

# Green Hydrogen, an Alternative Renewable Energy Source: Based on Solar-Energy-Driven Water-Splitting Technology

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## **Abstract:**

The need for zero-emission, eco-friendly hydrogen fuel has increased enormously over the years due to adverse impacts on the environment caused by conventional fuels such as natural gas, coal, oil, fossil fuels, bio-mass etc. This chapter reports the safest and most efficient route for hydrogen-fuel production based on solar-energy-driven water-splitting technology over a heterogeneous photo-catalyst. Several challenges have been made for the extension of photo-catalyst, based on nano-sized semiconducting materials such as binary and ternary metal chalcogenides nano-materials, CuS, CdS, Fe<sub>3</sub>O<sub>4</sub>, CuInO<sub>2</sub>, CuInS<sub>2</sub>, CuGaS<sub>2</sub> and their composites with hetero-nanostructure. When the nano-structures have the ability to absorb solar-light-energy (having a narrow band gap energy < 3.6 eV), i.e., to utilise the most of the solar-spectrum, the photo-catalytic performances have increased much more. The catalytic performances of the semiconductors have also been improved for enhanced hydrogen production using nano-engineering technology, i.e., different modifications to the nano-catalyst surface and electronic energy structure, so that they can act as an efficient photo-catalyst for solar-energy driven water electrolysis to produce enhanced large-scale hydrogen-fuel. The possible mechanism of the photo-chemical processes has also been explored through the formation of free electron-hole pair (e<sup>-</sup>/h<sup>+</sup>) on suitable heterogeneous catalyst's surface and controlling the kinetics of hydrogen evolution reaction and oxygen evolution reaction. How the proposed nano-catalyst materials have been designed to optimize solar-to-hydrogen conversion efficiency, improve the rate of hydrogen production and commercialized for the sake of society has been deliberated.

**Keywords:** *Electro-Catalytic Activity; Photo-Catalysis; Semiconducting Nano-Materials; Solar-Energy-Driven Chemical Reactions; Water-Splitting; Zero Emission Hydrogen*

## **Introduction:**

Natural fuel supplies are gradually running out, which is why there is a growing need for alternate, renewable, and non-fossil energy sources. Again Recently, much attention has been paid to 'hydrogen-fuel', as a next-generation energy carrier. Hydrogen is commonly known as 'Zero emission fuel (ZEF)' (Nnabuife *et al.*, 2023) (Figure 1)

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because when hydrogen enters into vehicles that run on hydrogen fuel, it produces only water vapour and generates almost no harmful air pollution, unlike conventional fuels such as natural gas, coal, oil, fossil fuel, bio-mass etc. which emit equally large amount (830 million tons) of carbon dioxide annually into the atmosphere (Höök & Tang, 2013). Due to presence of simplest chemical structure, where only two hydrogen atoms are stuck together by electrostatic force of attraction, hydrogen-fuel is non-toxic, odorless, and tasteless, unlike conventional fuels such as natural gas, coal, oil, fossil fuel, bio-mass etc. that contain toxic substances. With tremendous development of science and technology, Japan first achieved full-scale use of hydrogen-fuel as renewable energy source, like solar and wind-energy. In 2015, world's first publicly available Hydrogen Vehicle, commonly known as fuel cell electric vehicle, was launched in Japan, where energy is generated by converting chemical energy of hydrogen to mechanical energy in a fuel cell to rotate electric motor (Turoń, 2020). In this case, when hydrogen enters into fuel-cell device of a Hydrogen Car or Bus, it has been used as fuel and combines with oxygen from the air, creates electricity and water vapour through an electrochemical process. In this way, hydrogen and fuel cells can play an important role in the country-wide energy strategy, with the potential for use in a broad range of applications across all sectors—transportation, commercial, industrial, residential, etc.

