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Plenary Paper

Towards a global solar fuels project- Artificial photosynthesis and the transition from anthropocene to sustainocene

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Abstract

The development of an economy based on practical solar fuels is chiefly predicated on obtaining cheap and abundant hydrogen by using photons to split water, then cooling or compressing that gas; or on combining such hydrogen with carbon dioxide obtained from abundant industrial sources and eventually the atmosphere to create methanol. The construction of devices to make such fuels will be a major step in shifting the biosphere from what has been termed the Anthropocene to the Sustainocene epoch. Solar Fuels, particularly those derived from nanotechnology-based artificial photosynthesis represent an 'off-grid' energy, water and climate change solution that may directly challenge substantial investments in 'ancient photosynthesis' fuels by the World bank and multinational corporations in the energy sector, as well as government subsidies. This paper will examine immediate and long-term prospects and potential mechanisms for facilitating collaboration between the major existing national and regional Solar Fuels projects or establishing a macrosience Global Solar Fuels (GSF) initiative.

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1. Background to a Global Solar Fuels Project

1.1. United Nations Year of Sustainable Energy

The United Nations General Assembly has declared 2012 the *International Year of Sustainable Energy for All*, recognizing that "...access to modern affordable energy services in developing countries is essential for the achievement of the internationally agreed development goals, including the Millennium Development Goals, and sustainable development, which would help to reduce poverty and to improve the conditions and standard of living for the majority of the world's population." It has appointed Charles Holliday, Chairman of Bank of America, and Kandeh Yumkella, Chair of UN-Energy

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and Director-General of the UN Industrial Development Organization, to co-chair the Secretary-General’s High-Level Group on Sustainable Energy for All. With the help of a High-Level Group, they will mobilize commitments from governments, the private sector, and civil society partners to take actions that will make sustainable energy a reality for all over the next two decades.^[1] The main targets of this endeavour, as set out in Table 1, should be kept in mind in the context of the arguments to be made in this paper for the establishment of a Global Solar Fuels (GSF) Project.

Table 1. United Nations Year of Sustainable Energy for All

Targets	
1.	Modern cooking appliances and fuels
2.	Distributed electricity solutions:
3.	Grid infrastructure and supply efficiency off grid, micro and mini grid
4.	Large-scale renewable power: grid-connected
5.	Industrial and agricultural processes:
6.	Transportation: Increasing fuel efficiency for all classes of vehicles, increasing the share of renewables in the fuel supply
7.	Buildings and appliances: Improving efficiency through design, insulation, and retrofit of buildings and incorporating renewable self-generation options with more efficient consumer appliances and equipment.
8.	Energy planning and policies: Promoting direct public action and improving the legal and administrative context for successfully engaging the private sector and civil society.
9.	Business model and technology innovation: to overcome barriers to sustainable energy services and technologies.
10.	Finance and risk management: increase private investment in sustainable energy through the targeted use of public and philanthropic capital.
11.	Capacity building and knowledge sharing for faster replication across the world.

1.2 From Anthropocene to Sustainocene

The development of an economy based on practical solar fuels (whether focusing primarily on hydrogen, methanol or even formic acid) will be a major step in shifting the biosphere from what has been termed the Anthropocene to the Sustainocene epoch. The Holocene (“recent whole”) period was the term given to the post-glacial geological epoch by the International Geological Congress in Bologna in 1885. It began 10,000 years ago and from that time till about 1800 CE, humanity’s activities were not enough to alter much the natural systems of this world; for example atmospheric carbon dioxide concentration did not rise above their natural variability. Since 1800 with the onset of the industrial revolution, the development of the capacity to fix atmospheric nitrogen as a fertilizer, improved sanitation healthcare and transport human population and its impact have dramatically increased. Land ecosystems, for instance, were globally converted from mostly wild to mostly anthropogenic by the mid 20th century.^[2]

It has been argued that human activity has pushed this planet from the Holocene into what has been termed the Anthropocene period.^[3] The term ‘Anthropocene’ was coined by Crutzen in 2002.^[4] It refers to an epoch when human interference with earth systems (particularly in the form of influences on land use and land cover, coastal and maritime ecosystems, atmospheric composition, riverine flow, nitrogen, carbon and phosphorus cycles, physical climate, food chains, biological diversity and natural resources) have become so pervasive and profound that they are not only becoming the main drivers of natural processes on earth, but are threatening their capacity to sustain life.^[5]

