Nanophotocatalysts for hydrogen production applications

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Introduction

Traditional fuel sources produce global warming due to the generation and emission of carbon dioxide, carbon monoxide, and methane products, which leads to serious global disasters. Examples for the old sources are mineral and fossil fuels, hydroelectric, and nuclear energy sources. Nowadays, there is a desired reduction in the usage of these old sources and to begin using new renewable energy sources to decrease environmental pollution throughout the world. Therefore, researchers have developed new renewable energy sources to meet the needs of humans. However, different types of these new sources are still under research; already, some sources have been developed, and hydrogen-based energy is a most suitable source to satisfy our day-to-day needs. It is produced from renewable sources and does not rely on the production of carbon dioxide.

Hydrogen is a clean energy carrier, which provides a solution to environmental issues [1,2]. Mostly it is generated from the sources including, wind, solar, coal, biomass, thermal, nuclear, and hydraulic power. Commercially production of hydrogen can be achieved by reduction of coal using gasification and steam reforming of methane [3,4]. But the aforementioned two processes

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emit harmful carbon dioxide. Storage of hydrogen in the form of liquid, gas, or solid hydride can be supplied through pipelines over large distances. The studies discussed the important factors in storage of hydrogen fuel [5–10].

More hydrogen energy sources are supplied by sunlight and water, which could be used to produce hydrogen. Hence, photocatalytic water splitting is the method to generate clean solar hydrogen energy. This energy has been used for large-scale applications [11]. In 1972, Honda and Fujishima used water-splitting techniques for hydrogen production by the crystal of TiO_2 as an anode and Pt as a cathode [12]. Later, more research works on this technique were explored, which leads to more than 100 new catalysts that are developed including oxides, carbides, and sulfides. All catalysts have different factors that directly influence the hydrogen production efficiency. The following factors are very important for selection of catalysts, such as low cost, stability, nontoxicity, and resistance under light [13–16].

The following nanomaterials are commercially used materials for production of photocatalytic hydrogen in a cheap and clean manner such as SiC, TiO_2, CdS, and $CuInSe_2$ [17–20]. Recently, some more nanomaterials are developed by researchers such as Ta_2O_5 [21], ZnO [22,23], Nb_2O_5 [24], WO_3 [25], TaON [26], α-Fe_3O_3 [27,28], and $BiVO_4$ [29,30]. The XRD patterns of nanomaterials and its intensity were shown in the Fig 12.1.

Fig. 12.1 shows of XRD patterns of some photocatalysts. Limitation of band gap is a major issue in most of the photocatalysts, which results in reduction of hydrogen production [32]. To solve this problem, it could be modified with the doping processes including ion doping, metal doping, sensitization, and joining of metal-ion. Ion doping process involves anions of sulfur and nitrogen, transition metal, earth metal ions, etc. In

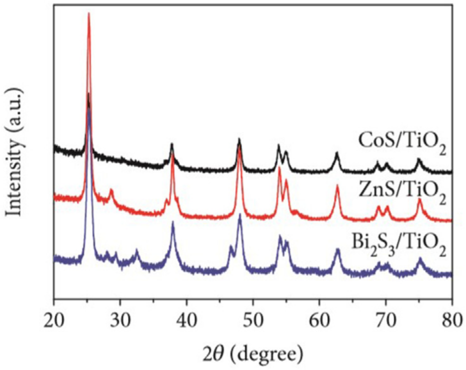

Figure 12.1 XRD patterns of CoS/TiO_2, ZnS/TiO_2, and Bi_2S_3/TiO_2 [31].

metal doping process, Pt was identified as noble metal, but it is very high cost. The other cheaper metals are also used, such as Cu, Ni, Ag, Pd, Ru, and Ir [33]. Sensitization process involves joining of semiconductors and dye-sensitization. Also, investigators are very much interested to produce co-catalysts with nanomaterials for production of hydrogen energy. This chapter is focused on developing of nanophotocatalysts for production of hydrogen fuel and to provide various key factors affecting the efficiency and structures.

Hydrogen production via water splitting

Under the illumination of ultraviolent and light, nanophotocatalysts have been used to split water into hydrogen and oxygen. This is the best method to produce recyclable and clean hydrogen fuel via water-splitting technique using a particulate photocatalyst [34,35]. But still there is a lack to find the appropriate materials with required band gap for splitting of water for industrial applications, because most of the metal oxides that have optical band gaps lie outside the range of visibility, which is greater than 3 eV. As a result, although they are active catalysts, it could not be used in an effective manner via solar spectrum. For instance, TiO_2 has an optical band gap range of 3.2 eV which was used to produce limited conversion efficiency of about 1%. At the same time, Fe_2O_3 has a smaller optical band gap of 2.2 eV due to this range, and solar to hydrogen conversion efficiency was increased to 15% [36]. Practically, 10% of solar to hydrogen conversion efficiency is normally required for electrolysis of water. Hence, there is a need to develop a highly active nanophotocatalysts for large-scale production of hydrogen through water-splitting processes [37]. The following sections is discussed the two types of nanophotocatalysts materials for the production of hydrogen through water-splitting processes.

