

## Towards Global Artificial Photosynthesis (Global Solar Fuels): Energy, Nanochemistry, and Governance

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### Introduction

This special open access edition of the *Australian Journal of Chemistry* represents a collection of papers from the first international conference dedicated to creating a Global Artificial Photosynthesis (GAP) or Global Solar Fuels (GSF) project, held at Lord Howe Island on 14–18 August 2011. Conceived and coordinated by the author of this article, the conference had endorsement from the UNESCO Natural Science Sector and was an official event of the UNESCO 2011 International Year of Chemistry. The federal Department of Industry, Innovation, Science and Research (DIISR, as it was then called) contributed to the funding, as did the Australian National University (ANU) College of Medicine, Biology and the Environment and ANU College of Law. Speakers included over 50 national and international experts in various aspects of artificial photosynthesis, as well as related areas including photovoltaics, hydrogen fuel cells, quantum coherence in electron transfer, and international governance systems.

Lord Howe Island is a jewel in the UNESCO World Heritage List with its unique southerly coral reefs, mountain microclimate, flora, and fauna (Fig. 1). It provided a perfect symbolic backdrop for discussions about how nanochemistry in particular could devise new mechanisms for powering the planet for this and future generations and what governance structures could assist our move from the Anthropocene towards what has been termed the Sustainocene era.<sup>[1]</sup> An expert naturalist (Ian Hutton) who was closely involved in that UNESCO listing process for Lord Howe Island gave a presentation to the conference about the energy and pollution challenges facing this beautiful island and donated copies of his illustrated book as gifts for the conference presenters.

An innovative feature of the inaugural GAP conference was the involvement of over 40 high-achieving senior year Australian high school science students (from James Ruse Agricultural

College in Sydney, Geelong Grammar in Victoria and Narrabundah High School, Radford College, and Canberra Boys Grammar in the ACT).

Proceedings began each day at 8 a.m. in the beautifully renovated 1930s-era community hall overlooking the lagoon. There were no parallel sessions and afternoons were free to allow collaborative discussions whilst exploring the island. The island community generously assisted with accommodation and food. Sessions recommenced for a couple of hours after dinner. Each session was constructed to be a multidisciplinary mix of topics and concluded with short presentations by the high school students that provided an insightful and often hilarious commentary on the presentations. Ending most evenings was a panel discussion on how to advance governance of global artificial photosynthesis.

We are very grateful that many of the GAP conference presenters have produced contributions for this special edition of the *Australian Journal of Chemistry*. Amongst these and other attendees were world leaders in many fields connected with solar fuels. Their active contributions during question time vitally helped shape the papers in this issue. Videos of their talks are available at the GAP conference website: <http://law.anu.edu.au/coast/tgap/conf.htm>. A brief survey of the overall GAP conference contributions is important in understanding the unusually high quality, interdisciplinary context in which this edition of the journal evolved.

Some notable presentations at the GAP conference included those on the use of gallium phosphide nanowires in light-driven hydrogen production by Peidong Yang, one of the leaders of the newly established Joint Centre on Artificial Photosynthesis at Berkeley.<sup>[2]</sup> Dan Nocera from MIT spoke about his ‘artificial leaf’ that configures a triple junction silicon photovoltaic cell with a cobalt catalyst (Co-OEC) for O<sub>2</sub> evolution and a ternary alloy (NiMoZn) as the H<sub>2</sub>-evolving catalyst.<sup>[3]</sup> Professor Nocera



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Fig. 1. View from Lord Howe Island during the *Towards Global Artificial Photosynthesis* conference, August 2011.

indicated that X-ray spectroscopy supported his claim that his self-assembling, earth abundant Co-OEC was a structural relative of the  $\text{Mn}_3\text{CaO}_4$ -Mn cubane of the OEC in Photosystem II (PSII), but with Co replacing the Mn and the cubane extended in a corner-sharing head-to-tail dimer. It was thus fascinating to see his interaction with another presenter, Nobuo Kamiya of Osaka University, a lead author on the most recent detailed publication on the cubane configuration of the OEC in PSII to a level of 1.9 Å (1.9 Ångströms or  $1.9 \times 10^{-10}$  m) using an electron density map to locate all of the metal atoms of what Professor Kamiya termed the  $\text{Mn}_4\text{CaO}_5$  cluster.<sup>[4]</sup> The author of this article presented a study of governance challenges and options for a GAP-powered world.<sup>[5]</sup>

