A Photocatalytic Process for Hydrogen Production: Selecting New Semiconductors as Co-Catalysts

Literature- Based Review

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1 Introduction

- There is an urgent requirement for an alternative and sustainable energy vector as reserves of fossil fuels are exhausted.
- Hydrogen is thought to be an attractive solution because it is renewable and abundant in nature. It is a clean fuel: during power generation only water is formed as the oxidation product of hydrogen.

2 Problem

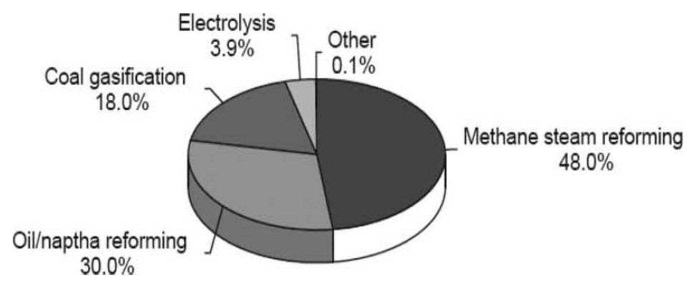

Fig.1 Distribution of H_2 production technologies [Ewan, et al., 2005].

The major challenge for the hydrogen economy is that only few of the technologies for its production can be considered environmentally friendly.

The further development of the photocatalytic methods, especially photocatalytic water splitting, and modifying the photocatalysts' bandgap so they can be used for the production of hydrogen simultaneously with the degradation of organic contaminants in the wastewater are the key in the advancement of solar-hydrogen production.

3 Motivation

The production of hydrogen fuels by the decomposition of water with solar light is the most promising source of the renewable energies since Fujishima and Honda published the innovative report in 1972 for photoelectrochemical water splitting by irradiating UV-light to TiO_2 electrodes.

4 Objective

- Harvesting clean energy from the wastewater: the feasibility of the dual approach of the production of hydrogen by photocatalytic methods via the use of solar-powered sources simultaneously with the degradation of organic contaminants in the contaminated water.
- Identifying alternate options for modification of Pt/TiO_2-based catalyst with suitable doping oxides/semiconductor agents (CdS, Mn, MC, Fe3O4, Bi_2O_4, etc.) for the production of hydrogen with the simultaneous degradation of model contaminants (pesticides, herbicides, etc.).

5 Photocatalytic (PC) Hydrogen Production

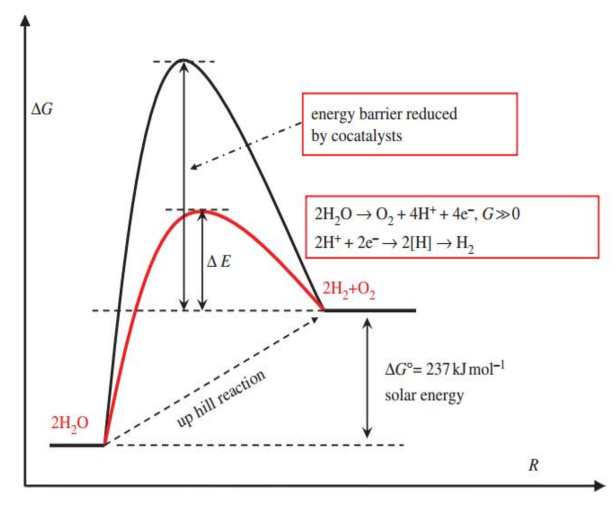

Fig. 2 Energy diagram for Photocatalytic Water Splitting [Yang et al., 2013].

- Photocatalytic water splitting is often regarded as an artificial photosynthesis due to its similarities to photosynthesis by green plants (both are uphill reactions).
- In this process, the photon energy is converted to chemical energy accompanied with a large positive change in the Gibbs free energy.

