University of Toronto Solar Fuels Cluster

Where Did We Come From and Where are We Going?

Past

University of Toronto, Solar Fuels Team, December 2017, www.solarfuel.utoronto.ca

Much of our group's research at the University of Toronto over the past fifty years has been in the field of nanochemistry, a 'bottom-up' chemical approach to nanomaterials fabrication, www.nanowizardry.info. It has been widely recognized for enabling innovative research in advanced materials and biomedical science and engineering. Most recently, we have expanded our research towards the field of energy nanomaterials, specifically those that facilitate heterogeneous catalytic conversion of carbon dioxide to synthetic fuels, powered by the heat and light of the sun.

Curiously, this elaboration of our research was sparked by our work in the field of 'green nanochemistry'. The initial focus of this work, beginning about seven years ago, was on size-separated, quantum size effect silicon nanocrystals. With the knowledge that these nanocrystals were made of earth-abundant, low-cost, and non-toxic silicon, we decided to direct the attention of our group towards nanochemistry concepts and principles that could enable the utilization of silicon nanocrystals in multicolor light-emitting diodes, high-coulombic efficiency lithium-ion batteries and biomedical theranostic devices – see 2011-2017 publications.

Our foray into the field of quantum-confined silicon nanocrystals in the size range of 1-5 nm began in 2011, when we succeeded in using density gradient ultracentrifugation and size-selective crystallization to separate poly-dispersions of silicon nanocrystals, with surface alkyl functionalization, into monodisperse fractions with good colloidal stability and size-tunable

photoluminescence. This advance opened up a cornucopia of heretofore impossible investigations into the size-dependent chemical, physical and biological properties of 1-5 nm silicon nanocrystals.

These studies focused on the following topics:

(i) silicon monoxide, a convenient precursor for large scale synthesis,

(ii) chemical reactivity with oxygen and water,

(iii) control of surface charge, water solubility and colloidal stability,

(iv) air stability and superhydrophobicity through 'Teflon-like' perfluorodecyl surface functionalization,

(v) n-doping and p-doping,

(vi) kinetics of thermal- versus microwave-induced hydrosilation,

(vii) absolute photoluminescence quantum yields,

(viii) switching on and off quantum size effects,

(ix) self-assembly and operando inner workings of a multicolor light emitting diode,

(x) perfluorodecyl-capped anodes enabling high initial coulombic efficiency lithium-ion battery,

(xi) cellular uptake and cytotoxicity, and

(xii) uv-blocking porous nanocomposites with siloxane polymers.

This has proven to be a successful and prolific research endeavor for our group, resulting in many breakthrough papers in high impact journals, as seen in our portfolio of 2011-2017 publications.

In a recent and surprising discovery, we found that hydride-terminated silicon nanocrystals, ncSi:H, with average diameter of 3.5 nm, could function as an efficaceous reducing agent, able to selectively convert gaseous carbon dioxide to carbon monoxide using the heat and light of the sun, at a rate of hundreds of μmol. h^{-1}. g^{-1}. Published in Nature Communications 2016, this report concluded that the large surface area and broadband visible/near infrared light-harvesting ability of silicon nanocrystals, coupled with the reducing power of silicon-hydride surface sites, synergistically played key roles in the carbon dioxide reduction reaction.

Most recently, we managed to double the reduction rate of carbon dioxide to carbon monoxide by doping the hydride-terminated silicon nanocrystals with phosphorous. Published in Advanced Sustainable Systems 2017 the improved reduction rate was attributed to the enhanced hydridic character of the surface silicon-hydride active sites induced by the n-doping effect.

Present

These foundational discoveries from hydride-terminated silicon nanocrystals, together with others in our group during the past five years, piqued our interest and inspired our foray into the wider fields of CO_2 nanomaterials chemistry, catalysis and chemical engineering approaches to synthetic fuels; a transition motivated by the desire to help ameliorate global warming and climate change.

The development of these research interests led to our group founding and spearheading the University of Toronto Solar Fuels team, a multi-disciplinary group of chemists and engineers whose goal is to convert CO_2 greenhouse gas to fuel and thereby close the carbon cycle (www.solarfuels.utoronto.ca). This is the backgound behind our decision to devote our ongoing and entire research effort to this worthwhile endeavor.

