Chapter

Hydrogen as a Clean Energy Source

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Abstract

Sustainable development of the world is mainly dependent on the use of present energy resources, which primarily includes water, wind, solar, geothermal, and nuclear power. Hydrogen as a clean and green energy source can be the resolution of the energy challenge and may satisfy the demands of several upcoming generations. Hydrogen when used it does not produce any type of pollutant and this makes it a best candidate as a clean energy. Hydrogen energy can be generated from natural gas, oil, biomass, and fossil fuels using thermochemical, photocatalytic, microbiological and electrolysis processes. Large scale hydrogen production is also testified up to some extent with proper engineering for multi applications. Alas, storage and transportation of hydrogen are the main challenge amongst scientific community. Photocatalytic hydrogen production with good efficiencies and amount is well discussed. Till date, using a variety of metal oxide-sulfide, carbon-based materials, metal organic frameworks are utilized by doping or with their composites for enhance the hydrogen production. Main intents of this chapter are to introduce all the possible areas of hydrogen applications and main difficulties of hydrogen transportation, storage and achievements in the hydrogen generation with its applications.

Keywords: energy, hydrogen, photocatalysis, storage

1. Introduction

The fast and uncontrolled growing population is a result of urbanization and industrialization. States economic growth is dependent on the number of working industries in it. Also, to fulfill the demands of growing population textile, food, petrochemical, plastic, leather, and metal factories are emerging day by day [1–3]. Each of these industries helps to the mankind for their betterment and responsible for creating several pollutants, destroying agricultural lands and natural habitats. On the other hand, all these industries are working on non-renewable energy sources like wood, coal, natural gas, and petroleum products [4, 5]. Non-renewable energy sources are of one-time use, once used one cannot utilize them again. Two main problems are associated with non-renewable energy sources firstly when they burnt the produces harmful pollutants which is not acceptable [6, 7]. From past couple of decades scientific community, is engaged to solve the pollutants removal/degradation problems which are not economical. When fossil fuel gets extensively used, they produce global warming. Global warming is mainly caused by carbon dioxide emission. Carbon dioxide is when produce it remains in the atmosphere and absorbs the harmful infrared radiations which are reflected from earth surface. Secondly, after consumption these energy sources are going to be extinct as their availability is limited [8]. Geographically, non-renewable energy stock is located only to certain territories hence, it might be the reason for clashes between energy enriched and energy deficient countries which may leads to the world war again. Because of all these problems like pollution, environmental and health hazards the use of non-renewable energy sources for long period are not viable [9, 10].

Use of renewable energy sources like solar energy, hydro energy, wind energy, geothermal energy and nuclear energy are the only alternatives for all above said problems. Major advantages of renewable energy sources are that they when used does not create any type of pollution as well as one can use them in cyclic manner. Only one thing that we must keep in mind that these can not be used directly as an energy, but one must convert in the form of energy [11]. Also, sometimes for the energy conversion process complex, huge and expensive machinery may require. The ultimate solution for all above discussed problems is the use of hydrogen energy. The sustainable and better future is the motivation for the production and use of hydrogen energy.

Hydrogen gas is also known as a green fuel, as it when used does not produced any harmful and toxic pollutants. Hydrogen is a very first element from the periodic table with symbol H and atomic number 1. It is present in a S block, first A (IA) group with electronic configuration $1S^1$. Because of only one electron present in its outermost shell, it can form only a single sigma bond with many other atoms. It is a nontoxic, colorless, odorless, and combustible element. Hydrogen is a nonmetal, present in a gaseous form under normal conditions. Hydrogen is at the top list in terms of abundance in the universe. Many studies shows that hydrogen is not only present on the planet earth but also it is present on and other planets too. Stars are producing helium from hydrogen under high temperature and pressure at their core. Being a smallest and lightest element hydrogen atom consist of one proton and one electron without any neutron.

