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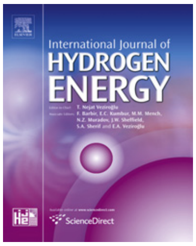

Editorial

Photosynthetic and biomimetic hydrogen production

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A B S T R A C T

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_2 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.

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_2S or NH_3, 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 was the most popular energy fuel. 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 hydrogenase and link hydrogenase (nitrogenase) to the electron-transport chain [6,7,22–28].

The study of biological hydrogen production in green algae began as a curiosity, and after 75 years of research, its evolutionary origin still remains an enigma ([22–24] (and references therein)). General progress in the field has been ongoing since early 1940s, when Hans Gaffron discovered that the green alga *Scenedesmus obliquus* produced hydrogen [29]. However, the last decade was marked by dramatic advances that have re-energized photobiological hydrogen production r&d activities. Certain algae under anaerobic conditions can use starch as a source of H^+ and e^- for H_2 production using hydrogenases. In cyanobacteria, the H^+ and e^- derived from H_2O can be converted to H_2 via nitrogenases or fermentation. Specifically, the hydrogenase genes for several species of green algae have been sequenced and the crystal structure determined. In addition, the mechanism by which a hydrogenase creates molecular hydrogen has been elucidated from extensive research on the structure, assembly, and biological properties of all hydrogenases [6–8,22–29].

We know that commercial photosynthetic hydrogen production will not be available until progress is made to solve two major problems that prevent the hydrogenase enzyme from producing significant amounts of molecular hydrogen. First, the hydrogenase has a short half-life that prevents it from producing hydrogen for longer than a minute. Second, it is necessary that the hydrogenase be tolerant to oxygen. Since all known hydrogenases have a short half-life even in the presence of very low concentration of oxygen, only a modified hydrogenase with increased hydrogen production and/or decreased oxygen sensitivity will allow for the commercial production of photosynthetically generated hydrogen [6,7,22–29].

On the other hand, it is clear that humans have always been fascinated by nature, and have constantly made efforts to mimic it. Rapid advancements in science and technology have now made them to act beyond, rather than just mimicking nature. They have now begun to understand and implement nature's principles like never before. By adapting mechanisms and capabilities from nature, scientific approaches have helped them to understand the related phenomena in order to engineer novel devices and design techniques to improve their capability. This field is now called as biomimetics or bioinspired technology. The term biomimetics is derived from bios meaning life and mimesis meaning to imitate. While some of nature's designs can be copied, there are many ideas that are best adapted if they are to serve as an inspiration using man made capabilities. There are many characteristics that can uniquely identify a biomimetic mechanism, and a major characteristic is to function autonomously in a complex environment, being adaptable to unpredictable changes and to perform multifunctional tasks. Some of the major benefits of biomimetics include development of artificial photosynthesis for hydrogen production [22–26,30–32].

As mentioned above, oxygen is released into the atmosphere where it is available for us to breathe and to use it for burning our fuels. The H_2 is not normally released into the atmosphere, but instead is combined with CO_2 to make high energy containing organic molecules of various types. When we burn fuels we combine the "stored hydrogen" of these organic molecules with oxygen. In this respect, the goal of making artificial photosynthesis-biomimetic is to utilize solar energy and convert it into chemical energy through a series of electron-transfer events. The design of such systems must adhere to the same principle as that in the natural photosynthesis. Today we have considerable knowledge of the working of photosynthesis and its photosystems, including water oxidation reaction. However, many questions and details remain unanswered. To fully understand photosynthetic reactions is not only a satisfying intellectual pursuit, but is also an important goal as we strive to improve agricultural yields and develop new solar technologies for splitting of water and generating fuels [3–8,22–26].

The human life has existed, and exists today, due to photosynthesis and thanks to all the plants, algae and cyanobacteria for doing photosynthesis for us and giving us oxygen, food, biomass, and bioenergy. The present day life, as we know it, is dependent on oxygenic photosynthesis. It provides breathable air, and photosystem II can derive an unlimited source of electrons from water for oxygen and hydrogen, by using energy from the sun [7].

We are pleased to bring out this special issue. This issue contains selected and invited papers presented at the International Conference in Baku, Azerbaijan. We provide a brief report on the conference (for further information, see Allakhverdiev et al. [33]).