Innovative, significant and technologically relevant contributions having emerged from this early phase of our research in the field of solar fuels can be summarised as follows:

1. Discovery and development of novel classes of nanostructured metal oxide, metal-metal oxide and metal oxide-metal oxide materials that enable efficient photochemical and photothermal heterogeneous catalytic hydrogenation of CO_2 to CO, CH_4 and CH_3OH, using the entire range of the solar spectrum;

2. Experimental and theoretical studies of the energetics and dynamics of the "excited state" surface chemistry and catalytic reactions responsible for solar-powered hydrogenation of CO_2;

3. Recognition that frustrated Lewis pairs comprising proximal Lewis base hydroxyls and coordinatively unsaturated Lewis acid metal sites can exist in the surface of nanostructured metal oxide photocatalysts, and that these pairs are able to function as the photoactive sites in heterolytic H_2 dissociation to form surface metal-hydride and metal-hydroxide sites. This proves to be a key step in the heterogeneous hydrogenation of CO_2, where the 'solar advantage' is found in the enhanced Lewis basicity and Lewis acidity of the excited state compared to the ground state, which decreases the activation energy for the rate determining CO_2 reduction step;

4. Chemical tailoring of 'designer defects' in nanostructured metal oxides, which facilitate optimisation of solar-powered heterogeneous CO_2 hydrogenation;

5. Enabling photocatalyst and photoreactor engineering to improve the efficiency of solar-powered heterogeneous CO_2 hydrogenation.

This CO_2-to-synthetic fuels phase of our research has also turned out to be a fruitful research endeavor for my group, resulting in many breakthrough papers in high-impact journals, as seen in our portfolio of 2013-2017 publications.

Imagining the Future

Circular Economy in which natural resources used in manufacturing products for a consumer society are recycled to enable maximum benefits to both the environment and the economy, www.eucolight.org.

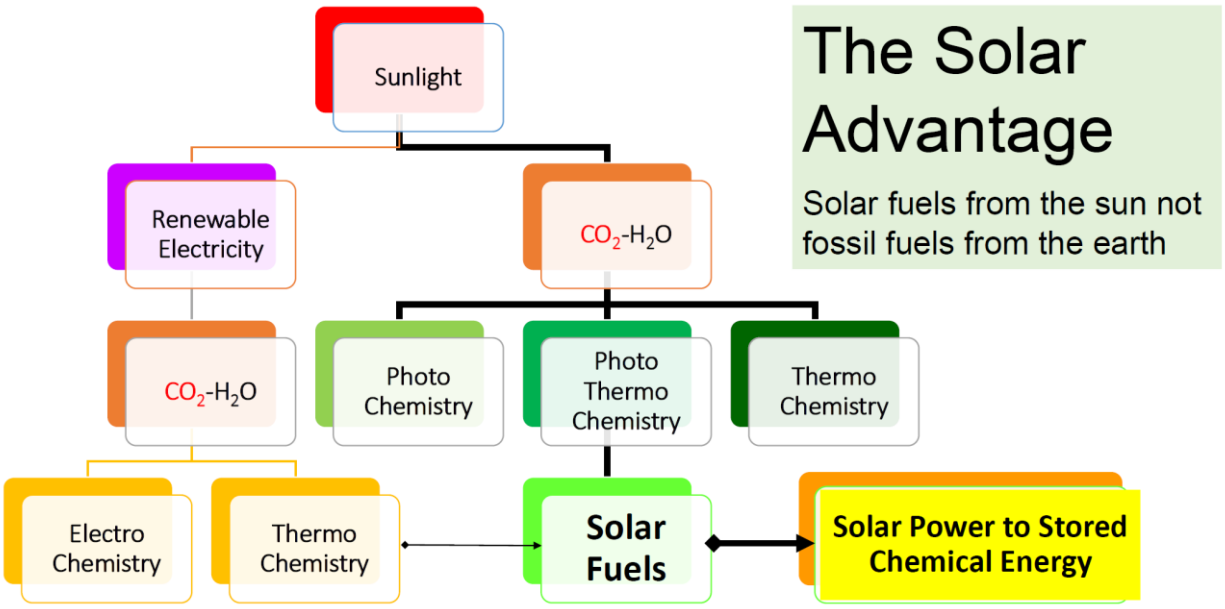
Canada, together with other countries, has embraced the opportunity to transition its unsustainable consumer economy to a sustainable one that "closes the loop" on the full life span of a product by recycling waste generated from manufacturing, consumption and use. The goal of this circular economy, illustrated in the accompaning scheme, is to bring benefits for both the environment and the economy by extracting the maximum value and use from all raw materials, products and waste, thereby fostering energy savings and reducing greenhouse gas emissions. This paradigm envisions carbon dioxide as a feedstock and asset, rather than a waste product and liability, one that can be converted into value-added chemicals and fuels for a carbon neutral carbon cycle.

