



Photocatalytic Water Splitting by Modified Titania For Hydrogen Production Using Visible Light Irradiation

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ABSTRACT

Sustainable hydrogen production is a key target for the development of alternative, future energy systems that will provide a clean and affordable energy supply. Photo catalytic water splitting can contribute to a green sustainable chemistry and can find solutions to many energy and environmental issues. Even though a number of modification techniques and chemical additives have been developed in recent years to improve the photo catalytic activity of TiO₂ under visible light irradiation, efficient photo catalytic splitting of water to generate hydrogen using sunlight still remains as an unachieved goal from a technological standpoint. For efficient water splitting into H₂ and O₂ under visible light irradiation, the conduction band (CB) and valence band (VB) of the photo catalysts should meet the potential requirements of reduction and oxidation of H₂O simultaneously. The hydrogen production efficiency of TiO₂ reported so far is still lower than the required 10% for practical applications, but the efficiency has been considerably improved by the continuing breakthroughs in the synthesis, modification with catalysts, and by tailoring the electronic structure of TiO₂. In this paper, we evaluate the efficiency of our modified catalyst and compared it with the unmodified titania for production of hydrogen through water splitting reaction.

Summary : In this paper, we discuss the brief history of hydrogen production through photo catalytic water splitting reaction. It also includes the different materials and techniques behind hydrogen production, the general mechanism of photo catalytic water splitting reaction on semiconductor materials. In addition to this, the advantages of titania as a photo catalyst with its drawbacks and modifications are also discussed.

KEYWORDS

Photo catalysis, Water splitting, Solar energy, metal co-doping.

1. Introduction

The Sun which is a source of silent and precious energy, is distributed fairly all over the Earth and is a clean, safe and economical potential energy source that cannot be exploited unless the energy is converted to other useful forms. The conversion of solar energy into hydrogen via the water splitting process, assisted by photo-semiconductor catalysts, is one of the most promising technologies for the future since large quantities of hydrogen can be generated in a clean and sustainable manner. Moreover, since the sunlight source is carbon-free, it can facilitate the use of more efficient power generation systems such as fuel cells and hence can chemically reduce carbon oxides (CO, CO₂) to chemical fuels. Renewable hydrogen production (solar and wind) is not yet popular since the cost is high¹ and non-renewable sources such as fossil fuels can produce only 95% commercial hydrogen. Among the various materials for the hydrogen production, the water gets prominent role due to its large availability, easy to handle etc. The approaches for hydrogen production from water includes, (i) electrolysis, (ii) thermo chemical water splitting, and (iii) photo electrolysis and photo catalyzed water splitting. Among these, photo catalytic water splitting is the most attractive and rewarding work because of the renewability and abundance of water, and since this process can occur at ambient conditions using renewable sunlight and a semiconductor photo catalyst².

Water splitting into H₂ and O₂ is accompanied by a large positive change in the Gibbs free energy i.e., an uphill reaction. In this reaction, photon energy is converted into chemical energy as in photosynthesis by green plants and hence such reactions

can be termed as artificial photosynthesis. On the other hand, degradation reactions such as the photo-oxidation of organic compounds using oxygen molecules are generally downhill reactions which are irreversible. Such type of reactions are regarded as photo induced reactions and have been extensively studied with titanium dioxide photo catalysts³⁻⁵. Although photo catalysis by titania has been reported much earlier by Markham in 1955^{6,7}, the historical importance regarding the discovery of photo electrolysis of water evolving oxygen at a titania electrode and hydrogen at Platinum electrode by illumination of light greater than the band gap of titania is attributed to Fujishima and Honda. Also extensive work has been carried out to produce hydrogen from water by novel oxidation reduction reaction using varieties of semiconductors⁸. From the view point of large scale hydrogen production, specific photo catalysts are considered to be more advantageous over complex multilayer or tandem structure devices since they provide wide range of potential applications⁹⁻¹¹. Many types of semiconductors, with over 130 materials including oxides, nitrides, sulphides, carbides, and phosphides, have been reported to act as efficient photo catalysts for hydrogen evolution via water splitting with varying degree of both positive and negative results. A few of them are semiconductors containing elements such as Ga or In, compounds such as GaAs, CdTe and CdSe, metal oxides such as ZnO, TiO₂, ZrO₂, SnO₂, WO₃, Fe₂O₃, RuO₂, sulphide such as CdS, ZnS, GaS, metal (oxy) sulfide, metal (oxy) nitride, tantalates, niobates, Indates, Tungsten based materials, metal oxides with d⁰ and d¹⁰ electronic configuration, Perovskite type materials, Inorganic complexes

etc¹²⁻¹⁸. The objective of the present study is to investigate the effect of N, S co-doped and N doped titania for the production hydrogen through water splitting reaction. The studies involved the effect of amount of catalyst, effect of time and also contains a comparison of results with pure titania prepared in laboratory and a commercial one.

