

50 Years of Materials Research and Still Searching

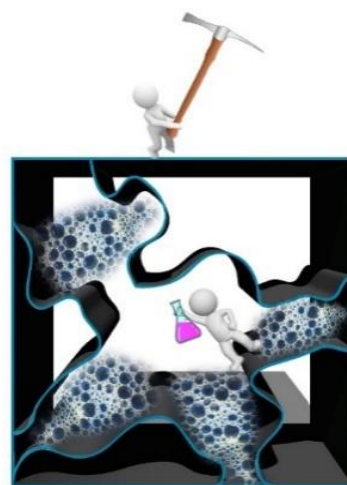
Vignettes of the 1967-2017 Research Contributions

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My first publication in a peer-reviewed journal was as a graduate student in 1967. It was in the field of materials chemistry. Realizing my dream to be a Professor, I set out on a research journey that transitioned my materials chemistry to the world of diminishing dimensions, which I called nanochemistry. Considered to be amongst the most important scientific disciplines, nanochemistry today is a dynamic interdisciplinary field in its own right, and a powerful driver of emerging nanotechnologies. Work in this discipline continues to catalyze multidisciplinary collaborations leading to innovations that benefit humankind in outstanding ways, helping us meet our global energy, environmental and health challenges, among other urgent concerns.

Where Did It All Begin? In reminiscing about a half a century of research, I use a few graphical depictions of how I stumbled into the field of nanochemistry. In the early seventies, the century-old field of colloid chemistry, pioneered by Thomas Graham (1805-1869), was undergoing its metamorphosis to today's nanochemistry, and colloid science, propagated by Wolfgang Ostwald (1883-1943), was nucleating as today's nanoscience. Graham had described the distinctive behavior of matter in the nanometer to micron size range, and Ostwald had enriched the subject in his book 'The World of Neglected Dimensions' (1914). I was inspired by this work to address the challenge of self-assembling materials with nanoscale dimensions using a bottom-up chemistry approach. As a synthetic chemist, however, I confronted an important unanswered question: How could one use chemistry to prepare nanoscale forms of well-known metals, semiconductors and insulators, with physical dimensions in the quantum size regime of around 1-100 nm? To this end, I studied the size-tunable behavior of these materials with an eye to elucidating function and determining utility. The 'eureka' moment of performing chemistry with 'naked' metal atoms under cryogenic conditions opened my mind to the tantalizing possibility that one could control nucleation and growth to 'atom-precise' metal nanoclusters M_n , by allowing them to diffuse around and self-assemble in low-temperature solid matrices. This scientifically significant feat had never been accomplished before. In this way, I observed metal atom-by-atom nucleation and growth reactions, and monitored and quantified their aggregation kinetics for the first time. Furthermore, I established that it was possible to observe previously undetected and unseen M_nL_m compounds in the presence of ligand L. (*Nature* 1972, *Nature* 1975).



One of my favorite early initiatives, undertaken while working as a Fairchild Fellow at Caltech in 1977 with William Goddard, was an experimental and theoretical study of $Ni_n(C_2H_4)_m$. This described for the first time the chemistry of 'naked' nickel atoms and nickel clusters with ethylene, envisioning them as a localized bonding model for ethylene chemisorbed on bulk nickel (*JACS* 1978). The ingenuity behind these 1970's experiments, summarized in *ACR* 1973 and *ACR* 1977 and expanded upon in some of my later papers, unveiled an unprecedented view of controlled size metal nanoclusters, the synthesis of which enabled the first explorations of the transition from molecular to quantum confined to bulk forms of metals (*JACS* 1980). They also provided a unique platform for investigating cluster-surface relations. It is worth mentioning that I later enriched this work with my discovery of a collection of unprecedented metal atom and metal cluster photo-processes. These processes included 'naked' metal atom photo-aggregation, 'naked' metal cluster photo-dissociation and 'naked' metal cluster photo-isomerization reactions as well as 'naked' metal atom photo-insertion reactions into the carbon-hydrogen bonds of saturated hydrocarbons, such as methane (*ACIE* 1983, 1986, *JACS* 1985). Together, these early experiments on the chemistry and photochemistry of 'naked' metal atoms and 'naked' metal clusters, laid the groundwork for the development of nanochemistry.

