H₂ on an industrially significant scale to power a global hydrogen economy. Graphic courtesy of Chenxi Qian.

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 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 H₂ evolution reaction from H₂O at a sufficiently large scale to facilitate a TW H₂ 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 H₂ evolution reaction from aqueous phase H₂O, the champion catalyst remains Pt despite much research devoted to find a more abundant cheaper alternative. This is simply because Pt as a H₂ 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 H₂ 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 H₂ evolution rate in a

photo-electrochemistry experiment using an exceptionally well-defined Pt-TiO₂-Ti-pn⁺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 H₂ evolution reaction was 5 nm at a loading level of 100 ng/cm² 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 H₂ 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 3.7x10⁻⁶ %) 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 H₂ clean and green global technology founded upon the photo-electrochemical splitting of H₂O 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 H₂ evolution reaction maintained if not improved [5]. Encouragingly in this context, a recent report revealed that the readily accessible, nanoporous layered material carbon nitride (C₃N₄), 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 C₃N₄-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 H₂ 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 H₂ fuel is seen with Toyota. After more than twenty years of rigorous research and development they have manufactured automobiles with H₂ fuel-cell powered engines to become commercially available later this year [9]. To enable this transition, H₂ fuel stations as well as H₂ 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 H₂ 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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Materials Views - Opinion Editorial

Photothermal Desalination

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Materials Views - Opinion Editorial

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

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



Metaphorming reverse osmosis RO, thermal distillation TD and photothermal desalination PD. Courtesy of Todd Siler and Geoffrey Ozin, www.artnanoinnovations.com.

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

Another 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.

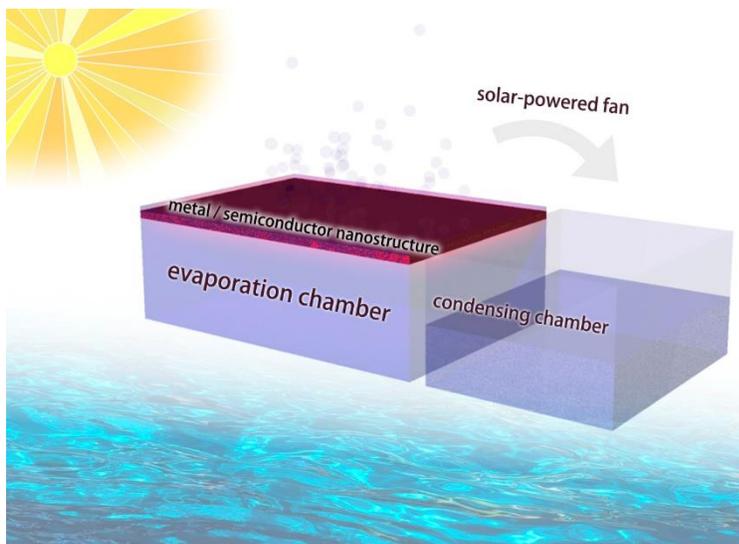


Illustration of an all-in-one solar distillation system for producing fresh water from salt water. Graphic courtesy of Chenxi Qian

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. The design needs 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. Presently, 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.

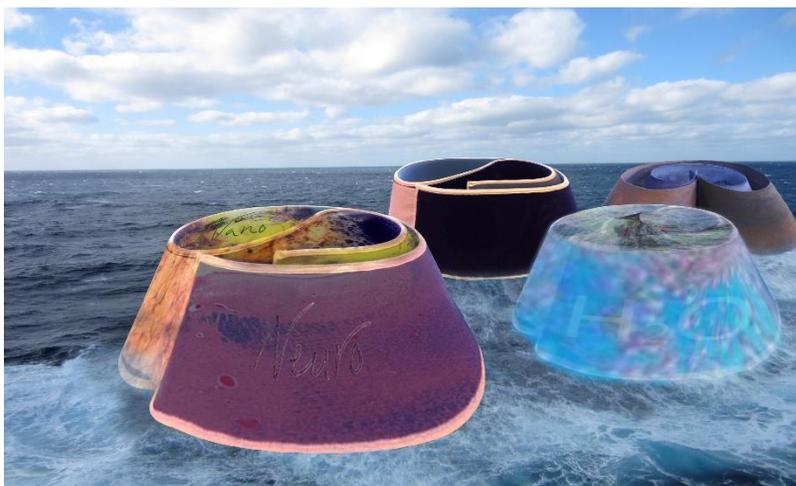
The photothermal effect can also operate through the non-radiative relaxation of phonons when organic or inorganic semiconductors are excited at energies above the electronic bandgap and when metals are excited at intra-band and inter-band energies. These excitations can result in localized heating of 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. This desalination system may take myriad forms to function in a wide range of environments. Moreover, it can be combined, integrated and scaled to accommodate every type of climatic condition anywhere.

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 due to 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

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SUN
ELECTRICITY
GREEN ENERGY
PHOTOCATALYSIS
WIND
WATER

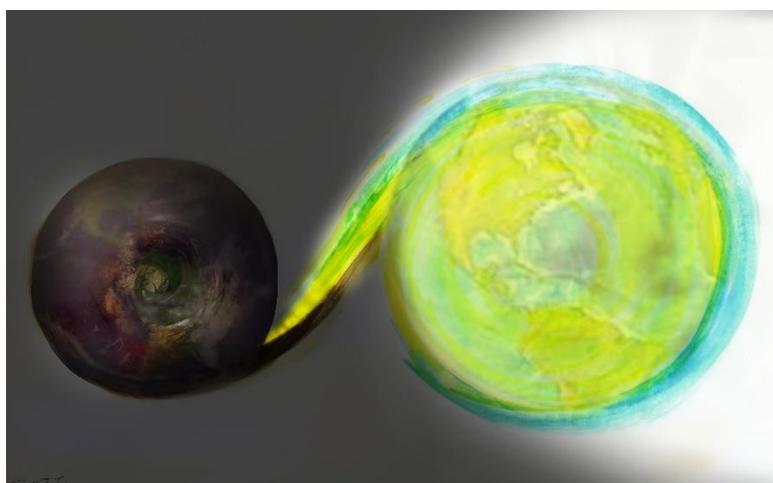
Electrified World, Art Work Courtesy of [Chenxi](#) Qian

Materials Views- Opinion Editorial

Electrified World

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It's Your Choice! An Unsustainable Fossil and Nuclear Energy Economy or a Clean and Green Energy Economy? Art Work Courtesy of Todd Siler, www.toddsilerart.com, www.artnanoinnovations.com

Humanity is only as secure and sustainable as the solutions we create to wisely manage our interrelated energy, climate and environment needs. The long-term use of fossil and nuclear energy sources leads to a dark and narrow cul-de-sac. Needless to say, these forms of energy are unsustainable and insecure. No doubt many people will initially react negatively to the far-reaching vision of a clean and green planet, one that's safe from climate change and environmental pollution. They'll say it's impossible to achieve this energy transition in practice citing the usual log jams or obstacles, namely, the technological and economic hurdles, not to mention the social and political barriers. However, it can be shown today that many of the obstacles or problems have already been solved or can be overcome by providing quantitative information on the technological and economic changes that are possible and the economic and social benefits that will result if they are implemented. Nevertheless, serious changes are hardly easy to actualize; and they're rarely welcomed. Change is often resisted by those in the fossil and nuclear energy industries who stand to lose out financially. However, a recent detailed technical, economic and social analysis

Imagine a world roughly 30 years into the future, in which all fossil and nuclear energy producing systems are converted into clean, safe and renewable ones producing electricity powered solely by wind, water and sunlight, to enable the operation of all transportation, heating and cooling systems, homes and industry, supplemented by some renewable hydrogen, generated electrochemically or photo-electrochemically.

Humanity is only as secure and

from a team of Stanford University Civil and Environmental Engineers, shows this is not necessarily true and the gains easily compensate for the losses if such an energy transition can be reduced to practice in an efficient and effective 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 and social 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 100% conversion to wind, water and sunlight electrical systems. These energy systems include onshore and offshore wind, concentrated solar, geothermal, photovoltaics, tidal, wave, and hydroelectric power systems.

Here a few points are worth noting. First, the conspicuous absence from the pan-electrical roadmap are nuclear power, coal with carbon capture, natural gas and liquid and solid biofuels. Notably biofuels are excluded on the grounds that greenhouse gas emissions are on a 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 with 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, super capacitors, hydrogen and conversion of carbon dioxide to liquid hydrocarbon fuels using hydrogen. The latter is 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. Airbus have a prototype 2-seater electric plane with a lithium battery plus a small gasoline engine to charge the battery. While this plane could serve as a test bed for a small hybrid electric commuter plane of the future it is hard to imagine an Airbus 380 plane being battery powered for a long time yet [3]. This is where solar thermochemical and photochemical catalytic conversion of CO₂-to-fuel will have a role to play in a pan-electrified utopia. Fourth, the benchmark to produce liquid fuels from H₂O, CO₂, and solar energy is based on the following process chain: 1) solar electricity; 2) H₂O electrolysis; 3) reverse water-gas shift (RWGS) of H₂+CO₂, 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 are 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, 7.2% rooftop photovoltaics, 7.3% concentrated solar power with energy 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 the replacement plan is expected to create 3.9M and 2.0M construction and operation jobs for building and running the renewable energy facilities respectively. This opportunity more than adequately accommodates the 3.9M jobs lost in the conventional fossil and nuclear energy sectors.

The associated health and economic benefits of this energy transition are also remarkable. 46,000 mortalities per year from air pollution in the United States would be eliminated following full conversion in 2050, saving \$600B per year in 2013 dollars in 2050. This amounts to an amazing 3.6% of the 2014 U.S.GDP!

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

On a personal basis the economic benefits are significant, whereupon by 2050 roughly \$260 per person per year in energy costs will be saved in 2013 dollars with additional savings of \$1,500 and \$8,300 per person per 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 make these people aware of what changes are technically and economically possible 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 powered entirely by wind, water and sunlight.

Based on 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 from 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 [4]. 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.

Acknowledgments

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Materials Views Opinion Editorial

Race for a CO₂-to-Fuel Technology

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For the first time since the tracking of CO₂ 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 CO₂ emissions could be recycled back to a synthetic transportable fuel using only H₂O and renewable forms of energy such as solar, wind and hydro power, in a carbon-neutral CO₂-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.

Materials Views Opinion Editorial

Race for a CO₂-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 CO₂-to-Fuel, the first pilot demonstration to successfully take CO₂ 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 CO₂ 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 CO₂-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 CO₂-to-Fuel technology to beat.



Priming the petrol pump with recycled CO₂ from thin air

Materials Views Opinion Editorial

Race for a CO₂-to-Fuel Technology

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The stakes have been raised in the quest for a commercially viable CO₂-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 CO₂ and H₂O and renewable energy sources, such as wind or solar or hydro power. The CO₂ supply was obtained mainly from a biogas plant supplemented with some CO₂ captured directly from the air.

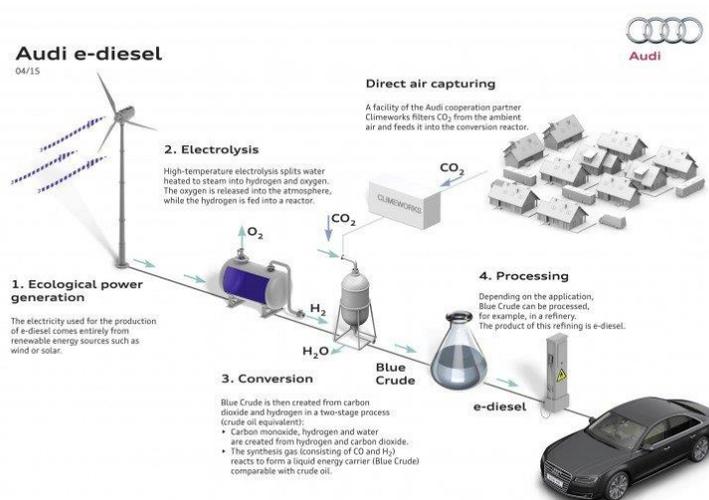


Figure 1: Audi process for producing diesel fuel from carbon dioxide and water, <http://www.sciencelert.com/audi-have-successfully-made-diesel-fuel-from-air-and-water>

While very few techno-economic details are currently available for an independent critical life-cycle-assessment, the publicized estimated price at the pump of 1-1.5 Euro/liter seems to make the future prospects for CO₂-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 CO₂ from thin air; the *second* involves electricity generation from renewable sources; the *third* uses electrical energy to electrochemically split water into a hydrogen (H₂) and oxygen (O₂) mixture from which the H₂ must be separated; the *fourth* uses this H₂ to reduce the CO₂ captured from the atmosphere, to form a mixture of carbon monoxide (CO) and water (H₂O) in a high temperature and high

pressure Reverse Water Gas Shift (RWGS) process, from which the H₂O and unreacted CO₂ is separated; and the *fifth* mixes the CO with the H₂ 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 CO₂-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 H₂O. It does not account for all remaining capital costs including CO₂ capture, conversion and separation nor for the additional required energy inputs, such as, the electricity to compress captured CO₂ 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.

Concerning the most promising alternative CO₂-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 CO₂-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

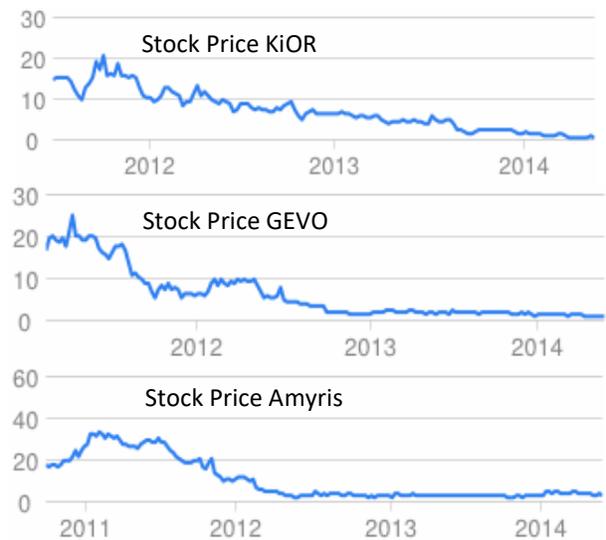


Figure 2: Boom and bust record of some biofuel spin-off companies <http://finance.yahoo.com/>

the material and energy balances of CO₂-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 CO₂ and H₂O 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 CO₂-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, CO₂ 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 H₂ by the photochemical splitting of H₂O 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 H₂ for a viable CO₂-to-Fuel economy that could impact greenhouse gas climate change.

