Chapter 16
Generation of Green Hydrogen Using Semiconductor-Based Nanomaterials

Ajay Mittal and Rajeshwar Mahajan

Abstract Photocatalytic water splitting using semiconductors-based nanomaterials has recently attracted attention from scientists and businesses for its potential to produce hydrogen in a sustainable manner. This article discusses the mechanism of photocatalytic water splitting and production of green hydrogen using semiconductor-based nanomaterials, different approaches for structural modification for better efficiency and the challenges in the selection of best semiconducting material. According to the study, oxide-based semiconductors are preferred to other semiconductors because they are abundant, affordable, and stable, but their low efficiency limits their commercial application. The fundamental difficulty can be overcome by combining binary, ternary, or quaternary photoelectrode materials. This research will contribute to the creation of stable tertiary or quaternary photoelectrode materials, which will enhance the efficiency of green hydrogen production.

Keywords Green hydrogen · Semiconductor · Water splitting · Photoelectrolysis

16.1 Introduction

In recent years, green hydrogen's potential as a renewable energy source has risen to a higher level of attention because of its low environmental impact [1, 2]. Green hydrogen can be produced in a sustainable manner through photocatalytic water splitting using nanomaterials based on semiconductors [3, 4]. As shown in Fig. 16.1, lots of semiconducting materials like TiO_2, Fe_2O_3, WO_3, CdS, Ta_2O_5, $BiVO_4$, ZnO, Cu_2O and many more have been the focus of extensive study over the past decade because of their suitable band gap, stability, and efficient response to solar irradiation in the creation of hydrogen gas but lack mass scale production due to low efficiency due to their low reactivity to visible light, low reduction potential, and high charge carrier recombination rate [5, 6].

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A. K. Sahu et al. (eds.), *Energy Storage and Conservation*, Springer Proceedings in Energy, https://doi.org/10.1007/978-981-99-2870-5_18

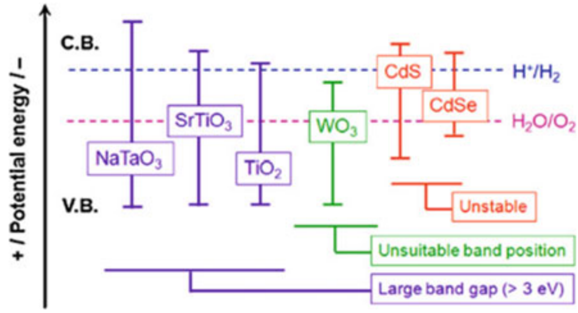

Fig. 16.1 Band structure of most used semiconductors for photocatalytic water splitting [7]

Semiconductor materials with band gaps that do not match the water splitting redox potentials are ruled out by the redox potential criterion unless the structure is adjusted. TiO_2, ZnO, Cu_2O have attracted the most attention from researchers interested in structural modification because of its low toxicity, excellent stability, and near-visible light photocatalytic activity [8, 9]. This article discusses the mechanism of photocatalytic water splitting and production of green hydrogen using semiconductors-based nanomaterials, different approaches for structural modification for better efficiency and the challenges in the selection of best semiconducting material. Additionally, this article facilitates the development of hybrid oxide–semiconductor materials, thereby facilitating future research that is more informed and fruitful.

16.2 Methods of Hydrogen Production

Hydrogen can be produced either from fossil fuels or renewable source of energy like biomass, solar energy, wind, or hydropower. The production of hydrogen from fossil fuels or biomass is not environmental-friendly and energy intensive. The splitting of water using solar energy, wind energy, or hydropower are the greener methods that can be utilized to produce hydrogen from renewable sources. The most promising technique for producing green hydrogen is water splitting using solar energy, which is also fortunate because it is less constrained by geographical location than hydropower and wind energy [10].

In the past decade, researchers utilized various techniques which water splitting solar energy for production of green hydrogen illustrated in Fig. 16.2. The photoelectrochemical (PEC) and photocatalysis water splitting technologies are the most promising methods for the creation of hydrogen. This is since both methods employ the limitless energy source of solar light and do not generate any CO_2 [6, 11, 12].