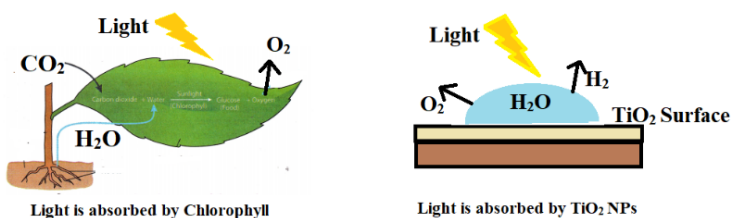


**Figure 1:** Zero emission future (Net Zero) (Source: Nnabuiife et al., 2023)

Hydrogen is the simplest and most abundant chemical element in the universe. It was discovered in the Sun, Stars and the gas planets, but on earth, hydrogen doesn't exist in free form and is generally found in compounds with other elements such as carbon and oxygen, it exists mainly as methane ( $\text{CH}_4$ ) and water ( $\text{H}_2\text{O}$ ), respectively. To obtain pure hydrogen for industrial applications, it must be separated from the compounds to which it is bound. Since the beginning of the 19<sup>th</sup> century, hydrogen-fuel has been so chosen to be used to fuel cars, airships, spaceships etc. and most of the cases of hydrogen (in environment sense Grey Hydrogen) have been extracted commercially from fossil-fuels such as natural gas, coal, oil, bio-mass etc. that emit equally large amount of carbon dioxide into the atmosphere. So, focus needs to be put on replacing

that grey hydrogen with one that can reduce global warming, decrease fossil-fuel dependency through improving technologies for fully utilizing unlimited water resources. Since then, water-splitting or water-electrolysis process has become much desired, where pure green hydrogen can be produced by separating hydrogen from the oxygen in water. In 2022, Govt. of India established the national Green Hydrogen Mission and India's first 99.99% pure green-hydrogen-pilot-plant was commissioned by OIL (Oil India limited) where pure hydrogen has been generated by the electrolysis of water or water-splitting (Harichandan, Kar & Rai, 2023; Vardhan *et al.*, 2022).

Now-a-days, solar-energy-driven water-splitting, over a nano-sized photo-catalyst material, is the most acceptable method for enhanced large-scale hydrogen production (Kim *et al.*, 2019; Maji *et al.*, 2012). Light is an outstanding source of energy and has been used as driving force to conduct chemical-pathways. When solar-energy is used in a photo-chemical reaction, it will be the most beneficial alternate sustainable-energy source as the abundance is virtually unlimited and free, making the hydrogen production process more cost-effective for the sake of society (Dutta *et al.*, 2012). In the year 1967, Prof. Fujishima and Honda (1972) of Tokyo University of Science, Japan, first discovered the Photo-catalytic hydrogen production technology, which is basically analogous to the natural photo-synthesis technique in plant-leaves and similar types of photo-chemical reactions have been carried out under light irradiations (Figure 2). In their research works, it has been observed that, in a photo-electrochemical set up with Titanium dioxide ( $\text{TiO}_2$ ) nano-material based working electrode and a Platinum cathode, when light falls on the  $\text{TiO}_2$  surface, gas bubbles consisting of hydrogen have evolved from the surface of the  $\text{TiO}_2$  anode while simultaneously oxygen gas has been generated at the Pt counter electrode from water splitting.



**Figure 2:** Photo-catalysis technology on  $\text{TiO}_2$  surface, basically analogous to the photo-synthesis technique in plant (Source: Fujishima & Honda, 1972)

The possibility of hydrogen production from water opens the door for the development of hydrogen production technology by employing different nano-materials with very interesting physico-chemical features. As a catalyst material, nano-sized inorganic materials show remarkable efficiency in the field of photo-catalysis technology (Hoffmann *et al.*, 1995). As the dimension of the nano-scaled materials is so small, new interesting properties have been generated, such as interesting chemical and physical

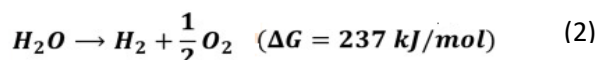
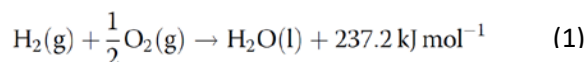
properties, large specific surface area, large specific surface-to-volume ratio, greater surface tension, greater surface activity, high catalyst-loading capacity and better light absorption capacity. Again, the nano-dimension having large surface-to-volume ratio can enormously increase the number of active sites at the nano-catalyst's surface, their interaction with different target-molecules/moieties and hence catalytic performances. Now-a-days, using nano-engineering technology, the nano-structure can be manipulated during nano-materials synthesis with specific control over size (quantum confinement), shape, morphology and hence the catalytic performances towards hydrogen production can be optimized.