Craig Hill of Emory University spoke at the GAP conference of his research involving a polyoxometalate water oxidation catalyst capable of strongly binding multiple transition metal centres proximal to one another, so facilitating multi-electron processes such as the 4-electron oxidation of  $\text{H}_2\text{O}$  to  $\text{O}_2$ .<sup>[6]</sup> David Tiede of the Argonne National Laboratory reported on a new strategy for solar fuel production involving insertion of high abundance first-row transition metal molecular catalysts (cobaloxime) into Photosystem I (PSI) as a mechanism for  $\text{H}_2$  production.<sup>[7]</sup> Klaus Hellgardt from Imperial College London spoke of developing a flat plate photoelectrochemical (PEC) reactor for hydrogen production.<sup>[8]</sup> Gary Brudvig from Yale University and Chris Moser from University of Pennsylvania independently discussed how insights from the natural photosynthetic system might develop bio-inspired materials for photochemical water oxidation and fuel production.<sup>[9]</sup> Kylie Catchpole from the ANU evaluated enhancing the light capture part of artificial photosynthesis with plasmonic solar cells.<sup>[10]</sup> Andrew Blakers, also from the ANU, discussed his innovative 'sliver' photovoltaic cells, but also the challenge posed by the reduction of solar electricity prices and intercontinental super electricity grids.<sup>[11]</sup>

A sense of the high quality and wide research range of the talks at the GAP conference (but also the necessary context in

which to evaluate the significance of the papers in this volume) is conveyed by the following additional brief survey. GAP presentations were made on  $\text{H}_2$  evolution photocatalysts based on  $\text{SrTiO}_3$  doped with Cr, tantalum oxynitrides and organic Dyes (Ryu Abe, Hokkaido University), use of cyclic porphyrin nanorings as artificial light-harvesting antennae (Naoki Aratani, Kyoto University), cyanobacterial  $\text{H}_2$  production as a model for efficient electron transfer (Eva-Mari Aro, University of Turku), nafion/carbon nanotube-based membranes for mixed proton and electron conduction after water splitting (Stefano Bianco, Italian Institute of Technology), using plasma to engineer nanoparticle  $\text{TiO}_2$  light-absorbing thin films and efficient proton exchange membrane fuel cells for  $\text{H}_2$  production (Rod Boswell and Christine Charles, ANU), the relationship of artificial photosynthesis to the European Union's renewable energy and climate change policy (Katharina Brinkert, Uppsala University), whether low cost PV units will make chemical storage of solar energy unnecessary (Gavin Conibeer, University of New South Wales [UNSW]), as well as balancing of quantum coherent dynamics dissipation and dephasing in interconnected nanoscale components of an artificial photosynthetic system (David Coker, University College Dublin and Boston University).

Further GAP presentations providing a background to the papers in this volume included insights from the study of natural light-harvesting complexes (Roberta Croce, VU University, Amsterdam), use of purified samples of the antenna complexes of photosynthetic bacteria to study quantum physics-based exciton energy transfer (Arvi Freiberg, University of Tartu), use of self-assembled quantum dots and nanowires for efficient PV devices (Lan Fu, ANU), a survey of each unit in artificial photosynthesis and a discussion on the use of  $\text{H}_2$  peroxide as a fuel (Shunichi Fukuzumi, Osaka University), studies of the efficiencies in  $\text{CO}_2$  reduction of different forms of RuBisCO (Jill Gready, ANU), manipulation of donor-acceptor composition and distance in fullerenes and carbon nanotubes to enhance charge separation quantum yields and lifetimes (Dirk Guldi, Friedrich-Alexander-Universitaet), international collaborations

around co-location of water oxidation and reduction catalysts on base semiconductors (Hongxian Han, Dalian Institute of Chemical Physics) and the study of biological systems to refine design of  $H^+$  coupled electron transfer (Felix Ho, Uppsala University).

