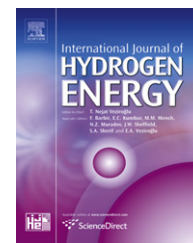


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## Editorial

# Photosynthetic and biomimetic hydrogen production

### ABSTRACT

#### Keywords:

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It is clear that three of the great challenges facing humanity in the 21st century are energy supply, climate change, and global food security. Although global energy demand is expected to continue to increase, the availability of low cost energy will continue to diminish. Coupled with increasing concerns about climate change due to CO<sub>2</sub> release from the combustion of fossil fuels, there is now an urgent need to develop clean and renewable energy system for the hydrogen production. This special issue contains selected papers on photosynthetic and biomimetic hydrogen production presented at the International Conference “Photosynthesis Research for Sustainability-2011”, that was held in Baku, Azerbaijan, during July 24–30, 2011, with the sponsorship of the International Society of Photosynthesis Research (ISPR) and of the International Association for Hydrogen Energy (IAHE). This issue is intended to provide to our readers recent information on the photosynthetic and biomimetic hydrogen production. The web site of this international conference is at: <http://www.photosynthesis2011.cellreg.org>. At this conference, awards were given to nine young investigators. We have included here some photographs to show the pleasant ambiance at this conference. (Also see <http://www.photosynthesis2011.cellreg.org/Photos.php> and <http://www.life.illinois.edu/govindjee/g/Photo/Baku.html> for some additional photographs). We invite the readers to the next conference on “Photosynthesis Research for Sustainability-2013” to be held in May or June 2013, in Baku, Azerbaijan. Information will be posted at: <http://www.photosynthesis2013.cellreg.org>.

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## 1. Special issue

More than 3 billion years ago, living organisms, developed the capacity to efficiently capture solar energy and use it to power the synthesis of organic molecules using photosynthesis. The photosynthetic process set into motion an unprecedented explosion in biological activity, allowing life to prosper and diversify on an enormous scale, as witnessed by the fossil records and by the extent and diversity of living organisms on our planet today. Indeed, it was the process of photosynthesis over eons of time which has provided us with the oil, gas and coal needed to power our technologies, heat our homes and produce the wide range of chemicals and materials that support everyday life [1–7].

Prior to the evolution of photosynthesis, biology had been dependent on hydrogen/electron donors such as H<sub>2</sub>S or NH<sub>3</sub>, which were in limited supply compared with the ‘oceans’ of water with which the planet Earth is blessed [2]. For background on various processes involved in photosynthesis, see

special issues of journals [3–7], reviews [8–10] and books [11–15].

Accumulation of the oxygen evolved resulted in aerobic atmosphere. Formation of an ozone layer allowed organisms to move from the ocean to the land. With oxygen available, the efficiency of metabolism increased dramatically since aerobic respiration provides almost 20 times more cellular energy than anaerobic respiration. This improved efficiency in energy conversion was likely a major factor responsible for the subsequent evolution of eukaryotic cells and multicellular organisms. The build-up of the ozone layer in atmosphere provided a shield against harmful UV radiation allowing organisms to explore new habitats and, in particular, to exploit the terrestrial environment, i.e. to move from the ocean to the land. Therefore, it can be argued that one of the most important events in the Earth’s history is the evolution of photosynthetic organisms capable of water oxidation [1–17].

Today, it is estimated that photosynthesis produces more than 100 billion tons of dry biomass annually, which would be

equivalent to a hundred times the weight of the total human population on our planet at the present time and equal to a global energy storage rate of about 100 TW. The success of this energy generating and storage system stems from the fact that the raw materials and energy needed to drive the synthesis of biomass are available in almost unlimited amounts; i.e., sunlight, water and carbon dioxide. In other words, the solar power is the most abundant source of renewable energy and photosynthetic machinery uses this energy to power the thermodynamically and chemically demanding reaction of water splitting. At the heart of the reaction is the splitting of water by sunlight into oxygen and hydrogen. In so doing, it provides biological systems with an unlimited supply of the 'hydrogen' (electrons and protons) needed to convert carbon dioxide into the organic molecules of life [6,7].

Photosynthesis can be either oxygenic ( $O_2$  producing) or anoxygenic. Oxygenic organisms use solar energy to extract electrons and protons from water mainly for the  $CO_2$  assimilation cycle, and  $O_2$  as an incidental product is produced. Anoxygenic organisms do not possess the necessary redox potential to oxidize  $H_2O$  and are therefore obliged to take electrons from electron donor substrates like  $H_2S$  or organic acids. Oxygenic photosynthesis takes place in higher plants, algae and cyanobacteria, whereas anoxygenic photosynthesis occurs in organisms such as green sulfur and purple non-sulfur bacteria (see e.g., [2–9,15–17]).