2. Experimental

The photo activity of all the samples were analyzed under irradiation with a medium pressure mercury lamp (Hg, Ace Glass Inc., 450W) in a closed rectangular quartz cell equipped with sampling and evacuation ports. The irradiated samples were placed in an outer irradiation quartz cell with the lamp being surrounded with water circulation jacket to absorb IR radiation. The lamp exhibits broad range emission spectra with maxima at both UV and visible range. 16% radiation of the lamp is in UV and the remaining in visible region. The catalytic activity experiments were conducted in static mode for water in methanol (2:1 v/v %) mixture, in the presence of a well dispersed catalyst. The reaction products were analyzed over a period of 6 hrs with an interval of 2 hr. A gas chromatogram (Netel (Michro-1100), India) equipped with a thermal conductivity detector (TCD) and a molecular sieve column (4m length) with argon as the carrier gas was employed in the isothermal temperature mode at a temperature of 50°C. The number of photons falling on the reaction cell or flux of the light was determined with a light flux meter and was observed to be about 19 x 10⁴ lux or 278.2 watts/m² in horizontal geometry irradiation with a UV-visible photo irradiator.

2.1 Synthesis

The catalytic activity strongly depends on the methods of preparation. Small deviations in preparation conditions can give large variations in activity. Therefore, intense care should be taken during the selection of methods. The procedure of catalytic preparation and its characterizations was already discussed in our earlier work^{19,20}. The catalysts used in this study is labeled as given below.

N,S-TiO₂ - Nitrogen and Sulphur codoped titania

N-TiO₂ – Nitrogen doped titania

L-TiO₂ – Pure titania prepared in our laboratory

A-TiO₂ – Pure titania obtained commercially (Sigma Aldrch)

2.2 Mechanism

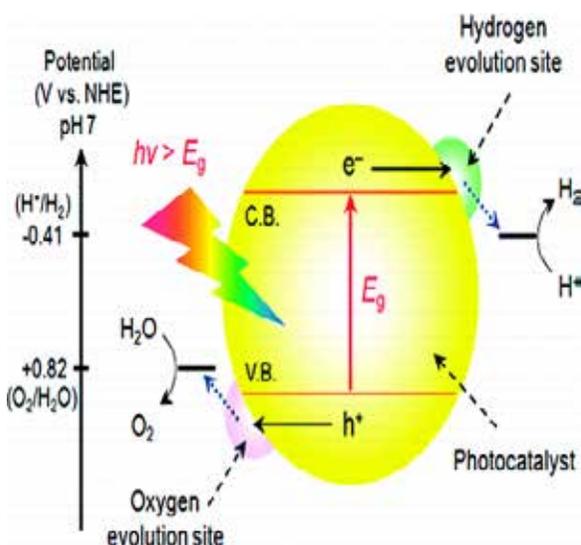
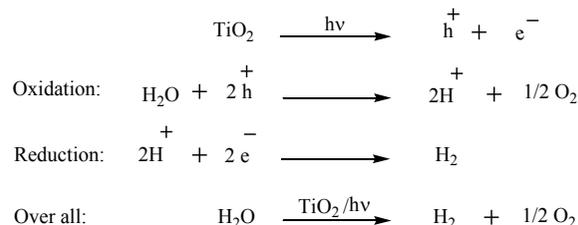


Fig.1. Schematic representation of photo catalytic water splitting reaction over a semiconductor material.

The schematic representation of water splitting reaction by photo catalytic materials are shown in Fig. 1. Upon irradiation

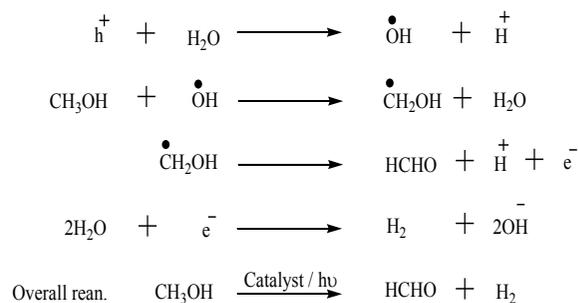
with energy greater than or equivalent to the band gap of semiconductor photo catalyst, electrons and holes gets generated in the conduction band and valence band of the photo catalyst respectively and hence causes reduction and oxidation in semiconducting materials. To achieve better splitting of water, the bottom of the conduction band must be located at a more negative potential than the reduction potential of H⁺ to H₂ (0 V at pH 0), while top of the valence band must be positioned more positively than the oxidation potential of H₂O to O₂ (1.23 V at pH 0). Hence, minimum photon energy thermodynamically required to drive the reaction is found to be 1.23 eV²¹.



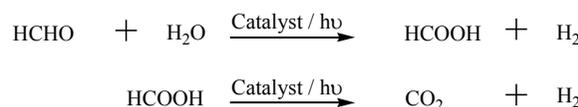
Titania becomes a prominent one because of its favourable band gap, high chemical and photochemical stability, biological inertness, low cost and ease of method. One of the main drawback of titania is its wide band gap energy which permits only its activity suitable by UV irradiation. The anatase phase of titania exhibits better photocatalytic activity than others with a band gap of 3.2 eV. Among various methods such as dye sensitization, doping with metals and non metals, coupled with other semiconductors etc²²⁻²⁹, non-metal doping predominates over others due to its strong visible absorption by reducing the band gap by mixing their orbitals with valence band titania.