The same efficiency, scalability and cost considerations apply to aqueous phase photochemical conversion of CO₂-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 H₂O to H₂ followed by the H₂ reduction of CO₂, 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 H₂ 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 H₂ generated in this way can be transformed to electricity using fuel cells or converted to transportable liquid fuels by

heterogeneous catalytic reduction CO₂ *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 CO₂-to-Fuels. However, as mentioned above, the cost of scaling up an aqueous phase solar-powered CO₂-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 CO₂-to-Fuel, the overall process is simplified as the electricity generation and electrolysis requirements of H₂O 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 H₂ 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 H₂, 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 CO₂ + H₂O into CO + H₂ 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 H₂-CO Syngas using a two-step H₂O-CO₂ 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 CO₂ 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 CO₂ + H₂O 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 CO₂ + H₂O or H₂ 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 CO₂-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 CO₂ + H₂O to a fuel such as CH₄ or CH₃OH to be realized in practice.

One way to transcend the complexity and efficiency of the multi-step Audi CO₂ + H₂O to fuel process is to discover a “dream” catalyst dubbed the “techno-leaf”, which is able to directly convert gaseous CO₂ + H₂O under mild conditions to a fuel, using just the energy contained in sunlight as the renewable power source. The gas-phase “techno-leaf” CO₂ + H₂O 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 CO and step 5 if we make fuels such as such as CH₃OH, (CH₃)₂O, HCO₂H or CH₄.

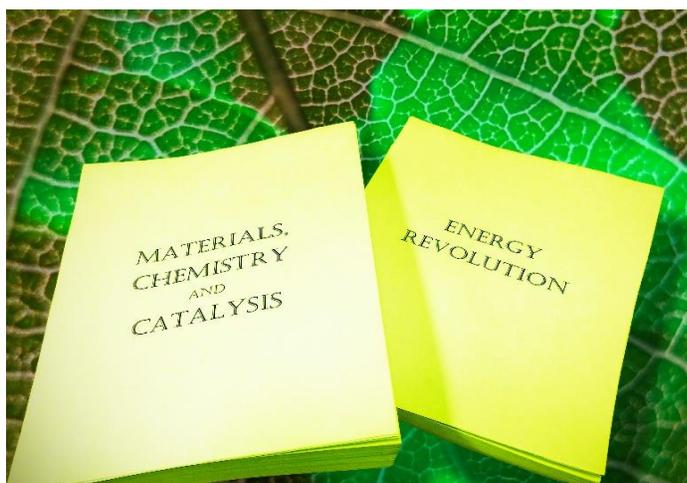


Figure 3: You can't have an energy revolution without materials, chemistry and catalysis; Graphic image courtesy of Chenxi Qian.

If the “techno-leaf” could also capture CO₂ and H₂O from thin air and operate with low concentrations of CO₂ in the presence of O₂, 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 CO₂-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 CO₂-to-Fuel technology to enable an energy

revolution and resolve greenhouse gas climate change.

In the case of a light-assisted process that converts CO₂ and H₂O 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 CO₂ for processing with H₂O to synthetic fuels by any of the aforementioned methods. In the Audi process, much of its CO₂ 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 CO₂ and H₂O 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 H₂O 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 CO₂ and H₂O 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 CO₂ and H₂O co-extraction process. By combining this process with the conversion of CO₂ and H₂O to fuel, energy can be conserved and costs reduced because the need to transport CO₂ and consume fresh water resources are eliminated [16].

It would be interesting to invent photoactive materials that can simultaneously capture CO₂ and sunlight and convert the CO₂-to-Fuel. This might be a way to reduce the entropic penalty pervasive in carbon capture and conversion processes. In a “one-step” solar-powered gas-phase CO₂-to-CO “techno-leaf” the effluent of CO₂ capture and conversion will have 80% N₂, 20% O₂, and a few ppm of CO₂ and CO. Assuming 50% conversion, there will be, very roughly, 250 ppm CO₂ and 150 ppm CO. This means that to get the product CO, it will have to be extracted from the mixture by a selective CO adsorbent. Currently, most research is targeted at CO₂ separations, so although we only have one separation, designing materials that would extract CO from N₂+O₂+CO₂ mixtures will be required. The alternative of removing N₂, O₂, and CO₂ from the mixture is a prohibitive option because it would require the removal of huge amounts of gases and thus require a lot of energy compared to the production rate of the main product. Another approach is to capture CO₂ and H₂O on the photo-catalyst surface and convert the mixture to a liquid product, such as MeOH. One would still have to remove ppm amounts, but this time we have to separate a liquid product from a gaseous one, which can be done by simply cooling. In this case one would kill two birds with one stone, namely carry out separation and reaction in one step and have an easy separation for the final MeOH product.

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 CO₂-to-Fuel in the long term.

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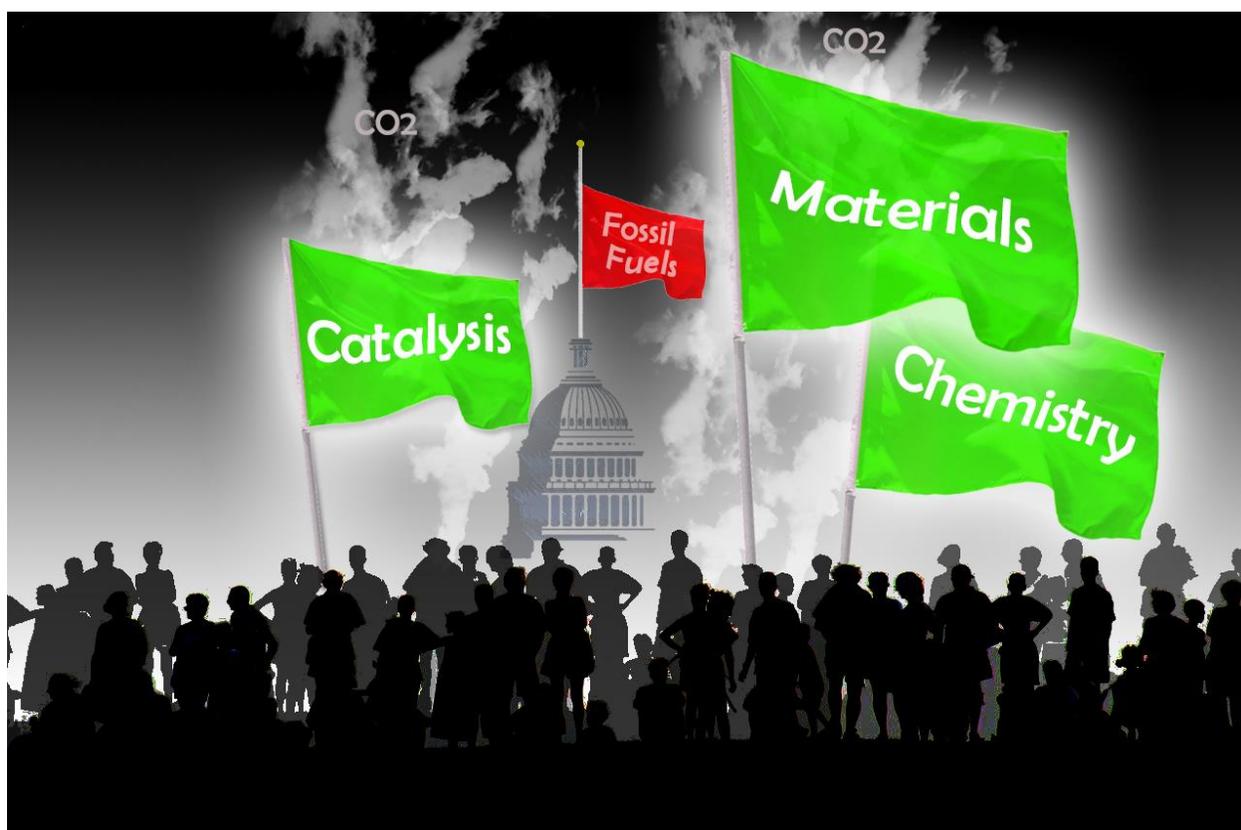
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Materials Views Opinion Editorial

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

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The central postulate of this article is that CO₂ 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 belief 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].

In this context I have been pondering whether the grand challenge faced by the materials research community of creating the science and technology to enable the transformation of CO₂-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/or action?

Because CO₂ 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



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

use of a catalyst. Synthesis of a champion CO₂-to-fuels catalyst requires an in-depth understanding of how the structure, properties and activity relate to each other to make it work efficiently.

Catalysts are an essential part 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 physicochemical principles of catalysis began to take shape in the 20th 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 21st century based on a CO₂ economy. We are now well aware of the deleterious effects of the continuous emission of CO₂ 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 CO₂ reactions we can now envision an economically viable and secure energy supply, where CO₂ is treated not as a waste product, but rather as a valuable and bountiful chemical feedstock for making renewable fuels in a CO₂-to-fuel carbon neutral catalytic cycle.

Ideas and practice on CO₂-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 CO₂-to-fuels to policy and industry implementation [2,3].

Seen in this new light, the CO₂ 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 CO₂-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 CO₂-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 CH₄ and CH₃OH, to store renewable solar energy in the form of chemical bonds, using CO₂ as a carbon source [4]. These ambitions are at the conceptual stage globally. Nevertheless they come with feasible strategic plans for implementing these CO₂ 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 CO₂ conversion efficiencies. Their collective vision continues to inspire and forge essential global research collaborations committed to moving mutually beneficial discovery forward for a sustainable CO₂-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 CO₂ 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 CO₂ 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 CO₂-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 CO₂-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 CO₂-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 CO₂-to-fuels knowledge dissemination should greatly increase the capacity to inform policy in individual countries, validated by basic and translational science across countries. As such, CO₂-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 CO₂-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 CO₂-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 CO₂ to stored energy in the chemical bonds of CH₄ and CH₃OH at rates, efficiencies and scales required for large volume production of fuel from CO₂.

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 CO₂ economy will depend upon. It will likely be predicated upon a gas-phase conversion of a CO₂-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 CO₂ available to be exploited.

Recently several promising candidate 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 CO₂ 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 = 1.1×10^6 TJ = 0.033 TW-year = 1×10^9 MBTU = 172MBOE). This is equivalent to about 70 billion barrels of oil which translates into about 20 billion ton equivalents of CO₂ 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 CO₂ in our atmosphere in the next couple of decades then the sum total of all kinds of CO₂ refineries around the globe will have to cope with CO₂-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 CO₂-to-fuel are currently scattered amongst isolated groups around the world, and information and education about these research projects are not targeted at policy makers and the public in an effective way, which is unnecessarily delaying the transition. A global CO₂-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!

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Materials Views Opinion Editorial

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

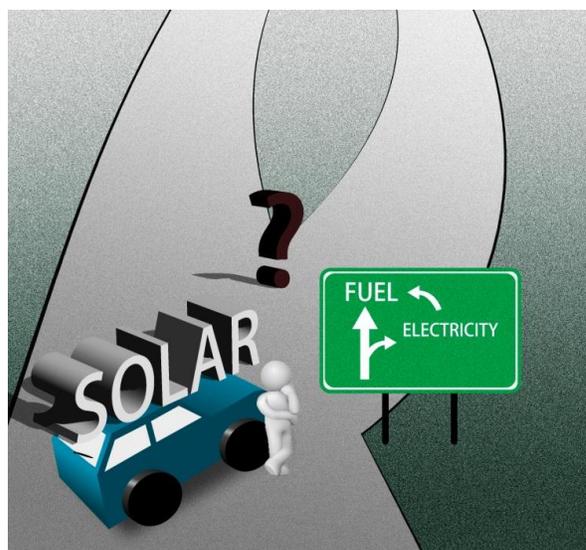
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Materials researchers around the world, who are trying to discover materials and processes, abiological, biological or a hybrid of both, to enable solar powered conversion of H_2O and CO_2 into chemicals and fuels, such as H_2 , CO , CH_4 , HCO_2H or CH_3OH , 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 CO_2 function as a carbon-neutral renewable energy supply for making chemicals, powering transportation and running industrial infrastructure.



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 H_2O and/or 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.

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 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 H₂. One can then convert the gaseous H₂ and CO₂ to CH₄, CH₃OH or (CH₃)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 CO₂.

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 H₂O/CO₂ to form CO or CH₄ 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^2 - 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_2 , (2) separate CO_2 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.

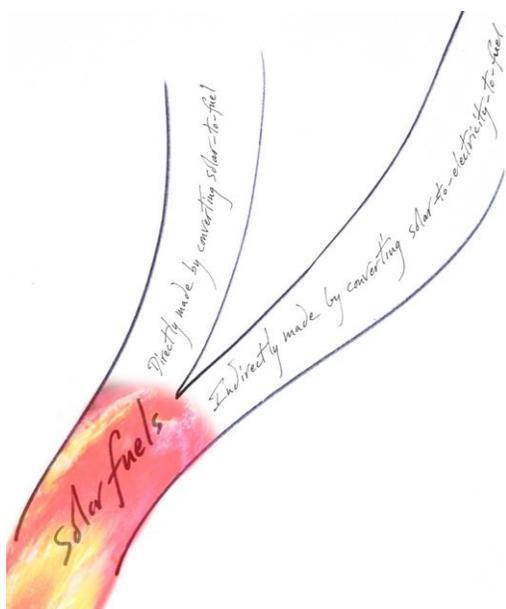
Hopefully materials researchers will find the insight derived from this type of brainstorming discussion, with energy engineering experts, to be helpful for placing basic-directed research aimed at the discovery and development of materials and processes for generating solar fuels directly from H_2O and CO_2 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_2 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 CO₂, 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 CO₂.

An equally important and related societal and ethical question concerning the utilization of CO₂ as a source of renewable energy is: do we value economic cost more than environmental cost? 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?



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.

There is a strong focus on cost in the solar fuels community, which is unfortunate because mature technologies to avoid extra CO₂ 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.

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 Brey, Thomas Bein, and Avelino Corma is deeply appreciated.

Materials Views Opinion Editorials

“Charge” of the “Sunlight” Brigade

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Figure 1 Concept of a sustainable solar fuels earth founded upon the light-assisted photo-conversion of CO₂ and H₂O to solar fuels such as CH₄, adapted from 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 photocatalyst and the hydrogen so produced will reduce carbon dioxide using sunlight and a second photocatalyst, to produce a solar generated fuel such as carbon monoxide, methane, methanol, formic acid and dimethylether.

While these photochemical transformations are well known, photocatalysts 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”.