Other GAP presentations considered mono-site ruthenium catalysts with high turnover rate for hundreds of thousands of cycles (Khurram Joya, University of Engineering and Technology, Lahore), problems of globally regulating new technologies (Michael Kirby, AC), use of NMR to detect photochemically induced dynamic nuclear polarisation in photosynthetic reaction centres (Jorg Matysik, Leiden Institute of Chemistry), a critical analysis of quantum mechanisms in relation to artificial photosynthesis (Gerard Milburn, University of Queensland), layer-by-layer assembly of sintered nanocrystal solar cells (Paul Mulvaney, University of Melbourne), military implications of GAP (Hitoshi Nasu, ANU), advancing artificial photosynthesis with renewable energy incentive laws (James Prest, ANU), developmental opportunities for GAP (Rocque Reynolds and Michael Heinrich, Southern Cross University), two-dimensional electronic spectroscopy on the PSII reaction centre for information on the quantum effects involved in photosynthesis (Elisabet Romero, VU University, Amsterdam), long-range quantum coherence in photosynthetic excitation energy transfer (Tom Stace, University of Queensland), electron transfer at semiconductor quantum dots and metal oxide nanostructures (Yasuhiro Tachibana, RMIT University), a ruthenium-cobalt oxide nanoparticle catalyst for photochemical water oxidation (Anders Thapper, Uppsala University), site, rate and mechanism of photoprotective quenching in cyanobacteria (Herbert van Amerongen, Wageningen University), ferritin as a charge separation photocatalyst (Richard Watt, Brigham Young University), optimising carbon dioxide fixation and solar energy conversion inside a long-lived photosynthetic foam derived from the Tungara frog (David Wendell, University of Cincinnati), tandem photoelectrochemical cells for direct water splitting (Haixiang Zhang, UNSW), tuning electrolytes for enhanced photooxidation of water (Chuan Zhao, UNSW) and a quantum mechanical study of ZnO- and  $TiO_2$ -based dye sensitised solar cells (Giancarlo Cicero, Politecnico of Torino).

## Overview of this Edition

The above background, as mentioned, facilitates appreciation of the extent to which the papers selected for this volume are not only beautifully representative of the interdisciplinary spirit and quality of the GAP conference, but are at the cutting edge of their respective fields. Those papers will now be specifically introduced.

### *Institutional Approaches*

The initial paper in this special edition by Ann Magnuson and Stenbjorn Styring ('Molecular Chemistry for Solar Fuels: From Natural to Artificial Photosynthesis') provides a valuable overview of the field. The authors highlight the policy priority that as the global population approaches 10 billion by 2050, future energy carriers allow the non-fossil fuel legacy world to increase their standard of living without deleterious impacts on the global climate or on security as well as responding to the understanding that most of the world's energy is used as fuel rather than electricity. They highlight that even with a modest 10% energy conversion efficiency, only 0.1% of the earth's surface need be utilised to capture photons to provide our energy

needs. The paper considers the indirect options for making a solar fuel: processes that convert sunlight into the intermediaries of electricity or biomass. They then evaluate direct molecular approaches for light-driven water oxidation via catalysts that are amenable to fine tuning. They further consider indirect non-molecular systems where catalysis occurs on metal surfaces, semiconductors or nano-structured materials, as well as semi-direct systems involving photosynthetic microorganisms. The paper concludes by highlighting some of the main challenges in the field, including the race to develop non-molecular oxides of cobalt instead of manganese.<sup>[12]</sup>

The paper by Johannes Messinger ('An Institutional Approach to Solar Fuels Research') flows naturally on from this by providing a valuable case study on how discrete solar fuels projects are being established around the world. As the author notes, such organisations gain from physical co-location that stimulates spontaneous contacts and collaborations across traditional disciplinary borders: chemistry departments being located next to those of plant physiology, ecology, biophysics, and physics to facilitate common utilisation of electron microscopy, vibrational spectroscopy, NMR, mass spectrometry, proteomics, biochemical imaging, greenhouse facilities, and computational equipment. The capacity of such a structure to create high profile projects that attract funding is a notable feature.<sup>[13]</sup>

An institutional approach to solar fuels is also reflected in the paper by Gerry Swiegers, Doug MacFarlane, David Officer, Amy Ballantyne, Danijel Boskovic, Jun Chen, Charles Dismukes, Graeme Gardner, Rosalie Hocking, Paul Smith, Leone Spiccia, Pawel Wagner, Gordon Wallace, Bjorn Winther-Jansen and Orawan Winther-Jansen ('Towards Hydrogen Energy: Progress on Catalysts for Water Splitting'). The paper details research at the Australian Research Council's Centre of Excellence for Electromaterials Science (ACES) at Monash University and University of Wollongong in three areas of hydrogen-based energy technology. The first of these involves work suggesting that many recently discovered active Mn or Co molecular or inorganic water oxidation catalysts (for example, the Co-pi catalyst of GAP presenter Dan Nocera<sup>[14]</sup> or the Co-polyoxotungstate catalyst of GAP presenter Craig Hill<sup>[15]</sup>) utilise a cubane core that structurally resembles the catalytic core in the PS-II WOC. The second area involves the study of conducting polymers as electro-catalysts, particularly utilising heterojunctions so that photo-excitation in one conducting polymer followed by rapid charge separation across the junction suppresses recombination. The third area investigates the efficacy of nanostructured porphyrin arrays to drive water splitting either as the light-harvesting component or the oxidation or reduction catalyst.<sup>[16]</sup>