When the nano-structures are semiconducting in nature, they possess suitable band-gap energies and flat band-potential levels that can easily absorb UV, visible, even solar-light-energy and accelerate the photo-chemical reaction rate (Nakata & Fujishima, 2012). Most of the metal chalcogenides nano-particles such as metal oxides, metal sulfides TiO<sub>2</sub>, ZnO, CuO, FeS, ZnS NPs etc. are semiconducting in nature and have proper redox potentials, excellent electron transfer ability and outstanding stability in air and solutions (Sun *et al.*, 2008).

Keeping in mind low-cost and large-scale hydrogen production for the sake of society, this chapter comprehensively summarizes how pure green hydrogen production technology has been developed in such a way that low-cost, large-scale commercially hydrogen has been obtained from unlimited and free water resources using unlimited and free solar-energy. It has also been discussed in detail about the fundamental principle of water-splitting technologies based on simplest photo-catalytic water-electrolysis. The possible mechanism of the photo-chemical processes has also been explored through the creation of free electron-hole pair (e<sup>-</sup>/h<sup>+</sup>) on suitable heterogeneous catalyst's surface and controlling the kinetics of hydrogen evolution reaction (HER) and oxygen evolution reaction (OER). A brief overview of recent trends in solar-energy-driven hydrogen-fuel production has been deliberated.

### **Fundamental principle of water-splitting technologies**

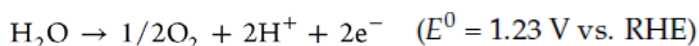
Water is the most copious resource for hydrogen-production. Water-splitting technology breaks the water molecule into hydrogen and oxygen when suitable amount of energy is provided according to thermodynamic equation 1 and 2.



As equation 1 involves thermodynamically uphill transformation, which is associated with positive 237.2 kJ/mol Gibbs free energy (Li & Li, 2017), in water-splitting reverse reaction

(equation 2), a certain amount of energy equivalent to Gibb's free energy (~237 kJ/mol) has to be supplied to the system comprising water, leading to the conversion (thermodynamically) into hydrogen and oxygen. Generally, in simplest way, electrical energy has been used to split water, which is commonly known as water-electrolysis. In this case, an electrical current has been passed through two electrodes (anode and cathode) of an electrochemical set-up containing water molecules to conduct two half-cell reactions, oxidation and reduction, leading to the formation of hydrogen and oxygen, respectively (Holladay *et al.*, 2009). From the redox point of view, the reduction reaction by electrons to form H<sub>2</sub> (at the cathode) and oxidation reaction to form O<sub>2</sub> (at the anode) are commonly known as hydrogen evolution reaction (HER) and oxygen evolution reaction (OER), respectively (Li, Wang & Wang, 2021).

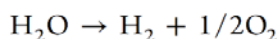
anode



cathode



overall process



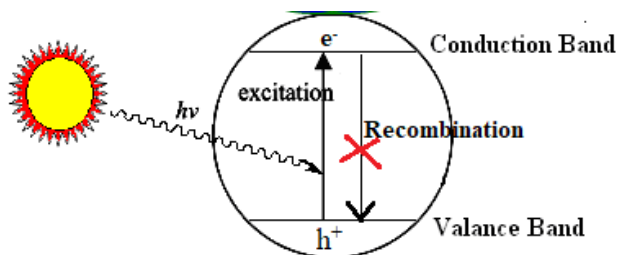
The kinetics of HER requires redox potential of H<sup>+</sup>/H<sub>2</sub> i.e., 0 V vs. NHE and standard reduction potential of 1.23 V vs. NHE (E<sup>0</sup> of O<sub>2</sub>/H<sub>2</sub>O) requires for evolution of oxygen. The total Gibb's free energy (237.2 KJ/mol) corresponds to 1.23 eV per electron have to be supplied to overcome the overall thermodynamic barricade of the water-splitting reaction is 1.23 V.

### ***Photo-catalytic mechanism on water-splitting***

When a heterogeneous semiconductor photo-catalyst has been employed in the above water-splitting chemical pathway, enhanced large-scale hydrogen-production has been obtained. Under light illumination. In a photo-chemical set up, suitable catalyst material plays important role in quickening the kinetics of both the OER and HER.

