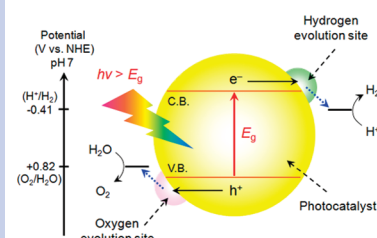


Photocatalytic Water Splitting: Recent Progress and Future Challenges

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ABSTRACT Water splitting to form hydrogen and oxygen using solar energy in the presence of semiconductor photocatalysts has long been studied as a potential means of clean, large-scale fuel production. In general, overall water splitting can be achieved when a photocatalyst is modified with a suitable cocatalyst. It is therefore important to develop both photocatalysts and cocatalysts. In the past five years, there has been significant progress in water splitting photocatalysis, especially in the development of cocatalysts and related physical and materials chemistry. This work describes the state of the art and future challenges in photocatalytic water splitting, with a focus on the recent progress of our own research.



Photocatalytic overall water splitting to form hydrogen and oxygen has attracted considerable attention as a potential means of renewable energy production with no reliance on fossil fuels and no carbon dioxide emission.^{1–5} As illustrated in Figure 1, current successful photocatalytic systems for overall water splitting can be divided into two primary approaches. One approach is to split water into H₂ and O₂ using a single visible-light-responsive photocatalyst with a sufficient potential to achieve overall water splitting. In this system, the photocatalyst should have a suitable thermodynamic potential for water splitting, a sufficiently narrow band gap to harvest visible photons, and stability against photocorrosion. Because of these stringent requirements, the number of reliable, reproducible photocatalysts suitable for one-step water splitting is limited.^{6,7} The other approach is to apply a two-step excitation mechanism using two different photocatalysts.⁸ This was inspired by natural photosynthesis in green plants and is called the Z-scheme. The advantages of a Z-scheme water splitting system are that a wider range of visible light is available because a change in Gibbs free energy required to drive each photocatalyst can be reduced as compared to the one-step water splitting system and that the separation of evolved H₂ and O₂ is possible. It is also possible to use a semiconductor that has either a water reduction or oxidation potential for one side of the system. For example, some metal oxides (e.g., WO₃ and BiVO₄) function as a good O₂ evolution photocatalyst in a two-step water splitting system using a proper redox mediator, although they are unable to reduce water.^{9,10} Successful overall water splitting via two-step photoexcitation by visible light using several combinations of photocatalysts and electron relays has been reported.^{9–16} However, challenges remain in the promotion of electron transfer between two semiconductors and in the suppression of backward reactions involving shuttle redox mediators.

As we can expect from the reaction scheme shown in Figure 1, photocatalytic activity for overall water splitting is strongly dependent on the physicochemical properties of a

photocatalyst, the nature of the active sites (so-called cocatalyst), and the reaction conditions.^{2,4} In the past decade (in particular, from 2000 to 2005), a number of materials have been reported as visible-light-driven photocatalysts capable of producing both hydrogen and oxygen under visible light.^{1–4,17} Some have successfully achieved overall water splitting without any sacrificial reagents. In the past 5 years, significant progress has been made on cocatalyst development and the elucidation of reaction mechanisms. This Perspective highlights some important aspects of recent water splitting research.

Loading nanoparticulate cocatalysts onto a photocatalyst significantly improves the water-splitting rate.

Nanoscale Design of Hydrogen Evolution Sites. Although some of the photocatalysts developed to date (e.g., layered compounds and tantalates) can decompose water without a cocatalyst,⁴ most require the loading of a suitable cocatalyst (such as NiO_x and RuO₂) to obtain a high activity and reasonable reaction rates. It is believed that the cocatalysts provide reaction sites and decrease the activation energy for gas evolution. Noble metals such as Pt and Rh are excellent promoters for H₂ evolution but can also catalyze a backward reaction, forming water from H₂ and O₂, limiting their usefulness as cocatalysts for photocatalytic overall water