Hydrogen has three isotopes adds proton (H), deuterium (D) and tritium (T) along with these chemists succeeded in the synthesis of 4H and 7H in a laboratory, which are not occurring naturally. Arrhenius theory of acids and bases is very useful in chemical science is depends on the hydrogen. Most of the chemical compounds which are synthesized in lab or naturally occurring are bonded to hydrogen because of its high reactivity. Water is a most important source for living organisms which is also known as a universal solvent is composed of two hydrogens and one oxygen. In the present chapter, different sources of hydrogen as an energy with photocatalytic hydrogen production methods mechanism from water and toxic hydrogen sulfide is depicted along with respective photocatalytic reaction setup for the generation of hydrogen. Both water and H_2S splitting set ups are being reported in our latest work with the help of organic and inorganic semiconductor and composite photocatalyst materials.

2. Hydrogen production methods

After realizing the importance of hydrogen in clean energy and future fuel till date, many methods are well known for the generation of hydrogen.

Hydrogen can be produced mainly from biological, electrolytic, photocatalytic, steam reforming and thermochemical methods as shown in **Figure 1**. Microorganisms (algae and bacteria) can also be responsible for the generation of hydrogen using biological processes. Water can be spilt by using both electrolytic and sunlight (photo) into hydrogen and oxygen. Also, hydrogen sulfide can used as

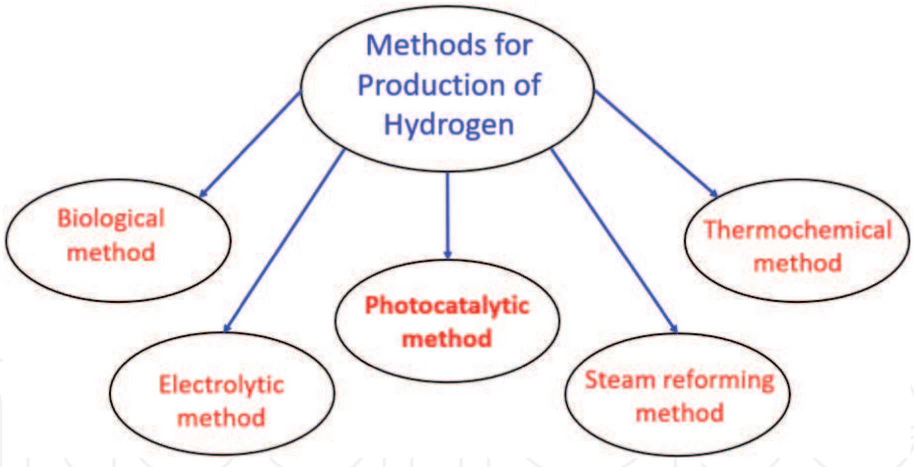

Figure 1.
Hydrogen production methods.

a rich source for hydrogen, which photocatalytically splits into hydrogen as a clean energy and sulfur for agriculture [12].

2.1 Biological method

Microorganisms such as algae and bacteria in absence of sunlight with organic matter can produce hydrogen using many biological reactions. In this method bacteria (microorganisms) break down the organic matter such as biomass, sugar, corn or waste and releases hydrogen gas. This method is also known as dark fermentation as no light is involved [13]. Biological method is under research and development stage as the efficiency of this process is not up to the mark.

2.2 Thermochemical method

Natural gas, coal, hydrocarbons and biomass is also rich with the hydrogen content. Thermal process like steam reforming is responsible for releasing hydrogen from these sources. Hydrogen when combines with carbon produces a hydrocarbon which are available naturally and are one of the main sources of hydrogen. Hydrocarbons like methane, ethane and propane (alkene and alkyne) are key compounds of hydrogen. More than 90% of hydrogen which we get nowadays is coming from hydrocarbons which has a fossil origin. These hydrocarbons are quite stable than the other sources of hydrogen and does not leave hydrogen easily unless catalysis process is used. Breaking of sigma bond present in carbon and hydrogen is most difficult but can be achieved by steam reforming in case of methane.

$$CH_4 + H_2O \rightarrow CO + 3H_2 \tag{1}$$

Generally, in steam reforming process water (steam) and methane are mixed in presence of catalyst (noble metals) inside a tube in appropriate proportion. Main advantage of using this process to produce hydrogen is that many companies/industries are already with all the equipment's setups are present. Perfect engineering and research and development in hydrogen generation from hydrocarbons field will fulfill the need of many upcoming generations [14].

