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Advances in solar hydrogen technologies

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Hydrogen produced from water or biomass through a solar-driven process provides a low-polluting alternative to fossil fuels.

Hydrogen is a clean and efficient fuel that has gained popularity as an alternative source of energy. Because hydrogen is not readily available as a gas, it has to be obtained from sources such as water and biomass where it exists in combination with other elements. For example, it can be produced by the electrolysis of water using a simple process. This method is, however, very energy consuming and expensive.

It has long been hoped that solar power could be used to produce hydrogen from renewable resources, making it an attractive option to help satisfy the world's demand for energy while ensuring environmental sustainability. Recent developments in solar-driven photocatalytic and thermochemical technologies that directly convert water and/or biomass into hydrogen have made this possibility real. Our group has been working to advance these technologies for high-efficiency and low-cost solar hydrogen conversion for the past 15 years.[1]

Since the pioneering work of Fujishima and Honda in 1972,[2] a high volume of research on semiconductor photocatalysis has yielded significant results. These include a better understanding of how this process can be used for hydrogen production with enhanced energy conversion efficiency.[3] From a systematic point of view, catalytic materials (semiconductor photocatalyst), reaction media (sacrificial reagent solutions) and reactor-related systems (pilot-scale demonstrations) are considered the three key issues in photocatalytic hydrogen production. When the basic mechanisms and processes are considered, the essentials are efficient visible-light harvesting and enhanced charge separation.[3] Our research gives particular attention to the optimization of the latter two issues while taking into account the systematic aspects.

We have developed different kinds of visible-light-sensitive photocatalysts by band-structure engineering (ion doping and the making of solid solutions are examples) and enhancement of photo-induced charge separation (nanostructure design, semiconductor combination and co-catalyst loading).[4] Nano-twin CdS-ZnS (cadmium sulfide, zinc sulfide) solid solutions without co-catalyst loading are particularly interesting. They exhibit superior photocatalytic activity with very high quantum efficiency (43% at 420nm) when solar hydrogen is produced from an aqueous solution containing SO_3^{2-}/S^{2-} (sulfite anion and sulfide anion composite) as a sacrificial reagent. These activity and efficiency values are due to the effective separation of photo-induced electron-hole pairs by a twin-boundary potential (see Figure 1).[5] Sacrificial reagents (preferentially polluting

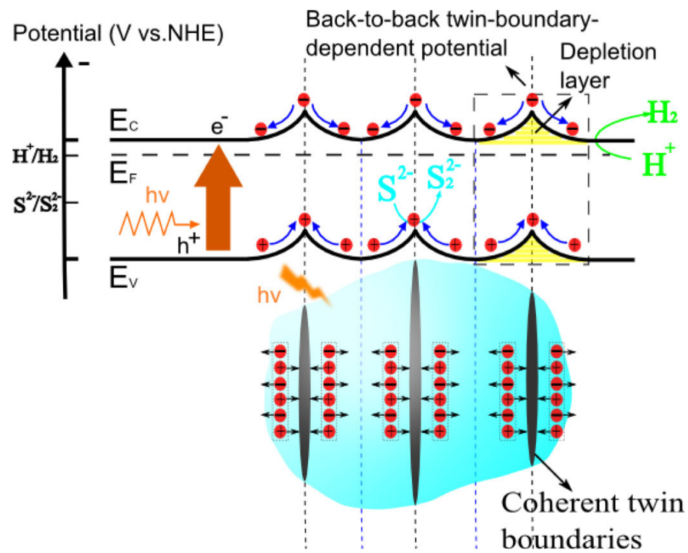

Figure 1. *The migration of free charges and photocatalytic hydrogen production from an aqueous solution over nano-twin CdS-ZnS solid-solution crystals. Parallel boundaries provided the twin-boundary-dependent potential deriving the 'back to back' Schottky barrier that controlled the charges' migration. V: Potential. NHE: Normal hydrogen electrode.* hv*: Planck constant (*h*) × photon frequency (*v*).* E_c*,* E_F*,* E_v*: Electron energy of conduction band, Fermi level and valence band, respectively.* H^+*: Proton.* h^+*: Hole.* e^-*: Electron.* S^{2-}*: Sulfide anion.* ${S_2}^{2-}$*: Persulfide anion.*