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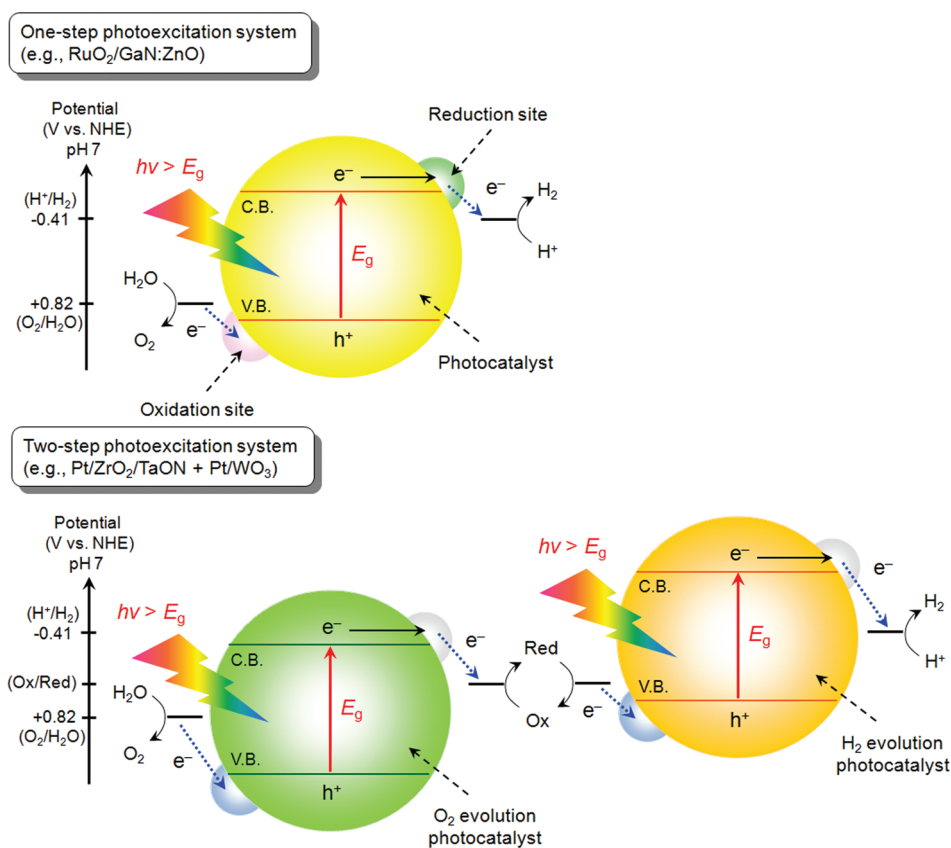


Figure 1. Schematic energy diagrams of photocatalytic water splitting by one-step and two-step photoexcitation systems. C.B., conduction band; V.B., valence band; E_g , band gap.

splitting. To avoid the backward reaction, transition-metal oxides that do not exhibit activity for water formation from H_2 and O_2 are usually applied as cocatalysts for overall water splitting. However, no cocatalyst more effective than NiO_x or RuO_2 was found, until recently.

Our report on a nanoparticulate rhodium and chromium mixed oxide with a solid solution of GaN and ZnO (represented GaN:ZnO hereafter), published in 2006,¹⁸ highlighted the important role of cocatalysts in photocatalytic water splitting and stimulated additional research on such cocatalysts.^{19–21} After the initial study, we attempted to develop a new cocatalyst using nanotechnology.^{22–25} Core/shell-structured nanoparticles (with a noble metal or metal oxide core and a chromia (Cr_2O_3) shell) were presented as a new type of cocatalyst for photocatalytic overall water splitting.²² As schematically illustrated in Figure 2A, core/shell nanoparticles can be readily prepared by the photo-reduction of Cr(VI) ions using noble metal or metal oxide loaded photocatalyst powders in air-free conditions. Figure 2B shows high-resolution transmission electron microscope (HR-TEM) images of metallic Rh-loaded GaN:ZnO, before and after photoreduction of Cr(VI) ions. The figure shows that a shell approximately 2 nm thick was deposited on the Rh metal, forming a core/shell structure. X-ray photoelectron spectroscopy and X-ray absorption spectroscopy revealed that the shell consisted of Cr_2O_3 . As shown in Figure 2C (left panel), Rh-loaded GaN:ZnO exhibited little

photocatalytic activity for overall water splitting, most likely due to rapid water formation on the Rh nanoparticles. However, GaN:ZnO loaded with a Rh core/ Cr_2O_3 shell cocatalyst exhibited stoichiometric H_2 and O_2 evolution from pure water (Figure 2C, right panel). Therefore, significant water formation from H_2 and O_2 occurs on uncovered Rh nanoparticles during overall water splitting, and the suppression of water formation is essential for achieving efficient evolution of H_2 and O_2 in this system. The use of Cr_2O_3 shells on other noble metal cores, such as Pd and Pt, produced similar results.