Extraordinary problems facing society require extraordinary measures for achieving solutions. This is especially true of the greenhouse-gas-induced climate change facing the world today. We decided to rise to this challenge with an interdisciplinary team of chemists and engineers. Our thesis is that chemistry created the greenhouse gas effect by combusting legacy fossil fuels, and chemistry can reverse the effect by converting CO_2 into synthetic fuels, in a closed-carbon-cycle. To actualize this utopian idea of a green and sustainable future, one needs to discover nanostructured materials that can accomplish this conversion efficiently, safely, and economically on a large scale.

At the heart of this challenge lies the exceptionally high thermodynamic and kinetic stability of CO2. In the case of solar fuels, this requires the discovery of highly active photocatalysts and the development of high performance photoreactors. To meaningfully impact climate change, targeted catalysts must be able to make synthetic fuels from CO_2 at industrially practical scales and rates of conversion, while maintaining long-term performance stability. In addition, the catalyst must comprise earth-abundant, low-cost, non-toxic elements, to ensure economically viable and environmentally sound CO_2 refineries. This is no easy challenge and the climate

change clock is ticking.

Our experience and intuition drove us to choose one of six viable approaches to enable the conversion of CO_2 to fuels, namely, homogeneous catalysis, heterogeneous catalysis, bio-catalysis, photo-catalysis, electro-chemistry, photo-electrochemistry, solar thermal chemistry. We decided the clear choice was heterogeneous catalysis and the preferred source of power was sunlight. It is incredible to realize the sun bombards the Earth with enough light in one hour to satisfy our energy needs for a year. In the context of using sunlight to make fuel from carbon dioxide, it is important to appreciate the 'solar advantage'. This concept, illustrated in the scheme, depicts the use of sunlight directly to convert CO_2-H_2O to solar fuels through photochemistry, thermochemistry or photo-thermal chemistry means. Compare this pathway to the indirect route of first converting sunlight electricity, which subsequently converts CO_2-H_2O to solar fuels through electrochemistry or thermochemistry means.



Our group decided that heterogeneous catalysis is the most practical route to developing CO_2 solar refineries that, as a turnkey system, would seamlessly integrate with existing industrial infrastructure. To this end, we have been working on design rules and implementation strategies for the synthesis of novel classes of nanostructured materials with optimized composition, structure, size, shape and self-assembled architecture, in order to enable the heterogeneous catalytic conversion of gaseous CO_2 to fuels. Our first breakthrough has been exploitation of the entire wavelength range of the solar spectrum, using photothermal heterogeneous catalysis to make efficient use of both the light and heat of the sun to drive the conversion.

To this end, we have developed a suite of solar-activated, nanostructured catalysts that facilitate conversion of CO_2 into methanol, methane, and carbon monoxide. These catalysts enable the

energy of the sun to be stored in the chemical bonds of the products, which, in many cases, offer a direct substitute for the fossil-based products used as automotive fuels or for electricity production. Furthermore, synthetic liquid fuels offer a significantly higher volumetric energy density than batteries and have the capacity to store daily and seasonally intermittent renewable electricity at a large scale, thereby helping to balance supply and demand on the electricity grid. This innovation outcompetes alternative solutions, and foresees modular, self-contained CO_2 refining systems operating at industrial scales, and straightforwardly integrated into existing fossil-fuel-based infrastructure. These systems would operate as compartmentalized turnkey units to serve distributed emitters and remote communities with unique energy demands. This approach presents fast and flexible commercialization opportunities and is ideal for scale-up because such units can suit a wide range of applications, from individual households, to communities, to central power stations, thereby helping to mitigate financial risk. Our technological-readiness-level currently comprises engineered solar-powered methanol production and methane reforming lab-scale demonstration units, which are able to operate under industrially relevant conditions.

Through these small-scale, yet all-important, test reactors we can understand process performance in the presence of waste gases from existing industrial operations. A team of twelve young chemical engineering students is currently working on the energy and economic life cycle analysis of our envisioned solar powered CO_2 refinery as their final-year capstone project. We have teamed-up with the U of T Central Steam Facility to integrate our solar-powered CO_2 synthetic fuels system into their existing plant, in order to demonstrate the viability of our technology for reducing the carbon footprint of the university community. Such solar fuel refineries could help enable the energy transition toward a sustainable future by 2020. We are passionate and proud to work on this project as our social responsibility and for future generations.