2.3 Electrolytic method

This method uses electricity to get hydrogen and oxygen from decomposition of water. Now a days electrolytic water splitting is well developed and available in market commercially. This method is more efficient as compared to previous methods for production of hydrogen. Ultra-pure hydrogen can be produced by using electrolysis method. Also, bulk amount of hydrogen can be produced using this method but, the assembly required for this purpose is expensive [15]. Excess amount of energy is required in the form of overpotential to overcome activation barriers. If excess energy is not supplied the rate of hydrogen production is merely slow. Lately, hydrogen production using this method is not in demand as hydrogen can be generated in affordably amount from fossil fuels.

2.4 Photocatalytical method

In any chemical conversion reactants are converted into useful products either by photocatalytic or thermal reaction. The photocatalysis reaction method in which light/ photon is used to stimulate a photocatalyst substance (catalyst) which alters the rate of chemical reactions/process favorably without taking actual part in chemical process. Photocatalysis can also explained as a process in which light energy is used to activate the substance, which enhances the rate of a reaction without used in the chemical reaction [16]. Generally, electron-hole pairs are generated after absorption of light when the energy of the incident light/photons exact matches or exceeds the bandgap of that semiconductor photocatalyst material.

3. Mechanism of photocatalysis

In presence of light photocatalyst material shift the electron from valance band (VB) to the conduction band (CB). VB which has oxidative potential of +1.0 to +3.5 V versus the normal hydrogen electrode (NHE), and CB have a chemical potential of +0.5 to −1.5 V versus the NHE, hence they can act as reductants. **Figure 2**

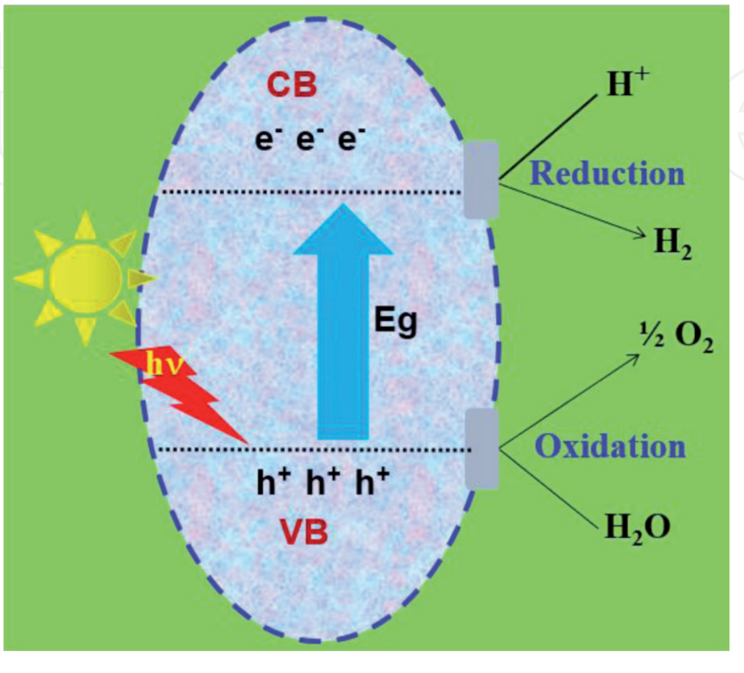

Figure 2.
Mechanism of photocatalytic H_2 production.

describes, photocatalysis method in three steps (1) migration of electrons (negative charge) from VB to CB, by leaving exact vacant holes (positive charge), (2) movement of excited holes and electrons to the surface and (3) excited electrons-holes they react with absorbed electron donors and electron acceptors for reduction and oxidation reactions. Along with proper band gap of semiconductor photocatalyst material its charge recombination rate, mobility and lifetime of electron and holes also plays a crucial role in overall hydrogen production [17].