The above results strongly suggest that a Cr_2O_3 shell can suppress water formation from H_2 and O_2 on noble metals, thereby allowing for the forward reaction ($2H_2O \rightarrow 2H_2 + O_2$). Although this functionality is essential for a noble metal loaded photocatalyst to achieve overall water splitting, it is not necessarily required for metal oxide loaded photocatalysts because metal oxide cocatalysts generally exhibit negligible catalytic activity for water formation, as mentioned earlier. In some cases, however, metal oxide cocatalysts undergo degradation due to a change in the cocatalyst state by exposure to the reactant solution. They can also catalyze O_2 photoreduction (another backward reaction of water splitting), leading to a decrease in activity. When loaded metal oxide nanoparticles are covered with Cr_2O_3 , this deactivation and the resulting O_2 photoreduction is suppressed by the reduced accessibility of the reactants to the loaded metal

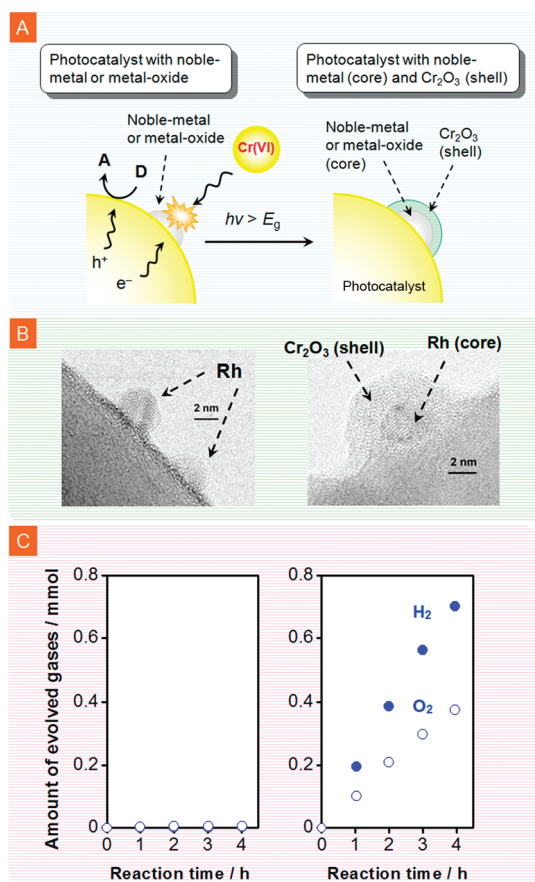


Figure 2. (A) Schematic illustration of Cr_2O_3 deposition through the reduction of Cr(VI) ions (D and A indicate electron donor and acceptor, respectively). (B) HR-TEM images of GaN:ZnO with photodeposited Rh (left) before and (right) after photodeposition of a Cr_2O_3 shell. (C) Time course of overall water splitting under visible light ($\lambda > 400 \text{ nm}$) using GaN:ZnO modified with (left) Rh and (right) core/shell-structured Rh/ Cr_2O_3 .

oxides. It has been reported that the photocatalytic activity of metal oxide loaded GaN:ZnO for overall water splitting was improved by forming a core/shell-like configuration with a Cr_2O_3 shell.²⁴ Therefore, this method is applicable not only to noble metals but also to metal oxides.

Among the noble metals and metal oxides examined as nanoparticulate cores, Rh was the most effective at enhancing activity. However, in the original preparation method, the Rh-based nanoparticles tended to aggregate on the catalyst.^{22,23} As the activity of a catalytic system is, in general, dependent on the surface area available for reaction, the activity of this system should improve further if aggregation of the cocatalyst nanoparticles can be prevented. Therefore, attempting to increase the dispersion of cocatalysts in a given system is a reasonable strategy for improving the photocatalytic activity.