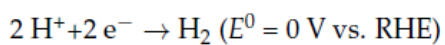
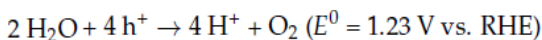
Numerous attempts have been covered to develop photo-catalyst materials in such a way that they can function under visible, even solar-light irradiation to efficiently utilize solar-energy. In photo-catalysis process, metal chalcogenide-based nanomaterials are chosen as heterogeneous photo-catalyst because they are semiconducting in nature and possess suitable band gap and flat band potential levels with filled valance band (VB) and vacant conduction band (CB) (Figure 3). Titanium dioxide (TiO<sub>2</sub>) nano-material has been selected as the model material for basic investigation and to demonstrate

general surface photo-catalytic reactions of semiconductors. It is generally accepted that the main reaction responsible for photo-catalysis is the interfacial redox reaction of carriers generated when a certain amount of energy is absorbed by the semiconductor catalyst. If the band gap energy of the catalyst is equivalent to or less than the energy of incident light energy, the electrons ( $e^-$ ) residing in VB will absorb the photon and be promoted to the CB, thus leaving behind a hole ( $h^+$ ) in VB of the semiconducting nanomaterials (Figure 3).

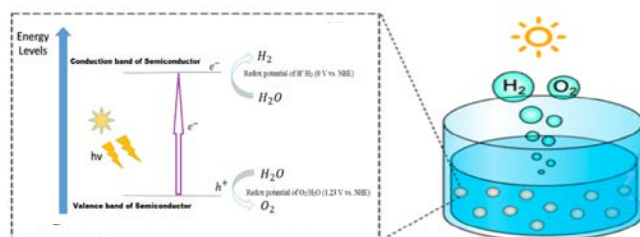


**Figure 3:** Illustration of photo-catalytic mechanism (Source: Dutta, Maji & Adhikary, 2014)

The photo-chemical reactions basically start with the free electron-hole pair ( $e^-/h^+$ ) formation (Dutta, Maji & Adhikary, 2014). That ' $e^-$ 's and ' $h^+$ 's pass to the active sites of the surface of semiconductor photo-catalyst, acting as reducing or oxidizing agents to drive reduction/oxidation reaction on that surface. In water-splitting process, water molecules are reduced by the photo-induced electrons to form  $H_2$  and similarly, water molecules are oxidized by the photo-induced holes to  $O_2$  (Almomani, Shawaqfah & Alkasrawi, 2022) (Figure 4) according to equation:



The hydrogen gas that produced was collected using gas-tight syringe and analysed by gas chromatography.

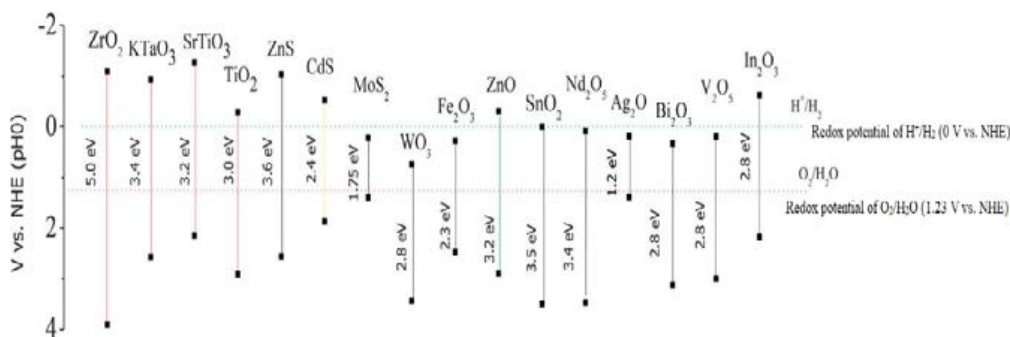


**Figure 4:** General illustration for photocatalysis-based water splitting on  $TiO_2$  nano-materials (Source: Almomani, Shawaqfah & Alkasrawi, 2022)

### Recent trends of Photo-catalytic (PC)-based hydrogen-fuel production

Inspiring from the first research work of Fujishima and Honda in 1972, so many researchers have paid considerable attention to increasing hydrogen production efficiency in a large-scale way using efficient catalyst materials such as metal oxides, metal sulphides, carbon-nitrides, polymers, hetero-nanostructures, even under natural solar-light illumination (Teixeira *et al.*, 2018). In these cases, the catalyst materials can act as catalytically active sites to facilitate the corresponding HER, lowering the kinetics overpotentials of water-splitting.