Zeeting Zeolite My passion to take the insights gained from my nanochemistry work on 'naked' metal atom and 'naked' metal cluster cryochemistry 'out of the cold' provided the link between my early works to the field of zeolite science. I envisioned making and stabilizing these tiny pieces of matter so that detailed studies of their structure, property, function, utility and relations could be undertaken. In this context, it occurred to me that because these M_n and M_nL_m nanoclusters were inherently metastable with respect to further agglomeration

to thermodynamically stable bulk materials, they needed stabilization by some kind of surface protecting sheath. I performed the nucleation and growth reactions within the nanometer-sized voids of zeolites, 'capping and trapping' the nanoclusters in a 'zeolate' ligand cage (**AM** 2004), confirming that zeolites could serve as nanoporous hosts for synthesizing and stabilizing metal and semiconductor nanomaterials.

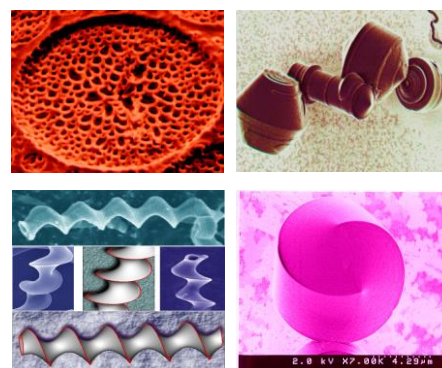
During this period, thinking within the zeolite community focused solely on the properties and applications of zeolites in catalysis and gas separation. I preferred however, to look at zeolites as solids filled with nanoscale voids and wondered how they could perform and compete in the advanced materials research space. I saw their potential in areas such as information storage, photovoltaics, batteries, fuel cells, photo-catalysts, chemical sensors and drug delivery systems. Exploring these opportunities, I worked with Edith Flanigen at Union Carbide, Tarrytown New York for five years to bring some of these ideas to practical fruition, ultimately describing my vision for the future direction of the field in one of my favorite papers, 'Advanced Zeolite Materials Science' (**ACIE** 1989). Coincidentally, around this time the Union Carbide team made the extraordinary discovery that it was possible to synthesize nanoporous materials from elements across the periodic table. This breakthrough expanded the composition field of zeolites way beyond aluminosilicates and silicates. This advance inspired me to focus my attention on advanced materials applications of nanoporous metal chalcogenides, which I envisioned as semiconductors filled with nanometer holes (**Nature** 1997) with perceived utility in molecular size- and shape-discriminating sensing devices. This work enabling the development of an early prototype 'electronic nose', (**SC** 1995).

