

# Chem Soc Rev

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Reviewing the latest developments in renewable  
energy research

Guest Editors Professor Daniel Nocera and Professor Dirk Guldi

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# Living healthy on a dying planet†

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Living healthy on a dying planet—we are a world out of balance. We seek immortality at the individual level and are oblivious to the health of our humanity at a global level. The average life expectancy in the world is 66 years and in the developed world it is >78 years.<sup>1</sup> But this is not enough. We stridently seek to extend our existence. One of the great discoveries of recent science is the mapping of the human genome. And what is the hopeful outcome of this human genome project? Most of all practitioners say it is to cure disease at a genetic level. While this is a noble cause for the young, at what cost does an octogenarian society aspire to eternal life when the environment on which humanity finds sustenance is in peril?

A clear picture is emerging about the change that confronts our planet in the near future. Professor James Anderson of Harvard has determined that the current level of CO<sub>2</sub> in our atmosphere now ensures sufficient heating to melt the Arctic summer ice cap within the next decade. The ice in the Arctic Ocean acts as a heat shield for our planet by preventing the flow of warm ocean currents to the furthest reaches of the northern hemisphere. With the polar ice cap gone, significant global changes to our environment are assured the most concerning of which is the collapse of the Greenland ice cap and the loss of permafrost. Much of the world's industrial centers and population are situated near coastline, which will be submerged under the water accompanying the 7 metre rise in ocean levels with the collapse of the Greenland ice cap. Even more troublesome is the inability of living organisms to adapt to our quickly changing environment. Environmental biologists have documented the disappearance of entire ecosystems

from our planet in a single human generation. The worrisome concern is whether humans can adapt quickly enough to our changing world.

With our humanity blindly staggering toward an ominous future, we are swayed by the folly of futurists who promise immortality. We allocate resources as if we believe that dying is an option. In the US, which is no different from most societies in the developed world, GDP is roughly divided equally between health and energy. However, the emphasis we place on immortality is plainly evident in the 30 : 1 ratio of R&D funding for health : energy science.<sup>2</sup> Despite this imbalance in resources, a global cohort of scientists, undeterred by societal indifference, confronts the energy challenge head on.

These scientists, some of which are collected in this issue, provide hope for our global future. The problem they tackle is daunting. In the past several years, it has been well documented that our global energy need will roughly double by mid-century and triple by 2100.<sup>3,4</sup> Holding atmospheric CO<sub>2</sub> levels to even twice their preanthropogenic values by mid-century will require invention, development, and deployment of schemes for carbon-neutral energy production on a scale commensurate with, or larger than, the entire present-day energy supply from all sources combined. One pre-eminent solution to the energy challenge is offered by the sun. More energy from the sun strikes the Earth's surface than humans currently use in a year. However, current options to harness and store this energy are too expensive to be implemented on a large scale. Hence the objective to science is to develop new materials, reactions and processes to enable solar energy to be sufficiently inexpensive to penetrate global energy markets.

This themed issue of *Chemical Society Reviews* on Renewable Energy collects the work of scientists that seek to transform the dream of a solar-powered

society into reality. To do this, they undertake science to (i) uncover the secrets of bioenergy conversion and biocatalysis, (ii) design novel solar *capture* and *conversion* materials and (iii) create catalysts that can store energy in hierarchical materials or in the form of the chemical bonds of fuels.