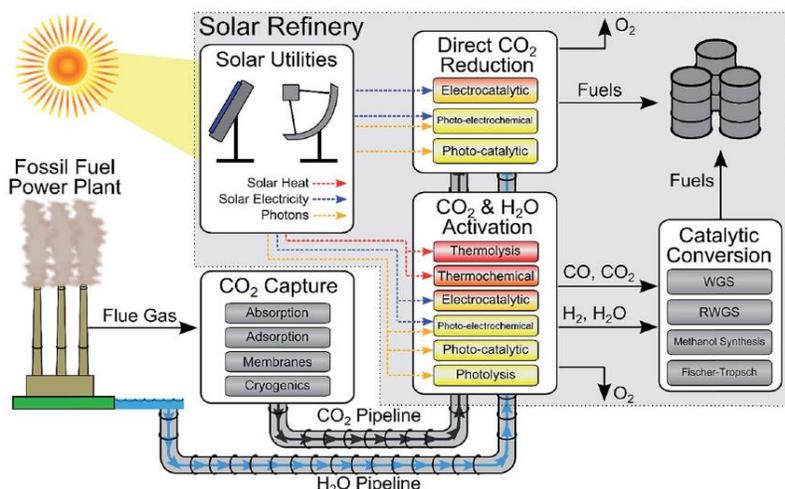
In view of the impending climate change and energy security challenges confronting the human race, the prescience of Giacomo Luigi Ciamician, Thomas Edison and Melvin Calvin is extraordinarily close to actuality today and the “Sunlight” Brigade is “Charged” with their mission to make the Utopian vision of a sustainable solar fuels earth, founded upon the light-assisted photo-conversion of CO₂ and H₂O to solar fuels such as CH₄, a reality, **Figure 1**.

Materials Views Opinion Editorials

Solar Refinery: Can we have our carbon cake and eat it too?

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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 CO₂ emissions, to a new and sustainable 'carbon dioxide economy' that instead uses the CO₂ as a C1 feedstock, together with H₂O and sunlight, for making solar fuels.

Scheme Futuristic 'solar refinery' for making fuels and chemicals from CO₂, H₂O and sunlight, Energy and Environmental Science, 2014, DOI: 10.1039/c4ee01958j

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 CO₂, and (iii) converting CO₂ and H₂O directly or indirectly into 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 CO₂ facility uses absorption, adsorption, membrane or cryogenic techniques for capturing, purifying and releasing CO₂ on demand; and (iii) The CO₂ is piped with H₂O and either *directly* transformed to fuels using electrochemical, photoelectrochemical or photocatalytic methods or *indirectly* converted to CO and H₂ by thermochemical, electrochemical, photoelectrochemical or photocatalytic means. The CO and H₂ formed by these processes 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.

However what has been sorely missing in the open literature, to assist the teams of materials chemists, scientists and engineers around the world who are eager to contribute to the development of this solar refinery, is a life-cycle-assessment, a holistic techno-economic 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 CO₂ reduction is currently lagging far behind that of solar driven H₂O splitting and more research is needed to improve the activity of photocatalysts and the efficacy of photoreactors. In the indirect process of transforming CO₂/H₂O to fuels, it is apparent that if the currently achievable solar H₂O-to-H₂ conversion (>10%) can be matched by solar CO₂/H₂-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 process that can directly transform CO₂/H₂O 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 CO₂ 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, even though the cost of the

CO₂ reduction step, which is estimated to be quite costly, was not included in the estimates. Improvement in the activity of CO₂ 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 CO₂ 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 Climeworks AG (www.Climeworks.com) with commercially available equipment that enables an efficient two-step process involving (i) CO₂ capture and purification using specialized sorbents followed by (ii) CO₂ release using solar power. This positive development, together with advances in CO₂ 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 paper by Christos Maravelias and his colleagues 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 too? 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 CO₂ 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 solar refinery of the future.

Materials Views Opinion Editorials

CO₂: War and Peace?

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Figure 2 Every day we influence the dynamic balance between The CO₂ War and Peace, by messing with the equilibrium level and steady-state concentration of CO₂ and O₂ 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

sunlight to oxidize water to form molecular oxygen. As a result of this astonishing event, a symbiotic balance and synergy evolved between the O₂ required to sustain life and the life needed to sustain O₂. In this biological era - and up until recent times - a delicate equilibrium was established that maintained a steady-state concentration of CO₂ and O₂ in the atmosphere. This equilibrium enabled all life processes to flourish on Earth. Essentially, **life was at peace with CO₂**, and has remained so ever since, **Figure 1**.

At War with CO₂ It started around the period of the industrial revolution (1760-1840) as the concentration of CO₂ 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

At Peace with CO₂ 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

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 CO₂ in the Earth's atmosphere to gradually increase from its equilibrium level 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 CO₂ 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 CO₂ into the atmosphere and at today's increased emission rate of 40-50 billion tons of CO₂ per year we are on track for a 2°C rise). Cut global CO₂ 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 CO₂ into the atmosphere since the industrial revolution or those nations currently emitting the greatest amount of CO₂ 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 CO₂ 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!

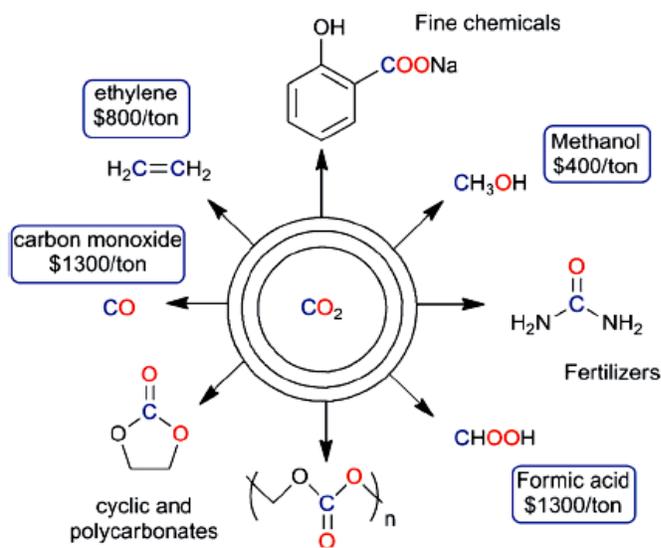
The big challenge for the global community is whether we have the scientific, technological, economic and political means and motivations for commercial implementations to agree upon

an approach to accelerate the transition of fossil fuels to renewable forms of energy fast enough to avoid the ramifications of a CO₂ 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) While the storage element of this procedure is likely to be different if CO₂ 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 CO₂ 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 CO₂**, Figure 1.

At Peace Again with CO₂ Perhaps the toughest challenge of ameliorating climate change and facilitating a sustainable energy future, in which life is at peace with CO₂, is stopping ourselves from treating CO₂ as a waste product endangering life on Earth. Instead we need to utilize CO₂ as an abundant, non-toxic and low cost feed stock for making fuels and chemicals, enabling life to flourish indefinitely.



Scheme CO₂ is not a waste product to fear, it is an abundant, non-toxic, low cost C₁ 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 CO₂ 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 CO₂ would be over.

In actualizing this possible reality, CO₂ 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 CO₂ 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 CO₂ 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 CO₂ 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 CO₂ 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 CO₂ to useful products around the world and could be scaled to produce Gigatons per year, thus making a pretty big dent in the CO₂ footprint.

The main contenders under active investigation for CO₂ 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 CO₂ conversion processes with the overall capacity of utilizing Gigaton amounts of CO₂ 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 CO₂ conversion to fuels and



Figure 3 Peace → War → Peace with CO₂ again enabled by the endeavors of chemists and chemical engineers; Courtesy of Chenxi Qian

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 CO₂ 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 CO₂ into the atmosphere should be strongly regulated by a global CO₂ watchdog commission. In this way again, **life at peace with CO₂**, will become an ‘ideal made real’, **Figure 2**.

Materials Views Opinion Editorials

Jarring Fears – CO₂ War or Peace?

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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 (CO₂) 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 CO₂ 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 CO₂ driven climate change. In the absence of any aspirations on mitigation of CO₂ 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 CO₂/kWh into our atmosphere compared to 0.4kg CO₂/kWh from coal, 0.28kg CO₂/kWh from oil, 0.05kg CO₂/kWh from biomethane, and from wind and solar a mere 0.01kg CO₂/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 CO₂ 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 H₂O where the H₂ so produced can be used to reduce CO₂ to CH₄ 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 CO₂ emissions in the process but globally CO₂ 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 CO₂ 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 CO₂ 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 CO₂ – from both thin air and more concentrated localized sources. This strategy could be made compatible with existing CO₂ 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 H₂ and then using the H₂ to reduce gaseous CO₂ 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 CO₂ 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 CO₂ 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.

Materials Views Opinion Editorials

Do we have a Plan B?

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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 CO₂ into the atmosphere through the burning of fossil fuels (see references: <http://trillionthtonne.org/>, <http://www.climatecommuniques.com/>, <http://www.carbontracker.org/>).

CO₂ is the thermodynamic 'default molecule' of fossil fuel combustion. Hence, I believe a Plan B strategy can be built around a 'New CO₂ Economy', the premise of which is (i) CO₂ is not a waste product to fear, (ii) CO₂ is a bounteous carbon resource, (iii) CO₂ belongs to all and (iv) through innovative chemistry CO₂ 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 CO₂ feedstock. These CO₂ emissions are needed for Plan B in order to maintain sustained petrochemical and chemical production using CO₂ driven by light and heat from the sun. Once this transition is completed, atmospheric CO₂ 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 reach whereby CO₂ is converted to solar fuels, which is consumed to produce CO₂, 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 CO₂ 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 CO₂.

I would argue therefore that the infrastructure exists for the development of a global scale CO₂ capture and conversion economy, which leads to recycling of CO₂ 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 CO₂ in the atmosphere.

What is missing in the transition from a fossil fuel based economy to one based on CO₂ is a globally sustainable supply of clean energy to enable the heterogeneous catalytic processes that can transform CO₂ 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 CO₂ and harvest both light and heat from the sun and convert CO₂ into fuels and chemical feed stocks. This can be exemplified by the economically viable production of CO, CH₄ and CH₃OH at a relevant rate and scale.

To place this grand challenge into perspective, a conversion rate of 10 moles of CO₂ per hour per gram of catalyst translates into a conversion rate of 1 Gigaton of CO₂ 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_x nanomaterial with average density of 5 g.cm⁻³.

One can appreciate from this 'back-of-the-envelope' calculation that the development of a global scale CO₂ economy could readily handle the yearly global emission of 40 to 50 Gigaton of CO₂. This conversion rate is sufficiently high in that it can maintain a steady-state concentration of CO₂ 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 CO₂ 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.

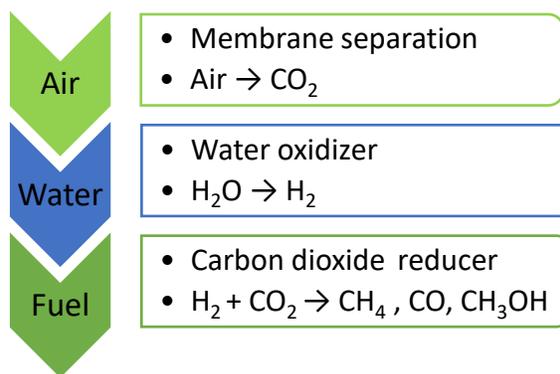
To further build upon this proposal, a Plan B vision for a sustainable future is to make the solar fuels technology (i.e. capturing and utilizing CO₂ in both air and in concentrated localized sources) compatible with existing infrastructure on land and sea around the world. The scheme illustrates the envisioned Air-to-Fuel technology, which utilizes solar-assisted heterogeneous catalysis materials science and chemical engineering methods. The three-step process involves CO₂ separation or capture. Next gaseous water is split into H₂. Then this H₂ is utilized to reduce gaseous CO₂ to CO, CH₄ and CH₃OH 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 CO₂ capture and conversion technology that will enable the creation of a new and sustainable CO₂ 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 CO₂ being a critical component of the energy endgame.

The goal of a new CO₂ 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.



Materials Views Opinion Editorial

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

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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.

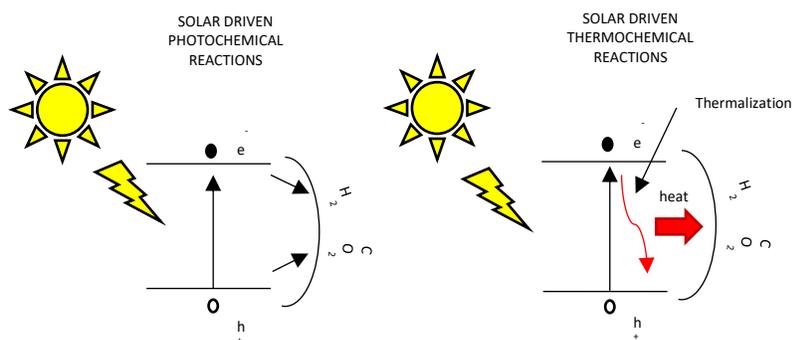


Figure 4 Gas-Phase Photocatalysis: powered by light, heat or a combination of both? Graphical illustration courtesy of Paul O'Brian.

An equally important question relevant today, especially in the rapidly emerging field of solar fuels and solar chemicals, is what proportion of a claimed gas-phase 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' heterogeneous catalytic 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 thermally equilibrate through phonon relaxation and supply heat energy to enhance reaction rates. The questions are which of these processes dominate and what their contributions are? This discussion 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 gas-phase CO₂ photoreduction on 'black' catalysts, exemplified by Ru-RuO_x and Ni-NiO_x 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 (CO₂) 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 CO₂ 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 gaseous CO₂ 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 dominantly provided 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 H_2O to H_2 , the photocatalytic reduction of CO_2 remains a significant challenge and has been studied to a much lesser extent. This is especially true for gas-phase CO_2 photoreduction, which can be readily engineered into existing industry heterogeneous catalytic infrastructure and 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 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 for the catalyst integrated into light absorbing versus non-absorbing supports.

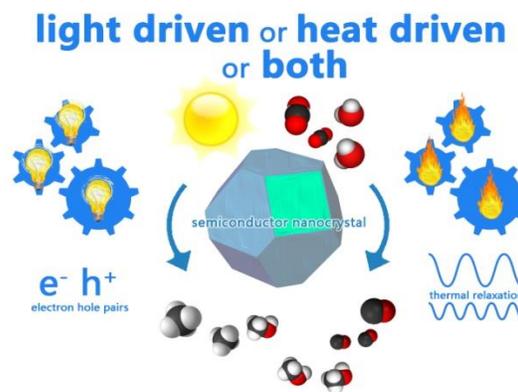


Figure 2 Is your photocatalytic reaction powered by light or heat or both? Graphical illustration courtesy of Chenxi Qian

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 CO₂ economy for the production of solar fuels and solar chemicals using light from the sun!