### *Light-Harvesting*

The starting point of any practical solar fuel system is harvesting of sunlight and a critical part of this is the understanding that efficiencies may be improved by incorporating quantum coherence techniques. The paper by Gabriela Schlau-Cohen and Graham Fleming from Lawrence Berkeley National Laboratory ('Structure, Dynamics, and Function in the Major Light-Harvesting Complex of Photosystem II') shows how two-dimensional electronic spectroscopy (2DES) is used to study the pigment-protein complexes (PPCs) in the light-harvesting complex of PSII (LHCII). It reveals dense packing of the PPCs (they comprise 80% of the thylakoid membrane) which not only

allows maximal absorption of all polarisations of incident sunlight, but gives rise to strong electronic coupling and ultrafast unidirectional energy transfer with quantum coherence that allows the excitation to reach the reaction centre before other photochemical processes (quenching) can occur. The authors conclude that such characteristics should be included in any practical light-harvesting device.<sup>[17]</sup>

#### *Electron Transport*

The next paper by Joseph Hughes and Elmars Krausz from ANU ('The Chemical Problem of Energy Change: Multi-Electron Processes') follows on nicely in evaluating the centrality of the relatively poorly understood role of multi-electron processes in the ultrafast kinetics, energy-trapping events, and catalytic four-electron water oxidation chemistry of PSII. An important aspect of such research is proton-coupled electron transfer where multi-electron aspects do not sit easily within the dominant Marcus Theory framework. The authors generalise that new avenues of chemistry research leading to inexpensive, small-scale, portable solar-to-fuel energy devices will open up through evaluation of the hypothesis that if the energy barrier producing stepwise single electron transfer intermediate states is sufficiently greater than another reaction pathway that involves the simultaneous or cooperative transfer of two electrons, then the latter will be preferred.<sup>[18]</sup>

#### *Elucidating Fine Structure*

The significance to artificial photosynthetic constructions of the paper by GAP presenter Nobuo Kamiya and others on the cubane configuration of the OEC in PSII to a level of 1.9 Å has already been highlighted.<sup>[19]</sup> In this edition, Ron Pace and Rob Stranger of the ANU ('The Biomimetic Inspiration for Renewable Hydrogen Fuel Production from Water Oxidation within Artificial Photosynthesis') detail how their high-level computational chemical analyses of this structure reveal that one region of the Mn<sub>4</sub>/Ca cluster is dominantly involved in substrate water binding, while a separate Mn is principally responsible for the redox accumulation function, acting as a 'battery', and so is capable of being replaced by another constant voltage electron sink (i.e. an electrode). The authors note that amongst potential metal catalysts, Mn is unique in that its values are consistently poised from oxidation level II to IV to fit precisely into the narrow gap of redox potentials required for OEC function. Various similarities between Mn and Co catalyst systems are being examined by these computational methods and the authors posit that the resultant system may work best with 'light excluded' electric power input, including that from the grid.<sup>[20]</sup>

The paper by Rosalie Hocking, Shery Chang, Doug MacFarlane, and Leone Spiccia from Monash University ('Preparation and Characterization of Catalysts for Clean Energy: A Challenge for X-rays and Electrons') opens a group of papers in this edition considering the problem of how to construct an effective water-splitting catalysis system for solar fuels. The authors explain that approaches to improving the efficiency of water-splitting can involve studying how enzymes (such as hydrogenase) catalyse hydrogen oxidation processes in biology, or investigating materials such as photocatalysts (TiO<sub>2</sub>, WO<sub>3</sub>, MnO<sub>2</sub>) and electrocatalysts (RuO<sub>2</sub>, IrO<sub>2</sub>, Co-Pi). Yet, the most efficient materials approach to water splitting reported involves a catalyst (Cu<sub>2</sub>O, Al-doped ZnO, TiO<sub>2</sub> and Pt) which loses activity after one hour in operation.<sup>[21]</sup> The authors highlight the importance of elucidating the atomic and molecular level