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

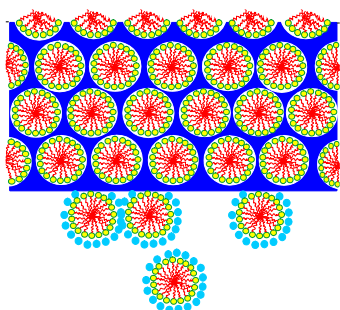
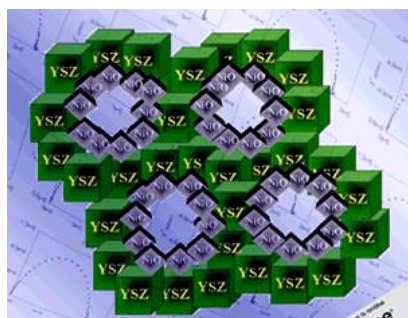
Birth of Nanochemistry My ensuing research laid out the essence of a chemical approach to nanomaterials - a futuristic field that I called 'Nanochemistry', (**AM** 1992). This paper set the scene for a nanomaterials revolution that continues unabated today. I envisioned the novel world of nanochemistry with its 0-D dots, 1-D wires, 2-D layers and 3-D open frames, configurations that surprised, shape- and size-dependent behaviors that startled. Here were the conceptual foundations, the description of a bottom-up paradigm for synthesizing nanoscale materials with nanometer-level command over their size, shape, surface and self-assembly. The potential I saw was breathtaking. It would be possible to produce nanoscale materials - perfect down to the last atom - from organic and inorganic components, with structure-property relations designed to yield new materials characterized by an array of novel behaviors and these materials would have real-world applications. The field of nanochemistry crystallized in 1992 and gave birth to journals that publish nanochemistry with citation impact-factors matching or exceeding the flagship journal in their respective society and include, *Small*, *Nano Letters*, *ACS Nano*, *Nature Nanotechnology*, *Nanoscale* and the list continues to grow. Chemistry and nanotechnology united forever through nanochemistry, evidenced by the astronomical growth of nano chemistry ISI citations since 1992, more than 50M hits on Google, and the creation of numerous global initiatives in academic, industry, government, and defense institutions around research and education in nanochemistry. These initiatives inspired others to employ fundamental scientific principles and practices of nanochemistry to solve challenging real world problems in nanotechnology.

Micro-, Meso-, Macro-Scale This work mapped the foundation for much of my research on nanomaterials which underpinned my 'panoscopic' vision of materials self-assembly over 'all' length scales (**ChemComm** 1999), a synopsis of which is described below with graphical illustrations.

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



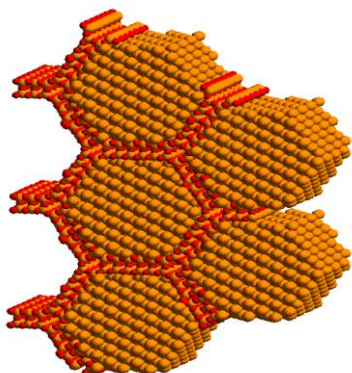
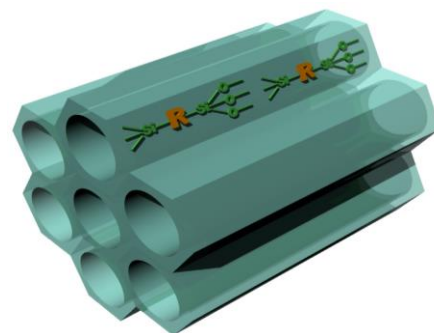
2. **Mesosopic materials** – This biomimetic way of thinking about template-directed co-assembly of materials led to my discovery of periodic mesoporous silica in the form of 'oriented thin films' formed at liquid-solid and air-solid interfaces (**Nature** 1995, **Nature** 1996). These



seminal papers inspired a world-wide effort on finding utility for periodic mesoporous silica film in optics, fluidics, microelectronics and sensing, to name a few applications. I also advantageously used template directed co-assembly of meso scale-inorganic materials with compositions beyond the archetype silica. These meso-materials included semiconducting germanium sulfide (*Nature* 1999), electrochromic nanocrystalline titania (*NL* 2004), transparent conducting indium tin oxide (*AM* 2009) and fast ion conducting yttria stabilized

zirconia (*AFM* 2001), which displayed structural features intermediate between the nanoscopic and macroscopic length scales, and compositions that led to many meso-materials useful in today's energy nanotechnologies