3.1 Semiconductor photocatalyst material

Recently, charge recombination is delayed using either use of co-catalyst (platinum) on the surface of semiconductor photocatalyst which boosts the overall efficiency of hydrogen. Sacrificial agents such as methanol, EDTA, sulfides, sulfates and benzyl alcohol are also act as an oxygen scavenger in the process by enhancing the total yield of hydrogen production. After first report on TiO_2 for hydrogen production by Gratzel *et al.* the hydrogen generation field is considered as of immense importance [18]. Many researchers have published in the photocatalytic hydrogen generation field by changing catalysts, co-catalysts, combination of two catalysts (composites, coupled system). Till date, nano metal oxides, sulfides, niobates, tantalates and vanadates which contained the metal of d^0 or d^{10} electronic configurations such as In, Ga, Sb, Bi and Ag. Further, binary and ternary nano sulfides (CdS, ZnS, SnS_2, ZnI_2S_4, CdI_2S_4 and Sb_2S_3) nitrides oxynitrides, carbon based, and organic semiconductor materials has been reported as alternative photocatalysts for H_2 generation. Nanomaterial based semiconductor photocatalyst systems (TiO_2, SnO_2, WO_3, ZnO, Si_2O_7, ZrO_2, $SrTiO_3$, $LaCrO_3$, $BaTiO_3$) have many advantages as compared to their bulk counterparts and hence preferred in photocatalytic hydrogen generation [18–20]. These advantages are, high surface area, higher optical absorption, shorter charge migration length, higher solubility, tunable electronic structure, plasmonic resonance assisted charge injection and separation. All these plus points can be utilized to scale up photocatalytic hydrogen production using nanostructured semiconductor photocatalyst system. Following are the two photocatalytic hydrogen production setups are discussed with schematic representation using water and hydrogen sulfide as a source of hydrogen.

4. Photocatalytic hydrogen generation setups

4.1 Water splitting

Many attempts were taken place for the construction and engineering of setup for photocatalytic hydrogen generation [16]. Depending on the light source used (in sunlight or in a lab) reaction setup is modified, and the simplest form is described here with schematic representation **Figure 3**.

Generally, photocatalytic hydrogen production experiments were carried out in a wooden cupboard box which is known as a photocatalytic water splitting setup. This box is having the dimensions around 30 × 30 × 30 inch with closed wooden/stainless steel chamber with observing window as shown in schematic. **Figure 3** represents the schematic of setup and can be divided into three main parts as shown in figure. Firstly, the light source fitted vertically in quartz tube having water circulation (a) arrangement for cooling purpose. 400–600 W lamp with emission wavelength 200–800 nm can be used depending upon the photocatalyst. Secondly, inside this box a two neck 250 mL borosilicate round bottom flask (b) act as a photoreactor. In photoreactor water, co-catalyst, magnetic needle and scavenger

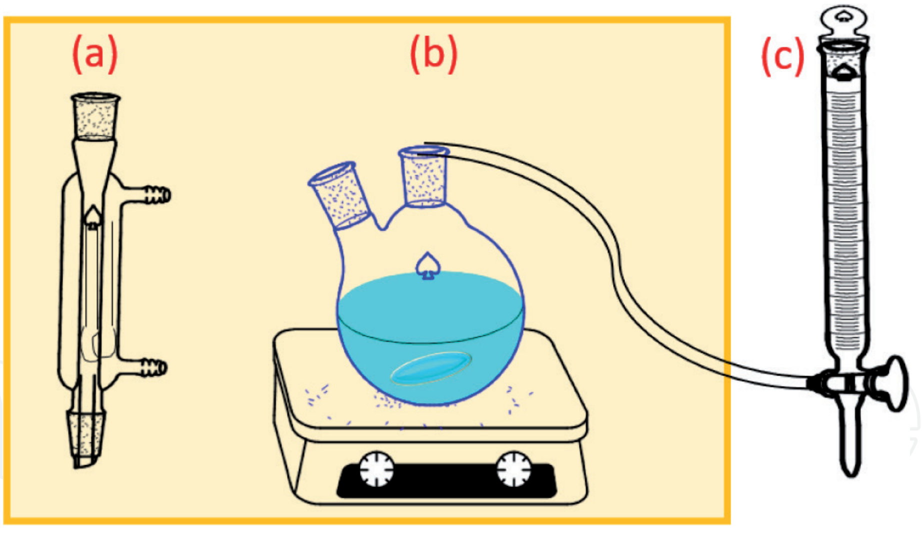

Figure 3.
Schematic representation of photocatalytic water splitting, (a) Light source fitted vertically in quartz tube having water circulation, (b) photoreactor, (c) a eudiometric tube.