We owe to photosynthesis that solar energy is captured and accumulated in the form of biofuel as coal, oil and gas. However, the fuels provided by photosynthetic organisms have been intensively used and are becoming limited. Out of the global energy consumption in 2008, 81% was obtained from fossil fuels (oil 33.5%, coal 26.8%, gas 20.8%), renewable (hydro, solar, wind, geothermal power and biofuels) 12.9%, nuclear 5.8% and other 4%. Oil and coal combined represented over 60% of the world energy supply in 2008 [18,19]. Moreover, global energy consumption will increase from the current level of 12.8 TW to 28–35 TW by 2050. This will lead to further global warming on our planet [6,7,18–21] as the levels of  $CO_2$  and other greenhouse gases rise in Earth's atmosphere. During the last 50 years, the concentration of atmospheric  $CO_2$  has increased by more than 20% [20]. The surface temperature of the Earth has increased by 0.6–0.9 °C (1.1–1.6 °F) over the period 1906–2005, and the rate of temperature increase has nearly doubled in the last 50 years. Temperatures are certain to go up further (see e.g., [6,7,21–29]). It is still debatable how much the activity of human industry is responsible for this global change of our climate, since there are just too many variables. Nevertheless, the reason for which human activity is definitely responsible seems to be the invention of many ways to liberate  $CO_2$ , and hardly any to assimilate it. This is problematic, because we are distorting the balance of the carbon cycle by the consumption of our inherited carbon resource, without much hope for its renewal.

It is clear that fossil fuels (i.e., petroleum, natural gas and coal), which meet most of the world's energy demand today, are being depleted fast. Also, their utilization is causing global problems, such as the global warming, climate change, ozone layer depletion, acid rains, oxygen depletion and pollution,

which are posing great dangers for our environment and eventually for the life on the planet Earth. Many engineers and scientists agree that the solution to these global problems would be to replace the existing fossil fuel system by the Hydrogen Energy System. Hydrogen is the most efficient and the cleanest fuel. Its combustion will produce no greenhouse gases, no ozone layer depleting chemicals, little or no acid rain ingredients, no oxygen depletion and no pollution [26].

Hydrogen is a clean, zero carbon emission, and renewable energy carrier, with a high specific heat of combustion. Hydrogen can be used in internal combustion engines to generate mechanical power or in fuel cells to generate electricity. As hydrogen can be produced from many natural sources, it is expected to have a stable price in the future, independent of the fluctuation in price and availability of single sources. Hydrogen also allows flexibility in balancing centralized and decentralized power supply [22–29]. Of course, hydrogen is a synthetic fuel and it must be manufactured. There are various hydrogen manufacturing methods such as direct thermal, thermochemical, electrochemical, biological, etc. Among the hydrogen production methods, biological method has the potential of resulting in the most cost effective hydrogen. Because of this, many research groups around the world are working on biological hydrogen production [26].

Now it is time and it is important to develop renewable and clean energy sources for the future. In this regard, photosynthesis provides a successful example of how solar energy can be converted into fuel when electrons are extracted from water by using light as the only energy input. It would be wise to look into photosynthesis in further detail, because the photosynthetic processes contain many clues from which we could learn. An economy and an infrastructure for transport, based on molecular hydrogen and fuel cells could decrease our dependence on oil and the concomitant environmental consequences. Such approach would also positively affect energy security, while mitigating air pollution and global climate change. Biological production of hydrogen using photosynthesis may someday become a valuable alternative to chemical and electrochemical technologies. Firstly, solar energy and water are cheap and renewable energy sources. Secondly, burning  $H_2$  is clean, emitting water as end product, and a renewable process [6,7,22–26]. Photosynthesis is at the basis of all biological solar-driven methods of  $H_2$  production in green algae, cyanobacteria and higher plants.

Some of the anoxygenic organisms are able to generate hydrogen quite efficiently. However, as they cannot get electrons from water, their use is not commercially viable for the photoproduction of hydrogen on a large scale. All oxygenic phototrophs extract electrons and protons from water and use them to reduce plastoquinone and  $NADP^+$  as energy sources for the metabolism. In this case, oxygenic phototrophs including cyanobacteria and microalgae can transiently produce  $H_2$  under anaerobic conditions via proton reduction catalyzed by the key enzyme hydrogenase (or nitrogenase) in competition with other intracellular processes. In this case, the electrons and protons, ultimately produced by water oxidation, are transferred via ferredoxin/ $NADPH$  to hydrogenase. Thus, the photosynthetically reduced ferredoxin (or  $NADPH$ ) can serve as the physiological electron donor to

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