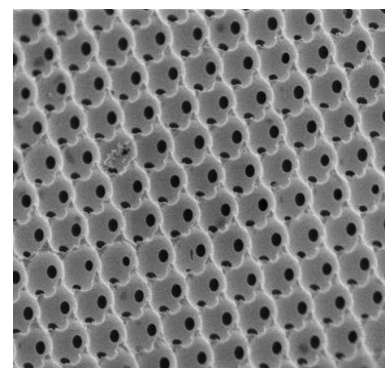
3. **Hybrid nanomaterials chemistry** – a new class of nanocomposite materials called periodic mesoporous organosilicas (PMOs) were invented in this phase of my work (*Nature* 1999). These distinctive hybrid materials contain bridge-bonded organic molecules integrated into the silicate pore walls. The organic moieties include aliphatics, alkenes, aromatics, dendrimers, fullerenes and polyhedral oligomeric silsesquioxanes. Today, having undergone extraordinary growth across the globe and across the borders of the science disciplines, PMOs deliver properties that transcend the sum of their inorganic and organic components and are finding widespread application as interlayer dielectrics in microelectronic packaging, chromatography stationary phases, chiral catalysis, dental implants and drug delivery vehicles (*Science* 2003, *Science* 2004, *ACR* 2005).



4. **Host-guest inclusion chemistry** – using chemical vapor and metal organic vapor deposition within the spatial confines of nanoporous hosts, I discovered how to control the nucleation and growth, stabilization and protection of size- and shape-controlled quantum confined semiconductor nanomaterials. Examples include, nanometer dimension Si, Ge, Ag, AgCl, CdS, SnS₂, MoO₃ and WO₃, (*ACR* 1992) This genre of research inspired subsequent work on ligand-stabilized colloidal nanocrystals that underpin some of today's most promising nanotechnologies including solar cells and batteries, supercapacitors and fuel cells, medical diagnostics, imaging and theranostics.

5. **Photonic crystal materials** – Thinking big, I discovered how to employ self-assembly to synthesize the world's first 3D silicon photonic crystal with an omni-directional photonic bandgap operating at optical telecom wavelengths (*Nature* 2000). This genre of research

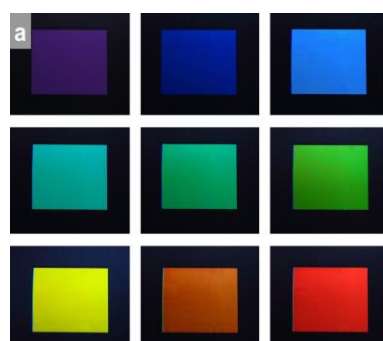
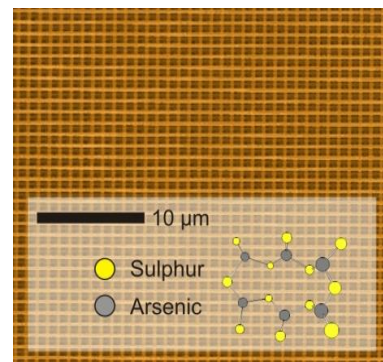
inspired me to synthesize photonic crystals with a wide range of compositions that could display the full gamut of 'color from structure' as found in the natural world. I also discovered how the 'slow light' attributes of these photonic crystals could be used to amplify light absorption, which inspired me to use them to enhance the efficiency of silicon and titania solar cells and titania photocatalysts (*NL* 2011, 2013, *AM* 2007, 2009). I also showed how to incorporate nanoscale planar defects into photonic crystals and how to implement them as a new class of chemical and biological color sensors (*AM* 2006).





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

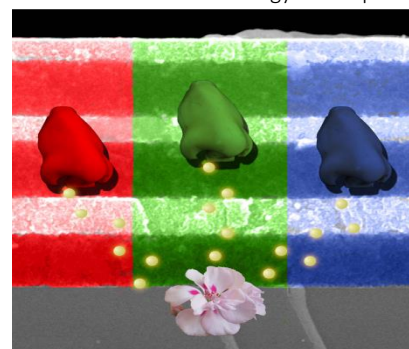
7. **Multi-photon direct laser written (DLW) photonic bandgap nanomaterials** – in collaboration with colleagues at the Karlsruhe Institute of Technology, I used this nanofabrication method to invert a DLW polymer template in silica by atomic layer deposition. This enabled a subsequent inversion in silicon by disilane chemical vapor deposition, creating thereby a silicon replica of the original polymer template (Nature Materials 2006). Silicon photonic bandgap nanomaterials created by this inventive ‘double inversion’ method facilitate the development of silicon-based all-optical devices, circuits and chips with utility in optical telecommunication and computer systems. I spearheaded a creative extension of this work with single-step DLW in a high refractive index ‘inorganic’ photo-resist, arsenic sesquisulphide, As_2S_3 . This opened the door to a large variety of new photonic bandgap materials and architectures that can be made by DLW without inversion of a sacrificial polymer template (ChemMater 2008).