Materials Views Opinion Editorial

Real or Artifact: CO₂ Photo-Catalysis *versus* Carbon Contamination

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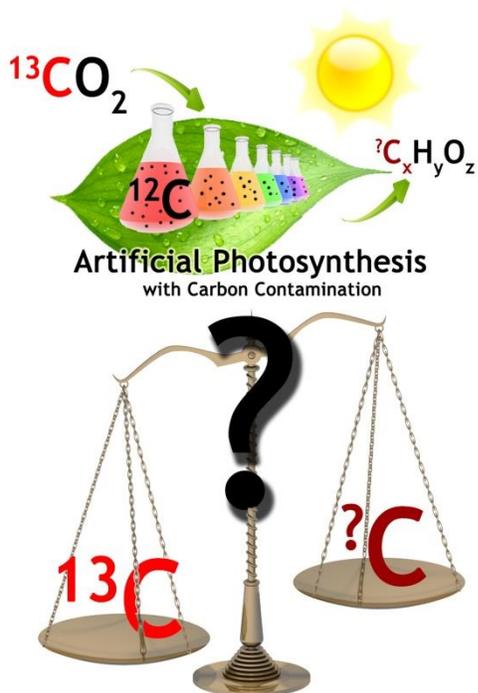
Because of energy and climate concerns, research into carbon dioxide capture and utilization has skyrocketed in the past decade. Of all the different approaches proposed to solve this problem the only one that appears to offer the capacity to have a significant impact on greenhouse gas emissions, is a solar-to-chemical conversion gas-phase artificial photosynthesis process with an efficiency that can surpass natural photosynthesis. The goal is to sequester carbon dioxide either from concentrated sources and/or thin air and transform it to an organic fuel or chemical feedstock using sunlight as the only energy input.

The intergovernmental panel on climate change, the trillion tonne communiqué and the carbon exchange in 2014 aptly put the intertwined climate and energy conundrum into stark perspective with some key facts and messages that include:

- Consensus on a trillion tonne carbon limit to prevent global warming above 2°C
- Fossil fuel share of that limit = 2,900 Gt CO₂
- Current total CO₂ emissions = 1,430 Gt CO₂
- 50% of troposphere space for CO₂ is used up
- 66% chance at keeping global temperature rise $\Delta T < 2^\circ\text{C}$
- Remaining fossil fuels should stay in the ground
- Stranded carbon assets have created a carbon bubble for global investments
- Regulation, guidance, transparency needed to shift capital market carbon practices
- The world needs to get to net zero annual emissions by 2050 or shortly thereafter

Clearly we need an economically competitive global artificial photosynthesis silver bullet initiative to help solve this problem.

To amplify on the science and technology of artificial photosynthesis, the Holy Grail is to discover a carbon dioxide photo-catalyst that is at least an order of magnitude more efficient than natural photosynthesis, one that can convert at least 10% of sunlight into organic fuels or chemicals.



Leaf Mimic - Fact or Fiction. Graphic illustration courtesy of Chenxi Qian

organic products are usually characterized by gas-chromatography.

Generally speaking the majority of reported carbon dioxide conversion rates and efficiencies are currently well below the US Department of Energy 10% target required for a practical artificial photosynthesis process that could be engineered at a large enough scale to have a meaningful effect on the reduction of greenhouse gas emissions.

Even though valiant measures are taken through solvent and chemical removal, oxygen plasma and high temperature oxidation post-treatment methods to strip nano-structured photocatalysts of adventitious carbon, the problem of artifacts arising from such carbon residues can remain.

The main concern comes from carbon contamination on the surface and within the bulk of photo-catalysts. This kind of carbon residue, which can originate from organics in the environment as well as from incomplete removal of solvents, precursors, surfactants and additives and their decomposition products, can complicate the analysis of organic products by gas-chromatography, giving artificially elevated rates of photo-conversion.

Translated into the recommended United States Department of Energy metric of 10% efficiency for the solar powered transformation of carbon dioxide to carbon monoxide, methane or methanol requires the discovery of a photo-catalyst that can achieve conversion rates of millimoles per gram of catalyst per hour at a solar irradiance of AM 1.5.

Research on photo-catalytic water splitting into hydrogen and oxygen greatly outweighs that on carbon dioxide reduction to organic chemicals and fuels where the bulk of the work today is conducted in the aqueous phase with relatively little effort being expended on the more practical gas phase process. For water splitting in the aqueous phase state-of-the-art photo-catalysts achieve rates of $10 \text{ mmol gcat}^{-1} \text{ hour}^{-1}$ with photonic efficiencies of 56%

Of the dozen or so reports that do describe gas phase carbon dioxide photo-reduction the photo-catalyst is based on single or multi-component nano-structured materials, mainly metals and metal oxides, and

This is a problem that can arise from carbon residues as low as 0.001- 0.1 wt % of the photo-catalyst, which can only be revealed and quantified by $^{13}\text{CO}_2$ isotope tracer experiments best analyzed by on-line and coupled gas-chromatography mass-spectroscopy.

Very few literature reports have included this kind of isotope tracing data so any conclusions drawn about photo-catalysts boasting champion photo-conversion efficiencies that lack this information must be considered dubious at best.

Of the very few that have employed $^{13}\text{CO}_2$ isotope labeling it is important to realize that it is not only evidence of ^{13}C labeling that matters but also the $^{12}\text{C}/^{13}\text{C}$ ratio of unlabelled to labeled organic photo-products, enabling one to define the selectivity towards real products of carbon dioxide photo-catalysis relative to artifacts of deleterious carbon contamination.

Another pitfall that can go unrecognized with $^{13}\text{CO}_2$ isotope labeling experiments which are required to differentiate reality from artifact in the formation of solar fuels is the specified purity of the $^{13}\text{CO}_2$ from the supplier, which for the cheaper lower grade ^{13}C enriched carbon dioxide often contains significant amounts of $^{13}\text{CH}_4$, so buyer beware!

Without this pivotal isotope tracer confirmatory information it is exceptionally hard to judge fact from fiction in the burgeoning field of gas-phase carbon dioxide photo-catalysis, a difficulty which is severely impeding the rate of progress towards the vision of global artificial photosynthesis. Hopefully practitioners in this vitally important and rapidly expanding field will realize this predicament exists and will make every effort to improve the current situation.

On closing it is worth mentioning that unrecognized carbon contaminations of carbon dioxide reduction nano-structured photo-catalysts can have a disastrous affect on the work and lives of researchers and students who expect published work in the literature to be reliable and reproducible. My solar fuels group knows firsthand how much time, effort and money can be wasted pursuing promising leads published in top-rank, peer-reviewed journals that prove to be specious. Unfortunately such false positives can terribly mislead newcomers trying to enter the field with similarly devastating consequences.

It is instructive to recognize however that water splitting photo-catalysts have evolved from conversion rates of nanomoles to milimoles per gram of catalyst per hour within a decade, so there is no reason to believe carbon dioxide photo-catalysts cannot follow suit.

Materials Views Opinion Editorials

A Fossil Fuel Free World

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Carbon Dioxide Economy Imagine a time in the not-too-distant future when all our legacy fossil fuels have been depleted because of our incessant demand for energy and chemicals, obsession with consumerism and never ending drive for economic growth. Ignoring for a moment that a global catastrophe will almost certainly ensue, what will be left for our newly fossil fuel free society but carbon dioxide, the combustion product of our long-time addiction? And there will be plenty!

In a fossil fuel-free world it is unlikely that our global hunger for energy, chemicals, consumerism and growth will be satisfied by renewable sources of energy. So what choice will we have? I would suggest that we need to learn how to run the world in reverse: we need to make our carbon dioxide-rich atmosphere our source of fuels and chemicals. The sun then becomes our fusion reactor, the engine to sustain life.

In order to rise to the challenge of developing a global economy founded on carbon dioxide it is vital to get government, investment, and university and industry leaders, together with the public, to understand that carbon dioxide is not a waste product to dread. Instead carbon dioxide should be showcased as a feedstock for making fuels and chemicals, a bountiful resource of latent carbon spread uniformly around the globe. With the right chemistry it can be transformed into a boundless supply of carbon neutral renewable energy and chemicals to sustain and support a high quality of life for eternity.

This vision of carbon dioxide as the powerhouse that drives a new economy is based on artificial photosynthesis. This is the approach upon which a sustainable future could be founded. The support of the global community must be enlisted to make it happen.

Our journey to mimic nature has just begun. Imagine a carbon dioxide economy inspired by biological photosynthesis, a process honed to perfection over an evolutionary time scale.

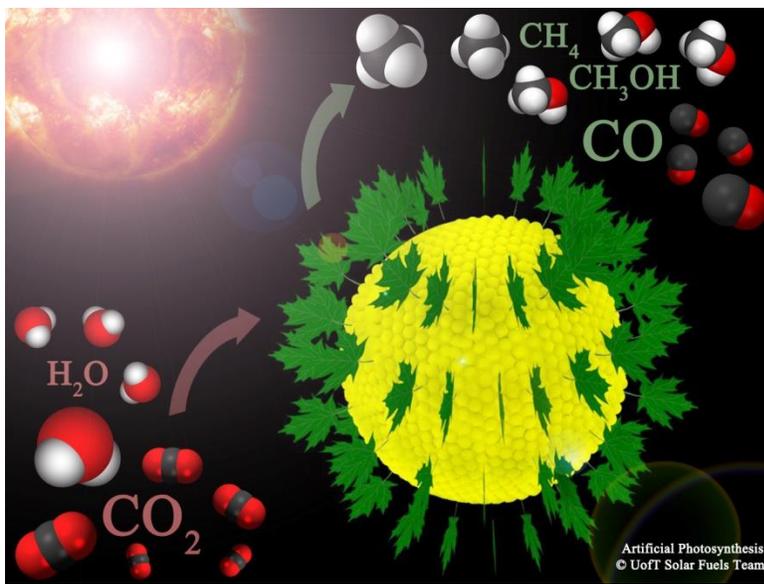


Illustration depicting how the leaf's photosynthetic machinery for processing carbon dioxide, water and sunlight to solar fuels such as carbon monoxide, methane and methanol, is integrated into the nanoworld - graphical illustration courtesy of Chexi Qian.

the obvious perils of continuing to increase the concentration of anthropogenic carbon dioxide in our atmosphere, could be more deaths than all those caused by war, terrorism, famine, poverty and disease throughout the history of humankind.

The scientific challenge is to discover a class of materials made of earth-abundant, low cost, sunlight stable and non-toxic materials. Such materials would then be able to generate solar fuels and chemicals, such as carbon monoxide, methanol or methane, from carbon dioxide at a technologically significant rate and efficiency at global proportions.

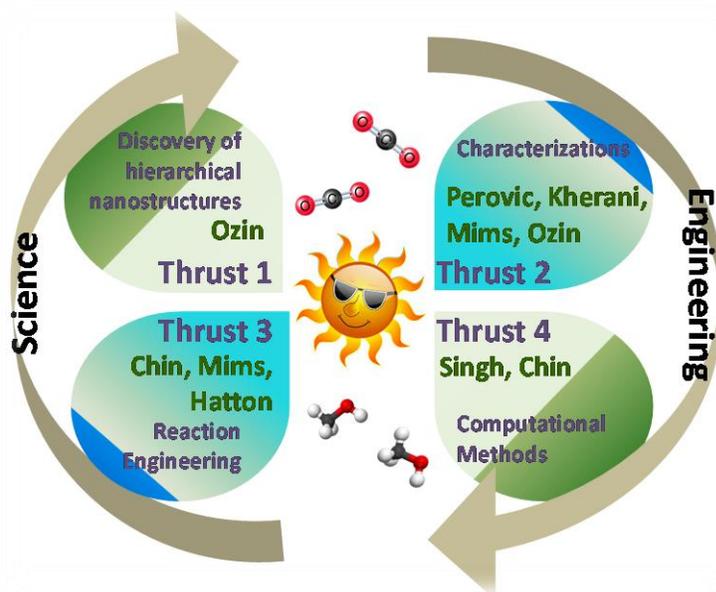
The Payoff If this Utopian dream is realized it will forever change the way we see carbon dioxide: instead of a foe, it will become our greatest friend. The development of a practical artificial leaf will in turn seed the development of a global CO₂ economy that will provide a carbon neutral replacement for fossil fuels. Recycling carbon dioxide in our atmosphere and converting it to solar fuels and solar chemicals seems to be the only silver bullet solution to enable the human race to sustain its existence in a world depleted of fossil fuels.

What will it take? As the debate over greenhouse gas emissions and climate change intensifies with no signs of consensus being reached any time soon, governments in the United States, Europe and Asia have already determined the value of investing considerable funds in artificial photosynthesis research and development.

An impressively large global network of scientists working on artificial photosynthesis through

Global Challenge Copying the leaf is a most appealing vision, but it is not yet a reality. No material is known today that can use energy from the sun to convert carbon dioxide into a storable and transportable fuel or chemical feedstock at an efficiency that outperforms biological photosynthesis and a scale that can handle hundreds of billions of tons of carbon dioxide a year. This is a challenge for the global community, and it is incomparable in complexity and magnitude to any other faced before. The consequences of 'willful blindness' on climate change, namely ignoring

team science and collaborative research emerged in 2012 (www.solar-fuels.org). This network is composed of a dozen European research partners, including the Solar-H₂ Network, supported by the European Union, and the Institute for Chemical Energy Conversion, a 100 million Euro foundation in Germany supported by Max-Planck Society. The US Department of Energy (DOE) Joint Center for Artificial Photosynthesis (JCAP), led by the California Institute of Technology (Caltech) and Lawrence Berkeley National Laboratory, has been awarded US\$ 122 million over 5 years to demonstrate a scalable solar fuels generator using earth-abundant elements that robustly produces fuel from the sun at ten times the efficiency of current crops. Some Energy Frontier Research Centers (EFRCs) funded by the US DOE are focused on solar fuels-related endeavors, including the Argonne-Northwestern Solar Energy Research (ANSER) Center led by Northwestern University, the Center for Bio-inspired Solar Fuel Production (BISFuel) and Light-Speed Solutions and Light Works led by Arizona State University, and the Center for Solar Fuels led by the University of North Carolina. Other prominent international examples include the Energy Futures Lab at Imperial College London, the Australian Centre of Excellence on Electromaterials Science (ACES) Energy Research Program and the Solar Fuels Lab at Nanyang Technological University in Singapore. In Japan, the Advanced Low Carbon Technology Research and Development (ALCA) project aims to produce a carbon-free fuel based on hydrogen peroxide. In South Korea, the Pohang Steel Company is contributing to the Korea Center for Artificial Photosynthesis (KCAP). In China, the first national lab for clean energy research has been set up with the broader mission of also reducing carbon emissions.