Five characteristic features of the Anthropocene epoch that tend to dominate its policy debates include: population; poverty, preparation for war, profits and pollution.^[6] Salutary facts driving academic and policy interest in moving from the Anthropocene to a different type of human-controlled epoch are not only the greenhouse-gas driven increase in severe weather events, but the projected increase of global human population to around 10 billion by 2050 with associated energy consumption rising from $\approx 400\text{EJ/yr}$ to over 500EJ/yr beyond the capacity of existing fossil-fuel based power generation.^[7] The research underpinning the push to develop Sustainocene-oriented energy and climate policy also emerges strongly from influential commentaries such as the Intergovernmental Panel on Climate Change^[8] and the Stern Report,^[9] as well as the United Nations *Millennium Development Goals*.^[10]

The term ‘Sustainocene’ was coined by the Canberra-based Australian physician Bryan Furnass in 2012.^[11] It refers to a period where governance structures and scientific endeavour coordinate to achieve the social virtues of ecological sustainability and environmental integrity as influentially propounded by eco-economists such as the EF Schumacher (with his concept of ‘small (and local) is beautiful’) and Kenneth Boulding (with his idea of ‘Spaceship Earth’ as a closed economy requiring recycling of resources) as well as Herman Daly with his notion of ‘steady state’ economies drawing upon the laws of thermodynamics and the tendency of the universe to greater entropy (dispersal of energy).^[12]

One area of academic research and policy development that fits well with ‘Sustainocene’ thinking is that centred on the idea that this planet should be treated not just as a distinct living entity (James Lovelock’s Gaia Hypothesis), but as a patient.^[13] ‘Planetary medicine’ as this field has become known has become a symbolic rubric focusing not just public and governmental attention on the interaction between human health, technological development and sustainability of the biosphere.^[14] In this emerging discipline, characteristic features of the Anthropocene epoch such as anthropogenic climate change and environmental degradation, as well as gross societal imbalances in poverty as well as lack of necessary fuel, food, medicines, security and access to nature, are targeted as intrinsically global pathologies the resolution of which requires concerted efforts to implement a wide range of not just renewable energy technologies (such as those using nanotechnology) but bioethical principles including those related to protecting the interests of future generations and preservation of biodiversity.^[15]

Table 1. Comparison of Anthropocene and Sustainocene

	Anthropocene	Sustainocene
Powered by ‘Old’ Photosynthesis Fuels	Yes	No
Powered by ‘New’ photosynthesis Fuels	Yes	No
Corporate-led Governance	Yes	No
Community-led Governance	No	Yes
Governance protecting future generations	No	Yes
Governance protecting ecosystems	Yes	No
Governance protecting biodiversity	Yes	No

1.3 Towards a Photon or Hydrogen-based Economy in the Sustainocene

There has been much policy interest in developing what is termed the ‘hydrogen economy’ in which hydrogen is used ubiquitously as a carbon-neutral energy vector (for example source of electricity via fuel cells or as a fuel itself when combined, for example, to form methanol) and source of small amounts of fresh water (when combusted). Major policy documents have outlined the case for such an economy.^[16] ^[17] ^[18] ^[19] Some of the challenges include the need to lower the cost of hydrogen fuel production to that of petrol, the difficulties in creating a sustainable and low carbon dioxide route for the mass production of hydrogen, the need to develop safe and more efficient storage (including the difficulties of compressing and cooling the hydrogen), the need to develop regulations and safety standards at national and international levels as well as the need to develop stable incentive systems for large scale investment in this area that will not fluctuate with oil prices.