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

Seeing the Light One of the hallmarks of my research is the exploitation of the unique properties of regular arrangements of nanopores with dimensions that traverse nanometers to microns. For example, my research on periodic macroporous materials, which I call ‘light-scale’ materials, a focus has been electrically, thermally, mechanically, and chemically tuned ‘color from structure’. This revolutionary concept forms the basis of a new ‘photonic color’ nanotechnology developed

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

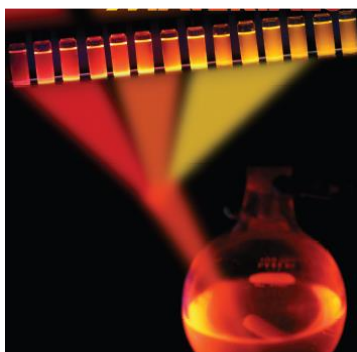


It is worth pointing out that the **P-Ink** photonic colour technology developed by Opalux was recognized by the Technical Development Materials Award in the USA in 2011, which identifies the most innovative and significant technical achievement in the field of materials development (<http://www.idtechex.com/printed-electronics-usa-11/awards.asp>). Opalux follows in the footsteps of many previous illustrious industry winners of this award in the US, Europe and Asia. In 2013, Opalux P-Ink Photonic Technology received the Global Innovation Award for its potential impact on the specialty colour displays industrial sector (http://techconnectworld.com/World2013/participate/innovation/innovation_awards.html). Opalux Opal-Print Technology was runner-up in the 2013 Excellence in Tax Stamps Awards for best new innovation in anti-counterfeiting, anti-diversion, document security, brand protection and holography technologies (<http://www.taxstampnews.com/awards>).



New nanochemistry twists I was amongst the first few scientists to demonstrate chemically powered ‘nanolocomotion’. This work relied on chemical control of the motion of barcode nanorod motors, whose power originated from the decomposition of hydrogen peroxide into water and oxygen localized at the catalytic segment of the nanorod (*ChemComm* 2005, *AM* 2005). My first experiments aimed at nanorod rotors and motors, a goal being to understand the origin and control of their motion and speed. Subsequently I was the first to show how to make them flexible by integrating polymer hinges between the segments of the nanorod (*Nature Nanotechnology* 2007). These papers on catalytic nanomotors inspired a veritable ‘nanomotor industry’ with conferences on the subject increasingly being organized around the world. Activity in this field is now burgeoning globally with envisioned nanomachine applications that include the removal of pollutants from water and as drug-carrying and delivery vehicles for targeted cancer therapy. In another innovation moment I discovered

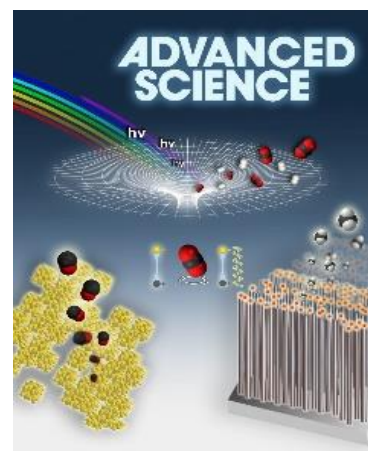
ultrathin inorganic nanowires (*ACIE* 2008), characterized by unprecedented small < 2 nm diameters. These amazingly thin nanowires look, grow and behave like organic polymers (*JACS* 2012, 2010, *NL* 2009, *AM* 2009). This work inspired a flurry of activity around the globe to explore the composition space and structure, properties, and functionality of these uniquely-thin one-dimensional constructs. This work raises an important question about how to expand and enrich the myriad applications enjoyed by organic polymers into the completely uncharted territory of ultrathin inorganic nanowires. The opportunities appear to be boundless!