2. The conference

There were 280 participants from 41 countries (Australia, Austria, Azerbaijan, Belarus, Bulgaria, Canada, China, Czech Republic, Denmark, Estonia, Finland, France, Germany, Hungary, India, Iran, Israel, Japan, Jordan, Kazakhstan, Korea, Latvia, Mongolia, Nepal, New Zealand, Pakistan, Poland, Roumania (Romania), Russia, Singapore, Slovakia, Spain, Sweden, Switzerland, Syria, Tajikistan, Turkey, The Netherlands, UK, Ukraine, and USA). This conference was held during July 24–30, 2011 and the participants discussed previous, present, and future research on photosynthesis, ranging from molecular to global aspects of this process (http://www.photosynthesis2011.cellreg.org/Conference-programme.php).

Fig. 1 shows a photograph of the opening ceremony of the conference, and Fig. 2 shows some of the audience at the opening ceremony.

Fig. 3 shows a group photograph of the participants and the organizers, whereas Figs. 4 and 5 shows some individual participants at the conference. For other photographs of this conference, see http://www.photosynthesis2011.cellreg.org/Photos.php and http://www.life.illinois.edu/govindjee/g/Photo/Baku.html.

The scientific program was quite exciting; it covered the breadth and depth of photosynthesis. In particular, this conference was very good for international students, postdocs and other young investigators to expand their knowledge and understanding of the entire field of photosynthesis.

The two organizing committees, international and local, are listed at: http://www.photosynthesis2011.cellreg.org/Organizing-committee.php. The honorary chairman of this conference was Jalal A. Aliyev, whereas co-chairmen were: T. Nejat Veziroglu (President of International Association for

Fig. 1 – Opening ceremony of the conference *Photosynthesis Research for Sustainability-201, Baku, Azerbaijan, July 24–30, 2011*. Place: The main building of the Azerbaijan National Academy of Sciences, Baku, Azerbaijan. *Left to right*: Suleyman Allakhverdiev (Coordinator of the meeting); Jalal Aliyev (Honorary Chairman); James (Jim) Barber (Chairman, Past President of the International Society of Photosynthesis Research, ISPR); Ali Abbasov (Chairman of the local organizing committee, Minister of Communication and Information Technology of the Republic of Azerbaijan); and William (Bill) Rutherford (Current President of the ISPR).

Fig. 3 – A group photograph of some of the participants at the conference on the grounds of the Crescent Beach Hotel.

Hydrogen Energy) and Gary Brudvig. The chairman of the International Committee of the conference was James Barber, whereas the chairman of the local organizing committee was Ali Abbasov. The coordinator of this meeting was Suleyman Allakhverdiev (the author).

This international conference covered almost all the important aspects of photosynthesis, and their relationship to global issues, as well as hydrogen production and artificial photosynthesis. Topics included: Type I and Type II reaction centers; photosynthetic electron flow and photophosphorylation; mechanisms of water oxidation; photosynthetic light harvesting; C3, C4 and CAM photosynthesis; regulation of photosynthetic gene expression; biogenesis of photosynthetic apparatus; photosynthesis and environmental stress; artificial photosynthesis; photosynthetic and biomimetic hydrogen production; photosynthesis in relation to crop and biomass productivity; photosynthesis education; and bioinformatics of photosynthesis.

There were sixty three speakers (listed alphabetically): Ali Abbasov, Jalal Aliyev, Suleyman Allakhverdiev, Seiji Akimoto, Eva-Mari Aro, James Barber, Marc Brecht, Robert Blankenship, Barry Bruce, Min Chen, Holger Dau, Leslie Dutton, Julian Eaton-Rye, Arvi Freiberg, Gyozo Garab, Carina Glöckner, John Golbeck, Govindjee, Joanna Grzyb, Kentaro Ifuku, Anjana Jajoo, Khurram Saleem Joya, Hazem Kalaji, Diana Kirilovsky, Vyacheslav Klimov, Ernst-Walter Knapp, Anja Krieger-Liszkay, Olaf Kruse,

Fig. 2 – Audience at the opening ceremony in the main building of the Azerbaijan National Academy of Sciences (*top, left and right*), and at the Crescent Beach Hotel (*bottom, left and right*).

Fig. 4 – Some of the participants. ***Top left to right*** **Mitsue Miyao with Elvin Suleymanoglu Allakhverdiev (a 13-year-old participant), Maria Leonova, Denis Yanykin.** ***Middle left to right*** **Masami Kusunoki with Zinaida Eltsova, Suleyman Allakhverdiev (the author) with Emina Dinc, Maria Mubarakshina.** ***Bottom left to tight*** **Olaf Kruse and Elvin Suleymanoglu with Hiroshi Nishihara. Khorcheska Batyrova, Anatoly Tsygankov.**

Steven Long, Heiko Lokstein, Mahir Mamedov, Tarlan Mamedov, Mitsue Miyao, Jun Minagawa, Norio Murata, Frank Müh, Nathan Nelson, Hiroshi Nishihara, Marc Nowaczyk, Jorg Pieper, Seeram Ramakrishna, Fabrice Rappaport, Gernot Renger, Jean-David Rochaix, Andrey B. Rubin, William Rutherford, Franz-Josef Schmitt, Ilham Shahmuradov, Jian-Ren Shen, Vladimir Shuvalov, Per Siegbahn, Victor Solovyov, Igor Stadnichuk, Miwa Sugiura, Ichiro Terashima, Tatsuya Tomo, Anatoliy Tsygankov, Esa Tyystjarvi, Imre Vass, Athina Zouni, Ismayil Zulfugarov, Akiho Yokota, and Vidadi Yusibov. In addition, we had about 90 posters.