Our work to date has been aimed at understanding the concepts and principles that underpin the gas-phase, light-assisted heterogeneous CO_2 reduction reaction. These early studies have set the stage for the next phase of our research, namely, discovery and optimization of high performance nanostructured catalysts for the solar-powered heterogeneous hydrogenation of CO_2 to synthetic fuels. In particular, it is essential to evaluate their activity, selectivity and stability, surface chemistry, kinetics and mechanisms under ideal reactor operating conditions of pressure, temperature, gas composition and flow rate. With this knowledge, best-performing photocatalysts can be scaled, and photoreactors designed, to enable the development of lab-scale demonstration units, and ultimately, pilot-scale plants for the conversion of CO_2 to synthetic fuels.

The focus of our planned research will be on the discovery of next-generation CO_2 conversion materials, through both experimental and theoretical methods, and the development of new and improved reactors and processes to enable these CO_2 conversions. This research will comprise:

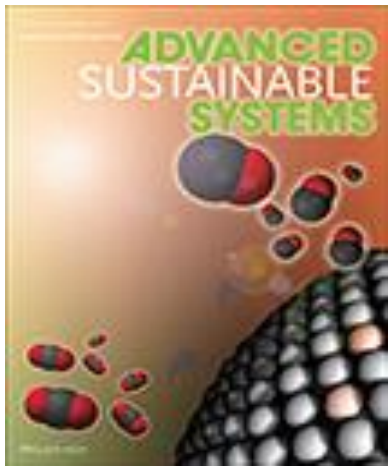
(i) Discovery, structure determination and property measurements of nanostructured materials active for light-assisted, gas-phase heterogeneous CO_2 reduction;
(ii) Evaluation of conversion rates, conversions and efficiencies for production of chemicals and fuels, such as CO, CH_4 and CH_3OH, through light-assisted, gas-phase heterogeneous catalytic reduction of CO_2;
(iii) Experimental in situ and computational studies of the surface chemistry, kinetics and mechanisms pertinent to thermochemically and photochemically driven CO2 conversion reactions.

These studies will be complemented by:

(iv) Optimizing the catalytic performance of materials;
(v) Developing material fabrication methodologies for up-scaling;
(vi) Developing and testing lab-scale demonstrators;
(vii) Evaluating effects of wavelength and intensity of light on CO_2 conversion rates, conversions and efficiencies;
(viii) Life cycle analysis - material, energy, economic flows and feasibility of developing a pilot CO_2 refinery.

