Toward Efficient Solar Light Hydrogen Generation from Water. Bioinspiration and Structuring by Zeolites

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Toward Efficient Solar Light Hydrogen Generation from Water. Bioinspiration and Structuring by Zeolites

There is an urgent need for developing renewable energy resources that can be alternative to fossil fuels.[1] Sunlight is the cleanest and almost inexhaustible source of energy that made possible and now sustains life on the Earth. By evolution of millions of years, green algae and plants have developed a complex and delicate system to convert the energy of sunlight into chemical energy. As our understanding of natural photosynthesis has become deeper and more detailed, we have realized the complicated machinery responsible for this process and, importantly, the crucial role played by the assembling and spatial structuring of the various components. The spatial arrangement of the individual pieces involved in the photosynthesis is very important in order to harvest the light and use its energy for charge separation and funneling of electrons and protons to the catalytic centers where they are converted into chemical energy.

Nature can serve in this regard of "bioinspiration" in the long-term design of photoresponsive systems to convert solar light into energy, showing the feasibility and the benefits of this process. However, we are still far from having comparable photosynthetic systems, and our current approach must be necessarily more realistic, looking for photoactive materials with a considerably lower degree of complexity than the natural photosynthetic centers. A part of the research concerning conversion of sunlight into energy has focused on visible light photocatalytic hydrogen generation.[2] Large-scale generation of hydrogen from water rather than from fossil fuels, as is currently obtained in industry, will have a tremendous economic impact that will revolutionalize the energy sector. Hydrogen, when adequately stored and used in fuel cells instead of combustion engines, is the ideal fuel for transportation because under these conditions, water will be the only byproduct without the formation of CO_2, NO_x, or SO_x, which are currently emitted in the combustion of fossil fuels and are responsible, among other effects, for climate change.

As simple as it may seem considering the chemical equation going from H^+ to H_2, hydrogen generation from water using solar light is a challenging process for the chemistry of the 21st century that still remains unsolved. The reason is that photocatalytic hydrogen generation involves many elementary steps, and all of them need to be optimized in order to achieve a decent efficiency. One of the most studied methodologies for visible light hydrogen generation consists of synthesizing a material (photocatalyst) that, upon light absorption of energy larger than their band gap, effects charge separation with the creation of an electron in the conduction band of the material and a hole in the valence band (Scheme 1). Electrons can act to reduce water to hydrogen, and holes can oxidize water to oxygen. Thus, the same material can effect oxidation and reduction simultaneously in each particle, provided that the energies of the valence and conduction bands are sufficient to abstract and donate electrons to the water, respectively.

This simple approach of synthesizing a photocatalytic material, although it constitutes a proof of principle of the feasibility of water splitting by light, suffers from a low yield due mainly to the mismatch between the solar spectrum and the absorption spectrum of the material and the occurrence of wasteful electron/hole recombination before effecting any chemical event. Charge recombination can be minimized when migration of electrons is very fast and through long distances and when the rate of the chemical processes is also fast. All of the strategies to improve the efficiency of the photocatalytic materials for hydrogen generation involve the development of photosynthetic systems more elaborate than just a simple material.

When looking for ways to overcome the limitations of the current photocatalytic materials, biomimesis and bioinspiration can be of large utility. The knowledge gained from the study of how the natural photosynthetic systems operate is a powerful source of ideas and concepts that can be translated to artificial photosystems. In this regard, in his Perspective appearing in this issue,[3] Vullev illustrates some of the key features of natural photosynthesis that should be implemented on the artificial photocatalysts in order to improve their efficiency for solar light hydrogen generation. In his article, Vullev emphasizes that assembling of different components with specific missions such as light harvesting, energy funneling, and water oxidation and their spatial structuring is the most salient feature of the photosynthetic machinery. In addition, he also remarks the importance of the concept of electrets, macromolecules in which electric dipoles have a defined orientation over tens of nanometers assisting electrons in moving in the correct sense. Protein helices in the thylakoid membrane have, besides the structural role, the mission to drive the electrons formed in the photoinduced charge separation event in the desired direction, favoring charge separation that, as already indicated, is one of the main problems limiting the efficiency in most photocatalytic materials. Learning more about the natural photosystems surely will inspire further improvements in artificial systems.