Synergistic integration of research thrusts of the University of Toronto solar fuels team that embrace the design, synthesis, structure determination and properties measurements, computational modeling and reaction engineering of nano systems capable of carbon dioxide photo-reduction, - illustration courtesy of Chandra veer Singh.

At the University of Toronto a multidisciplinary solar fuels team was founded in 2012 and has been investigating a portfolio of nanostructured materials that are active for the gas-phase photo-reduction of carbon dioxide to solar fuels like carbon monoxide, methane or methanol.

The focus of the team's research on a gas-phase process is predicated upon their collected belief that the development of a global scale process capable of handling hundreds of billions of tons of carbon dioxide annually, which would represent the

largest chemical factory ever on earth, for a host of practical and economical reasons is unlikely to work in aqueous solution.

To embrace all aspects of the problem the expertise of the University of Toronto solar fuels team has been designed to crisscross the borders of experimental and theoretical materials chemistry and nanochemistry, chemical, materials, and optical and photonic engineering. Our collective skill-set and know-how enables us to effectively collaborate on the grand challenge of how to discover a champion artificial photosynthesis material that can transform gaseous carbon dioxide at a technologically meaningful efficiency and scale.

The thrust of our research is to understand at a fundamental level the relations between the synthesis, composition, structure and properties of champion nanostructured materials that confer upon them the capacity to function as efficient gas-phase carbon dioxide photocatalysts.

All of our experiments employ the full gamut of diffraction, microscopy, spectroscopy, electrical, optical, thermal and adsorption analytical techniques to define structure-property relations of photocatalysts. We use isotope-labeled reagents to identify reaction intermediates and products, to elucidate kinetics and mechanisms, and to distinguish real products from artifacts arising from ubiquitous carbon contamination problems.

With this knowledge, photocatalytic conversion rates and efficiencies of materials can be engineered from a laboratory prototype and optimized to a technologically important archetype able to make solar fuels from carbon dioxide and sunlight at a globally significant scale.

We are all Passengers on Spaceship Earth It is clear from all the research activity on artificial photosynthesis that scientists understand the urgency of learning how to harness the energy of the sun to transform carbon dioxide into a renewable source of energy and chemicals to sustain life on earth. An equally important challenge is to change the perception of policy makers and the public in the fastest and most effective ways. We need to convince the world that carbon dioxide is a friend not a foe and can be used to carry and sustain our way of life long after the fossil fuel reserves have dried up.

By working together as a global community on the science and technology of artificial photosynthesis, carbon dioxide could be our savior rather than our downfall in the fossil fuel free world of the future.

A Burning Closing Thought Last year the International Energy Agency cautioned that [a third of the world's fossil fuel reserves must be put off limits](#) until 2050 if humanity is to stand a

chance of avoiding catastrophic climate change

(<http://www.worldenergyoutlook.org/publications/weo-2012/>). In this context it is worth noting that a recent report claimed if governments ever issued an edict to curb the use of fossil fuels because of climate change it could put \$6 trillion in fossil fuel reserves in jeopardy (<http://gofossilfree.org/files/2013/>).

In this scenario it has been [estimated that a number of oil behemoths could lose up to 50% of their market value](#) and trillions of dollars in revenues, <http://www.carbontracker.org/wastedcapital>. Investors are rightly concerned about the risks associated with multinational oil, coal and gas companies that could be left with trillions of dollars of stranded assets if carbon taxes and other emission limits reduce the demand for fossil fuels (<https://www.ceres.org/files/car-mats/car-release/companies-that-received-car-letter/>). Why, then, would they invest in climate catastrophe?

In a fossil fuel world whose unmitigated freedom to operate as usual is curtailed by the threat of climate devastation, a carbon dioxide economy based on artificial photosynthesis can come to the rescue not only to the benefit of all those who believe and invest in the initiative, but also to sustain the health and well-being of humankind.

Materials Views Opinion Editorials

Climate Conundrum

Sustainability - Solar Fuels from the Sun not Fossil Fuels from the Earth

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Why Worry? Being British by birth I was brought up in a climate where the main topic of conversation was often the weather and so I became acclimatized to it raining most of the time. Now a naturalized Canadian, I have learned to live with and enjoy the extremes of hot and cold weather. As a scientist working in the field of artificial photosynthesis, where worrying about the effect of carbon dioxide on the weather usually motivates funding, I am becoming increasingly concerned and frustrated about the dissent that currently permeates the debate on the evidence for anthropogenic causes of weather

change, even amongst climate scientists. This dispute is exacerbated by self-interest lobby groups, the press and media who benefit from climate confusion. The difficulty of unequivocally separating fact from fiction is disquieting for scientists who are incessantly searching for support from funding bodies, peer reviewers, media outlets and the public to further their thesis that artificial photosynthesis could provide a long-term solution to the intertwined climate change and sustainable energy problems facing society today. Climate confusion is also a conundrum for government, industry, institutional investors who are contemplating support of artificial photosynthesis research and anyone interested in following scientific advances. Suffice to state, the only 'truth' we know fairly certainly is that there is 'evidence' of anthropogenic climate change and due to the nature of the problem and the nature of science this 'evidence' will always remain what it is, 'evidence not certainty'. Despite the desire of the public and politicians for 'certainty', science provides only evidence. Science is not about certainty even if there is a tendency to treat it as such. It is about overwhelming evidence in support of a theory or hypothesis until a new one comes along. Like it or not, science cannot say anything with 100% certainty, only that there is strong or weak evidence in support of a particular model of an event or phenomenon.

Why Do We Care?

The United Nations Intergovernmental Panel on Climate Change, IPCC, considered the top authority in the world on global warming, has just declared with 95% certainty that humans are responsible for climate change.

As witnessed by this report and many similar ones, the climate change debate continues to generate much discussion amongst scientists, economists, sociologists, legal scholars and policy makers attempting to analyze the risks and costs posed by over-reacting or under-reacting to the potentially serious and adverse consequences that could flow from a scenario of increasing global warming from escalating greenhouse gas emissions. Scientists can estimate the risk associated with not doing anything as well as doing something and with this knowledge, political, social and economic decisions can be formulated and implemented.

With all this uncertainty, one thing is indisputable to chemists, materials scientists and engineers working on different forms of renewable energy, such as solar cells, wind mills and tidal mills that produce electricity. They all suffer from the intermittency and variability of solar irradiance, air stream and tidal power as well as the difficulty of storing large amounts of electricity, as it has to be used essentially as it is produced. Hence there exists an urgent need to find a green way of producing energy in a form that can be transported and stored for use on demand. A long-term solution to this important problem is to discover materials and processes that can make fuel from sunlight akin to the way the leaf utilizes sunlight to transform carbon dioxide and water to carbohydrates in a process called photosynthesis.

In this context, solar fuels research is aimed at harnessing solar energy *via* the paradigm of artificial photosynthesis to make an energy rich portable fuel. It is inspired by the belief that the long term use of fossil fuels is not sustainable and not practical and the rush to develop bio-fuels is short-sighted as evidence grows that its production, by any means, has a poor energy balance and does not lead to any appreciable reduction of carbon dioxide emissions that could be better achieved by modest energy conservation. Moreover, with a population increase of about 75 million per year, bio-fuels are considered a regrettable misuse of land and water resources sorely needed to maintain the earth's growing population.

There is also a debate whether carbon capture and storage (CCS) should be implemented to achieve climate change targets. Arguments against CCS is that it is a largely untested technology with health and safety concerns, it is energy intensive to apply and it will raise the cost of electricity, so much so that a renewable energy infrastructure could be developed quicker and cheaper.

The longer term investment in artificial photosynthesis research and development, rather than the shorter term focus on bio-fuels and carbon capture and storage, presents a more practical and appealing solution to the intertwined climate change and sustainable energy challenges faced by our society today. Whilst the scientific and technical hurdles of artificial photosynthesis are in the process of being understood and surmounted, through strong and sustained solar fuels basic directed research over the next 10-20 years, a global artificial photosynthesis strategic plan, akin to the human genome project of the 1990's, can be formulated and implemented to provide a lower cost and more sustainable green fuel, offering genuine rather than misplaced benefits promised by bio-fuels and carbon capture and storage.

Artificial Photosynthesis Goes Global Artificial

photosynthesis has gone global. The objective is to discover innovative uses for greenhouse gas emissions, namely turning a waste product into fuels or value-added chemicals. In the context of artificial photosynthesis, the top twelve performing solar fuels nations can be identified in the histogram of publications (Figure 1) since the inception of the field around three decades ago (<http://statnano.com/index.php?ctrl=index&lang=2>). In the last decade there has been an explosive increase in artificial photosynthesis research, which coincides with the emergence and expansion of global concerns over anthropogenic climate change. Governments in the United States, Europe and Asia have realized the social, political, economic and strategic ramifications of a breakthrough in artificial photosynthesis and have invested hundreds of millions of dollars in basic research to discover if materials and processes can be found that match or exceed the efficiency of nature's photosynthesis in the laboratory.

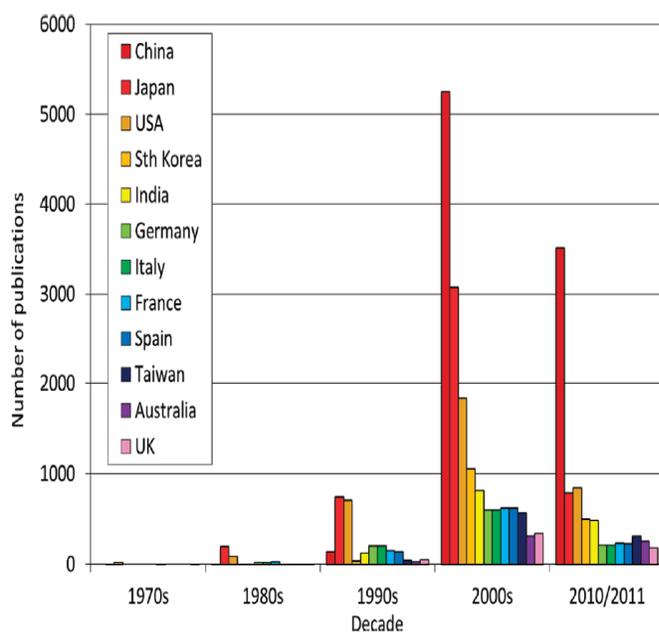


Figure 5: Top 12 solar fuels nations, ISI 2012.

Inspired by the words of Thomas Founce, *Energy & Environmental Science*, 2013, 6, 695, there are a number of ways to rationalize a global initiative in artificial photosynthesis, even as the climate change debate intensifies:

- (i) *Biological photosynthesis is complex and its understanding requires cross-disciplinary expertise and collaboration between teams of scientists.*
- (ii) *Discovering materials that can mimic photosynthesis is a grand challenge.*
- (iii) *Increasing the public visibility of fuel from the sun by artificial photosynthesis*

would encourage government, industry and institutional stakeholders to invest in the rapid deployment of solar fuels technology.

(iv) *Artificial photosynthesis research and development should be allowed to grow naturally and rationally and not motivated by a crisis that destabilizes societies.*

Unfortunately the low cost of, growing and easy access to, fossil fuels have meant that funding for artificial photosynthesis has remained small compared to bio-fuel and carbon capture and storage technologies. Nevertheless, activity in the field of artificial photosynthesis around the world is exponentially increasing and new materials ideas, innovative photocatalytic reactors, techno-economic analyses for scaling materials and processes and manufacturing solar fuels, are appearing daily in the literature. By coordinating the research efforts and knowhow of scientists around the world, progress will accelerate towards the practical realization of fuel from the sun, providing thereby a secure and long-term solution to a carbon neutral secure energy supply, to ensure the health and well-being of future generations.

It is worth contemplating that in an artificial photosynthesis world, a sustainocene (period where humans strive for renewable technologies to sustain the environment for future generations) rather than an anthropocene (period where human activities have had a significant global impact on the Earth's ecosystems), countries with fossil fuels in the ground would no longer have the political and economic power that they now have and for a period of time power may pass to countries or companies that own the intellectual property rights for artificial photosynthesis. An interesting question therefore, is whether there would be any attempt to agree on how rights to use the technology for artificial photosynthesis would be available for the benefit of humankind or whether it would be a strictly commercial arrangement? The problem is probably not the same as for the human genome project as the intellectual property rights for artificial photosynthesis will be much more conventional and less open to argument. Countries now charge high taxes on fossil fuels and no doubt countries would be looking at ways to tax solar fuels from the sun to compensate for the loss in tax revenue currently received for fossil fuels in the ground. Any change would obviously not come overnight and for a number of years the two sources would likely run side by side plus of course energy from alternative sources such as wind, solar, wave and tidal.

x1000 The discovery of the sunlight powered photocatalytic reaction: $\text{CO}_2 + \text{H}_2\text{O} + h\nu \rightarrow$

CH_4 or CH_3OH ignited the idea that anthropogenic greenhouse gas could be recycled from a waste product to a value-added fuel or chemical feedstock. This breakthrough inspired scientists around the world to search for materials and processes that could match or exceed natural photosynthesis. Three decades later, after exploring essentially every corner of structure-composition space in the periodic table of the elements, the rates and efficiencies of gas and

aqueous phase $\text{CO}_2 + \text{H}_2\text{O} + h\nu \rightarrow \text{CH}_4$ or CH_3OH photocatalysis by molecules or materials have improved very little over the initial report and researchers in the field of artificial photosynthesis continue to scramble for the magic bullet material that will provide at the very least a x1000 enhancement to make the process techno-economically competitive with alternative sources of methane or methanol.

So what is the origin of the x1000 problem? It is a kinetics conundrum where the challenge is to discover chemical and structural approaches to prolong the lifetime of photo-generated electron-hole pairs, which normally recombine at picosecond to nanosecond time scales, long enough so the slower reactions of water oxidation with the holes and carbon dioxide reduction with the electrons can compete. It is a matter of selectivity, namely how to tailor photoactive materials to gain control over the ratio of the rate of productive e-h reaction chemistry to unproductive e-h recombination processes, which currently stands at around x1000. This concept, simple in theory, is proving to be exceptionally difficult to implement in practice.