From the above thermodynamic restrictions, a semiconductor photo-catalyst that has the ability to split water to produce hydrogen must have flat band-positions in such a way that the bottom level of the conduction band (CB) position should be more negative than the redox potential of  $H^+/H_2$  (0 V vs. NHE) for evolution of hydrogen and the top level of the valence band (VB) needs to be more positive than the standard reduction potential of  $O_2/H_2O$  (1.23 V vs. NHE) for evolution of oxygen (Jafari *et al.*, 2016). So, the minimum band-gap energy of a semiconductor photo-catalyst necessary for driving water-splitting process is 1.23 eV. To efficiently use solar-energy, the band-gap energy ( $E_g$ ) should be in the range of  $3.0 \text{ eV} > E_g > 1.23 \text{ eV}$  (Qiao *et al.*, 2018). Figure 5 represents the band potential positions of several metal chalcogenide semiconductors relative to the water redox potential levels, which can efficiently split water to produce hydrogen.



**Figure 5:** Band potential position of several metal chalcogenide semiconductors against normal hydrogen electrode (NHE) as a reference (Source: Jafari *et al.*, 2016)

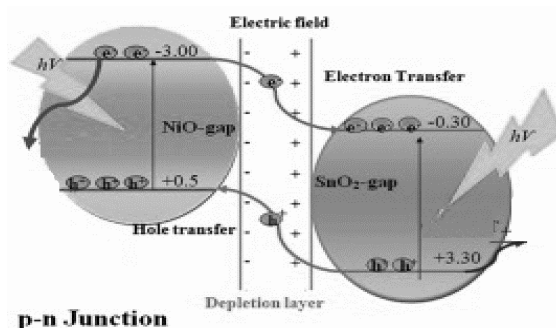
Though fulfilling thermodynamic potential level condition, some nano-materials cannot efficiently produce hydrogen, exhibit unacceptable photo-catalytic capability much below the expected level, due to their partial light utilization, inactive surface redox processes. Again, most of the photo-generated electrons and holes can re-combine (considerable electron-hole pair re-combination) on the photo-catalyst's surface in a very short-time.

### Exploration of Chemical Complexity



Again, after formation of hydrogen, the back-ward reaction of  $H_2$  and  $O_2$  to  $H_2O$  occurs immediately.

Under these circumstances, in the recent trend, numerous effective strategies have been explored to increase light absorption, photo-generated charge separation and lower kinetic overpotentials of hydrogen evolution using different efficient nano-semiconductors, such as metal oxides, carbon-nitrides, polymers, and hetero-structures (Teixeira *et al.*, 2018). In addition, different modifications on nano-catalyst surface, such as amalgamation of semiconductors with other components by ion-doping, hetero-structure fabrication, noble-metal loading, morphology or size modulation, defect engineering, tuning of active crystal facets etc. have also been adopted for enhancing the photo-catalytic capability. Using defect engineering, vacancy defects in semiconductors can enhance catalytic efficiency and improve photocatalytic water-splitting. Actually, vacancy defects can change the electronic structure of semiconductors and generate defective energy levels near the conduction-band (CB) or near the valence-band (VB) in case of n-type or p-type semiconductors, respectively. The newly formed energy level (Fermi level) in semiconductors can effectively prohibit electron-hole pair recombination, can effectively promote light absorption or improve visible light harvesting, promote charge carrier separation (photo-induced carrier separation) and photo-electron transfer, which really extend the carrier life-time, increase conductivity, and reduce the energy barriers for water-splitting. Again, in the cobalt sulphide/nickel sulphide hetero-structure, hybridization between two or more transition metal-based materials can synergistically enhance their catalytic performance and facilitate charge-transport ability, which provides a synergistic effect (Figure 6) toward HER and OER (Shit *et al.*, 2018).