Water decomposition is a very difficult and complex reaction. The various intermediate chemical steps present a kinetic limitation that decreases the efficiency of the reaction. One possible way to overcome this problem is the use of sacrificial electron donors or acceptors. The introductions of sacrificial agent (electron donor or proton acceptor) increase the efficiency of hydrogen production through suppressing the recombination electron-hole by react irreversibly with photo induced species or by reverse reaction between O₂ and H₂³⁰⁻³⁵.

Among various organic compounds, methanol was most widely used for the hydrogen generation process. The suggested mechanic route is depicted here³⁶.



The product, formaldehyde (HCHO), could be further oxidized to methanoic acid HCOOH and subsequently to CO₂ together with hydrogen generation.



3. Results and discussion

3.1 Activity

3.1.1 Effects of the amount of catalyst

The activity was studied with water to methanol volume ratio of 10:5 and with 0.05g, 0.1g and 0.15g of catalyst respectively. After 4 hrs of irradiation with visible light, the sample was

collected and analyzed using a gas chromatogram.

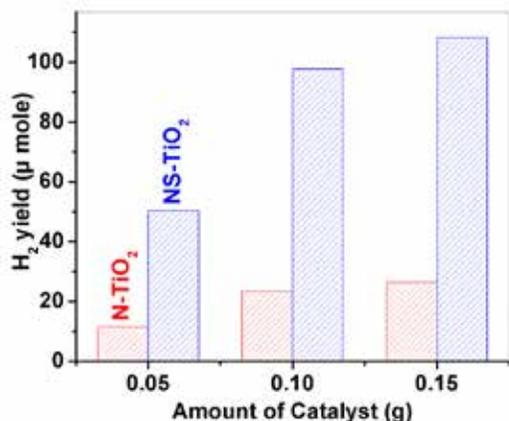


Fig. 2 Yield of hydrogen produced against amount of catalyst; Irradiation time: 4 hour; Water to methanol ratio 10:5.

Fig. 2 showed the yield of hydrogen (μmol) obtained against the amount of catalyst (g). It is clear from the figure that the yield of hydrogen increases with increase in the amount of catalyst. This is because with increase in the amount of catalyst, the active surface for the generation of photo excited species increases and hence the hydrogen yield increases. But after attaining an optimized range, there is no more increase in activity.

3.1.2 Comparison study

In this study all the catalyst is used for evaluate its activity in visible light for the water splitting reaction. Studies involve a 10:5 volume ratio of water to methanol ration with a catalyst amount of 0.1g. Samples are collected and analyzed at an interval of 2 hrs up to 6 hrs.

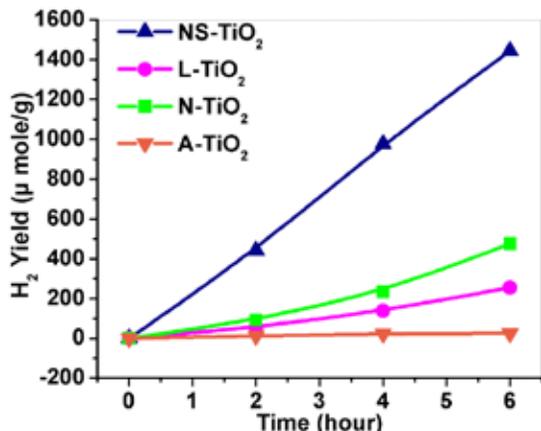


Fig. 3 Yield of hydrogen produced with time against different catalyst; Amount of catalyst: 1.0 g; Water to meth-

anol ratio 10:5.

A comparison of the amount of hydrogen produced with 1.0 g of different catalysts is shown in Fig. 3. Here the yield of hydrogen increases with increase in time for all the catalysts except the commercial titania (A-TiO_2), which has a very slight activity. It is also inferred that N, S co-doped titania shows better results than others due to the strong absorption band created by the dopants in the visible region by mixing with the valence band of pure titania. Moreover other factors such as crystallite nature of anatase phase, surface area, small particle size also contributed for its higher activity.

4. Conclusion

Even though titania is a very good photo catalyst, its activity is limited to the UV irradiation region based on its band gap. In order to bring its activity to visible region, we modified titania by doping with non-metals such as nitrogen and co-doping with nitrogen and sulphur. The crystallite defects can largely contribute to the efficiency of photo catalysts. The defects itself promote as trapping and recombination centers between photo generated electrons and holes, resulting in a decrease in the photo catalytic activity. The higher the crystalline quality, the smaller is the amount of defects. Therefore, a high degree of crystallinity, rather than a high surface area, is required for the photo catalysts, especially for an uphill reaction like water splitting. The results indicated that 0.1 g of NS-TiO₂ catalyst gives a good yield of hydrogen with visible light irradiation for 4 hrs when compared with the same quantity of other catalysts.

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