Assembling the right pieces of the puzzle in order to prolong the lifetime of photo-generated electron-hole pairs in photocatalysts, are well documented and include structuring and doping of materials at the nanoscale, tailoring junctions between semiconductors and liquids, semiconductors and metals, semiconductors and semiconductors, adapting and optimizing co-catalysts, and integrating blocking layers, hole scavengers, redox-shuttles, electron transport cascades, conducting substrates, and bias potentials.

Thirty four years since the pioneering 1974 artificial photosynthesis work of Honda and co-workers, researchers in the field of solar fuels are still searching for at least three-orders of magnitude enhancement in the conversion rate and efficiency, as well as long term thermal, chemical, photochemical and (photo)electrochemical stability, needed to endow a solar fuels material with the technological significance and commercial potential it promises. If this was an easy task it would have been done by now.

In some ways the long arduous adventure to discover a solar fuels material that can compete and beat nature's leaf reminds me of Michael Gratzel's 1991 landmark discovery of the dye sensitized solar cell with a reported efficiency 9% and the following twenty two years of determined heroic research and development effort it took to achieve 15% efficiency, bestowing upon it with the potential to make it a low-cost contender for the silicon Samurai!

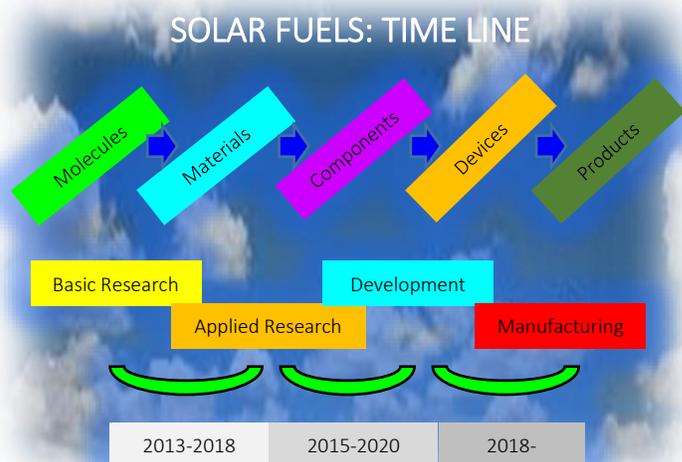
CO₂ Industry Road Map

Experts in the chemical industry have recently evaluated the science and technology challenges and time line for the cost-effective transformation of renewable energy to chemical energy in the form of organic molecules that

can be easily stored, transported and integrated as a raw material and source of power and fuel into the chemical production food chain.

Because the chemical industry is one of the largest consumers of energy from fossil fuels, it is in their self-interest to learn how to manage carbon dioxide as a chemical resource rather than treat it as a waste product and strive to develop a carbon dioxide based resource-efficient economy for powering their industrial processes and providing green fuels and energy for a sustainable society. The energy intensive chemical industry sees the introduction of carbon dioxide into the petrochemical value chain as a source of raw materials, power and fuels, using known catalytic processes working towards a viable and cost-competitive photocatalytic solar fuels technology.

By inspecting the timeline that the chemical industry proposes, to increase the use of renewable energy, one can see the short term perspective (2020) involves the utilization of excess electricity from wind and solar for electrolyzing water to hydrogen, which can be used in known



industrial catalytic processes to reduce carbon dioxide to chemical vectors such as syngas, methanol, formic acid, alkanes, olefins and dimethylether. For these processes to be cost effective the price of electricity has to be around \$0.05/kWh.

The medium term view of the chemical industry (2030) is that hydrogen production technology from the photo-electrochemical splitting of water, will improve in efficiency and cost competitiveness

compared to other sources of hydrogen and will be used to catalyze the reduction of carbon dioxide to organics providing the over-potential problem can be overcome. This technology becomes interesting from a commercial standpoint when the cost of producing hydrogen falls in the range \$2-3/kg.



Sustainability
Solar fuels from
the sun not fossil
fuels from the

Figure 4 Interplay between solar fuels from the sun and fossil fuels from the earth adapted from the internet web site <http://loadpaper.com/id27734/free-ipad-wallpapers-sun-moon-earth-ipad-wallpaper-ipadwallpaper-1024x1024-pixel.html>

In the long term view of the chemical industry (2030-) it is highly likely that materials for a practical artificial leaf technology will eventually be developed, which are able to efficiently capture and convert carbon dioxide, water and sunlight directly to specific chemicals and fuels in a distributed production system. Industry experts acknowledge huge challenges have to be overcome with regards to the discovery of photocatalysts that can mimic and even surpass the photosynthetic performance of the biological leaf.

Strong and sustained long-term basic research on solar fuels is envisioned to be able to deliver the fundamental knowledge that will enable the subsequent steps from basic to applied research to development and manufacturing, envisioned in the carbon dioxide to solar fuels time line, **Figure 3**.

Success in this endeavor will eventually be achieved and celebrated as a massive breakthrough that will ignite activity in the field of solar fuels thereby setting the scene for the development of global artificial photosynthesis renewable energy technologies and policies, **Figure 4**.

Artificial photosynthesis promises a new era of sustainability by gifting humanity with an unlimited supply of carbon neutral solar fuels from the sun rather than depleting the finite source of legacy fossil fuels from the earth and replacing them with increasing amounts of greenhouse gas in the atmosphere!

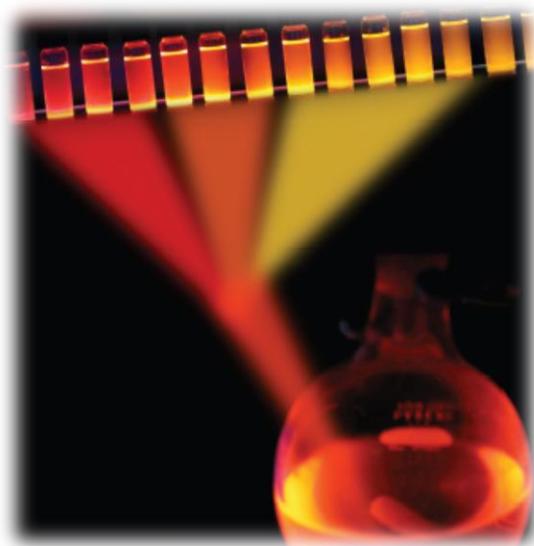
Materials Views Opinion Editorial

Nanochemistry Reproducibility

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Why Worry? The six concepts of nanochemistry that constitute the foundation of a chemical approach to nanomaterials are size and shape, surface and defects, self-assembly and utility in advanced materials and biomedical applications. In this bottom-up paradigm for making nanomaterials, synthetic methods for controlling the degree of perfection of nanomaterials have improved enormously compared to the early days of colloid chemistry that more recently underwent metamorphosis to nanochemistry but how well has the field progressed since then with respect to the reproducibility of a synthesis and why do we care?



Size-separated, color-tunable, colloidally-stable and allylbenzene-capped silicon nanocrystals by Melanie Mastronardi, Advanced Materials.

Nano Reproducibility The scientific method is founded upon the principle of reproducibility. It has been claimed that the reproducibility of research published in scientific journals is as low as 10-30% a worrying assertion for the long-term credibility of scientific results. In the context of a nanochemistry approach to nanomaterials, a fair question to ask is what do we actually mean by reproducibility and how reproducible is your nanomaterial synthesis? The degree of agreement between replicate syntheses, by the same or different persons under identical experimental conditions, is a measure of the reproducibility of the synthetic method described in the open literature or patent sources. In academic and industrial research, synthetic protocols reported in a paper or patent should

enable replication of the work as a platform for new discoveries, as validation of a claim and as an enabler for commercialization opportunities. So what is the best measure of reproducibility

for the synthesis of a nanomaterial, a unique state of matter having properties intermediate between molecules and materials but without the benefits of their atomic perfection and purity? And how reproducible does a nanomaterials synthesis method have to be in order to be useful?



Ultrathin inorganic nanowires that look, grow, and behave like polymers, Ludovico Cademartiri, Advanced Materials.

Size and Shape

The problem with nanomaterials is that the product of a synthesis is invariably a poly-dispersion, namely an ensemble of nanoparticles with a distribution of sizes and shapes rather than a collection of identical nanoparticles. Only recently have size separation and analytical techniques been applied to poly-dispersions of nanoparticles to narrow the size distribution in order to better define structure-property relations. So reproducibility in this context perhaps can be best measured and reported in terms of the ability to replicate the distribution of nanoparticle sizes and shapes in a given sample, defined by a poly-dispersity index, $PDI = [\sigma/d]^2 + 1$

where d and σ are the mean size and the estimated standard deviation of the nanoparticle size distribution. The trouble here is the precision with which one can measure the size and shape of a statistically meaningful population of nanoparticles in distribution. Because many properties of nanoparticles are described by quantum mechanical scaling laws that result from spatial confinement effects of electrons and holes, ideally the size and shape of nanoparticles could be defined with atomic exactitude but in practice this is not possible. Even for the best mono-dispersions typically with PDI of 1.05 the standard deviation of the measurement of nanoparticle size and shape within a distribution in atom equivalents may be tens to hundreds to thousands. Variability of this order of magnitude from nanoparticle synthesis to synthesis can manifest, for example, as inconsistent chemical, electrochemical and photochemical behavior; discrepant optical, electrical, optoelectronic, thermoelectric and piezoelectric properties; and variable activity in biomedical diagnostics and therapeutics.

Surface, Defects, Self-Assembly

External surfaces of nanomaterials present even more serious challenges with respect to reproducibility. The surface is perhaps the most poorly defined, difficult to control and hard to understand property of nanomaterials. Here one has to be cognizant of the surface structure and composition, charge, different kinds of defects (e.g., point, line, plane and cluster) and bonded and adsorbed impurities as well as the number and distribution of organic and/or inorganic capping groups bonded to these surfaces. These features are exceptionally hard to quantify and are never exactly the same from nanoparticle to nanoparticle and between repeat syntheses. Further,

because of the high surface to volume ratio inherent to nanoparticles, a large fraction of coordinately unsaturated atoms exist on the surface that can cause the composition to be inherently non-stoichiometric, a property that is exceedingly difficult to quantify analytically. The outcome of non-stoichiometry in nanoparticles can be manifest as doping, mixed valence and trap states. In addition, the forces that control the self-assembly of nanomaterials into functional architectures are varied and complex and the nature of the surface plays a dominant role in determining the structure and properties of the resulting nanoscale constructs. So the ability to control and quantify the reproducibility of nanoparticle surfaces and defects and their self-assembly is nearly impossible. This presents a serious challenge for many advanced materials and biomedical applications with their associated health and safety related issues that rely on command and control of the chemical and physical properties of nanoparticle surfaces.

Yield For molecules and materials that can be purified as single product and single phase, their yield is a quantity that in principle can be precisely defined but what do we mean by yield of a nanomaterial that is presented as an ensemble of nanoparticles with variable sizes, shapes, surfaces and defects? Is measured mass yield of the entire distribution with its estimated standard deviation the meaningful measure of yield and does it adequately define the reproducibility of the synthetic method or does one need to examine each component nanoparticle in the histograms of size, shape and surface?

Nano Care Because of these synthetic uncertainties, experiments conducted on nanomaterials emerging from different preparations are reporting results for an ensemble average, which for some applications might be quite acceptable but for others could prove to be problematical. Each situation has to be carefully scrutinized with respect to its tolerance to the variations in heterogeneity inherent in the reproducibility of all synthetic nanomaterials.

Towards Reproducibility Standards The misery about reproducibility of nanomaterials presented in the literature is a worrisome situation for the academic and government research community, and industries that manufacture nanomaterials and develop products and processes thereof. The crux of the problem is a lack of standards and procedures for quantifying reproducibility of known and new nanomaterials. Surely it is the responsibility of the authors of papers and inventors on patents as well as peer reviewers, examiners and publishers of these papers and patents to diligently attend to this aspect of the research, which is blatantly missing from most reports of nanomaterials syntheses.

One could resolve this problem by requiring evidence of the degree of reproducibility to be a prerequisite for publication of papers containing a nanomaterials synthesis. It is true that many analytical methods for defining reproducibility approach their limit of resolution for nanoscale materials therefore it is even more important to provide a sufficiently large set of data to inform the reader about the accuracy and reproducibility of the results.

In this regard, transmission electron microscopy TEM should not be regarded as science but art. At least for the purpose of reporting on reproducibility of a nanomaterials synthesis it cannot serve as a defining experimental diagnostic of the entire product but more often than not a biased slice of reality. Angle dependant dynamic light scattering, DLS and small angle X-ray scattering, SAXS could instead become mandatory standard characterization methods because they give meaningful information on the nanoparticle size and shape distribution of an assembly. Whenever quantum size effects come into play, preparative ultra-centrifugation could be practiced whenever possible in order to obtain and report upon narrower size distributions and the power of analytical ultra-centrifugation could be exploited to define the number of molecules on the surface and atoms in the core of nanoparticles in a distribution.

Ultimately a higher standard is expected of researchers and a tougher stance by referees and publishers for evidence of reproducibility of a nanomaterials synthesis as these higher standards of practice would greatly benefit the nanochemistry community as well as facilitate the transformation of nanomaterials ideas in the laboratory to innovative products and processes in the market place.

I am well aware of the problem to introduce these standards into every day practice and the additional time and effort required to implement them but all one can do is appeal to the scientific conscience of nanochemistry researchers to investigate and report on the extent of reproducibility of their synthetic nanomaterials work.

Nano Food for Thought

On a final note in the context of nano reproducibility, how does the nano community judge scientific quality? Some might say that the work with amazing images and routine science is looked upon more favorably than the work with amazing science and routine images. High quality images cannot be a substitute for high quality science. It should be science first and photography second! The question is, how representative are these art nano images of your pet nanomaterial and the reproducibility of the synthesis. The dilemma the nano community faces is that the literature is replete with the litter of irreproducible nanomaterials syntheses, which undermines progress in the field, diminishes its credibility scientifically and jeopardizes its commercial potential.

