A novel nanoscale semiconductor photocatalyst for solar hydrogen production

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Using solar power to derive hydrogen from hydrogen sulfide could reduce pollution and generate renewable energy.

The acidic gas hydrogen sulfide (H$_2$S) is an environmental pollutant because of its toxic, malodorous, and corrosive nature. Every year, millions of tons of H$_2$S are produced around the world from oil-refinery plants or natural-gas extraction, which is predicted to increase in the future. Decomposition of H$_2$S has therefore attracted attention because of the environmental problems it causes at levels higher than the threshold limit of 10ppm, above which its harmful effects on life are seen.

Current H$_2$S decomposition methods are broadly categorized as thermal, thermochemical, electrochemical, plasmochemical, and photochemical. Thermal decomposition methods, despite being the most direct for production of H$_2$ and sulfur (S), suffer from unfavorable thermodynamic equilibrium and a poor yield. The electrochemical and plasmochemical methods are not suitable for large-scale operation owing to the high cost of input electricity required, the expensive metal electrodes involved, and the need to render metals unreactive to S (passivation).

The Claus process is the most popular technique currently used for H$_2$S decomposition. The conventional Claus process involves the synproportionation reaction (a redox reaction in which two reactants that share an atom but differ in oxidation number react to a single chemical) of H$_2$S and SO$_2$, which yields elemental sulfur and water vapor, but a significant amount of hydrogen is wasted by burning the two H atoms in H$_2$S to make H$_2$O. In addition, photocleavage of H$_2$S to H$_2$ by a semiconductor-particle photocatalyst has been considered to convert solar energy into fuel (see Figure 1).

The photochemical strategy, which is still at an early stage of development and has received little meager attention, is promising because it is driven by abundant solar energy and—as a renewable ‘green-chemistry’ pathway—could play a pivotal role in the degradation or mineralization of toxic pollutants.

Although H$_2$ can also be produced through photocatalytic splitting of water, efficient decomposition of water into H$_2$ and O$_2$ over a visible-light photocatalyst has yet to be achieved. Since H$_2$S decomposition requires much less energy ($\Delta G^\circ$=33.44kJ/mol, where $G^\circ$ is the standard-state free energy of the reaction or ‘Gibbs energy’) compared to the energy necessary for water splitting ($\Delta G^\circ$=237.19kJ/mol), these combined considerations suggest that H$_2$S decomposition could be an ideal parent for H$_2$ production. Moreover, H$_2$S decomposition with concomitant H$_2$ generation offers sustainable-energy production and environmental-pollution abatement.

To achieve solar production of H$_2$, our research is directed by two primary strategies. First, intelligent design of a quantum-mechanical photocatalyst and second, the synthesis of an innovative photocatalyst material using special soft-chemistry techniques.

The initial design of a new generation of photocatalysts from

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metallic compounds (in the d block of the periodic table) with a d0 or d10 configuration, or by coupling d0 and d10 ions will be completed through the computational quantum-mechanical route (see Figure 2). The mixing of electronic energy levels of the constituent ions in single or composite metal-oxide photocatalysts will first be investigated to obtain the appropriate density of states in valence and conduction bands, and suitable band positions for reduction and oxidation. Finally, the effect of chemical modification, for example by nitridation or sulfurization, on band positions, and highest occupied and lowest unoccupied molecular orbitals, will be investigated during the design process.

The quantum-mechanically designed photocatalysts will be synthesized using innovative methods. Both conventional and non-conventional techniques, as well as our proprietary soft-chemical approaches (which include using ceramic, hydrothermal, modified hydrothermal, and sol-gel materials) could be adopted. Chemical modification of the photocatalysts by processes such as nitridation, sulfurization, and boration, among others, will be examined to convert the UV photocatalysts, so that they are activated by visible light. Individual or composite metal-oxide or nonoxide photocatalysts in the form of oxynitrides, oxycarbides, oxynitrides, oxysilicides, and oxysilicides can thus be prepared. For unstable or chalcogenide photocatalysts, photostability impartation will be attempted host-material anchoring, such as in special glass, zeolites, silica, and polymer materials, so that they can be investigated safely under visible radiation (see Figure 3).

A host of noble and transition-metal cocatalysts to boost and optimize the activity of the main photocatalysts will also be examined. Specially nanostructured metal-compound photocatalysts, such as nanometal chalcogenides, will also be designed and synthesized in host, template, and template-free media. After the photocatalysts have been subjected to thorough structure and functionality investigation, a new type of structural design and molecular assembly could emerge.

Our next steps involve developing evaluation methods to measure the photoelectrochemical properties of the new photocatalysts and designing a demonstrative reaction system.

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References