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Figure 2. *(A) Reaction array with every module connected in parallel by inlet and outlet. (B) Single-reaction module used for the assembly of a pilot demonstration.*

by-products from industries or low-cost renewable biomass from animals or plants) are typically included in aqueous reaction media for enhanced and sustainable hydrogen production.[3]

To use direct sunlight for photocatalytic hydrogen production in the open air, we set up a compound parabolic concentrator (CPC)-based reactor and a pilot-scale demonstration of the process. We found that hydrogen was produced efficiently when a tubular reactor was coupled to the CPC concentrator.[6] We also developed a modified pilot-scale demonstration using full-spectrum solar energy. In this case, we suspended photocatalyst powders in the reaction solution in the tubular reactor using natural gas circulation (typically for 55min per hour or more) and interval forced circulation (for 5min per hour). The cost of solar energy conversion decreases with this method because the external energy required for the continuous circulation of the reaction suspension is greatly reduced. Our demonstration system is composed of nine modules (see Figure 2) with an effective area for sunlight of more than 30m^2. We anticipate the solar-hydrogen energy conversion efficiency to be no less than 7% when a high-efficiency photocatalyst like PdS/CdS (composite of palladium and cadmium sulfides) and a suitable sacrificial reagent solution such as SO_3^{2-}/S^{2-} are used.

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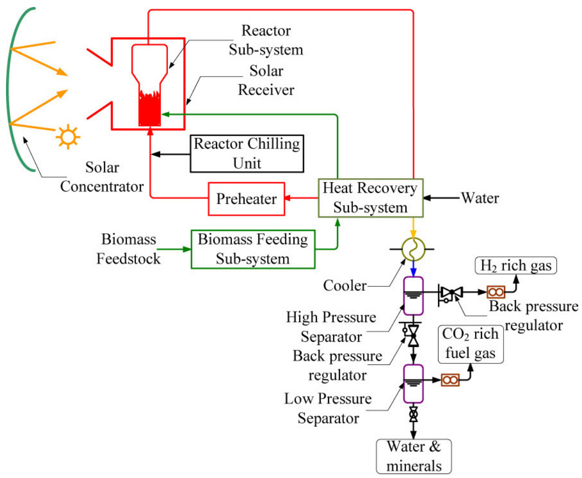

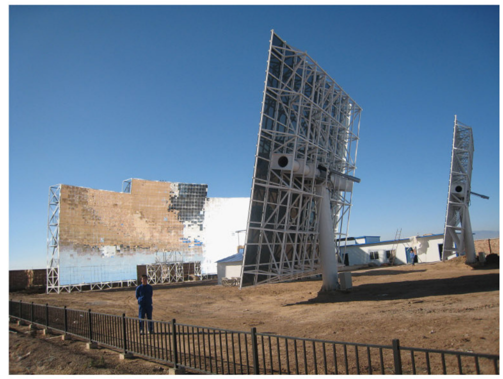

Figure 3. *Schematic diagram (left) and photo (right) of the pilot-scale demonstration for hydrogen production by biomass gasification in supercritical water using concentrated solar energy.*

In addition to water, biomass (such as energy crops, agricultural residues, organic wastes, and forestry waste) is another potential source for hydrogen production. Supercritical water (SCW) is a promising reaction medium to gasify this biological material. The process can achieve a gasification ratio as high as 100% and a hydrogen volumetric ratio up to 50%. Moreover, the technology needed to produce hydrogen by this method has already been shown to be economically competitive.

Since 1997, we have conducted a series of systematic studies on hydrogen production from biomass in SCW.[1,7–9] the fraction of hydrogen approached 55.6%, and the thermal efficiency of the reactor sub-system reached a maximum of 73.1%.

We believe that our pilot-scale demonstration can be used as an experimental platform for research on biomass gasification in SCW and other solar hydrogen technologies. To realize large-scale hydrogen production driven by solar energy, further research will continue to focus on improving conversion efficiencies, reducing capital costs, and enhancing reliability and operating flexibility.

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