Materials Views Opinion Editorial

Fuel from the Sun

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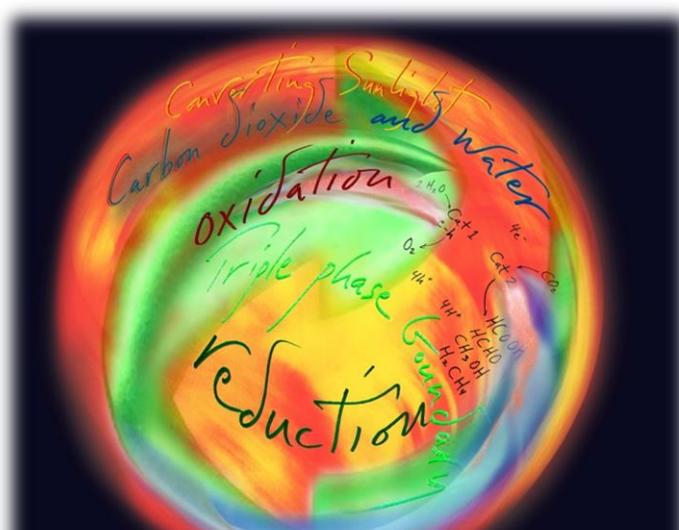


Why Do We Care? Nature is the archetype chemist having synthesized everything ‘under the sun’. Nowhere is this more apparent than in photosynthesis practiced by plants, algae and bacteria that convert sunlight, carbon dioxide and water into stored chemical energy and oxygen and maintains life on earth. Moreover, the chemical capacity of photosynthetic organisms to convert carbon dioxide to organic compounds is around 100 G Tons annually making it the ‘largest chemical factory on earth’.

For a billion years since the emergence of oxygenic photosynthesis on earth the symbiotic cycle of carbon capture, carbon fixation and carbon utilization has remained in balance but in recent times with population growth and increasing demands for food, clean water, air and energy the concentration of carbon dioxide in the troposphere from the combustion of fossil fuels is gradually increasing by about 2 ppm annually, has attained record highs and is continuing to increase. As global consumption increases especially in the developing world, carbon dioxide emissions are expected to keep on rising to levels that potentially threaten life on earth.

Whether one is a believer or a disbeliever in the greenhouse gas effect, a controversial and divisive issue scientifically, socially, economically and politically, it is surely a moral imperative that decisive preventative action be taken now in order to stabilize the concentration of carbon dioxide in earth’s atmosphere to minimize the risks of the doomsday scenario resulting from global warming, ice-cap and glacier melting, ocean acidification and geopolitical instability.

In the words of Nobel Laureate Jean Marie Lehn, “if it exists it can be



Nanosolution – Clean Fuel from the Sun – Todd Siler and Geoffrey Ozin - ArtNanoInnovations©

synthesized” implying the ability of chemists to make materials that mimic the redox chemistry of photosystem II and photosystem I in photosynthetic plants, algae and bacteria to produce fuel from the sun, carbon dioxide and water is within our grasp.

Imagine life in a ‘clean house gas’ rather than a ‘green house gas’ world; this will require a change of human behavior from that practiced in the Anthropocene era where the Earth’s ecosystems have been negatively impacted by humans to the Sustainocene age where humans strive to heal the Earth through renewable technologies to make things better.

If this utopian vision of solar fuels from carbon dioxide capture and recycling could be reduced to practice to make greenhouse gas an enabling chemical resource rather than a waste stream and if the process could be conducted at a technologically significant efficiency, at a globally relevant scale and at a cost competitive with fossil fuels, then the development of a sustainable future for following generations becomes an attainable goal.

Solar Fuels Materials Dilemma The challenge in designing and making materials that can transform carbon dioxide, water and sunlight to an energy rich fuel akin to Nature’s photosynthesis, is the one often faced by scientists and engineers working in the field of advanced materials technology, namely one of providing processes and devices that either perform at high efficiency but utilize critical materials that are in short supply and too pricey or rather work at low efficiency but use materials that are earth abundant and accessible at a competitive cost. So the difficult choice one has to make in today’s solar fuels research is whether or not to focus ones efforts on reducing the cost of a high efficiency process based on rare expensive materials or improving a low efficiency process founded on common cheap materials.

An added requirement for a viable artificial photosynthesis process, which is able to handle the rising concentration of greenhouse gas in the troposphere at a level that can rival natural photosynthesis, necessitates searching for a material that can transform carbon dioxide, water and sunlight to an energy rich fuel with economy of scale and cost of manufacturing. From a practicality standpoint this will likely favor a gas phase light driven heterogeneous photocatalytic process rather than aqueous phase dispersion photocatalysis or aqueous photoelectrochemistry with control over pH and ionic strength and an applied voltage bias to overcome the extra potential required to drive an energetically uphill solar fuel reaction.

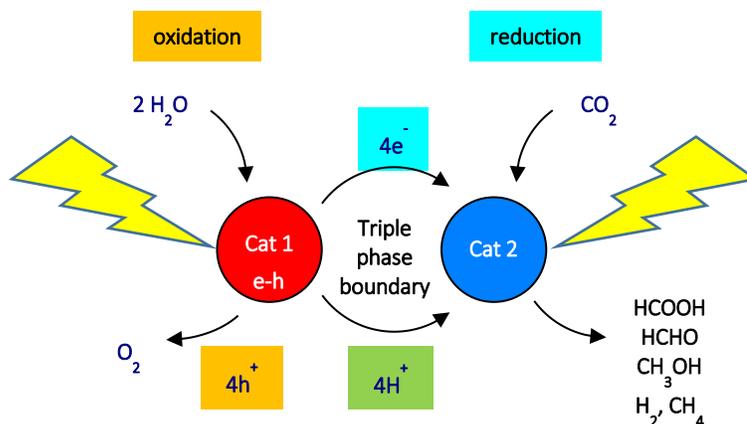
Hence one is forced to direct research efforts on a gas phase photoprocess using what tantamount to be ‘zero cost’ photoactive materials with elemental compositions in abundance and lacking toxicity, exemplified by metal oxides, carbon and silicon. These will require shrewd

size, shape, surface and interface materials engineering, judicious incorporation of additives and control of defects, and thoughtful design of the way these materials are integrated to an architecture that optimizes the optical, electrical, photophysical and chemical requirements of the system.

All of these considerations are important to avoid future production issues associated with materials scarcity and economy of scale, commonplace requirements for the successful operation of large volume production chemical manufacturing industries.

Can we Match Nature?

Establishing photosynthetic efficiency of plants, algae and bacteria for converting sunlight, carbon dioxide and water to chemical energy is a complex issue that depends on the type of organism and environmental conditions and whether the efficiency is averaged over an annual cycle estimated at 1-3% or growing season at 3-7% (Science, 2011, 332, 805-811). These natural photosynthesis efficiencies are to be compared with the best laboratory mimics researched over the past thirty years which currently are roughly three orders of magnitude less.



The challenge therefore is to discover materials that are able to more efficiently harvest and utilize sunlight, and catalyze the photo-oxidation of water and photo-reduction of carbon dioxide to energy rich fuels such as methane or methanol, illustrated in the scheme. The goal is to synthesize photoactive materials able to chemically couple these light driven redox reactions together and achieve conversion rates and efficiencies of carbon dioxide and water into energy rich fuels at a level that begins to match nature's photosynthesis.

About 85% of the world's energy supply is transported in the form of gaseous and liquid, carbon containing fuels!

Why Has Progress Been So Slow? While water oxidation and carbon dioxide reactions that generate solar fuels look simple on paper in practice they are exceptionally demanding to implement in practice as they involve thermodynamically uphill, multi-electron, multi-hole and multi-proton processes occurring on a multi-component photo-catalyst as envisioned in the scheme. The photo-catalysts needed to facilitate these processes, besides having to be made of earth abundant, non-toxic, light-stable, scalable and low cost materials also have to satisfy additional requirements that include, high surface area and porosity to maximize

the adsorption, transport and desorption of reactants, intermediates and products as well as strong visible light absorption to enable the efficient generation, transport and utilization of electrons, holes and protons at water oxidation and carbon dioxide reduction centers. Perhaps the greatest challenge is how to tailor nanomaterials with long-lived charge-separated states required to power multi-electron, multi-hole, multi-proton chemistry that underpins the formation of solar fuels.

In the context of light absorption, a number of optical techniques are potentially useful for boosting the effectiveness by which light is harvested in the photo-active material including:

1. structuring to increase the effective optical path length by multiple light scattering or photonic crystal slow photon amplification
2. surface plasmon resonance to enhance local electric fields and optical absorption strength
3. up-conversion to transform non-absorbed infrared to absorbed visible light
4. multiple-carrier generation to achieve quantum yields greater than 100%

One paradigm in the field of solar fuels is that a single nanostructured material can provide electronic band energies and band gaps that under solar insolation facilitate both water oxidation and carbon dioxide reduction. Another is that these requirements are best achieved in a multi-component heteronanostructure in which electronic band energies and gaps of the constituent materials are matched to the solar spectrum and oxidation and reduction potentials for water and carbon dioxide. The interface between the components of the hetero-nanostructure ideally should be lattice matched and their band energies and gaps tailored to optimize the photo-generation and separation of electron-hole pairs to be competitive with their recombination. In addition their electrical conductivity and diffusion length should be as high as possible to minimize recombination of these electrons and holes and facilitate their transport to surface reaction sites to do productive chemistry.

Equally important is that co-generated protons from water need to be able to rapidly diffuse from the surface of the oxidizing component of the hetero-nanostructure to the reducing one and react with carbon dioxide and electrons to form the carbon-hydrogen bonds of the organic product. This may need the assistance of an organic or inorganic or organic-inorganic hybrid proton conducting material to assist simultaneous proton and electron transport between the oxidizing and reducing components.

Additional considerations involve complications arising from carbon residues formed on the surface of the hetero-nanostructures during their synthesis originating from organics in precursors, ligands and solvents. Adventitious carbon on the surface of the hetero-nanostructure could be hydrophobic and would have the effect of reducing the adsorption of water and carbon dioxide and the absorption of light thereby reducing the efficiency of producing solar fuels.

Other difficulties concern competing photo-oxidation reactions of methane or methanol by co-generated oxygen and formation of hydrogen from recombination of photogenerated protons and electrons from the photo-oxidation of water, both of which can reduce the efficiency of converting carbon dioxide and water to solar fuels.

If a photosynthetic mimic is to really produce solar fuels on a globally significant scale it will have to efficiently and economically capture and cleanup carbon dioxide from thin air and in a chemically and optically engineered gas phase photocatalytic process convert it and water into methane or methanol and separate these organic products from co-generated oxygen, at a cost that is competitive with their production from fossil fuels.

What Have We Learnt? In all studies reported to date, conversion rates and efficiencies are about three orders of magnitude too low to be of practical significance and the challenge has been to try to understand the reasons for the poor performance and to find materials, chemical and optical engineering remedies for its improvement.

A major impediment in earlier work has been finding reliable means to sort out fact from fiction in the production of solar fuels. The literature since the beginning of the field has been replete with reports that as-synthesized and post-treated materials produce organics at significant rates but only very recently have $^{13}\text{CO}_2$ isotope tracer methods been employed to decide unequivocally whether they originate from carbon dioxide or carbon residues on the surface of the photo-catalysts or both. After much study the consensus is that one of the best ways to reduce adventitious carbon to manageable levels is through ultraviolet light post-treatment of photo-catalysts in humid air or in pH and ionic strength controlled aqueous solution.

Designing and making well-defined nanostructures with all the necessary features mentioned above, to reduce to practice an efficient solar fuels photocatalyst, has proven to be much more challenging than originally anticipated by research scientists and initially expected by government, industrial and private sponsors of this research.

At this point in time a number of key questions still remain to be answered to realize the dream of fuel from the sun at a technologically significant rate, efficiency and scale. These include:

1. how to choose solar fuels nanomaterials
2. how to integrate them into a higher level architecture
3. how to harvest and amplify the absorption of sunlight to optimize the formation, separation and transportation of multiple electrons, holes and protons
4. how to retard the recombination of photo-generated electron-hole charge-separated states and favor the formation of solar fuels

5. how to utilize these photo-generated charge carriers to oxidize water and reduce carbon dioxide to store solar energy in the form of energy rich chemical bonds, at a rate and efficiency that matches or exceeds photosynthesis
6. how to scale fuel from the sun technology to cope with the global emission rate of anthropogenic carbon dioxide at a cost that is economically competitive with fuel from the earth

The 'super-leaf' challenge is x1000!

Steps Toward, a Sustainable Future

Approximately 75% of the current 48 Gt CO₂ equivalents per year of anthropogenic emissions of greenhouse gases are due to combustion of fossil fuels and until these emissions are reduced to zero, human interference with the climate and its associated social, economic and political uncertainties will continue.

Solar fuels research aimed at the sunlight powered conversion of carbon dioxide and water vapor to methane holds out the promise of large-scale electrical generation fueled entirely by the energy of the sun. One could envision a photo-reactor system would be employed as a 'bolt on' technology used in conjunction with existing, well-established energy systems and combustion technologies, minimizing the capital and infrastructure cost of effecting the transition to sun-powered electricity. The result would be to wean electrical generation off fossil fuels and to reduce to zero the CO₂ emissions of existing gas-fired electrical generating plants – an enormous step toward creating a sustainable energy future.



Recreating Nature Inventing a Sustainable Future:
Todd Siler and Geoffrey Ozin - ArtNanoInnovations©

Alternatively, the photo-reactor system might be configured to generate methanol – a clean-burning liquid fuel that can readily be stored and transported. This methanol could be used in a wide variety of applications ranging from the very large (e.g. production of industrial chemicals) to the very small (e.g. power generation in homes and businesses). It could also be used in internal combustion engines with minimal modifications to energy infrastructure and engine design, enormously reducing reliance on fossil fuels and reducing the contribution of vehicles to global CO₂ emissions.

What is needed now are rudimentary materials, chemical and optical engineering analyses of various options imagined for these kinds of solar fuels technologies in order to gain a preliminary understanding of the scientific, technical, economic, and commercialization challenges that different approaches to carbon capture and solar recycling will inevitably face with respect to competing renewable and non-renewable energy sources.

While the 'super-leaf' concept is elegant in its simplicity and powerful in terms of its promises for a sustainable future, it will only transition from laboratory curiosity to technological reality if the materials and engineering costs are understood and proven to be competitive with alternative approaches for making methane and methanol.

Materials Views Opinion Editorials

Ode to CO₂

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Oh small molecule
Friend or foe
To love or hate
To understand you better
Before it's too late!

Geoffrey A Ozin, April 2012



Of the three small molecules that dominate the composition of our earth's atmosphere, it is the minor component, CO₂ that we are beginning to fear because of the looming Armageddon global warming scenario arising from the accumulation of *greenhouse gas* in the troposphere. While O₂, N₂ and CO₂ brought about and maintain life on our planet, CO₂ the combustion product of the human race now threatens its demise.

It is the innate ability of humans to recognize and react defensively to danger and in doing so learn how to survive that has inspired a global effort to understand how to transform CO₂ into a *clean house gas*!