Hydrogen (H_2) requires 3000 times more space for equivalent amount of energy, but on a weight basis H_2 has 3 times the

energy content of gasoline. Liquifying H₂ requires complex and expensive process (pre-cooled with liquid ammonia to -40°C then to -196°C with liquid nitrogen, then helium in compression-expansion to get liquid H₂ at -253°C) 30-40% of H₂ energy is lost in liquifaction and 1-5% must be lost to atmosphere each day to avoid pressure build up and explosion. Compression similarly requires 10-15% energy and requires cylindrical shape.^[20] One of the main problems at present with moving to a global hydrogen economy is the carbon-intensive energy required to produce hydrogen in large quantities by steam reformation of hydrocarbons, generally methane. ^[21]

Yet a cheap and abundant source of H₂ is readily at hand as an output of technology that enhances the splitting of water using sunlight. One of the reasons for focusing on this as the main energy supply of the Sustainocene is 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.^[22] ^[23] At present the average daily power consumption required to allow a citizen to flourish with a reasonable standard of living is about 125kWh/day. Much of this power is devoted to transport (~40 kWh/day), heating (~40 kWh/day) and domestic electrical appliances (~18 kWh/day), with the remainder lost in electricity conversion and distribution.^[24] Global energy consumption is approximately 450 EJ/yr, much less than the solar energy potentially usable at ~1.0 kilowatts per square metre of the earth— 3.9×10⁶ EJ/yr even if we take into the earth's tilt, diurnal and atmospheric influences on solar intensity.^[25]

Photosynthesis as a natural process is equally important with DNA in the progress of humanity. Photosynthesis provides the fundamental origin of our oxygen, food and the majority of our fuels; it has been operating on earth for 2.5 GYr.^[26] Photosynthesis can be considered as a process of planetary respiration: it creates a global annual CO₂ flux of 124 PgC/yr ^[27] and an annual O₂ flux of ~10¹¹ t/yr.^[28] In its present nanotechnologically-unenhanced form, photosynthesis globally already traps around 4,000 EJ/yr solar energy in the form of biomass.^[29] The global biomass energy potential for human use from photosynthesis as it currently operates globally is approximately equal to human energy requirements (450 EJ/yr).^[30]^[31]^[32]

Contemporary energy policy analysts appear to have overlooked the capacity of nanotechnology to not only substantially improve but make more widespread the photosynthetic process on earth. When photosynthesis is considered in an energy or climate change policy context it is usually as a source of biofuels, often with a deleterious cost to rainforests or agricultural lands. Further, even if 3000m² per person is devoted to biomass production this will provide only fuel only 36 kWh/day per person (well short of the 125kWh/day required for people to live comfortably).^[33] Photovoltaic (PV) energy systems are improving their efficiencies towards 25%, and the cost of the electricity they produce is nearing or has past grid parity in many nations. The development of “smart-grid” (allowing energy carrying capacity to fluctuate coherently in accord with input and output) and “pumped-hydro” (using diurnal PV electricity to pump water to high reservoirs so it can be run down through turbines at night) will assist the viability of this as a national energy source. But even large solar farms (for example taking up 200 m² per person with 10%-efficient solar panels) could produce but ~50kWh/day per person.^[34]

Table 3 Energy Consumption and Solar power

Parameter	Energy/Power
Annual solar energy intercepted by the Earth at ~1.37 kW/m ²	5.5×10 ⁶ EJ/yr
2008 primary energy consumption	352.8 EJ
2050 primary energy consumption	590-1,050 EJ
2100 primary energy consumption	880-1,900 EJ
Ratio of potentially usable annual solar energy to current primary energy consumption/yr	~9,000 to 1

Sources: H-H Rogner. Ch 5 in United Nations Development World Energy Assessment. United Nations 2004 p162 and International Energy Agency. Key World Energy Statistics. IEA. Paris. 2010 p30.

Artificial photosynthesis can facilitate other energy options H₂ –based fuels, for example by reduction of CO₂ and mixing it with H₂ to make methanol (CH₃OH) or derived dimethyl ether (DME). Methanol is relatively simple to make, safe, easy to store and transport liquid oxygenated hydrocarbon. It can be prepared from reductive hydrogenative recycling of industrial or domestic emissions or atmospheric CO₂ with H₂ from solar-driven water splitting. It can also be used as chemical building blocks for polymers, paints, building materials and almost all currently utilized old photosynthesis fuels (OPF). Use of CO₂ in this way may transform it from being an atmospheric pollutant to classification as a global public

good.^[35]