Green Nanochemistry

Cover Illustrations 2011-2017



Green Nanochemistry

Solar Fuels Publications, 2014-2017

1. Alexandra Tavasoli, Geoffrey A. Ozin, 2018, Solar Dry Reforming, submitted.
2. Geoffrey. A. Ozin, Meikun Xia, Chenxi Qian, Lu Wang, Hong Wang, 2018, Greening of Ammonia
3. Michael Ertl, Corina Andronescu, Jonathon Moir, Mirijam Zobel Friedrich E. Wagner, Geoffrey Ozin, Wolfgang Schuhmann, Josef Breu, 2018, Mössbauerite – A New "Iron-Only" Oxygen Evolution Electrocatalyst, submitted.
4. Yuchan Dong, Kulbir Kaur Ghuman, Wenjie Zhou, Joel Y. Y. Loh, Abdinoor A. Jelle, Jia Jia, Paul N. Duchesne, Di Wang, Xiaoke Mu, Radian Popescu, Christian Kübel, Lu Wang, Le He, Mireille Ghoussoub, Laura M. Reyes, Qiang Wang, Nazir P. Kherani, Chandra Veer Singh, Geoffrey A. Ozin, 2018, Tailoring Surface Frustrated Lewis Pairs of $In_2O_{3-x}(OH)_y$ for Gas Phase Heterogeneous CO_2 Reduction by Isomorphous Substitution of In^{3+} with Bi^{3+}, submitted.
5. Hong Wang, Lu Wang, Qiang Wang, Shuyang Ye, Wei Sun, Yue Shao, Zhiping Jiang, Qiao Qiao, Pengfei Song, Debao Li, Le He, Xiaohong Zhang, Jiayin Yuan, Tom Wu, Geoffrey A. Ozin, 2018, Champion Electrocatalyst for Nitrogen Fixation at Ambient Conditions, submitted.
6. Lu Wang, Mireille Ghoussoub, Hong Wang, Yuchan Dong, Yue Shao, Athan Tountas, Thomas E. Wood, Hai Li, Wei Sun, Meikun Xia, Young Li, Shenghua Wang, Jia Jia, Chenyue Qiu, Chenxi Qian, Le He, Xiaohong Zhang, Geoffrey A. Ozin, 2018, Solar Methanol: Photocatalytic Hydrogenation of Carbon Dioxide with High Selectivity to Methanol at Atmospheric Pressure, 2017, submitted.
7. Abdinoor A. Jelle, Kulbir K. Ghuman, Paul G. O'Brien, Mohamad Hmadeh, Amit Sandhel, Doug D. Perovic, Chandra Veer Singh, Charles A. Mims, Geoffrey A. Ozin, 2018, Highly Efficient Ambient Temperature CO_2 Photomethanation Catalyzed by Nanostructured RuO_2 on a Silicon Photonic Crystal Support, *Advanced Energy Materials*, 8, 1702777.
8. Wong, A.P.Y., Sun, W., Qian, C., Jelle, A., Jia, J., Zheng, Z., Ghoussoub, M., Dong, Y., Ozin, G.A., 2017, Tailoring CO_2 Reduction with Doped Silicon Nanocrystals, *Advanced Sustainable Systems,* 1(11), DOI: 10.1002/adsu201700118 (front cover).
9. Ozin, G., 2017, "One-Pot" Solar Fuels, *Joule* 1, 19-23.
10. Jia, J., Wang, H., Ozin, G.A., 2017, Photothermal Catalyst Engineering: Hydrogenation of Gaseous CO_2 with High Activity and Tailored Selectivity, *Adv. Sci*. 4, 1700252 (back cover).
11. Wang, H., Jia, J., Wang, Q., Li, D., Qian, C., Wang, L., Min, S., Ma, C., Wu, T., Yuan, J., Antoniettie, M., Ozin, G.A., 2017, Efficient Electrocatalytic Reduction of CO_2 by Nitrogen-Doped Nanoporous Carbon/Carbon Nanotube Membranes - A Step towards the Electrochemical CO2 Refinery, *Angew. Chem*. 129, 7955- 7960.
12. Jia, J., Qian, C., Dong, Y., Li, Y-F, Wang, H., Ghoussoub, M., Butler, K.T., Walsh, A., Ozin, G.A., 2017, Heterogeneous Catalytic Hydrogenation of CO_2 by Metal Oxides: Defect Engineering - Perfecting Imperfection, *Chem. Soc. Rev.* 46, 4631 – 4644.