Metal oxide photocatalysts

Some research works are reported based on the density function theory for production of hydrogen through water-splitting techniques under the conditions of ultraviolet and visible light irradiation. Most of the investigations were reported based on TiO_2 photocatalysts. Kaur et al. [38] examined the amorphous TiO_2 photocatalyst using the density function theory for hydrogen production. It was resulted that the amorphous TiO_2

photocatalyst acted as a cheaper and abundant material, however it was low efficient when compared with nano-TiO_2 photocatalyst. To enhance the photocatalytic property, the doping process was executed through various methods. Reynal et al. [39] investigated that the hydrogen production on Co electrocatalyst immobilized on TiO_2. It was faster (10^4 times) than the reverse charge recombination.

Bandura et al. [40] studied $SrTiO_3$ nanowires photocatalytic material for production of hydrogen and examined the band gap width under solar irradiation in the visible light, in which TiO_2 is the main key element for photocatalytic activity. Hanaor et al. [41] examined the relative stability of TiO_2 via density function theory. They also reported the doping of TiO_2 with the different atoms such as Al, Si, Fe, and F.

The main parameters such as solubility, stability, and reproducibility are along with the reduction of band gap and doping methods to increase the photocatalytic activity of TiO_2. The heterogeneous structure of TiO_2 with the combination of other oxides could increase the photocatalytic activity to enhance the absorption of solar light [42,43]. The following combination such as MgO-TiO_2 [44], Ga_2O_3-TiO_2 [44], and $Bi_4Ti_3O_{12}$-TiO_2 [45] can decrease the band gap, which leads to absorb high visible light and charge separation and enhanced photocatalytic activity than pure TiO_2. For example, $Bi_4Ti_3O_{12}$-TiO_2 band gap is 2.5 eV, which is lesser than the band gap of pure TiO_2 (3.2 eV). Currently, graphene material has attracted by the researcher because of their superior properties such as high photocatalytic efficiency and surface area. But only few research works are reports on the area of graphene sheets with nanoparticles. Farhangi et al. [46] developed graphene with TiO_2 nanofibers and Fe-doped TiO_2 nanofibers for high-efficient hydrogen production. WO_3 is the best metal oxides due to their attracted properties such as high photosensitivity, stability against photo corrosion, and better electron transport [47–49]. Also, the band gap for it is 2.8 eV which is smaller than the TiO_2 and leads to make it suitable for high absorption of visible light. Wang et al. [50] prepared the doped WO_3 with the elements such as Cr, Mo, Ti, Zr, and Hf, which leads to enhance the absorption of visible light with high benefits for high production.

Nonmetal oxide photocatalysts

Generally, in particularly surface modification of TiO_2 achieved by doping process with C, N, or some nanoparticles could not be used to offer better photocatalytic activity for absorption of light of the solar spectrum [51]. Afterwards, investigators have been researched in developing altered materials for the purpose of conversion of solar energy. Due to that, high volume production of photocatalysts remains a big challenge for the applications of industries [52]. The polymeric carbon nitride has been identified as a good photocatalyst active material that can be used to produce hydrogen from water, but it is required a sacrificial donor [53].

Likewise, kinds of photocatalysts materials such as sulfur [54], boron [55], phosphor [56], carbon carbide [57], and carbon nitride [58] have been developed. Currently conjugated polymer has developed as a best alternative for the conversion of solar energy applications. But there is a lack of research work in conjugated polymers area. Also, semiconductor-based photocatalytic materials have been reported for this application. Graphene is a two-dimensional materials which could be used as a promising photocatalysts [59,60]. This material has monolayer that offers the band gap is zero but h-BN offers a higher band gap of about approx. 5.5 eV. It is the medium band gap semiconductor which is achieved via chemical reactions [38,61]. Graphene oxide with carbon can improve the spontaneous and charge separation processes [62,63]. Recently, heterogeneous graphene-based materials can be used as photocatalytic materials because of their sp2 hybrid carbon networks, providing high-speed mobility at normal temperature, high work function and surface area [64,65].

Huang et al. [66] prepared a B—C—N nanosheets, which has a ternary structure to produce hyrogen from the reduction of water and carbon dioxide under illiumination of visible light condition. Kanda et al. [67] found the metal chalcogenides are to be a suitable photocatalyst material for the production of hydrogen because of their required band gap and band edge position.