3. Young researcher awardees

This conference enabled organizers to select 9 awardees from among the young researchers who presented their work at this conference. The awards/prizes were presented to these researchers who had done and presented outstanding research in the field of "photosynthesis for sustainability". These young researchers included Ph.D. students, as well as post-docs. For a list of the chairpersons and the selection committee, see Allakhverdiev et al. [33].

Fig. 5 – Some of the participants. *Top left to right* Hiroshi Nishihara at opening ceremony. Immediately behind Olga Avercheva, is Holger Dau, Keisuke Saito, Hazem Kalaji, Karolina Bosa, Lyudmila Vasiliyeva. *Middle left to right* Norio Murata, Elvin Suleymanoglu Allakhverdiev (a 13-year-old participant), with Vladimir Paschenko. Tatsuya Tomo with Yashar Feyziyev, Vasilij Goltsev. *Bottom left to right* Franz-Josef Schmitt, Esa Tyystjarvi, Martin Trtilek, with Miwa Sugiura, and Leslie Dutton with William (Bill) Rutherford.

The 9 awardees (listed alphabetically) are: (1) Tofig Allahverdiyev (Research Institute of Crop Husbandry, Ministry of Agriculture of Azerbaijan Republic, Baku, Azerbaijan). *Title of research*: Effect of soil water deficit on gas exchange parameters, relative water content and assimilating surface area of leaves from bread wheat genotypes. (2) Emine Dinc (Institute of Plant Biology, Biological Research Center, Hungarian Academy of Science, Szeged, Hungary). *Title of research:* Application of synthetic antisense oligodeoxy-nucleotides in higher plants. (3) Zinaida Eltsova (Institute of Basic Biological Problems, Russian Academy of Science, Pushchino, Moscow Region, Russia). *Title of research*: Purple bacteria mutants with low pigment content: do they have higher potential as hydrogen producers? (4) Vaclav Karlicky (Department of Biophysics, Faculty of Science, Palacký University, Czech Republic). *Title of research*: The acclimation of the photosyntetic apparatus to different intensity of PAR. (5) *Maria Leonova* (Institute of Basic Biological Problems, RAS, Pushchino, Moscow Region, Russia). *Title of research*: Electron transfer in *Rhodobacter sphaeroides* mutant reaction centers in

Fig. 6 – Expression of thanks to Jalal Aliyev. *Top left* Jalal Aliyev and Norio Murata with Gernot Renger and Gyozo Garab. *Right* William (Bill) Rutherford and Jalal Aliyev. *Bottom left* James (Jim) Barber and Jalal Aliyev. *Right* Jalal Aliyev, Asaf Hajiyev, Ali Abbasov and Jim Barber.

the absence of the monomer bacteriochlorophyll molecule B_A. (6) Roshan Sharma Poudyal (Department of Molecular Biology, Pusan National University, Korea). *Poster title*: Impairment of Photosystem II repair and accumulation of reactive oxygen species in STN8 kinase knock-out rice mutants. (7) Junji Uchiyama (Research Center for RNA Science, RIST, Tokyo University of Science, Noda, Japan). *Poster title*: The Sph two component signal transduction pathway of *Synechocystis* sp. PCC 6803 regulates transcription of the gene specifying acid stress-inducible protein Slr0967 and Sll0939. (8) Mai Watanabe (Department of Life Sciences (Biology), Graduate School of Arts and Science, University of Tokyo, Tokyo, Japan; *title of research*: Photosystem I specific phycobilisome in *Anabaena* sp. *PCC 7120*). (9) Ivelina Zaharieva (Frei Universität Berlin, Institute für Experimental Physik, Berlin, Germany). *Poster title:* A novel electrodeposited Mn film mimicking the Mn cluster in Photosystem II as an efficient catalyst for water oxidation.

Fig. 6 shows the expressing of thanks to Jalal Aliyev.

I end this Editorial by paying special Tribute to Jalal Aliyev for his pioneering contributions to the growth and support of Science in Azerbaijan, especially to this conference.

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