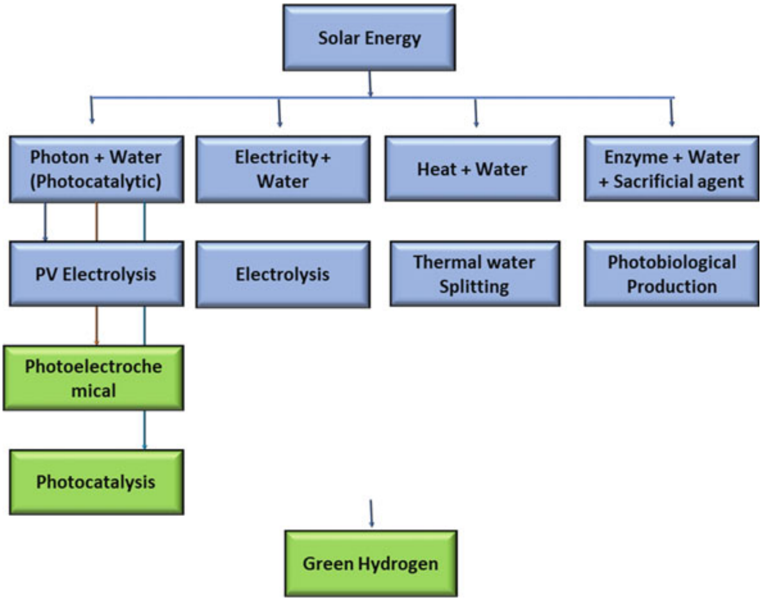

Fig. 16.2 Hydrogen generation techniques using solar energy (Created by adaptation of Fig. 16.1 from [8])

16.3 Technological Pathway of Photo-Electrochemical or Photocatalysis Water Splitting and Production of Hydrogen

Photocatalytic water splitting is photoelectrolysis of water, i.e., the absorption of solar energy and the electrolysis of water are brought together in both the photoelectrochemical and photocatalytic processes [13]. In a photoelectrochemical cell, water is reduced at the photocathode and oxidized at the photoanode, respectively [2, 11, 14–16] as shown in Fig. 16.3. In photocatalysis, reduction and oxidation reaction take place at photocatalyst and cocatalyst, respectively [11, 12, 14, 17, 18] as shown in Fig. 16.4. The reactions that take occur at the anode and cathode during water splitting are described below:

$$Anode : 2p^{+} + H_2O \rightarrow 0.5O_2 + 2H^{+}$$

$$Cathode : 2e^{-} + 2H^{+} \rightarrow H_2$$

In the process of photo electrolysis, solar irradiation with an energy equal to or greater than the band gap of the photoanode (photocatalyst) causes electrons in the valence band to be excited into the conduction band, leaving holes in the valence band. These photogenerated electrons and holes, respectively, create an oxidation

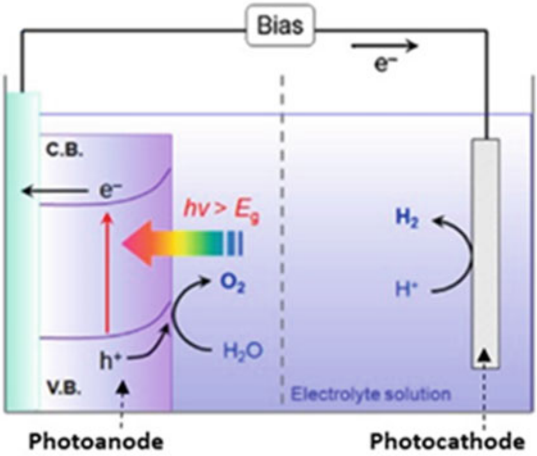

Fig. 16.3 Mechanism of photo-electrochemical water splitting process [7]

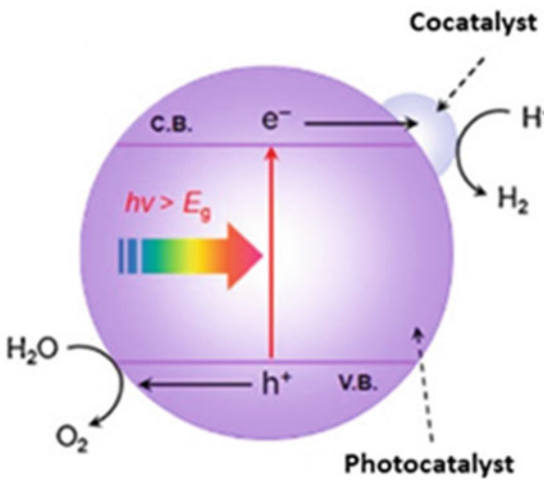

Fig. 16.4 Mechanism of photocatalysis water splitting process [7]