structure of a material before, during, and after catalysis. They point out that X-ray diffraction allows fine characterisation of bulk scale single crystals and, at the other end of the materials spectrum, inorganic spectroscopic techniques correlated with computational methods can discern equally well the molecular structure of a metal centre via its electronic transitions and/or magnetic signature. The authors then focus on X-ray absorption spectroscopy (XAS) (especially the X-ray absorption near edge structure [XANES] and extended X-ray absorption fine structure [EXAFS]) and transmission electron microscopy (TEM) as important techniques for elucidating the details of catalysis materials falling between these extremes. They apply XAS in particular to a molecular mimic of PSII, a tetranuclear manganese cluster inserted into a Nafion polymer matrix, to discover what component was responsible for the electro-catalysis.<sup>[22]</sup>

Adam Lee from Cardiff University ('Active Site Elucidation in Heterogeneous Catalysis via In Situ X-Ray Spectroscopies') similarly explores how recent breakthroughs in optic, detector, and reactor cell designs, in conjunction with global access to high energy radiation facilities, are helping in situ and bulk X-ray spectroscopies to identify and probe the active catalytic sites in wide-ranging liquid and gas phase chemistry and so assist in the development of (bio)inorganic nanostructured architectures for future solar fuel and chemicals synthesis.<sup>[23]</sup>

#### *Developing Catalysts*

Michael Nolan and Anna Iwaszuk from the Tyndall National Institute, and Hiroaki Tada from Kinki University ('Molecular Metal Oxide Cluster-Surface Modified Titanium (IV) Dioxide Photocatalysts'), review recent experimental and theoretical studies on the iron oxide-modified anatase/rutile and tin oxide-surface modified anatase TiO<sub>2</sub> photocatalysts. The former, for example, displays a narrowed band gap, giving visible light absorption compared with pure TiO<sub>2</sub>.<sup>[24]</sup>

The paper by Beniamino Iandolo and Michael Zäch from Chalmers University of Technology ('Enhanced Water Splitting on Thin-Film Hematite Photoanodes Functionalized with Lithographically Fabricated Au Nanoparticles') highlights why hematite or iron oxide ( $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>) is arguably preferable to Co and Mn as a catalyst in the race for development of a commercially viable device for water splitting-based solar fuels because of its low cost, high stability, abundance, and potentially high solar-to-hydrogen conversion efficiency.<sup>[25]</sup>

A focus on the practical commercial realities of water splitting technologies also characterises the paper from Alex Izgorodin, Orawan Winther-Jensen, and Douglas MacFarlane of Monash University ('On the Stability of Water Oxidation Catalysts: Challenges and Prospects'). The authors focus on developing strategies for testing or repairing the long-term mechanical and chemical stability of water oxidation catalysts. Examples of approaches for increasing mechanical stability include inclusion in the electrolyte of components that have the capacity to reform the catalytic layer via oxidation and precipitation, or surface modification to create a secondary lattice network that modifies the thermodynamics of the phases involved or absorbs the lattice strain during catalytic cycling.<sup>[26]</sup>

#### *Biological Approaches to Solar Fuels*

The next group of papers focus on the important biological approach to solar fuel development. Kastoori Hingorani and Warwick Hillier of the ANU ('Perspectives for Photobiology in Molecular Solar Fuels') discuss prospects for bio-inspired solar

energy conversion. One method is protein engineering, either by directed evolution of existing proteins or rational design of natural and novel proteins. The latter includes the construction of novel polypeptide sequences (maquettes), an area in which GAP participant Chris Moser specialises.<sup>[27]</sup> This field also involves synthetic biology and may lead to the full in vivo assembly of cofactors for solar-driven catalysis. The final topic considered here involves algal biofuels as ‘drop-in’ fuels requiring minimal downstream processing. The authors note that ethanol derived from fermentation can be a biofuel additive, but longer-chain lipids and alkanes from cyanobacteria and algae are better suited as aviation fuels.<sup>[28]</sup>