are added. Lastly, produced H_2 in a reactor is collected in a eudiometric tube (c) for characterization on gas chromatography (GC). The eudiometer tube is with a saturated solution of sodium chloride (NaCl) to avoid the dissolution of evolved gases [16].

4.2 H_2S splitting

Irritating smell of H_2S gas is the reason for less research and development in this area as compared to water splitting. Earlier, Claus process is used for H_2S splitting which is mainly focused on sulfur and not on hydrogen. Photocatalytic H_2S splitting

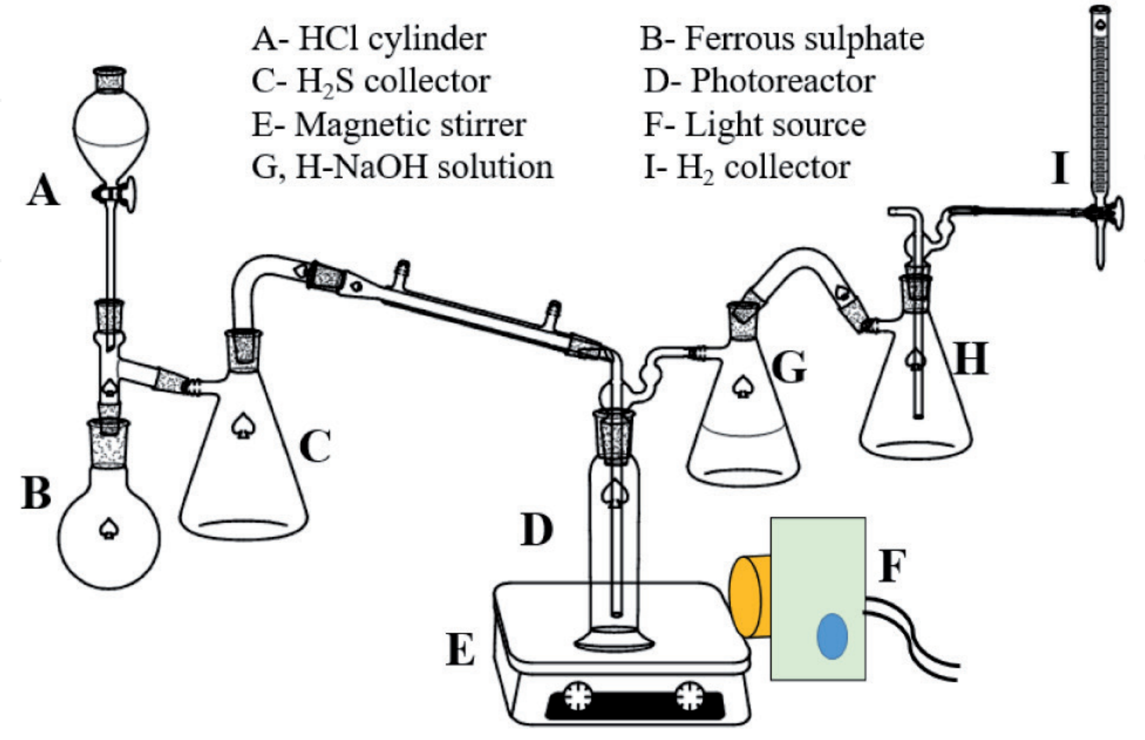

Figure 4.
Photocatalytic H_2S splitting reaction setup.

experiments for the generation of H_2 can be performed under light source or in sunlight depending upon the band gap of semiconductor photocatalyst [21, 22]. For light source (under lamp) an assembly is kept in a fuming hood to avoid bad smell and a schematic representation of a setup is shown in **Figure 4**. This setup can be divided in A to I parts as shown below.