Highly dispersed Rh nanoparticles were successfully loaded on GaN:ZnO without aggregation by adsorbing Rh nanoparticles that were stabilized by 3-mercaptopropylsulfuric acid (prepared by a liquid-phase reduction method) onto GaN:ZnO , followed by calcination under vacuum at 673 K for 30 min.²⁵ The average size of these Rh nanoparticles

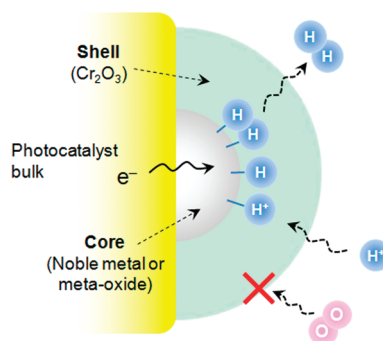


Figure 3. Schematic illustration of H_2 evolution on core/shell-structured nanoparticles (with a noble metal or metal oxide core and a Cr_2O_3 shell) as a cocatalyst for photocatalytic overall water splitting.

was calculated to be $1.9 \pm 0.6 \text{ nm}$, approximately one-fourth the size of particles prepared by photodeposition. After the Rh nanoparticles were coated with a Cr_2O_3 shell, the photocatalytic activity for overall water splitting was tested under visible light irradiation. As expected, the sample with a better dispersion of Rh exhibited three times the activity of an analogue containing poorly dispersed Rh nanoparticles. This follows the general trend in heterogeneous (photo)catalysis; highly dispersed catalytic species generally provide higher reaction rates.

It is very important to understand the reaction mechanism at the nanometer scale in order to design better photocatalytic systems. The mechanism of hydrogen evolution on core/shell-structured nanoparticles was therefore investigated using electrochemical and in situ spectroscopic measurements of model electrodes that consisted of Rh and Pt plates with electrochemically deposited 1.8–3.5 nm thick Cr_2O_3 .²⁶ For both Cr_2O_3 -coated and bare electrodes, proton adsorption/desorption and H_2 evolution currents were observed, and an infrared absorption band assigned to Pt–H stretching was apparent. Therefore, the Cr_2O_3 layer did not interfere with proton reduction or hydrogen evolution, and proton reduction took place at the $\text{Cr}_2\text{O}_3/\text{Pt}$ interface. However, the reduction of oxygen to water was suppressed only in the Cr_2O_3 -coated samples. It was concluded that the Cr_2O_3 layer is permeable to protons and evolved hydrogen molecules but not to oxygen. The reaction mechanism of H_2 evolution on core/shell-structured nanoparticles (with a noble metal or metal oxide core and a Cr_2O_3 shell) in photocatalytic overall water splitting is illustrated in Figure 3.

The above results indicate that Cr_2O_3 modification is a highly useful technique for improving H_2 evolution activity in overall water splitting. Another core/shell cocatalyst for photocatalytic overall water splitting, Ni core/NiO shell nanoparticles, has been applied to many heterogeneous photocatalytic systems.⁴ Compared with Ni/NiO, the present core/shell cocatalyst has several advantages, including (1) the possibility of using various noble metals and metal oxides as a core for the extraction of photogenerated electrons from the photocatalyst bulk, (2) the possibility of selectively introducing active species for overall water splitting at reduction sites on the photocatalyst, and (3) elimination of the need for activation

treatment by oxidation or reduction. The latter two advantages are effective when the core is introduced by an in situ photodeposition method. The elimination of activation procedures involving heat treatment is especially beneficial for nonoxide photocatalysts, which tend to be less heat-resistant.

Kinetic study on photocatalytic water splitting can provide us with rational strategies for improving the efficiency.