13. Su, B-L, Deparis, O., Hasan, T., Ye, J., Li, Y., Wu, M., Ozin, G., 2017, Slow Photons for Photocatalysis and Photovoltaics, *Adv. Mater*. 29, 1605349.
14. Jelle, A.A., Hmadeh, M., O'Brien, P.G., Perovic, D.D., Ozin, G.A., 2016, Photocatalytic Properties of all Four Polymorphs of Nanostructured Iron Oxyhydroxides, *ChemNanoMat* 2, 1047-1054.
15. Hoch, L.B., Szymanski, P., Ghuman, K.K., He, L., Liao, K., Qiao, Q., Reyes, L.M., Zhu, Y., El-Sayed, M.A., Singh, C.V., Ozin, G.A., 2016, Carrier Dynamics and the Role of Surface Defects: Designing a Photocatalyst for Gas-Phase CO_2 Reduction, *Proc. Nat. Acad. Sci*., 113, E8011-E8020.
16. Ghoussoub, M., Yadav, S., Ghuman, K.K., Ozin, G.A., Singh, C.V., 2016, Metadynamics-biased ab initio Molecular Dynamics Study of Heterogeneous CO2 Reduction via Surface Frustrated Lewis Pairs, *ACS Catal*. *6*, 7109–7117.
17. Hoch, L.B., O'Brien, P.G., Jelle, A., Sandhel, A., Perovic, D.D., Mims, C.A., Ozin, G.A., 2016, Nanostructured Indium Oxide Coated Silicon Nanowire Arrays: A Hybrid Photothermal/Photochemical Approach to Solar Fuels, *ACS Nano* 10, 9017-9025.
18. Ghuman, K., Hoch, L., Wood, T., Mims, C., Singh, C., Ozin, G., 2016, Surface Analog of Molecular Frustrated Lewis Pairs in Heterogeneous Catalysis, *ACS Catalysis* 6, 5764-5770.
19. Sun, W., Qian, C., He, L., Jia, J., O'Brien, P.G., Reyes, L.M., Wood, T.E, Mims, C.A., Ozin, G.A., 2016, Heterogeneous Reduction of CO_2 by Hydride-Terminated Silicon Nanocrystals, *Nature Commun.* 7, 12553.
20. Sun, W.; Qian, Chen, K., Ozin, G.A., 2016, Silicon Nanocrystals: It's Simply a Matter of Size, *ChemNanoMat* 2, 847-855.
21. Jia, J., O'Brien, P.G., He, L., Fei, T., Burrow, T.E., Reyes, L.M., Qiao, Q., Liao, K., Varela, M., Pennycook, S.J., Hmadeh, M., Helmy, A.S., Kherani, N.P., Perovic, D.D., Ozin, G.A., 2016, Ambient Temperature Visible and Near Infrared Photothermal Catalysed Hydrogenation of Gaseous Carbon Dioxide over Nanostructured Pd@Nb_2O_5*, Adv. Sci.* 3, DOI: 10.1002/advs.201670051 (front cover).
22. He, L., Wood, T.E., Wu, B., Dong, Y., Hoch, L., Reyes, L., Wang, D., Kübel, C., Qian,C., Jia, J., Liao, K., O'Brien, P.G., Sandhel, A., Loh, J.Y.Y., Szymanski, P., Kherani, N.P., Sum, T.C., Mims, C.A., Ozin, G.A., 2016, Spatial Separation of Charge Carriers in $In_2O_{3-x}(OH)_y$ Nanocrystal Superstructures for Enhanced Gas Phase Photocatalytic Activity, *ACS Nano* 10, 5578-5586.
23. Hoch, L.B.; He, L.; Qiao, Q.; Liao, K.; Reyes, L.M.; Ozin, G.A., 2016, Effect of Precursor Selection on the Photocatalytic Performance of Defected Indium Oxide Nanomaterials for Gas-Phase CO_2 Reduction, *Chem. Mater*. 28, 4160-4168.
24. Moir, J.W., Sackville, E.V., Hintermair, U., Ozin, G.A., 2016, Kinetics vs. Charge Separation: Improving the Activity of Stoichiometric and Non-Stoichiometric Hematite Photoanodes Using a Molecular Iridium Water Oxidation Catalyst, *ACS J. Phys. Chem. C* 120, 12999-13012.
25. Ghuman, K.K., Hoch, L.B., Szymanski, P., Loh, J.Y.Y., Kherani, N., El-Sayed, M.A., Ozin, G.A., Singh, C.V., 2016, Photoexcited Surface Frustrated Lewis Pairs for Heterogeneous Photocatalytic CO_2 Reduction, *J. Am. Chem. Soc*. 138, 1206-1214.
26. Ghuman, K.K., Wood, T.E., Hoch, L.B., Mims, C.A., Ozin, G.A., Singh, C.V., 2015, Illuminating CO_2 reduction on frustrated Lewis pair surfaces: investigating the role of surface

hydroxides and oxygen vacancies on nanocrystalline $In_2O_{3-x}(OH)_y$, *Phys. Chem. Chem. Phys.* 17, 14623-14635.
27. Ozin, G.A., 2015, You Can't have an Energy Revolution without Materials, Chemistry and Catalysis, *Energy and Environmental Science*, DOI: 10.1039/C5EE00907C.
28. Moir, J., Soheilnia, N., Liao, K., Burch, K., Ozin, G.A., 2015, Activation of Ultrathin Films of Hematite for Photoelectrochemical Water Splitting via H_2 Treatment, *ChemSusChem* 9, 1557-1567 (back cover).
29. Chen, C.; Soheilnia, N.; Hoepfner, V.; Hoch, L.B.; Moir, J.; Qian, C.; Mahler, B.; He, L.; Ozin, G.A., 2015, Morphology-Controlled Indium Oxide Nanostructures Vertically Grown on Fluorine-Doped Tin Oxide Enhance the Performance of Photo-electrochemical Water Oxidation, *Nanoscale* 7, 3683 – 3693.
30. Ozin, G.A., 2015, Throwing New Light on the Reduction of CO_2, *Adv. Mater*. 27, 1957-1963.
31. Hoch, L.B.; Wood, T.E.; O'Brien, P.G.; Liao, K.; Reyes, L.M.; Mims, C.A.; Ozin, G.A., 2014, The Rational Design of a Single-Component Photocatalyst for Gas-Phase CO_2 Reduction Using Both UV and Visible Light, *Adv. Sci.* 1, 1400013 (front cover).
32. O'Brien, P., Wood, T., Hoch, L., Sandhel, A., Jelle, A., Mims, C., Ozin, G.A., 2014, Photomethanation of Gaseous CO2 over Ru/Silicon Nanowire Catalysts with Visible and Near-Infrared Photons, *Adv. Sci*. 1, 1400001.
33. Mahler, B., Ozin, G.A., 2014, Colloidal Synthesis of 1T-WS2 and 2H-WS2 Nanosheets: Applications for Photocatalytic Hydrogen Evolution, *JACS* 136, 14121-14127.
34. Hmadeh, M., Hoepfner, V., Ozin, G.A., 2014, Photocatalytic Hydrogen Evolution over Platinum Nanocrystal Decorated Tri-Niobium Hepta-Oxide Hydroxide Nb_3O_7OH Nanorods, *ChemSusChem*. 7, 2104-2111 (back cover).
35. Mirtchev, P., Liao, K., Jaluague, E., Qiao, Q., Tian, Y., Varela, M., Burch, B.S., Pennycook, S.J., Perovic, D.D., Ozin, G.A., 2014, Fe_2O_3-Cu_2O Heterostructured Nanocrystals, *J. Mater. Chem*. A 2, 8525-8533.