process at the photoanode (cocatalyst) and a reduction reaction at the photocathode (photocatalyst). To achieve water splitting, the bottom of the conduction band needs to be more negative than the reduction potential of H + to H2, which is equal to 0; conversely, the top of the valence band needs to be more positive than the oxidation potential of H_2O to O_2, which is equal to 1.23. Both conditions must be met. Therefore, the minimum photon energy that is thermodynamically necessary to drive the reaction is 1.23 eV [14, 16]. Additionally, for the water splitting process to be extremely efficient, semiconductor materials should have a bandgap that is greater than 3 eV [11].

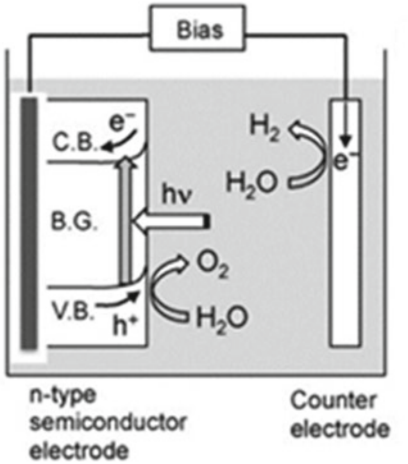

Fig. 16.5 n-type semiconductor photoanode used in photoelectrochemical water splitting [2]

Three types of photoelectrochemical frameworks are utilized by researchers that uses n-type semiconductor as photoanode (Fig. 16.5), p-type semiconductors as photocathode (Fig. 16.6), and a tandem system uses p-type semiconductors as photocathode and n-type semiconductor as photoanode (Fig. 16.7) are being developed for water splitting and production of hydrogen. n-type oxide semiconductors like TiO_2, $BiVO_4$, Fe_2O_3 are highly efficient and have frequently been used as photoanodes for the oxidation of water since they are resistant to photo corrosion and tend to be very affordable. p-type oxide semiconductors like Cu_2O are not efficient due to self-destruction [18]. Tandem system like p-GaP/n-TiO_2 [8] developed by researcher was inefficient but tandem system has promising potential for efficient photocatalytic water splitting but need structural modifications [8].

16.4 Semiconductor-Based Nanomaterials for Production of Green Hydrogen

In the past decade, chalcogenide, carbide, nitride and oxide semiconductors are extensively research for water splitting and production of hydrogen. Chalcogenide, carbide, nitride semiconductors found limited attention due to photo corrosion and chemical instability in water solution [8]. Metal oxide semiconductors become the preferred choice over other semiconductor materials for water splitting and production of hydrogen, due to their earth abundance and stability in water solution but the main challenge lies to meet the criteria suitable for effective water splitting like band-edge potentials suitable for overall water splitting, band-gap energy lower than 3 eV, stability in the photocatalytic reaction [7, 8]. Many oxide–semiconductor materials have been the subject of extensive study, but those whose band gap structures do not match the water splitting redox potentials are ruled out based on this

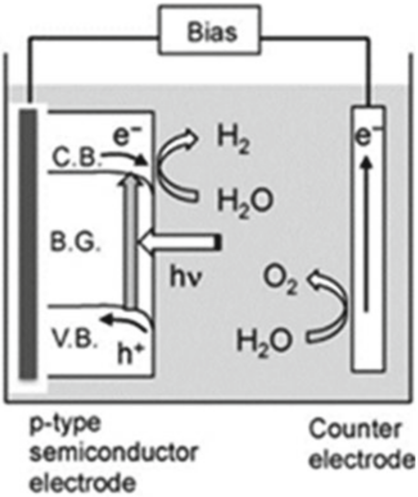

Fig. 16.6 p-type semiconductor photocathode used in photoelectrochemical water splitting [2]