Thus, it appears that spatial structuring is of extreme importance in natural photosystems. The thylakoid membrane acts as a scaffold separating the exterior from the interior of the photosynthetic organule, allowing different proton concentrations between the interior and the exterior and the creation of a electrochemical potential between the internal thylakoid lumen and the cytosol. The role of a membrane defining topologically an "in" and "out" is necessary when differences in

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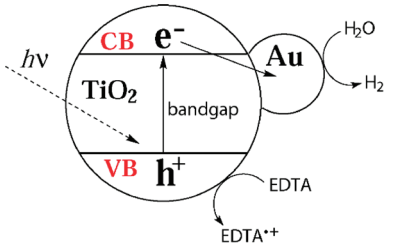
Scheme 1. Photocatalytic Activity of TiO_2 Having Gold As the Gas Evolution Center for Hydrogen Generation upon Excitation at the Band Gap in the Presence of a Sacrificial Electron Donor

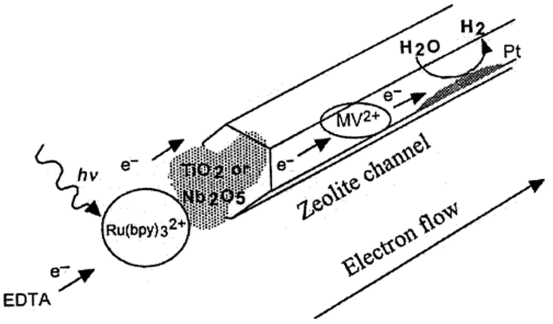


proton concentration and electrochemical potentials are required. In this context, inorganic porous materials such as zeolites can also be used as scaffolds to assemble in an ordered way different components assisting a vectorial electron transfer in a preferred direction. Dutta and co-workers have made substantial contributions showing how to use zeolites as structuring components to construct photocatalytic hydrogen generation.[4] Although the efficiency of these zeolite-based photocatalysts still needs improvement, at longer term, photocatalysts based on zeolite membranes are highly promising because the zeolite framework can act as a mimic of a thylakoid membrane and as a electride setting oriented dipoles in the space. Scheme 2 shows how the zeolite framework can be used to organize a photocatalytic system for water splitting. Fundamental work in this area has shown that the high polarity of the micropores increases considerably the lifetime of the charge separation beyond the microsecond time scale. Charge separation is a transient state that is typically very short lived (less than nanoseconds) in most semiconductors, this short life being a strong limitation to the overall efficiency.

The current status of the use of zeolites to develop efficient photocatalytic systems may still be far from commercial application, and many more fundamental studies are needed toward this goal. In this context, Hashimoto and co-workers have made large contributions toward the understanding of diffusion of molecules inside of the zeolite micropore system.[6] He has been applying optical microscopy to determine how the properties of the molecules and the composition and structure of the zeolite influence diffusion, a physical process that not only is important for the preparation of the photocatalytic system but also is an elementary step in any (photo)catalytic reaction. By a clever design of donor and acceptor pairs and using fluorescence microscopy, it has been possible to follow the migration of molecules on the time scale of days and months as well as to establish the influence of water and other conditions in diffusion and relocation of the embedded molecule.

With respect to other photocatalytic materials, photocatalytic systems based on microporous zeolites allow organization of the different components in a topologically defined arrangement, and the charge separation being favored by the polarity of the internal voids holds considerable promise for these systems. What is probably needed to further develop these materials, bringing them closer to application, is novel procedures for the well-defined preparation of multicomponent systems having included guests. The advantages of this approach are derived from the understanding of the natural photosynthetic systems and their most remarkable features. Thus, as far as they may seem to be coming from different worlds, the use of inorganic zeolites for photosynthesis can be envisioned as one original approach derived from bioinspiration.

Scheme 2. Pictorial Illustration of the Visible Light Photocatalytic Hydrogen Generation Based on a Multicomponent System Assembled in a Monodirectional Zeolite[a]



[a] Light absorption by $Ru(bpy)_3^{2+}$ triggers a photoinduced electron transfer to the semiconductor oxide located at the pore mouth. Subsequently, the electron is transferred to methylviologen (MV^{2+}), which acts as an electron relay pooling the electron on the platinum site. Ethylendiaminetetraacetate (EDTA) acts as sacrificial electron donor in the process (taken from ref 5).

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