Green Nanochemistry

Nano Silicon Publications 2011-2017

1. Qian, C., Zhao, J., Sun, Y., Lee, H.R., Luo, L., Makaremi, M., Mukherjee, S., Wang, J., Zu, C., Xia, M., Wang, C., Veer Singh, Ozin, G.A., C., Cui, Y., 2017, Electrolytephobic Surface Enables High Initial Coulombic Efficiencies for Porous Silicon Anodes, submitted.
2. Chen, D., Sun, W., Qian, C., Wong, A.P.Y., Reyes, L.M., Ozin, G.A., UV-Blocking Photoluminescent Silicon Nanocrystal/Polydimethylsiloxane Composites, 2017, *Advanced Optical Materials* 5 (10), DOI: 10.1002/adom.201700237.
3. Wong, A.P.Y., Sun, W., Qian, C., Jelle, A.A., Jia, J., Zheng, Z., Dong, Y., Ozin, G.A., 2017, Tailoring CO2 Reduction with Doped Silicon Nanocrystals, *Advanced Sustainable Systems* 1 (11), DOI: 10.1002/adsu.201700118.
4. Kusi-Appiah, A.E., Mastronardi, M.L., Qian, C., Chen, K.K., Ghazanfari, L., Prommapan, P., Kübel, C., Ozin, G.A., Lenhert, S., 2017, Enhanced Cellular Uptake of Size-Separated Lipophilic Silicon Nanoparticles, *Scientific Reports*, Nature Publishing Group, 7, 43721.