**Figure 6:** Illustration of synergistic effect on charge transport towards photo-catalytic reaction (Source: Shit *et al.*, 2018)

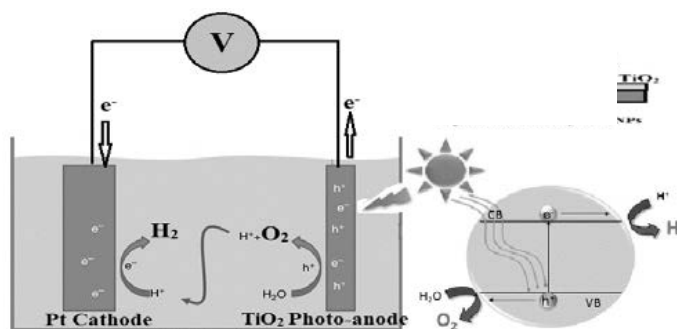
Similarly, when some semiconductors ( $TiO_2$ ) coupled with highly conductive supports such as metallic Silver, Gold, Pd, Pt or bimetallic PdPt NPs, they can strongly prevent the re-combination of photo-generated electrons in the semiconductor, enhance the



electron-transport behaviour and improve their photo-electrocatalysis performances towards water-splitting (da Silva *et al.*, 2020). Also, active co-catalyst loading (say Ni<sub>3</sub>N) onto semiconductor g-C<sub>3</sub>N<sub>4</sub> support, can produce hydrogen under visible-light illumination with hydrogen evolution rate of ~305.4/mol/h/g, which is about three times higher than that of pristine g-C<sub>3</sub>N<sub>4</sub> (Ge *et al.*, 2019). ZnS nano-structure has excellent potential in solar-energy-driven hydrogen formation because of its ability to quickly generate photo-induced carriers. Again, zinc vacancies can modulate the electronic energy-level of ZnS and affect the CB and VB positions in such a way that it can decrease the oxidation capacity of the holes, protecting the Zn-deficient ZnS from photo-corrosion, leading to long-term photo-catalytic stability and exhibiting an outstanding light-energy-driven hydrogen productivity of ~338 μmol/h/g. Besides, Bi-based photo-catalysts, Bi<sub>2</sub>WO<sub>6</sub> nano-bipyramids with “Bi–O” vacancy and BiVO<sub>4</sub> with enriched oxygen vacancies have been used for enhanced solar-energy-driven photocatalytic hydrogen production and show much stronger photo-sensitivity and photo-induced carrier separation ability owing to the formation of the intermediate defect energy-level in its band-gap (Kim *et al.*, 2015).

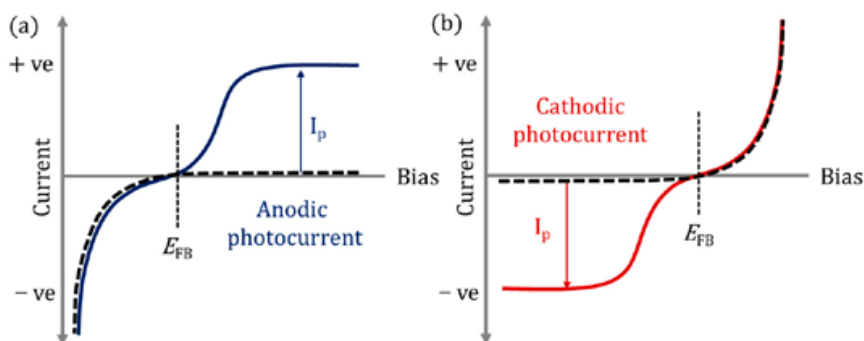
### **Photo-electrocatalysis (PEC) technology on water-splitting**

Photo-electrocatalysis technology (PEC) is gaining considerable interest for commercial green-hydrogen production owing to presence of lower system complexity, lower operation potential and higher hydrogen production efficiency. If in the above photo-chemical mechanism, an externally applied electrical bias (Figure 7) has been used in an electro-chemical setup having a photo-electrode (photo-anode) coating with a similar type of semiconducting nano-material and normal platinum counter electrode, photo-electrocatalysis i.e. ‘electrochemically assisted photo-catalysis’ technology, has been developed. Here, the photo-catalysis technology has been combined with electro-catalysis to make dual-functional catalysis work for green-hydrogen production (Chatterjee *et al.*, 2022).