Matsumura et al. [68] developed the CdS material as a good semicondutor photocatalyst for hydrogen production (Fig. 12.2). But some technical problems such as fast photogenerated charge carriers and photo corrosion is produced under visible light condition which act as barrier for extended application of CdS. Li et al. [70] studied the production of hydrogen by the activity of solid solutions $Zn_{1-x}Cd_xS$ with different molar ratios of CdS and Zns via density function theory. The highest rate of hydrogen proudction is 7.42 mmol/hg for Zn/Cd in equal molar ratio which is exceeding that of the pure ZnS and CdS materials by 54 and 24 times, respectively.

Several reserch works have been reported on the area of hybrid strutures with the combination of graphene and semiconductor materials via different phases either gas or liquid

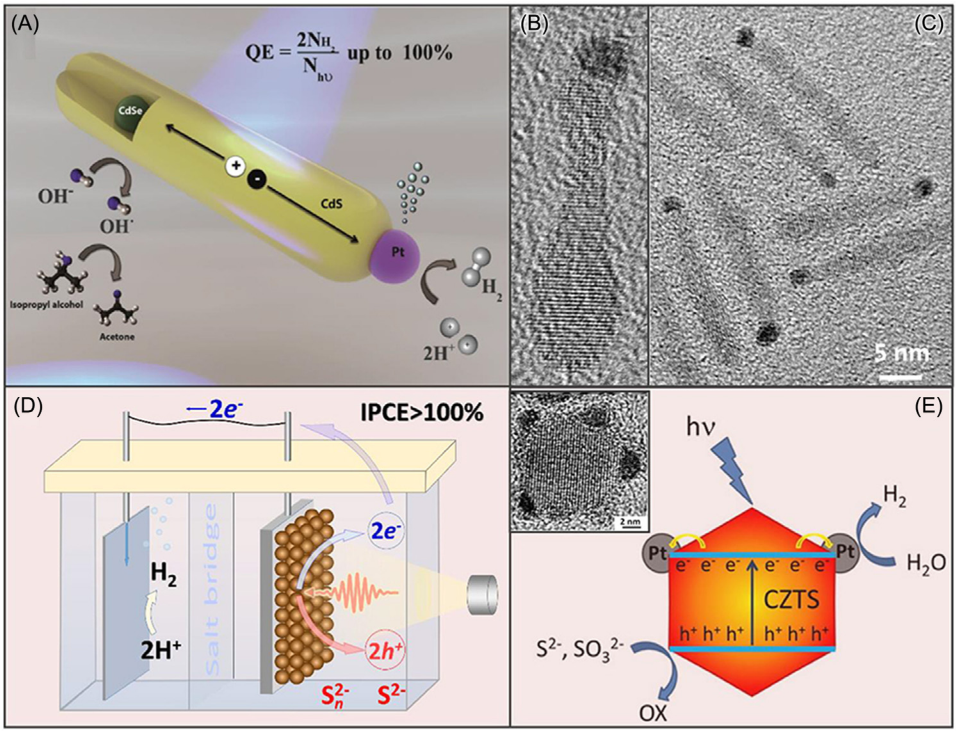

Figure 12.2 (A) CdSe/CdS nanorods appended with a Pt cocatalyst; (B,C) TEM images of CdSe/CdS nanorods; (D) photoelectrochemical hydrogen evolution; and (E) photograph of the hydrogen evolution [69].

[71,72]. Hou et al. [73] have prepared the different combination mateirals including CDS QDs, graphene, and $ZnIn_2S_4$ that provide better effective hydrogen production because of their efficient electron transfer and more hydrothermal stability. Graphene material also serves a major role in hydrogen production and it combines with other co-catalyst to enhance the efficiencty photocatalyst activity [74].

Zhu et al. [75] prepared ZnS reinforced with graphene (0.25 wt.%) and MoS2 (2 atom%) material for efficienct hydrogen production, and it is found that the rate of hydrogen production was 2258 μmol h-1, which is two times greater observation of pure ZnS.

Conclusions

This chapter reviewed the high-efficient production of hydrogen through water-splitting technique by the nanostructured photocatalysts materials including metal and nonmetal oxides under ultraviolet and visible light system. But there is a lack of research on semiconductor-based photocatalysts for hydrogen production. The present research works on this area does not explore the efficient and low-cost photocatalysts for hydrogen production via water-splitting technique. Since the present photocatalysts have high band gaps, which could not be absorbed, required light from the solar spectrum. To decrease this band gap, modified photocatalysts are developed; however it does not increase the efficiency of hydrogen production. The reason is that rapid charge and reaction are demerits via water splitting in solar energy. Nowadays the production of hydrogen is very low for the industrial applications. Therefore, there is a big research opening to research density function theory calculations for high-efficient hydrogen production on metal oxide and nonmetal oxide photocatalysts.

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