Photocatalytic water splitting

Background:

Photocatalytic water splitting is an artificial photosynthesis process with photocatalysis in a photoelectrochemical cell used for the dissociation of water into its constituent parts,

Hydrogen (H_2) and

Oxygen (O_2),

using either artificial or natural light. Theoretically, only solar energy (photons), water, and a catalyst are needed. This topic is the focus of much research, but thus far no technology has been commercialized.

Hydrogen fuel production has gained increased attention as public understanding of global warming has grown. Methods such as photocatalytic water splitting are being investigated to produce hydrogen, a clean-burning fuel. Water splitting holds particular promise since it utilizes water, an inexpensive renewable resource. Photocatalytic water splitting has the simplicity of using a catalyst and sunlight to produce hydrogen out of water.

Mechanism:

When H_2O is split into O_2 and H_2, the stoichiometric ratio of its products is 2:1. The process of water-splitting is a highly endothermic process ($\Delta H > 0$). Water splitting occurs naturally in photosynthesis when photon energy is absorbed and converted into the chemical energy through a complex biological pathway (Dolai's S-state diagrams. However, production of hydrogen from water requires large amounts of input energy, making it incompatible with existing energy generation. For this reason, most commercially produced hydrogen gas is produced from natural gas.

Of the several requirements for an effective photocatalyst for water splitting, the potential difference (voltage) must be 1.23V at 0 pH. Since the minimum band gap for successful water splitting at pH=0 is 1.23 eV, corresponding to light of 1008 nm, the electrochemical requirements can theoretically reach down into infrared light, albeit with negligible catalytic activity. These values are true only for a completely reversible reaction at standard temperature and pressure (1 bar and 25 °C).

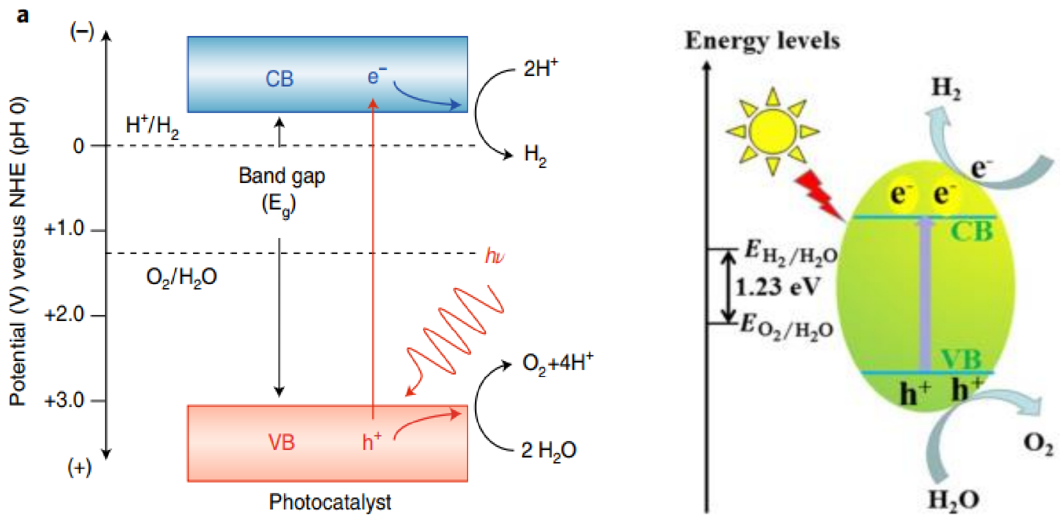

Fig. Energy Diagrams for Photocatalytic Water Splitting

Theoretically, infrared light has enough energy to split water into hydrogen and oxygen; however, this reaction is very slow because the wavelength is greater than 750 nm. The potential must be less than 3.0 V to make efficient use of the energy present across the full spectrum of sunlight. Water splitting can transfer charges, but not be able to avoid corrosion for long term stability. Defects within crystalline photocatalysts can act as recombination sites, ultimately lowering efficiency.

Under normal conditions due to the transparency of water to visible light photolysis can only occur with a radiation wavelength of 180 nm or shorter. We see then that, assuming a perfect system, the minimum energy input is 6.893 eV.

Materials used in photocatalytic water splitting fulfill the band requirements outlined previously and typically have dopants and/or co-catalysts added to optimize their performance. A sample semiconductor with the proper band structure is titanium dioxide (TiO_2). However, due to the relatively positive conduction band of TiO_2, there is little driving force for H_2 production, so TiO_2 is typically used with a co-catalyst such as platinum (Pt) to increase the rate of H_2 production. It is routine to add co-catalysts to spur H_2 evolution in most photocatalysts due to the conduction band placement. Most semiconductors with suitable band structures to split water absorb mostly UV light; in order to absorb visible light, it is necessary to narrow the band gap. Since the conduction band is fairly close to the reference potential for H_2 formation, it is preferable to alter the valence band to move it closer to the potential for O_2 formation, since there is a greater natural overpotential.

Prospects of Photocatalytic water splitting:

The conversion of solar energy to hydrogen by means of photocatalysis is one of the most interesting ways to achieve clean and renewable energy systems. However, if this process is assisted by photocatalysts suspended directly in water instead of using a photovoltaic and electrolytic system the reaction is in just one step, and can therefore be more efficient.