For avoiding over heating of the photoreactor (D) throughout the photoreaction water circulation is added, Photoreactors are of various capacity (100 to 1000 mL) can be used, the quantity of photocatalyst (0.05 to 1 gram) was decided in every photoreaction. A source of light (F) of intensity 450–600 W can be used as discussed in above water splitting set up. Hydrogen sulfide generated in (A-B) and collected extra amount in (C) is bubbled through the solution in the photoreactor under continuous stirring (E). Bubble rate differs as the capacity of photoreactor changes. The excess H_2S was trapped in NaOH solution (G-H). The amount of evolved H_2 was measured using graduated gas burette (I).

Large scale production of hydrogen using toxic H_2S is also possible like water splitting as discussed above in water splitting setup section.

5. Large scale hydrogen production and usage

Large scale production of hydrogen energy from water splitting is also possible by using this reaction setup. Appropriate photocatalyst with suitable band gap and light frequency source can leads to enhance hydrogen production. Quantity of photocatalyst and capacity of photoreactor promises the large-scale production of hydrogen energy. It can be achieved with proper engineering inside the lab as well as on roof of the lab under natural sunlight. Large scale production of hydrogen using toxic H_2S is also possible like water splitting as discussed above. Hydrogen is a clean energy which have applications in soil refining, methanol generation, steel production and ammonia production. Nowadays, it is also used for all type of transportation (alternative for Compressed Natural Gas, CNG), power generation, homes and fuel in jets and ships. Recently, the worlds first hydrogen-powered train rolled in Germany. After this many countries tested hydrogen fuel-cell passenger trains. Also, a UK-based car manufacturer company produced a two-seater hydrogen vehicle. The US, Europe and China are the top consumers of hydrogen mainly in refineries sector. Alas, all these emerging hydrogen applications are not economical than the other energy resources as hydrogen costs around USD 12–16/Kg.

6. Transportation and storage of hydrogen gas

Nowadays, the production of H_2 gas is not a new to a scientific community but the ways of transportation and storage of it is under continuous research. Transportation is mainly taking place either by road or by water routs in a cryogenic or compressed cylinders. As hydrogen is having low density the transportation is difficult and expensive so, for transporting H_2 from industry to working sites is achieved using pipelines [23]. In many cases gas is compressed and then filled in appropriate cylinders as per the quantity and requirement. Laboratories and research centers require hydrogen in small quantities and transportation of such cylinders can be takes place using small trolleys. On the other hand, the amount of hydrogen required for industrial purpose is in large quantities which are once received by transported kept in a gas bank.

Storage of hydrogen gas as a future fuel is important because one cannot produce it efficiently and in large amount at the domestic or small industry level.

For storage purpose research centers, industries and automobiles have well engineered tanks. The concept of adsorption is utilized for storage of gas, here a porous material with large surface areas like activated carbon are needed. In absorption metals are combined with hydrogen atoms to form a metal hydride. Palladium, zirconium and other transition metals are also reported for the large amount of gas absorption [24, 25].

Recently, photocatalytic solar hydrogen production from water splitting on a 100 m^2 scale panel, carbon films, closed systems, plates and sheets is demonstrated by K. Domen research group. A 100 m^2 array of panel reactors and other setup types effective for more than 90 days. Lately, chemical combination between hydrogen and boron or nitrogen is under investigation. During this combination hydrogen molecules are dissociated and forms hydrogen atoms which then goes in the empty spaces between the metals lattice structure [26].

7. Conclusions

Hydrogen produced from electrolytic, biological, steam reforming and photocatalytic methods can be utilized as a clean energy source. Still, plenty of research and development is needed to enhance the efficiency and to reduce the overall economy of the process. Though the various hydrogen production methods which are discussed here are better and less expensive, an effective method need to be developed for future energy crises. Photocatalytic hydrogen generation from water and hydrogen sulfide splitting using available setup is with opportunities to development for young researchers. Besides the transportation and storage of hydrogen gas it must be considered in a frame of the energy system globally.

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