One of the main issues facing policy makers seeking to drive the shift from Anthropocene to Sustainocene will be what principles should govern how emerging technologies (such as nanotechnology) assist in achieving the hydrogen economy. Nanotechnology is the science of making things from components that are not much bigger than a few atoms, less than 100nm (a nanometer is a billionth of a metre). The chief policy interest to date with nanotechnology to date has been concerned with ensuring its safety.^[36] Interest is growing, however, in focusing nanotechnology on such problems. Experts have encouraged nanotechnology researchers to systematically contribute to achievement of the United Nations *Millennium Development Goals* particularly energy storage, production and conversion, agricultural productivity enhancement, water treatment and remediation.^[37] As will be shown in section 3, one of the main ways nanotechnology may assist in relation to such issues concerns artificial photosynthesis and particularly its contribution to global domestic or locally-produced solar fuel.

2. Major Solar Fuels Hubs

Some researchers consider that only plants can do artificial photosynthesis (AP). Their focus is on genetically modifying plants and also using synthetic biology. They seek for example to genetically manipulate or even synthetically reproduce photosynthetic plants and bacteria to maximize their light capture and carbon reduction activities.^[38] But this approach surely has echoes of those in the 19th century experimentalists who considered that only birds could do flight and that perhaps one day we'd find a way to make huge birds that would allow us to travel across the Atlantic or Pacific Oceans.

When we travel in aircraft across the world it is easy to see the extent to which human concrete and asphalt structures are proliferating across the face of the planet. Such structures contribute little to the ecosystems around them. They do not enrich the soil or provide oxygen or absorb carbon dioxide. Yet we are almost at the point where nanotechnology and artificial photosynthesis can be engineered into such structures so they can be made to “pay their way” in an ecosystem sense.

Artificial photosynthesis is the subject of intense and advanced research by large groups of scientists in all developed nations.^[39] A dozen European research partners, for example, form the Solar-H2 network, supported by the European Union and coordinated by Stenbjorn Styring at Uppsala University, Sweden.^[40] The US Dept. of Energy (DOE) *Joint Center for Artificial Photosynthesis* (JCAP) at the California Institute of Technology (Caltech) and Lawrence Berkeley National Laboratory has US\$122m over 5 years to build a solar fuel system. At Caltech Harry Grey has initiated a Solar Army endeavour in which high school and college students are mentored to search the periodic table for suitable catalysts.^[41] In the US several Energy Frontier Research Centers funded by the US DOE are focused on scientific endeavours related to artificial photosynthesis.^[42] In Japan major artificial photosynthesis groups exist at Osaka, Kyoto, Tokyo and Hokkaido Universities.^[43] Other major solar fuels centres have been established in South Korea, The Netherlands and Singapore and numerous other competitively funded research teams have dedicated artificial photosynthesis-related projects already underway in many developed nations.^[44]

An international conference coordinated by the author at Lord Howe Island in August 2011 has linked senior artificial photosynthesis and global governance experts specifically as a precursor to a macroscale Global Artificial Photosynthesis (GAP) Project.^[45] It's not clear of course what name such a project would have. Some of the high achieving high school science students (from James Ruse Agricultural College, Geelong Grammar, Canberra Grammar, Radford College and Narrabundah College) argued that ‘artificial’ meant ‘fake’ or ‘not genuine’ and would have a negative public perception. They considered that a project entitled Global Solar Fuels (GSF) was more likely to be positively received.

3. Major Scientific Challenges in Global Artificial Photosynthesis

A basic idea of solar fuels research amongst the large national and regional projects mentioned above is to develop solar fuel prototype devices that improve on how plants absorb sunlight and use it to create an electron flow that splits water and reduces CO₂ resulting in a form of energy that can be stored in chemical bonds. Let's look at that process more closely as it is one of the great inventions of life and provides the template for the development of more efficient artificial systems.