While these days CO₂ might be considered the molecule to hate there are many reasons why our relationship with it could be transformed into an eternal love affair. In this article I will take a look at how CO₂ emerged into our scientific consciousness, how it became the molecule of choice for numerous products and processes, how its abuse and misuse are becoming a looming ecological, environmental and sociological nightmare, and how this fear of the consequences of global warming is driving a scientific and technological revolution aimed at making CO₂ into a friend rather than a foe, by learning how to capture and recycle it back into a useful fuel rather

than simply capture and store it, the latter considered an unsafe practice and banned in some countries.

Jan Baptista van Helmont (1580–1644) a Flemish chemist, physiologist and physician, whose research was contemporary with Paracelsus, remembered for his neologism of the word gas (Greek *chaos*), is given credit for the discovery in 1630 of carbon dioxide, as an off-gas in the combustion of wood, which he named *gas sylvestre*, wood gas.

The Scottish chemist Joseph Black (1728–1799) in 1756 first proved carbon dioxide occurred in the atmosphere and called it fixed air. He also showed it is a product of human and animal respiration and microbial fermentation and that it has a fascinating chemistry exemplified by the precipitation of limestone (calcium carbonate) by bubbling carbon dioxide into aqueous lime and reversed by heating the resulting limestone. He showed carbon dioxide to be denser than air and can extinguish both flames and life.

Joseph Priestley (1733–1804) could be considered the father of the soft drink industry with his discovery in the mid-1700's that carbon dioxide evolved from the action of oil of vitriol (sulfuric acid) on chalk (calcium carbonate) could be dissolved in water to produce a pleasantly flavored fresh sparkling soda water.

Imagine what these CO₂ pioneers would say today if they had known in addition to CO₂-driven photosynthesis in plants to produce carbohydrates which feed humans and animals and the beneficial effects of natural CO₂-based climate control of the planet to stabilize it at the right temperature for maintaining life, that if allowed to increasingly accumulate in the atmosphere, CO₂ could also cause long term harmful effects to the human race and life on earth.

Our love affair with CO₂ is seen in its many uses, including soft drinks, dry ice solid refrigerants, ingredients in frozen food, cooling bunches of grapes in wine making, atmosphere for reactive welding, capsules for air guns, extinguishers for electrical and oil fires that cannot be put out by water, supercritical solvent for the environmentally friendly and safe removal of caffeine from coffee to help the old to be put in the coca cola to help the young, the first infrared gas laser, and an enabler for enhanced oil recovery.

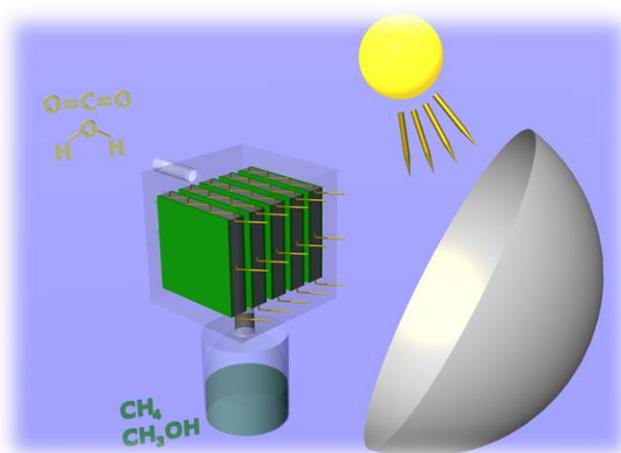
This affection is also found in chemically bound CO₂, pervasive as carbonate minerals with wide ranging uses that include construction, pharmaceuticals, food, glass, polymers, paper, coatings, pigments, paints, pottery and jewelry manufacture.

In the natural world carbonate biominerals are omnipresent in calcareous forms such as calcite and aragonite coccolithophores, sponge spicules, echinoderms, corals and the molluscan shell, the shapes and patterns of which continue to visually impress and intellectually challenge our understanding of morphogenesis, the origin and control of natural form.

The manufacture of chemicals and pharmaceuticals, fuels, and polymers from CO₂ using well established technologies is growing in importance but is currently having only a minor impact on

the roughly 10 Gt of yearly anthropogenic CO₂ emissions. It has been estimated that the implementation of these chemical technologies in large scale industrial processes could reduce CO₂ emission by as much as 350 Mt yearly however this only represents about 3-6% of annual anthropogenic CO₂ emissions even when added to the corresponding reduction in fossil fuel usage as a result of these kinds of CO₂ processes.

In this context, a promising area for research and development is the sunlight driven conversion of CO₂ and H₂O to energy rich and transportable fuels like CH₄, CH₃OH and HCO₂H but to achieve steady state in atmospheric CO₂ this will have to be implemented in a process that utilizes earth abundant, low cost, and non-toxic materials operating at globally significant rates and scales in order to stand a chance of making a real impact on the problem of anthropogenic CO₂.



While there are currently around half-a-dozen approaches competing for this CO₂+ H₂O + sunlight grand prize including solar thermal, homogeneous and heterogeneous catalysis, biomass, electrocatalysis and photoelectrochemistry, it is likely that the most practical and economically viable programs for large-scale CO₂ capture and recycling (CCR) to chemical fuels will involve gas-phase flow-based photocatalytic reactor units. They will likely work alongside CO₂ capture, purification and storage (CCS) technologies, possibly

based on metal organic frameworks, frustrated Lewis pairs or amine resins, integrated into CO₂ emitting fossil fuel power plants and iron, steel, cement and aluminum production facilities, working at low pressures and temperatures and driven by sunlight (image credit, Dr Wendong Wang).

One can also imagine personalized versions of these CCS+CCR units installed in homes and buildings, generating from CO₂ + H₂O solar fuels like methanol or methane used for heating and lighting as well as for powering cars.

So what will it take for CO₂ + H₂O + sunlight photocatalysis to outperform photosynthesis? Simple, the right (nano)material!

Materials Views Opinion Editorials

Powering the Planet with Energy Nanomaterials?

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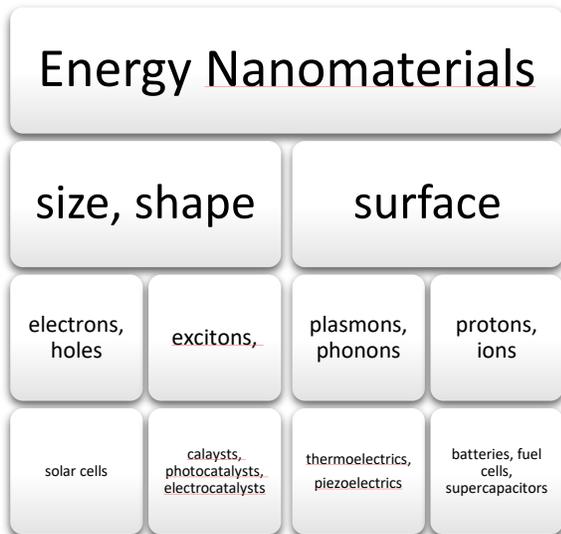
How can Nanochemistry help solve the energy problems that our world faces today? How can nanomaterials make a difference in the grand challenge: efficient and green global scale production, storage and use of energy?

It turns out that depending on how energy is generated; by making or breaking chemical bonds; exciting electrons or holes; creating excitons or multiple excitons; using plasmons or phonons; the physical size of materials involved in the process can make a big difference as below a critical dimension the chemical and physical properties of materials are subject to quantum mechanical scaling laws. So why is small often good for many kinds of energy materials and devices?

To answer this question we must understand the special properties of different classes of energy materials fashioned at the nanoscale and the role their size plays in energy or storage. A primary consequence of diminished size is to amplify surface effects and morphology will determine the crystal faces available for surface reactions. By reducing the physical dimensions of energy materials to the scale of nanometres the surface to volume ratio and number of active surface sites increase, which enhances the efficiency of any heterogeneous catalytic process whether thermo-, photo- or electro-catalytic.

For energy materials, with physical dimensions smaller than the wavelength of electrons, holes or excitons, the beneficial effects of spatial and quantum confinement on electrical, optical, thermal and mechanical properties are becoming apparent in the fabrication of solar and fuel cell, lithium ion battery, supercapacitor, piezoelectric and thermoelectric energy devices. At these tiny scales, enhancing the absorption, diffusion and scattering lengths and strengths of all the various particles and quasi-particles which contribute to energy generation processes are of paramount importance in the production of efficient energy materials and their implementation in energy devices.

I am really impressed by the many ways in which the unique properties of nanomaterials are being creatively applied to solve today's energy problems.



To amplify on the above with some representative examples, the intense electric fields associated with plasmons in silver and gold nanoparticles are being employed to enhance the harvesting of light, production of electrons and holes, and performance of metal oxide water splitting (γ -Fe₂O₃ nanoparticles) and carbon dioxide recycling (TiO₂ nanotubes) photocatalysts for the production of hydrogen, methane and methanol solar fuels. Noble metal nanoparticle plasmons are similarly being used for improving the light absorption and photon to electron conversion efficiency of different kinds of photovoltaics from silicon to dye sensitized solar cells.

In semiconductor nanocrystals, the effect of confinement of electrons and holes in a three-dimensional potential well is to transform the continuous energy levels of the electronic bands of the bulk semiconductor into discrete energy levels in the nanocrystal, whose energy spacing can be tuned by controlling the nanocrystal's physical size. This so called 'quantum size effect' in semiconductor nanocrystals can be usefully exploited in the construction of different kinds of solar cell, which take advantage of size tuneable electronic band gaps to optimize the harvesting of solar photons; size controllable electronic coupling between nanocrystals to enable efficient transportation and collection of charge; and multiple exciton generation from absorption of a single photon to maximize power conversion efficiency.

Colloidally stable dispersions of semiconductor nanocrystals have the additional advantage that they can be readily combined with organic polymers, dyes or other nanocrystals and processed into thin films and multi-layers on rigid or flexible substrates such as metals, transparent conducting oxides or polymers, all key attributes for the development of third generation solar cells.

In this context, the integration of photonic crystal architectures, such as those formed from multi-layers of colloidal nanocrystals, into solar cells has provided another means of improving their light collection and overall efficiency by increasing the effective path length and hence absorption of photons in the active semiconductor region of the device.

In lithium ion batteries, metal oxide nanoparticles based on titania, silica or alumina are replacing organic plasticizers in polymer-salt electrolytes because of their ability to stabilize the room temperature high ionic conductivity amorphous phase of the polymer and at the same time render the system less prone to explosion hazards during recycling. In this context, the deleterious charging-discharging volume swings of lithium ion battery anode and cathode materials, which occur due to intercalation of lithium ions at the negative electrode during charging and at the positive electrode during discharging, can be ameliorated

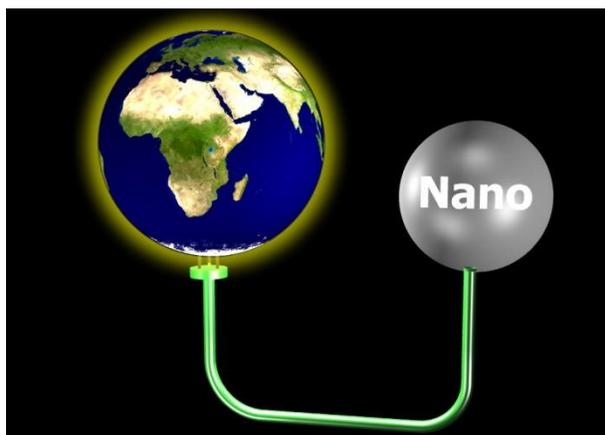
by reducing their scale to nanometre dimensions with the additional benefit of improved cycling times. A notable accomplishment in this regard is the development of high capacity silicon based-batteries which accommodate the substantial fourfold silicon anode volume changes on lithium insertion by fabricating the anode as an array of silicon nanowires, which provide small lithium ion diffusion lengths for rapid charge-discharge, nanowire conduits for transporting charge to current collectors as well as sufficient space in between nanowires to contain their volume expansion and contraction recycling requirements.

The development of high performance super-capacitors as electrical energy storage devices can also benefit from the use of high surface area electroactive nanomaterials. While the power density of super-capacitors is higher than that of batteries their energy density ($E = 1/2CV^2$ where C = capacitance and V = cell potential) needs to be improved for them to be widely deployed in electronic devices and industrial electrical systems. In this endeavour a notable research target is the high energy density asymmetric super-capacitor comprised of a high surface area carbon cathode and a metal oxide anode. A recent promising example is an interpenetrating porous network of vanadium pentoxide nanoribbons and carbon nanotubes, which enables easy accessibility of an organic electrolyte and facile charge transport into the electroactive nanomaterial network.

Reducing the scale of thermoelectric materials to the nanoscale provides a means of boosting the figure of merit ($Z = \sigma S^2/\kappa$ where σ = electrical conductivity, κ = thermal conductivity, and S = Seebeck coefficient) to values in the range $Z = 3-4$ that make their use in power generating systems a realistic prospect. Bismuth based nanomaterials - metal and metal chalcogenides in the form of dots, wires, sheets and assemblies thereof - can simultaneously display high electrical conductivity enabled by quantum size effects that enhance the electronic density-of-states and low thermal conductivity enabled through amplified surface phonon scattering effects.

Exploiting piezoelectric materials like zinc oxide, which generate electricity from the application of pressure, notably from tiny movements of easily deformable nanowires grown on different substrates (fibres, meshes and films), allows them to be fashioned into new kinds of mechanically actuated nanogenerating power systems targeted for mobile, implantable and personal electronic devices. Here the electrical energy to drive the device is created by some form of physical motion of the zinc oxide

nanowires, human or otherwise, originating in for example, sound, wind, heartbeat, muscle contraction and blood flow.



Powering the Planet with Energy
Nanomaterials – Graphic Illustration by
Wendong Wang

It is the nanochemical techniques which have been developed and refined over the past two decades, which have led to our ability to produce these potentially groundbreaking energy materials and devices. Nanochemists have strived to produce nanoscale materials with controlled size and shape and surfaces and well defined compositions, which are necessary for tackling these challenges.

Although there is still a great deal of work to be done, we have come a very long way in a very short time. Now the challenge is to make the leap from nanoscience to nanoengineering; from the simple

quest to discover and characterise new energy materials to the true goal of applying them in the solution of global energy problems, illustrated in the futuristic scheme of *nanomaterials powering the planet!*

In the emerging field of enhanced energy nanomaterials it has been the increasing application of nanochemistry synthetic strategies which has provided the enabling nanoscience that has led to the realization of improved performance energy nanotechnologies.