James Barber (DOI: 10.1039/b802262n) presents a review on the solar energy blueprint offered by nature. The primary steps of natural photosynthesis involve the capture of sunlight and its conversion into a wireless current. The anodic charge of the wireless current is used at the oxygen-evolving complex (OEC) in Photosystem II to oxidize water to oxygen, with the concomitant release of four protons. The cathodic charge of the wireless current is channeled to Photosystem I where protons are reduced to “hydrogen” by ferredoxin NADP reductase—with the reduced hydrogen equivalents stored *via* the conversion of NADP to NADPH. Maria Ghirardi (DOI: 10.1039/b718939g) exploits the photosynthetic properties of oxygenic and non-oxygenic microbes in combination with the H<sub>2</sub>-producing capabilities of hydrogenases and nitrogenases. By uniting these different enzymatic systems, she provides a photobiological path for storing sunlight by the production of hydrogen. Biological production of H<sub>2</sub> on a large scale brings certain practical requirements that need to be addressed at the molecular as well as the microbial level. The synthetic model compounds described by Frédéric Gloaguen and Thomas Rauchfuss (DOI: 10.1039/b801796b) permit detailed mechanistic studies by which hydrogenases operate. Fraser Armstrong's (DOI: 10.1039/b801144n) tutorial review shows how the H<sub>2</sub>-producing reactivity of hydrogenases may be deciphered using specialized electrochemical techniques. Especially crucial is to understand how hydrogenases can sustain high H<sub>2</sub> fluxes in the presence of the O<sub>2</sub> that the photosynthetic enzymes produce. Devens

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Gust, Ana Moore and Thomas Moore (DOI: 10.1039/b800582f) transition the themed issue from the world of biology to the world of technology. In their fascinating tutorial review, they show the parallels between energy conversion in biology, accomplished with proton-motive-force (pmf), and energy conversion in technology, accomplished by electro-motive-force (emf). They show aspects of biology that might be advantageously incorporated into emerging energy technologies, as well as ways in which technology might improve upon the design of biological energy-based systems.

The photosynthetic process may be realized artificially by spatially separating energy storage from the light capture and conversion system. For each component, the material must be earth-abundant and easily manufactured.

Charles Lieber (DOI: 10.1039/b718703n), Dirk Guldi (DOI: 10.1039/b802652c) and Gerald Meyer (DOI: 10.1039/b804321n) look to nanoscience for the construction of high efficiency and low cost solar energy capture and conversion devices. The effort from the Lieber group seeks to elucidate the properties and potential of semiconductor nanowires as building blocks for photovoltaic devices based on investigations at the single nanowire level. Si-nanowires with reproducible and carefully tunable PV properties are presented. The tutorial review progresses to show the rational design of more complex architectures based on nanowire tandem cell and quantum well structures. The use of carbon nanotubes as electron and photon carriers is detailed in the review of Dirk Guldi. He shows how superior transport properties may be achieved by tuning the properties of the carbon nanotubes. Gerald Meyer provides a review on Grätzel's original discovery that interfaced nanoscience to energy conversion—dye-sensitized TiO<sub>2</sub> solar cells. A comprehensive treatment of the current understanding of the charge-transfer processes at sensitized TiO<sub>2</sub> interfaces is offered. Against this backdrop of knowledge, new avenues of exploration are identified that have the potential for yielding dye-sensitized solar cells with high light-to-electrical power conversion efficiencies.

If solar energy is to be a major primary energy source for society, then it must be stored owing to the diurnal variation in

local insolation. Debra Rolison (DOI: 10.1039/b801151f) seeks to store the electricity from photovoltaics directly in novel 3D nanoarchitectures. Void space and disorder within the 3D architecture allow for rapid molecular fluxes that lead to amplification within the electrical interface. Alternatively, solar energy may be stored in the form of chemical bonds of fuels. The storage of solar energy in the bond is attractive in view of its high energy density.