David Ollis, Jian-Wei Liu, and Bradley Stevenson of the ANU (‘Engineering Enzymes for Energy Production’) lead on from this by focusing on the concept of modifying enzymes to make general fuel from biological materials. They note the approaches involving genetically engineering enzymes from bacteria to produce butanol as a petrol substitute, biodiesel, pinene as a jet fuel substitute, hydrogen, branched alcohols, and terpene-based chemicals. The authors discuss their approach of directed molecular evolution of glycolytic enzymes to produce ethanol.<sup>[29]</sup>

### Hydrogen Storage

This collection of papers is nicely rounded out with the paper by James Hanlon, Hazel Reardon, Nuria Tapia-Ruiz, and Duncan Gregory from the University of Glasgow on developing a safe and potentially ubiquitous hydrogen storage system involving a cheap, non-toxic solid state medium with minimal energy requirements to charge and discharge the store (‘The Challenge of Storage in the Hydrogen Energy Cycle: Nanostructured Hydrides as a Potential Solution’). The authors look at metal hydrides in this context, particularly nanostructured magnesium hydride. These storage systems can involve techniques such as mixtures ( $\text{MgH}_2$ ), encapsulation and synthesis in solvents using organic surfactants to prevent reaction with air and water. Other options explored include the use of borohydrides, alanates (on the back of the discovery in 1997 that doping with Ti results in destabilisation of  $\text{NaAlH}_4$ ) and amides (after the 2002 discovery that hydrogen could be reversibly stored within lithium nitride,  $\text{Li}_3\text{N}$ ). Hollow  $\text{Mg}(\text{NH}_2)_2$  or  $\text{Li}_2\text{NH}$  nanospheres, for example, have been prepared and studied for hydrogen absorption/desorption properties, by vaporising bulk Mg in the appropriate chemical atmosphere in a plasma-metal reaction. Nanoscaling of imides and amides has been shown to induce rapid kinetics at reduced temperatures compared with micron-sized materials.<sup>[30]</sup>

### Governance Challenges

The GAP conference uniquely focused on the governance as well as the scientific challenges for global artificial photosynthesis. The vision of a world powered by solar fuel is likely to involve much more than large coastal plants splitting seawater using sunlight captured in desert areas to produce carbon-neutral hydrogen-based fuels and fresh water. If rolled out globally as a cheap consumer and development aid for ‘off-grid’ local and domestic energy, fertiliser and food product, global artificial photosynthesis could replace policy models of corporate globalisation and ever-increasing economic growth predicated on preparation for war and use of non-renewable and polluting energy sources. A world powered by artificial photosynthesis, in which an increasing proportion of human-engineered structures

operate like trees in generating hydrogen fuel and oxygen while absorbing carbon dioxide to make basic food and fertiliser, will be much closer to being ecologically sustainable. It might even mark a shift from the hopefully short-lived Anthropocene to the Sustainocene. In the latter epoch, humanity may still control the earth and its ecosystems, but more as a steward exhibiting due respect for the flourishing of all life. To repay our ethical obligation to life, we should plan for a Sustainocene epoch lasting over two billion years.

In this context, it is worth reminding energy security policy makers that more solar energy strikes the earth’s surface in one hour of each day than the energy used by all human activities in one year.<sup>[31,32]</sup> World energy consumption is currently in the region of 450 EJ per year, but vastly more than this is the solar energy potentially usable at  $\sim 1.0$  kW per square metre of the earth –  $3.9 \times 10^6$  EJ per year.<sup>[33]</sup> Photosynthesis, the ultimate source of our oxygen, food and fossil fuels, has been operating on earth for  $2.5 \times 10^9$  years.<sup>[34]</sup> Photosynthesis creates a global annual  $\text{CO}_2$  flux of 124 PgC per year<sup>[35]</sup> and an annual  $\text{O}_2$  flux of  $\sim 10^{11}$  tonnes per year.<sup>[36]</sup> In its present technologically unenhanced form, photosynthesis already traps around 4000 EJ per year of solar energy globally in the form of biomass.<sup>[37]</sup> The global biomass energy potential for human use from photosynthesis as it currently operates globally is approximately equal to human energy requirements (450 EJ per year).<sup>[38–40]</sup>

Many of the papers in this volume reveal how natural photosynthesis can be substantially improved with nanotechnology. Nanotechnology-based global artificial photosynthesis arguably involves a moral imperative in addressing internationally agreed targets to reduce poverty and lack of necessary fuel and food as expressed in the United Nations’ *Millennium Development Goals*.<sup>[41]</sup> These critical survival issues for the poor will be exacerbated as global population grows towards 10 billion by 2050 and energy consumption rises over 600 EJ per year.<sup>[42]</sup>