Photosynthetic organisms absorb photons from a segment of the solar spectrum (~430-700nm) by so-called ‘antenna’ chlorophyll molecules in thylakoid membranes, or chloroplasts. The absorbed photons' energy creates unstable spatially separated electron/hole pairs. The “holes” are captured by the oxygen-evolving complex (OEC) in photosystem II (PSII) to oxidise water (H₂O) to what can be termed a natural form of hydrogen (protons) and oxygen (O₂). This process can be written as the following chemical equation: $2\text{H}_2\text{O} \Rightarrow 4 \text{ photons} \Rightarrow 4\text{e}^- + 4\text{H}^+ + \text{O}_2$. The protons released on water oxidation can be used to make hydrogen according to a chemical process recorded as: $2\text{e}^- + 2\text{H}^+ \Rightarrow \text{H}_2$. The electrons are subsequently captured in chemical bonds by photosystem I (PSI) to reduce NADP (nicotinamide adenine dinucleotide phosphate) to NADPH. Electro-chemical energy stored by the protons produces ATP (adenosine triphosphate). In the relatively less

efficient “dark reaction”, ATP and NADPH as well as carbon dioxide are used in the Calvin-Benson cycle to make a variety of energy rich chemicals, mainly sucrose and starch via the enzyme RuBisCO (Ribulose-1,5-bisphosphate carboxylase oxygenase).^[46] This capacity to store solar energy in potentially transportable and freely usable form in chemical bonds that makes enhanced photosynthesis so intriguing as a form of renewable energy.

Some nanotechnological innovations for artificial photosynthesis focus on improved ‘light capture.’ This ‘light capture’ involves nanostructured materials or synthetic organisms absorbing photons from a much wider region of the solar spectrum (photon absorption by antenna chlorophyll molecules in thylakoid membranes of chloroplasts, for example, currently is restricted primarily to ~430-700nm).^[47] Improved light capture system may involve multiple stacking of solar cells with increasing band gap energies to exploit the solar spectrum more profitably.^[48] Such systems may also use mesoporous thin film dye-sensitive solar cells of semiconductor nanoparticles^[49] and carbon nanotubes harvesting and conducting the resultant electricity.^[50] Nanomaterials and hybrid organic-inorganic nanostructures are improving the solar energy conversion efficiency of existing photovoltaic units that could be used in artificial photosynthesis light capture.^[51]

PSII in plants is a complex protein with 27 subunits and 32 co-factors involved in electron transfer and light harvesting. Researchers are working upon making a nanotechnological mimic of this protein (maquette) that is simpler^[52] and incorporates designer molecules that prolong charge separation.^[53] Nanotechnology is facilitating the construction of artificial photosynthetic electron pathways to this reaction centre that perform a single quantum computation, sensing many states simultaneously and so enhancing the efficiency of the energy capture and transfer at physiological temperatures.^[54]^[55]^[56]

The most globally widespread water catalytic system will probably involve inexpensive and self-repairing components that operate at neutral pH with non-pure (salty or bacterially and chemically contaminated) water^[57] and be stable to a variety of exposure conditions in air, water and heat.^[58] A major scientific challenge will be to optimise the free energy required for the overall water splitting process.^[59] Multiwalled carbon nanotubes^[60] and singlewalled carbon nanotubes may produce the critical breakthrough here.^[61]

In the artificial photosynthesis version of the “dark reaction”, ATP and NADPH as well as carbon dioxide (CO₂) will be used in an enhanced version of the Calvin-Benson cycle to make locally usable food or fuel (for domestic, heating, cooking, light and transport) in the form of carbohydrate via the enzyme RuBisCO.^[62] Bio-inspired self-repair strategies will ensure that this aspect survives damage from repeated cycles of thermodynamically demanding reactions.^[63] New catalysts for H₂ production and methods for efficient H₂ usage (in a fuel cell to make electricity) or storage (as a fuel after cooling and concentrating) will need to be built.^[64] It may be that methanol will turn out to be, at least in the short term, the most viable fuel produced from this side of the artificial photosynthesis process.^[65]