Mechanistic Aspect for Photocatalytic Water Splitting and a New Strategy to Improve Activity. During the development of photocatalytic systems for overall water splitting under visible light, a number of photocatalyst materials and preparation methods have been reported. Many studies have focused on the development of materials that are suitable for visible-light-driven overall water splitting by addressing light absorption properties, band edge position, crystallographic quality, particle morphology, and phase purity. However, it is difficult to understand what factor(s) dominates the net photocatalytic activity based on the above physical properties because the photocatalytic reactions proceed through a complicated sequence of competing multistep processes. This demonstrates the importance of understanding the kinetics and dynamics of a photocatalytic reaction to establish rational strategies for the immediate development of photocatalytic systems and for future practical applications.

Aspects of the photocatalytic water splitting mechanism on GaN:ZnO powder modified with a Rh–Cr mixed oxide cocatalyst were examined with respect to the effects of cocatalyst loading, light intensity, hydrogen/deuterium isotopes, and reaction temperature on photocatalytic activity.²⁷ The water splitting rate with the optimally modified photocatalyst was proportional to light intensity under solar-equivalent or weaker irradiation, indicating that accumulation of photoexcited electrons and holes was negligible. Excess loading of the cocatalyst did not improve the water splitting rate. The H–D isotope effect on overall water splitting was significantly lower than previously reported values for photocatalytic and electrochemical H₂ evolution reactions. The apparent activation energy for overall water splitting was as low as 8 kJ mol⁻¹ and was unchanged by the addition of electron donors or acceptors. These results reflect a shortage of photoexcited carriers available for surface redox reactions under steady light irradiation. In summary, the experimental results indicate that the balance between the rates of redox reactions on the photocatalyst surface and carrier generation/recombination in the photocatalyst bulk determines the steady-state charge concentration in the photocatalyst, that is, developing both a photocatalyst and a cocatalyst is important.

The proposed kinetic model of photocatalytic water splitting also suggests that the reaction probability of photoexcited

holes for O₂ evolution versus recombination with intrinsic electrons in the photocatalyst determines the water splitting activity of GaN:ZnO. It would be natural to expect that loading both H₂ and O₂ evolution cocatalysts onto the same photocatalyst would improve water splitting activity, compared to that for photocatalysts modified with either a H₂ or O₂ evolution cocatalyst. It is easy to imagine that the two different cocatalysts would separately facilitate H₂ and O₂ evolution, thereby promoting overall water splitting in harmony. Unfortunately, no successful, reliable example of this has been reported since the initial reports on photocatalytic water splitting in the 1980s, and a demonstration of the concept has remained a challenge.

Very recently, we demonstrated a proof of concept using GaN:ZnO loaded with Rh/Cr₂O₃ (core/shell) and Mn₃O₄ nanoparticles as H₂ and O₂ evolution promoters, respectively, under visible light irradiation ($\lambda > 420$ nm).²⁸ The goal was to generate both H₂ and O₂ evolution sites separately on the same photocatalyst surface. The preparation method developed by our group is a stepwise deposition involving the adsorption of MnO nanoparticles (9.2 ± 0.4 nm) followed by calcination to give crystallized Mn₃O₄ nanoparticles and a subsequent photodeposition of Rh/Cr₂O₃ (core/shell) nanoparticles, as shown schematically in Figure 4A. This procedure allowed the separate construction of H₂ and O₂ evolution sites, as revealed by TEM observation and energy dispersive X-ray spectroscopy analysis. As mentioned earlier, core/shell-structured Rh/Cr₂O₃ nanoparticles provide active sites for H₂ evolution.²⁶ On the other hand, photoelectrochemical analysis revealed that Mn₃O₄ nanoparticles on GaN:ZnO promote photooxidation of water. Finally, overall water splitting was attempted using the as-prepared samples under visible light. As expected, the activity of GaN:ZnO modified with both Rh/Cr₂O₃ and Mn₃O₄ provided a higher activity than modification with either Rh/Cr₂O₃ or Mn₃O₄, as shown in Figure 4B. This demonstrates the validity of the above idea and suggests a new strategy for improving photocatalytic activity for overall water splitting. The proposed reaction scheme of overall water splitting on GaN:ZnO modified with Rh/Cr₂O₃ and Mn₃O₄ is depicted in Figure 4C.