**Figure 7:** Schematic diagram of PEC water-splitting based on n-type photo-anode  
(Source: Chatterjee *et al.*, 2022)

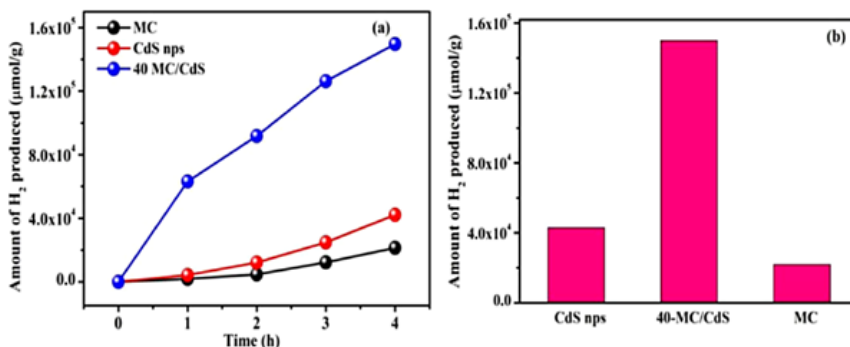
In PEC water-splitting technology, the first electron-hole pair ( $e^-/h^+$ ) is generated on the surface of a photo-electrode (generally photo-anode) upon light irradiation, followed by immediate transfer of those electrons to counter electrode through external circuit in the presence of external bias which promotes the HER redox reactions for hydrogen production (Figure 7). Here, the externally applied electrical bias plays an important role in preventing electron-hole pair ( $e^-/h^+$ ) re-combination through the migration of electrons to counter electrode and thereby increasing the life-time of the generated electron-hole pairs, which can improve the hydrogen production reaction-rates. The photo-anode, where electrons are the majority carriers, is generally fabricated by immobilising a n-type semiconducting nano-material onto an electrically conducting supporting substrate such as metals, carbonous materials or conductive films such as indium-doped tin oxide (ITO) or fluorine-doped tin oxide (FTO). Owing to large number of electrons that migrate to counter electrode upon light irradiation, which is commonly known as photo-induced carrier transport properties, an anodic photo-current response has been generated and can be measured experimentally through linear sweep voltammetry in comparison to current in dark (Figure 8a). Similarly, cathodic photocurrents have been observed from photo-cathodes coated with p-type materials, where holes are the majority carriers (Figure 8b) (Sato,1998).



**Figure 8:** (a) Anodic photocurrent ( $I_p$ ) response, (b) cathodic photocurrent ( $I_p$ ) response; solid lines under irradiation; dashed lines in dark; EFB flat band potential (Sato,1998)

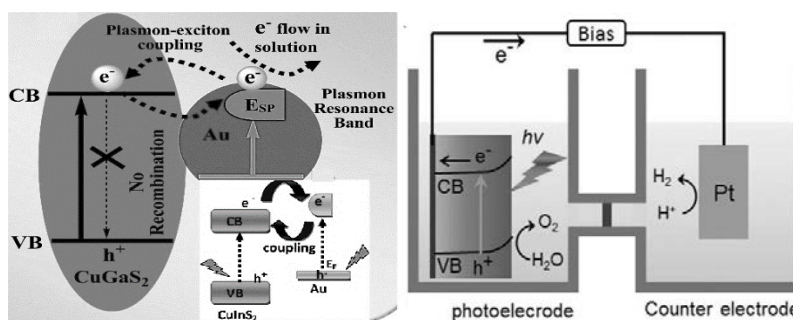
Various solar-energy-driven hydrogen production technologies have been greatly developed based on photo-electrochemical (PEC) water splitting with a high solar-to-hydrogen (STH) conversion efficiency. Different semiconductor electro-catalyst have been designed to optimize STH efficiency and improve rate of hydrogen production. Till now,  $\text{BiVO}_4$  has been established to be the best metal oxide electro-catalyst material and has been used as photoanode, which exhibits a photocurrent density of  $\sim 4.5 \text{ mA cm}^{-2}$  at 1.23 V under simulated sunlight irradiation, corresponding to high STH efficiency of 8.1% (Pihosh *et al.*, 2015). According to R. Banerjee and his co-workers (2021), the rate of  $\text{H}_2$  production from water over a heterogeneous photo-catalyst, CdS-

carbon nano-composite (40 MC/CdS of Figure 9), has been found to be much higher i.e., 37,641  $\mu\text{mol/g/h}$  due to the presence of a suitable flat band potential and photo-generated charge separation ability of catalyst.