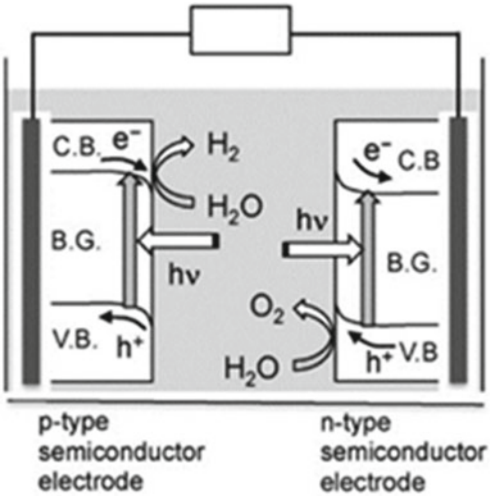

Fig. 16.7 Tandem system used in photoelectrochemical water splitting [2]

criterion until the structures are adjusted [11]. Thus, the focus of current studies is on developing improved methods for modifying oxide catalysts. For photocatalytic water splitting, researchers are investigating five ways for improving the hydrogen production efficiency of an oxide–semiconductor material. These include changes to the form and structure of crystals, doping a semiconductor with metallic and/or nonmetallic ions, the sensitivity produced by quantum dots in semiconductors, the development of stable heterojunctions or solid solutions, and the insertion of a cocatalyst into a process [11]. Developing effective composite photocatalysts for solar water splitting using metal–organic framework (MOF) materials like Ti-based

MOF (MIL-125-NH_2) achieved optical bandgap shifts towards visible light region (2.6 eV/475 nm) [16], Ti-MOF/TiO_2 composite semiconductors attains an improved photocurrent density by 50% in comparison to p-TiO_2 [16], the photocurrent density achieved by Ar-TiO_2 is over 500 times higher than that of p-TiO_2 [11]. Despite several years spent doing research, scientists have not been successful in identifying a single binary metal-oxide semiconductor that is superior to all the others. In this regard, it is vital to take into consideration semiconductor materials that have three or four components and are based on metal oxides. It is predicted that by combining three or four components in a variety of different ways and subsequently adjusting the bandgap structure, it will be possible to find the optimum photoelectrode material with outstanding photocatalytic efficacy for splitting water.

16.5 Challenges in Generation of Nanomaterials for Photocatalytic Water Splitting

16.5.1 Low Photoconversion Efficiency

Solar-to-hydrogen conversion efficiency using photocatalytic method for all the reported semiconductor-based nanomaterials is low and limit their use for commercial application. Also, there is a need to have a comprehensive method to calculate solar-to-hydrogen conversion efficiency [8, 19, 20].

16.5.2 Photocorrosion or Corrosion Stability

Most of the semiconductors such as CdS and SiC are not corrosion resistant and not suitable for water splitting [21] and limit their applicability. Proper method needs to be devised to calculate corrosion stability to avoid using semiconductors, which leads to photo corrosion [11, 14].

16.5.3 Chemical and Thermal Stability

Chemical and thermal stability of semiconductor materials are also crucial for improved photoconversion efficiency and commercial application.

16.5.4 Photostability

High photostability helps in semiconductor material resistant to change under the influence of solar energy and leads to increase in photoconversion efficiency [8, 14, 22].

16.5.5 Low Cost

Cost of the semiconductor material should be low for mass-scale production and widespread application [22, 23].

16.5.6 Non-toxic

Semiconductor material should be environmentally friendly and possess no harm to human beings [10, 13].

16.6 Conclusion and Future Perspective

Due to their natural abundance, high and tunable bandgaps, stability in aqueous conditions, low cost, and ease of manufacturing, semiconductor-based nanomaterials have shown remarkable potential to produce green hydrogen through photocatalysis and photoelectrical water splitting methods. The main challenge lies in achieving optimum properties of semiconductor like effective absorption of a wide spectrum, photochemical stability, low cost, low recombination possibility, efficient charge carrier, which is only possible through combination of semiconductor-based hybrid nanomaterials. Recent research in the production of green hydrogen through two-component metal oxide–semiconductor materials has shown increased efficiency of hydrogen production but lack commercial application. Even with current innovations, market viability still requires further enhancements in efficiency, durability, and cost. More research into developing three- and four-component photocatalytic semiconductor materials is needed to attain high efficiency, stability, and cheap cost in photocatalytic water splitting for green hydrogen production.

Acknowledgements I would like to thank the University of Petroleum & Energy Studies for providing all the necessary assistance for the completion of this project.

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