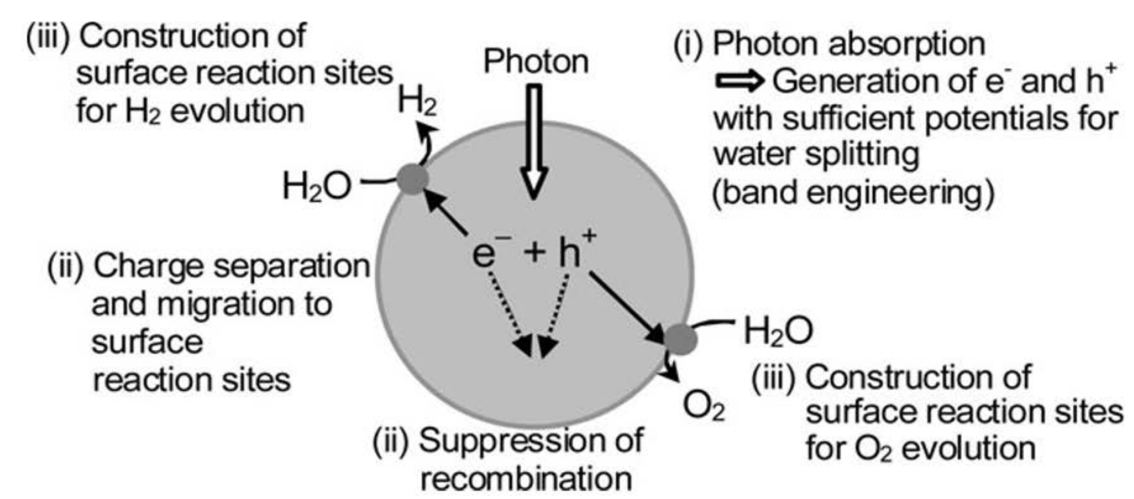

Fig. 3 Photocatalytic Water Splitting Scheme [Kudo et al., 2009].

Photoexcitation:

$$2h\nu \rightarrow 2e^- + 2h^+ \quad (1)$$

Reduction half reaction:

$$2e^- + 2H^+ \rightarrow H_2 \quad (2)$$

Oxidation half reaction:

$$H_2O + h^+ \rightarrow OH + H^+ \quad (3)$$

$$4h^+ + 2H_2O \rightarrow O_2 + 4H^+ \quad (4)$$

6 Photodegradation of Organic Contaminants

- The general stoichiometry of the photocatalytic degradation of an organic contaminant follows the general equation:

$$C_xH_yO_z + (x+0.25y-0.5z)\, O_2 \rightarrow xCO_2 + 0.5x\, H_2O \quad (5)$$

This is *complete mineralization.*

- If, instead one can achieve *partial mineralization* of the organic compounds, it should be possible to produce molecular hydrogen from the degradation of organic contaminants. This will be according to the stoichiometry as follow:

$$C_xH_yO_z + (2x-z)\, H_2 \rightarrow x\, CO_2 + (2x+.5y-z)\, H_2 \quad (6)$$

7 Titania (TiO_2)

- One of the major photocatalysts because it is stable, non-corrosive and cost-effective.
- The most active semiconductor photocatalyst for the degradation of organic compounds due to the ability to oxidize organic substrates in air and water through redox processes.
- Also, it has been a widely used photocatalyst for PC water splitting because its energy levels are appropriate to initiate water-splitting reaction.

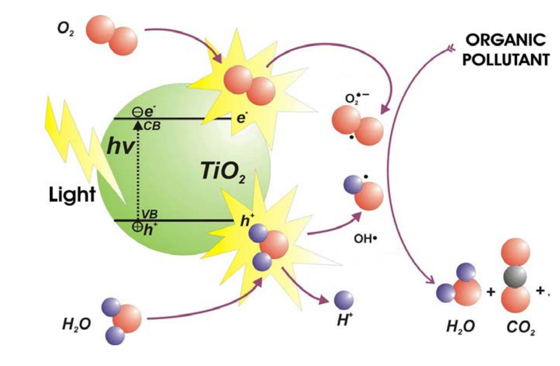

Fig. 4 TiO_2 excitation by band gap illumination [Ibhadon et al., 2013].

- Due to its relatively large energy band gap (3.2 eV for anatase), TiO_2 can be activated only by photons in the near UV-region and this produces electron-hole pairs:

$$TiO_2 \rightarrow e^-_{TiO2} + h^+_{TiO2} \quad (7)$$

8 Results

- [Shaban, 2013]: The simultaneous photocatalytic production of hydrogen and degradation of naphthalene in seawater was successfully achieved using carbon modified titanium oxide (CM-n-TiO2) nanoparticles under natural sunlight illumination.
- [Daskalaki et al., 2010]: The results showed that it is possible to produce hydrogen efficiently by using simulated solar light and by photocatalytically consuming either inorganic or organic substances. CdS-rich photocatalysts are more efficient for the photodegradation of inorganics, while TiO_2-rich materials are more effective for the photodegradation of organic substances.
- [Cho et al., 2015]: The simultaneous production of hydrogen and degradation of organic pollutants (4-chlorophenol, urea, and urine) was successfully achieved using titania photocatalysts which were modified with both anion adsorbates (fluoride or phosphate) and (noble) metals (Pt, Pd, Au, Ag, Cu, or Ni).

9 Conclusion

Most of the research done on TiO_2 so far is either about the photocatalytic hydrogen production (especially extending TiO_2 photo-response into the visible region) OR photodegradation of organic contaminants in both water/air.

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