A particularly attractive fuel forming reaction is the aforementioned water-splitting reaction of photosynthesis. In this process, solar energy is stored in the bond rearrangement of H<sub>2</sub>O to H<sub>2</sub> and O<sub>2</sub>. Oleg Ozerov (DOI: 10.1039/b802420k) explores the little studied activation of water by oxidative addition to a transition metal center. A popular design for achieving water splitting is to interface water reduction and oxidation catalysts to a photovoltaic membrane.<sup>5</sup> Daniel DuBois and Mary Rakowski DuBois (DOI: 10.1039/b801197b) describe the construction of a tool set for the development of highly active catalysts for the production of H<sub>2</sub>, whereas developments from my group have led to the discovery of a highly active cobalt phosphate catalyst for O<sub>2</sub> production (DOI: 10.1039/b802885k). This latter catalyst produces O<sub>2</sub> from neutral water at room temperature and low pressure and captures many of the functional elements of the OEC of Photosystem II. Akihiko Kudo (DOI: 10.1039/b800489g) combines photochemistry and catalysis in the creation of metal (oxy)sulfide and metal (oxy)nitride water-splitting photocatalysts. Bruce Parkinson (DOI: 10.1039/b719545c) seeks to improve the overall efficiency of heterogeneous photocatalysts by developing new methods for the combinatorial production and high throughput screening of metal oxides.

The use of hydrogen as a fuel requires its storage by materials with high volumetric and gravimetric hydrogen densities. Jason Graetz (DOI: 10.1039/b718842k) emphasizes the potential of metal hydrides as effective hydrogen storage materials, whereas Tom Baker (DOI: 10.1039/b800312m) explores the hydrogen-storing properties of BN compounds owing to their light weight and propensity for bearing multiple protic (NH) and hydridic (BH) hydrogens. Stephen Shevlin and Xiao Guo (DOI: 10.1039/b815553b)

complement these experimental approaches by demonstrating the power of density functional theory (DFT) simulations in evaluating, developing and discovering hydrogen storage materials. Hydrogen storage may be circumvented if production of oxygen from water is accompanied by reduction of CO<sub>2</sub> to a liquid fuel. Cliff Kubiak (DOI: 10.1039/b804323j) reviews electrocatalytic and homogenous approaches to CO<sub>2</sub> reduction and then defines benchmarks for accomplishing this reaction with high efficiencies.

I close with Kurt Vonnegut's paradoxical words of comfort shortly before his death. In a *PBS NOW* interview with David Brancaccio, Vonnegut describes the planet as a living organism. He reminds us that the immunological response of sophisticated life forms will eliminate irksome intruders when the organism is sufficiently compromised. Vonnegut sees humans as the irksome intruder of our planet. As we carelessly choose a path to suffocate the planet in CO<sub>2</sub>, Vonnegut assures Brancaccio that he need not worry: the planet's immunological system will respond and eliminate humans by not sustaining them in the dramatically altered environment that they created. Elaborating on Vonnegut's perspective, the "dying planet" in the title of this preface has little to do with the Earth, which will continue to exist and flourish at high CO<sub>2</sub> levels, though not as we know it. Rather, it is the humans on the Earth that are in a precarious state. When Brancaccio confronts Vonnegut about a solution to the "dying planet", Vonnegut responds, "join a gang and do something about it". In this themed issue on Renewable Energy, it is a pleasure to collect a "gang" of scientists who have taken up Vonnegut's call-to-arms by providing the discovery needed to answer the greatest challenge confronting humanity—the large scale supply of carbon-neutral energy.

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#### References

- 1 CIA: The World Fact Book, <https://www.cia.gov/library/publications/the-world-fact-book/rankorder/2102rank.html>.

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- 2 K. Koizumi, *AAAS Report XXXII, Research and Development FY 2008*, American Association for the Advancement of Science, Washington DC, ch. 2, 2008.
- 3 M. I Hoffert, K. Caldeira, A. K. Jain, E. F. Haites, L. D. Harvey, S. D. Potter, M. E. Schlesinger, T. M. Wigley and D. J. Wuebbles, *Nature*, 1998, **395**, 881.
- 4 *Climate Change and Water. Technical Paper of the Intergovernmental Panel on Climate Change*, ed. B. C. Bates, Z. W. Kundzewicz, S. Wu and J. P. Palutikof, IPCC Secretariat, Geneva, 2008, 210 pp.
- 5 N. S. Lewis and D. G. Nocera, *Proc. Natl. Acad. Sci. U. S. A.*, 2006, **103**, 15729.