5. Sun, W., Qian, C., He, L., Ghurman, K.K., Wong, A.P.J., Jia, J., Jelle, A.A., O'Brien., P.G., Reyes, L.M., Wood, T.E., Helmy, A.A., Mims, C.A., Veer Singh, C., Ozin, G.A., 2016, Heterogeneous Reduction of Carbon Dioxide by Hydride-Terminated Silicon Nanocrystals, *Nature Communications* 7, 12553, doi:10.1038/ncomms12553.
6. Sun, W., Qian, C., Chen, K.K., Ozin, G.A., 2016, Silicon Nanocrystals: It's Simply a Matter of Size, 2016, *ChemNanoMat* 2 (9), 847-855 (front cover).
7. Sun, W., Qian, C., Cui, Xiao, S., Ozin, G.A., 2016, Silicon Monoxide - A Convenient Precursor for Large Scale Synthesis of Near Infrared Emitting Monodisperse Silicon Nanocrystals, *Nanoscale*, 8, 3678-3684.
8. Chen, D., Sun, W., Qian, C., Reyes, L., Wong, A., Dong, Y., Jia, J., Chen, K., Ozin, G.A., 2016, Porous NIR Photoluminescent Silicon Nanocrystals-POSS Composites, *Adv. Funct. Mater*. 26 (28), 5102-5110
9. Chen, K., Liao, K., Casillas, G., Li, Y., Ozin, G.A., 2016, Cationic Silicon Nanocrystals with Colloidal Stability, pH-Independent Positive Surface Charge and Size Tunable Photoluminescence in the Near-Infrared to Red Spectral Range, *Adv. Sci*. 3, (front cover)
10. Mastronardi, M., Chen, K.K., Liao, K., Casillas, G., Ozin, G.A., 2015, Size-Dependent Chemical Reactivity of Silicon Nanocrystals with Water and Oxygen, *J. Phys. Chem. C* 119, 826-834.
11. Rinck, J., Schray, K., Kubel, C., Powell, A., Ozin, G.A., 2015, Size Dependent Oxidation of Monodisperse Silicon Nanocrystals with Allylphenylsulfide Surfaces, *Small* 11, 335-340 (front cover).
12. Chen, K., Mastronardi, M., Kübel, C., Ozin, G.A., 2015, Size-selective separation and purification of 'water-soluble' organic-capped brightly-photoluminescent silicon nano-crystals, *Particle & Particle Systems Characterization* 32, 301-306.
13. Qian, C., Sun, W., Wang, L., Chen, C., Liao, K., Wang, W., Jia, J., Hatton, B., Casillas, G., Kurylowicz, M., Yip, C., Mastronardi, M., Ozin, G., 2014, Non-Wettable, Oxidation Stable, Brightly-Luminescent, Perfluorodecyl-Capped Silicon Nanocrystal Film, *J. Amer. Chem. Soc.* 136, 15849-15852.
14. Sun, W., Qian, C., Mastronardi, M., Wei, M., Ozin, G.A., 2013, Hydrosilylation Kinetics of Silicon Nanocrystals, *Chem. Commun*. 49, 11361-11363.
15. Maier-Flaig, F., Kubel, C., Rinck, J., Bocksrocker, T., Scherer, T., Prang, R., Powell, A., Ozin, G.A., Lemmer, U., 2013, Looking Inside a Working SiLED, *Nano Letters* 13, 3539-3545.
16. Maier-Flaig, F., Rinck, J., Stephan, M., Bocksrocker, T., Bruns, M., Kubel, C., Powell, A., Ozin, G.A., Lemmer, U., 2013, Multicolor Silicon Light Emitting Diodes (SiLEDs), *Nano Letters* 13, 475-480.
17. Mastronardi, M.L., Henderson, E.J., Puzzo, D.P., Ozin, G.A., 2012, Small Silicon Big Opportunities: The Development and Future of Colloidally-Stable Monodisperse Silicon Nanocrystals, *Adv.Mater*. 24, 5890-5898 (front cover).
18. Maier-Flaig, M., Henderson, E.J., Valouch, S., Klinkhammer, S., Kübel, C., Ozin, G.A., Lemmer, U., 2012, Photophysics of Organically-Capped Silicon Nanocrystals – A Closer Look into Silicon Nanocrystal Luminescence using Low Temperature Transient Spectroscopy, *Chem. Phys.* 405, 175-180.
19. Mastronardi, M.l., Henderson, E.J., Puzzo, D.P., Chang, Y.L., Wang, Z.B., Helander, M.G Jeong, J., Kherani, N.P., Lu, Z., Ozin, G.A., 2012, Silicon Nanocrystal OLEDs: Effect of Organic Capping Group on Performance, *Small* 8, 3647-3654 (inside front cover).

20. Mastronardi, M.L., Maier-Flaig, F., Faulkner, D., Henderson, E.J., Kübel, K., Lemmer, U., Ozin, G.A., 2012, Size-Dependent Absolute Quantum Yields for Size-Separated Colloidally-Stable, Silicon Nanocrystals, *Nano Letters*, 12, 337-342.
21. Mastronardi, M.L., Hennrich, F., Henderson, E.J., Maier-Flaig, F., Blum, C., Reichenbach, J., Lemmer, U., Kübel, C., Wang, D., Kappes, M.M., Ozin, G.A., 2011, Preparation of Monodisperse Silicon Nanocrystals Using Density Gradient Ultracentrifugation, *J. Amer. Chem. Soc*. 133, 11928-11931.
22. Henderson, E.J., Shuhendler, A.J., Prasad, P., Baumann, V., Maier-Flaig, F., Wu, X.Y., Ozin, G.A., 2011, Colloidally Stable, Silicon Nanocrystals with Near-Infrared Photoluminescence for Biological Fluorescence Imaging, *Small* 7, 2507-2516.
23. Puzzo, D.P., Henderson, E.J., Helander, M.G., Wang, Z.B., Ozin, G.A., Lu, Z., 2011, Visible Colloidal Silicon Light Emitting Diode, *Nano Letters* 11, 1585-1590.
24. Xie, Z., Henderson, E.J., Dag, O., Wang, W., Lofgreen, J., Kübel, C., Scherer, T., Brodersen, P.M., Gu, Z.Z., Ozin, G.A., 2011, Periodic Mesoporous Hydridosilica – Synthesis of an "Impossible" Material and its Thermal Transformation into Brightly Photoluminescent Periodic Mesoporous Nanocrystal Silicon-Silica Composite, *J. Amer. Chem. Soc*. 133, 5094-5102.