**Figure 9:** (a) Photo-catalytic hydrogen-fuel production ( $\mu\text{mol/g/h}$ ) in presence of different CdS NPs (b) comparative study of H<sub>2</sub> production obtained after 4 h of light irradiation (Source: Banerjee *et al.*, 2021)

In recent years, there has been considerable attention to use hetero-structured semiconductor nano-composites in water-splitting technology to improve catalytic performances for enhanced hydrogen production and catalyst stability. Owing to presence of effective exciton-plasmon coupling (Figure 10) at hetero-junction, some semiconductors coupled with highly conductive supports such as metallic Silver, Gold, Pd or Pt can strongly prevent the re-combination of photo-generated electrons of the semiconductor, enhance the electron transport behaviour and hence improve their photo-electrocatalysis performances. The Au–CuGaS<sub>2</sub> and Au–CuInS<sub>2</sub> twin-structures similarly exhibit plasmon enhanced superior charge-transport ability, generate abruptly high photocurrent-density and have been used as potential candidates for photo-electrochemical water-splitting (Ghosh *et al.*, 2018).



**Figure 10:** Basic mechanism of plasmon–exciton coupling in the Au–CuGaS<sub>2</sub> hetero-structure (Ghosh *et al.*, 2018)

Again, water-splitting concerning OER and HER also depends upon overpotentials ( $\eta$ ) and those overpotentials have been enormously minimized with the help of efficient and bi-functional electro-catalysts, silver permanganate ( $\text{AgMnO}_4$  AMO)/Pd nano-composite (Mondal *et al.*, 2021). The catalytic performances of simple  $\text{AgMnO}_4$  (AMO) nano-materials had been improved for enhanced hydrogen production using nano-engineering technology through loading with highly conductive Pd over AMO and further modifying with PdOx ( $x = 1, 1.5, 2$ ), having different oxidation states of  $\text{Pd}^{\delta+}$  species produced at the AMO–Pd interface. It has been reported that the robust synergistic effect among AMO,  $\text{Pd}^{3+}$  and PdOx strongly contributes to remarkable OER/HER performances and AMO/PdOx/Pd-260 NComp (NComp-3) exhibits extremely low overpotentials ( $\eta_{10}$ ) (160 mV for OER, 58 mV for HER at  $10 \text{ mA cm}^{-2}$ ), highest Turnover Frequency (TOF) ( $3.7 \times 10^{-1} \text{ s}^{-1}$ ) and highest specific activity at  $\eta$  of 200 mV.

### Conclusion

This chapter aims to give an overview of different low-cost, large-scale pure green-hydrogen production technologies in such a way that commercially hydrogen has been obtained from unlimited, free water resources using unlimited and free solar-energy. Heterogeneous photo-catalyst materials have been successfully developed based on nano-sized semiconducting materials such as binary and ternary metal chalcogenides nano-materials, CuS, CdS,  $\text{Fe}_3\text{O}_4$ ,  $\text{CuInO}_2$ ,  $\text{CuInS}_2$ ,  $\text{CuGaS}_2$  and their composites. The catalytic performances of the semiconductors have been successfully improved for enhanced hydrogen production using nano-engineering technology i.e., different modifications to the nano-catalyst surface and electronic energy structure, which can act as an efficient photo-catalyst for solar-energy driven water-electrolysis to produce large-scale hydrogen-fuel. The possible photo-catalytic mechanism has also been discussed through the detection of free electron-hole pairs ( $e^-/h^+$ ) on a suitable catalyst's surface, which will act as reducing or oxidizing agents to drive reduction/oxidation reaction i.e., the hydrogen evolution reaction (HER) to form  $\text{H}_2$  and oxygen evolution reaction (OER), respectively. The catalytic performances have also been improved by tuning shape, size, morphology and band-gap energy during synthesis process. A brief overview of recent trends in solar-energy driven hydrogen-fuel production has been deliberated and successfully commercialized for the sake of society so that most of the solar-spectrum and light energies can be utilized for large-scale applications.

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