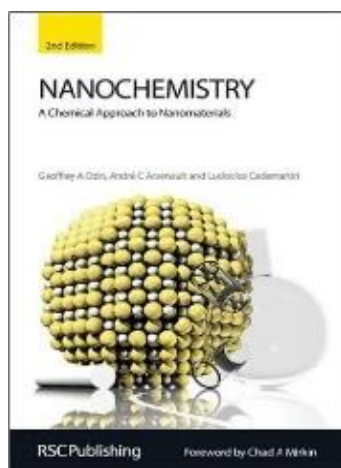
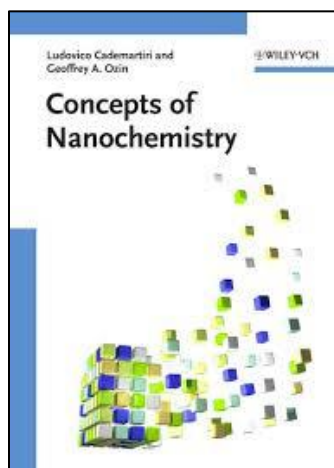


Lately, I have developed a passion for a greener kind of nanochemistry that focuses attention on nanocrystals made of the second most earth abundant element silicon. Silicon nanocrystals are non-toxic, low-cost and scalable. Most significantly, I recently figured out how to separate poly-dispersions of quantum-confined silicon nanocrystals into mono-dispersed colloiddally stable fractions with tailored organic surfaces (*JACS* 2011). Incredibly, for the archetype semiconductor silicon, this feat was the first of its kind since the discovery of silicon nanocrystals more than thirty years ago. The brightly colored visible to near infrared photoluminescence of these size-separated silicon nanocrystals enabled determination of their size-dependent absolute quantum yields, (*NL* 2012). These photoluminescence quantum yields were found to be surprisingly high and as a result are targeted for a range of ‘green’ nanotechnologies that include multicolor light-emitting diodes and biomedical diagnostics,

therapeutics and imaging for detecting and targeting tumors. I believe ‘green nanochemistry’ founded on benign nanocrystalline silicon will help alleviate the fear of cytotoxicity that currently pervades the use of heavy metal chalcogenide and pnictide nanomaterials currently favored for advanced materials and biomedical nanotechnologies (*NL* 2011, 2012, 2013, *AM* 2012, *Small* 2012).

Today, I am spearheading the U of T Solar Fuels Cluster, an interdisciplinary research team devoted to developing scalable, cost effective nanomaterials solutions towards using CO₂ as a chemical feedstock for making value-added fuels, www.solarfuels.utoronto.ca. Leveraging the expertise of a national and international team of leading chemists, engineers, and material scientists, he hopes to initiate a paradigm-shifting zero-emission CO₂ economy. Recently awarded the prestigious \$1M Connaught Global Challenge Award, this dynamic team is well positioned to be at the leading edge of CO₂-to-fuel technology development in the coming years. The ultimate goal of this is to facilitate an energy transition from today’s unsustainable “fossil fuel economy” to a new and sustainable “carbon dioxide economy” (*JACS* 2016, *EES* 2015, *AS* 2014).





Nanochemistry education A particularly important aspect of my research involves education. Textbooks '*Concepts in Nanochemistry*' and '*Nanochemistry: A Chemical Approach to Nanomaterials*', which I co-authored with former students Andre Arseault and Ludovico Cademartiri, are globally acclaimed as *the* gold standard reference works for teaching Nanochemistry to both undergraduate and graduate students. I tirelessly am involved in many outreach efforts through lectures and monthly opinion editorials in the family of Wiley materials journals www.advancedsciencenews.com/author/gozin, to inform scientists and laypersons alike on pressing issues affecting our collective future. These inspiring, thought-provoking perspectives offer viable ways of improving the state of the world.