International trade, and more particularly international trade and investment law, lies at the heart of the corporate globalisation process by which foreign capital takes advantage of abundant natural resources (particularly timber, oil, coal, and minerals) or cheap labour to manufacture products for distribution and profitable sale throughout the world using road, rail, sea, and air freight transport, reduced tariffs and mass marketing techniques. Governance changes must be made here to facilitate equitable international trade in GAP or solar food and fuel products.<sup>[43]</sup> In the Sustainocene epoch, such areas of global regulation must emerge from protracted, inclusive, and coherent social contract thinking – with a more obvious democratic mandate and a greater focus on protecting the interests of other species, ecosystems, and future generations.

An open-access model for research and marketing of GAP or solar food and fuel products could involve funding rules requiring public good licensing, technology transfer, ethical and social implications research, as well as rapid and free access to data. Patent pools between the public–private sectors with zero royalties could be used to promote GAP collaboration, but contributors will have to ensure the terms they agree on don’t violate anti-monopoly laws by excluding competitors. If the most widely used GAP component parts are subject to some form of open-access permission, then the research will proceed faster. An example of the type of research a GAP or GSF project could undertake might involve analysing a reasonably effective materials-based self-assembling, earth abundant, water-splitting catalyst (catalytic turnover frequencies for  $\text{O}_2$  production

$\geq 5 \text{ s}^{-1}$  at  $\text{pH} = 8^{[44]}$ ), then attempting to enhance its turnover frequency to  $>300 \text{ s}^{-1}$  (comparable with the reaction rate of  $100\text{--}400 \text{ s}^{-1}$  of the oxygen-evolving complex of PSII in vivo) by characterising and refining its structure at the molecular level.<sup>[45]</sup>

A GAP or GSF project governance structure emphasising international law might shelter photosynthesis from excessive patents promoting inequitable or unsustainable use within the class of United Nations treaties involved with protecting the common heritage of humanity (such provisions cover, for instance, outer space,<sup>[46]</sup> the moon,<sup>[47]</sup> the deep sea bed,<sup>[48]</sup> Antarctica<sup>[49]</sup> and world natural heritage sites<sup>[50]</sup>). One mechanism for this could be a UNESCO *Universal Declaration on the Bioethics and Human Rights of Natural and Artificial Photosynthesis (Global Solar Fuels and Food)*.<sup>[51]</sup> The five core components of the common heritage of humanity concept under public international law that might then apply to natural and artificial photosynthesis could include the following: First, there can be no complete private or public appropriation; no state, corporate or natural person can legally own the entire process of artificial photosynthesis. Second, representatives from all nations must manage the resource of artificial photosynthesis on behalf of all (this often necessitates a special agency to coordinate shared management). Third, all nations must actively share with each other the benefits acquired from exploitation of improved artificial photosynthesis. Fourth, there can be no weaponry developed using artificial photosynthesis. Fifth, natural and artificial photosynthesis should be preserved for the benefit of future generations.<sup>[52,53]</sup>

Apart from the common heritage of humanity, other international law concepts that could be influential are those that may declare GAP a global public good,<sup>[54]</sup> an aspect of technology sharing obligations,<sup>[55]</sup> or those arising under the international human right to health (set out for example in Article 12 of the United Nations' *International Covenant on Civil and Political Rights* [ICESCR]) or international human right to enjoy the benefits of science and its applications (as in Article 15(2) of the ICESCR).<sup>[56]</sup> A GAP or GSF project could even be promoted as being covered by a new class of ethical and international law principles in the category of 'planetary' common heritage.<sup>[57]</sup> To promote such ideas as part of a governance framework for a GSF project, since the 2011 GAP conference the author of this article has given invited presentations to the Solar H2 group in Uppsala (September 2011), the United Nations in Geneva (November 2011), the Joint Center on Artificial Photosynthesis (JCAP) at Berkeley (April 2012) and the Energy Futures Laboratory at Imperial College, London (April 2012).<sup>[58]</sup> He has also published a monograph setting the case for GAP to be considered the moral culmination of nanotechnology<sup>[42]</sup> and made submissions that this idea receive consideration by the High Level Group advising the United Nations for its 2012 *Year of Sustainable Energy For All*.<sup>[59]</sup>

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