Future Prospects for Photocatalytic Overall Water Splitting. As described above, in the search for visible-light-responsive photocatalysts, significant effort has been devoted to the development of active sites on photocatalysts and elucidating reaction mechanisms, leading to significant progress in the field of heterogeneous photocatalysis for water splitting, especially in the last 5 years.^{18–29} We have developed several promising systems, including Rh_{2–y}Cr_yO₃-loaded GaN:ZnO (one-step water splitting system) and a two-step system consisting of Pt/ZrO₂/TaON and Pt/WO₃ with an IO₃⁻/I⁻ shuttle redox mediator, with respective apparent quantum yields of about 5.1% at 410 nm and 6.3% at 420.5 nm. However, we continue to pursue more active photocatalytic systems capable of harvesting more visible photons. As shown in Figure 5, solar energy conversion efficiency increases when one can achieve overall water splitting under longer wavelength irradiation. Needless to say, this is because the number of available photons in solar spectrum increased with increasing wavelength.

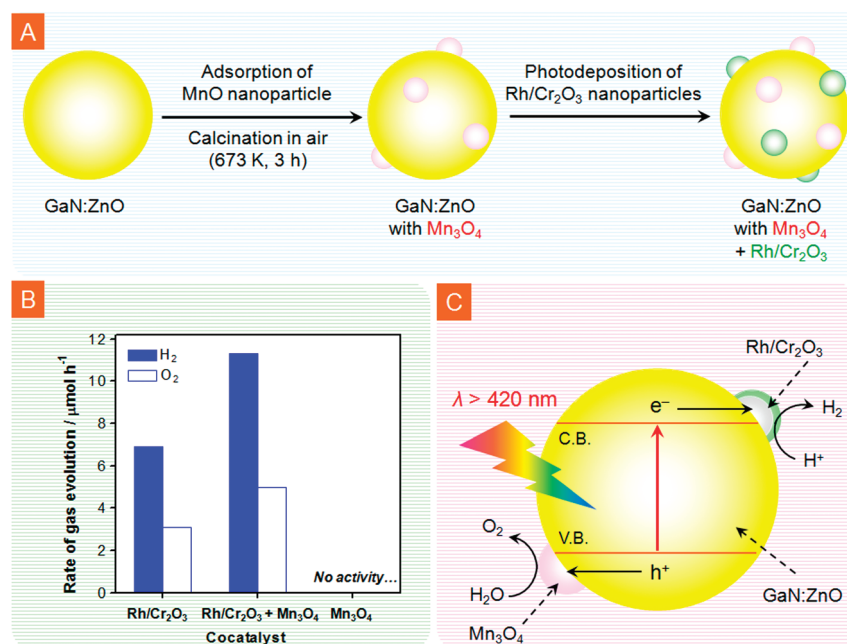


Figure 4. (A) Scheme for the preparation of GaN:ZnO loaded with both Mn₃O₄ and core/shell-structured Rh/Cr₂O₃. (B) Photocatalytic activity of GaN:ZnO modified with different cocatalysts under visible light ($\lambda > 420$ nm). (C) Illustration of the reaction scheme for overall water splitting on GaN:ZnO modified with Mn₃O₄ and core/shell-structured Rh/Cr₂O₃.

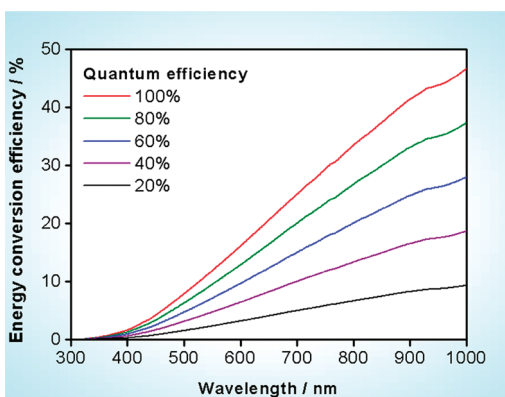


Figure 5. Calculated solar energy conversion efficiency as a function of wavelength for overall water splitting using photocatalysts with various quantum efficiencies. Solar irradiance used for the calculation is taken from AM 1.5G data.