Major researchers in the solar fuels area include Peidong Yang^[66] and Dan Nocera whose ‘artificial leaf’ configures a triple junction silicon photovoltaic cell with a cobalt catalyst for O₂ evolution and a ternary alloy (NiMoZn) as the H₂-evolving catalyst in a wireless configuration.^[67] Nobuo Kamiya of Osaka University, has encouraged the process of building mimics of the core part of the natural photosynthetic system with the publication by his team of a cubane configuration of the OEC in PSII to a level of 1.9Å³ (1.9 ångströms or 1.9×10⁻¹⁰ m) using an electron density map.^[68] Craig Hill of Emory University has developed a polyoxometalate water oxidation catalyst capable of strongly binding multiple transition metal centers proximal to one another, so facilitating multi-electron processes such as the 4-electron oxidation of H₂O to O₂.^[69] David Tiede of the Argonne National Laboratory has reported a new strategy for solar fuel production involving insertion of sustainable first-row transition metal molecular catalysts (cobaloxime) into Photosystem I (PSI) as a mechanism for H₂ production.^[70] Klaus Hellgardt from Imperial College London has developed a flat plate photoelectrochemical (PEC) reactor for hydrogen production.^[71] Gary Brudvig and Chris Moser are amongst the notable researchers who have focused on how insights from the natural photosynthetic system might develop bioinspired materials for photochemical water oxidation and fuel production.^[72]

4. GSF project as Planetary Nanomedicine

Planetary medicine is now a growing field in which the expertise of medical professionals is directed towards issues of global health and environmental protection, particularly including climate change.^[73] A GSF Project could well be promoted through domestic and international media as a defining symbolic endeavour of planetary nanomedicine.^[74]^[75] One significance of this for artificial photosynthesis researchers is that funding agencies respond indirectly to public and governmental national interest concerns and nanotechnology, despite its great promise, still has a problematic place in the popular imagination owing to safety issues. A GSF Project therefore represents an excellent opportunity to create a high profile awareness of nanotechnology as a positive contributor to overcoming major contemporary public health and environmental problems.

The process of photosynthesis is as central to life on earth as DNA; thus there are likely to be similar major debates over whether patents should be allowed over any part of the photosynthetic process. Such a debate will be unlikely to inhibit patents being taken out over many aspects of GSF. The US Supreme Court, for example, has ruled that genes (despite the symbolic importance of DNA to human heritage) can be patentable if they are isolated and purified.^[76]

A larger issue for such governance approaches is that nanotechnology, despite its great scientific novelty and promise, still has a problematic place in the popular imagination owing to unresolved safety issues.^[77] A macroscale project to promote equitable global use of artificial photosynthesis therefore represents an excellent opportunity to create a high profile awareness of nanotechnology as a positive contributor to overcoming major contemporary public health and environmental problems. Provided an appropriate ethical regulatory structure was in place, such a project could well be promoted through domestic and international media as a defining symbolic endeavour of planetary nanomedicine.^[78] ^[79]

5. Conclusion

No matter how significant the vision or advanced the science, the governance challenges of moving to a Global Solar Fuels Project are considerable.^[80] One model of a Sustainocene powered by solar fuels involves bio-mimetic polymer photovoltaic generators plugged in to the national electricity grid to power hydrogen fuel and waterless agriculture, chemical feedstocks and polymers for fibre production.^[81] This model has the advantage of the ‘light’ and ‘dark’ reactions being uncoupled in relation not only to energy/material flow balance, but also to the requirement to be co-located in space. Such an uncoupling will vastly extend the area for capturing light over otherwise barren land, and also allow the elimination or reduction of molecular oxygen in solar fuel reactions, enhancing longevity of the components. A model which the author favours emphasizes the greater potential for individual and community economic autonomy implicit in micro or local generation of fuel and food through solar fuel products installed as a policy priority on domestic dwellings and vehicles.^[82] Large GSF facilities providing fuel for industry or backup supply can still be preferentially located under such a model near large sources of seawater, CO₂, waste heat, high solar irradiation and proximity to end use facilities. In the longer term every human engineered structure on the planet will have a built in artificial photosynthetic capacity allowing it to be a positive contributor to the biosphere—improving the atmosphere, providing fuel and basic food and fertilizer. There is a simple public policy message at the core of a vision such as that of the Sustainocene. It involves telling people that nanotechnology will be used to make buildings function like trees. A device that can do this and is available to cheap purchase and installation, like the mobile phone or internet, by providing decentralised power equitably could rapidly transform society to one that is more community and values-oriented.

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