To provide one-third of the projected energy needs of human society in 2050 from solar energy, our preliminary estimation suggests that approximately 10 000 “solar plants” (5 km × 5 km in area per plant) with a solar energy conversion efficiency of 10% would be needed. The total required area, 250 000 km², corresponds to 1% of the earth’s desert area; 570 tons of H₂ gas would be produced per day, assuming an integrated solar energy of AM1.5G irradiation for a day with correction for sunlight angle. This H₂ would be available for use as a “recyclable” reactant in fuel cells and as a raw material for the production of important chemicals such as methanol and so on. Of course, a technology to separate simultaneously produced H₂ and O₂ would be required. This scheme is illustrated in Figure 6. In relation to such a system

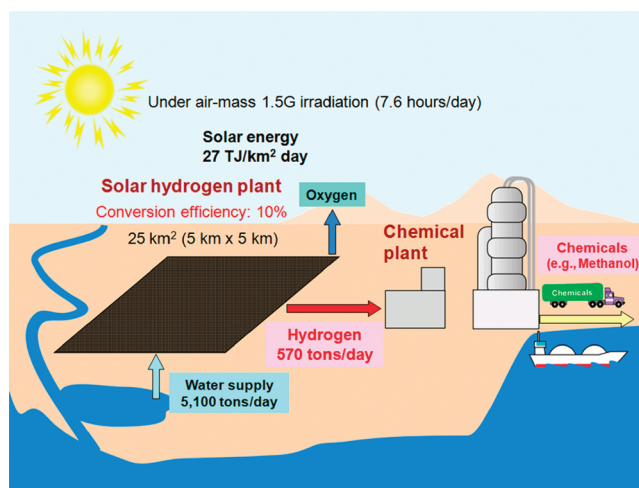


Figure 6. Possible scheme for large-scale H₂ production via solar water splitting.

processing, a unique reactor toward photoelectrochemical hydrogen production was proposed recently.³⁰ James et al. reported a techno-economic evaluation of conceptual photochemical H₂ production systems using solar energy. According to that report, shallow horizontal pools or beds consisting of a flexible clear plastic thin-film baggie, which contains a reactant solution and a photocatalyst, would be a potential candidate as an inexpensive water splitting reactor. Such a system-processing study, including the construction of the water splitting reactor, H₂ and O₂ gas separator, a solar hydrogen chemical plant, and so on, is expected to be more important for realizing practical application in the future.

Clearly, the development of a photocatalyst with a wider absorption band is highly desirable. While there is an activation barrier for surface chemical reactions that evolve H_2 and O_2 , a photocatalyst with a 600 nm absorption edge would be optimal. We have already developed several candidates, such as $LaTiO_2N$, Ta_3N_5 , and $Sm_2Ti_2S_2O_5$, which have a band gap of ~ 2 eV (an absorption edge near 600 nm).² Although the photocatalytic activities of these 600 nm class materials are insufficient to achieve overall water splitting at present, recent progress in materials chemistry toward reducing the density of defects should enable their use.^{15,31} Fortunately, in a two-step water splitting system, the absorption wavelengths available for H_2 and O_2 evolution have been increased to 660 nm (using $BaTaO_2N^{12}$) and 600 nm (using Ta_3N_5), respectively.¹⁶ It is also important to investigate the nature of the defects, which can facilitate the undesirable electron–hole recombination, in photocatalysts, because fewer than 10% of the incident photons are used by current reaction systems for photocatalytic overall water splitting. Our research is currently under way along with directions of both photocatalyst preparation and system processing in harmony.

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Biographies

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Kazunari Domen received his BSc. (1976), MSc. (1979), and Ph.D. (1982) in chemistry from the University of Tokyo. He joined the Tokyo Institute of Technology in 1982 as an Assistant Professor and was subsequently promoted to Associate Professor in 1990 and Professor in 1996. He moved to The University of Tokyo in 2004 and is currently a full Professor. His current research interests include heterogeneous catalysis and materials chemistry, with particular focus on surface chemical reaction dynamics, photocatalysis, solid acid catalysis, mesoporous materials, and fuel cell catalysts. Further information on the Domen research group can be found at <http://www.domen.t.u-tokyo.ac.jp/>.

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