# Nanomaterials For Hydrogen Generation: A Review

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**Abstract:** Hydrogen is proving its potential as most appealing and eco friendly energy fuels. Theorganic reforming based nano-sized composites and nanocatalyst for photocatalytic water splitting applications are attracting growing interest in the prospect of hydrogen generation from solar energy with minimal environmental impact. Because of the higher surface area and size-dependent features, such as increased absorption coefficient,reduced carrier-scattering rate and increased band-gap energy, the nano- semiconductors have potential advantages in PEC applications when compared to bulk materials. Despite recent research in producing materials having high specific photoactivity, the conversion efficiencies from solar-to-hydrogen are still far from achieving the basic requirements for actual solar applications, according to a literature review. The paper begins by providing an overview of the conventional hydrogen generation techniques. This paper also examines current advances and challenges in water splitting methods based on Photo Electro Chemistry based nanomaterials and various ways for improving hydrogen evolution.

***Keywords:*** **Hydrogen, nanomaterials, water splitting, PEC.**

## 1. INTRODUCTION

The greatest difficulty to be handled in the near future of the scientific period is the massive energy requirements. By 2040, global energy consumption is expected to have increased from 540.5 quadrillion Btu in 2011 to 815.0 quadrillion Btu[1]. A steady and affordable supply of energy is essential to our daily life. Fossil fuels have given a significant percentage of world energy, but they are not renewable, and their combustion has resulted in substantial environmental problems by emitting harmful chemicals and greenhouse gases.[2]. Because of its green (a clean and renewable energy source), storable, and high energy density features, hydrogen is one of the most potential energy alternatives beyond the fossil fuel age. Hydrogen is now produced mostly by steam reforming and water gas shift methods, both of which rely on fossil fuels[3].Furthermore, carbon dioxide is released during this process. The usage of sunlight and water for the

production of hydrogen can providethefuel which can almost meet global energy demands. This also aids to combat climate change by lowering carbon emissions[4]. Sunlight can be used in almost three ways to produce hydrogen from water. The oldest and most established method is electrolysis of water using electricity generated by solar cells. Photoelectrochemical hydrogen generation is a newer approach that Fujishima and Honda found in 1972 using TiO2 as a photoanode and Pt as a cathode[5]. Particulate photocatalysts capture photons and breakdown water directly to hydrogen and oxygen in photocatalytic water splitting.In this article, a brief summary of advanced nanomaterials for water splitting and hydrogen generation is provided.

## 2. Methods of hydrogen production

There are a range of manufacturing processes for hydrogen generation, which can be classified into conventional and renewable methods depending on the raw materials available.Various technologies exist for producing hydrogen from fossil fuels. Hydrocarbon reforming and pyrolysis are two of the most common.Because of their well-developed and widely utilised properties, these technologies can meet practically all of the hydrogen requirement.Natural gas accounts for 48 percent of hydrogen supply, with naptha and heavy oils accounting for 30 percent, and coal contributing for 18 percent[6], [7].The main ways for generating hydrogen from renewable sources are biomass and water splitting, both of which are currently under investigation. Biological and thermochemical processes are used in the biomass process[8], [9].In recent years, water splitting (artificial photosynthesis), which is based on the principle of photosynthesis, has received a lot of interest. Water splitting requires energy, which can come from both renewable and non-renewable sources.

## 3. Solar Water Splitting Mechanism and Material Requirements

### 3.1.Solar Water Splitting mechanism

The water splitting process using single component as photocatalyst is represented schematically as in Fig 1[10]. When the photocatalyst is irradiated with light that has a higher photon frequency or energy greater than the band gap energy, the electrons movefrom valence band to the conduction band, creating holes in the valence band. These electrons and holes move on to the surface, where they can start water oxidation/reduction to make oxygen and hydrogen. Without creating hydrogen or oxygen, theexcited electrons and the holes can recombine either through radiatively route or through nonradiative routes. Electron-hole recombination must be decreased to achieve higher energy efficiency.The sites required for water reduction and oxidation are be separated for preventing the backward reaction of oxygen with hydrogen to water.

### 3.2. Sequence of Water splitting process

The process of overall solar water splitting is shown schematically in Figure 1. The minimal free energy required for the breakdown of water into hydrogen and oxygen is 237 kJ mol1, or 1.23 V between the hydrogen and oxygen evolution potentials[11].

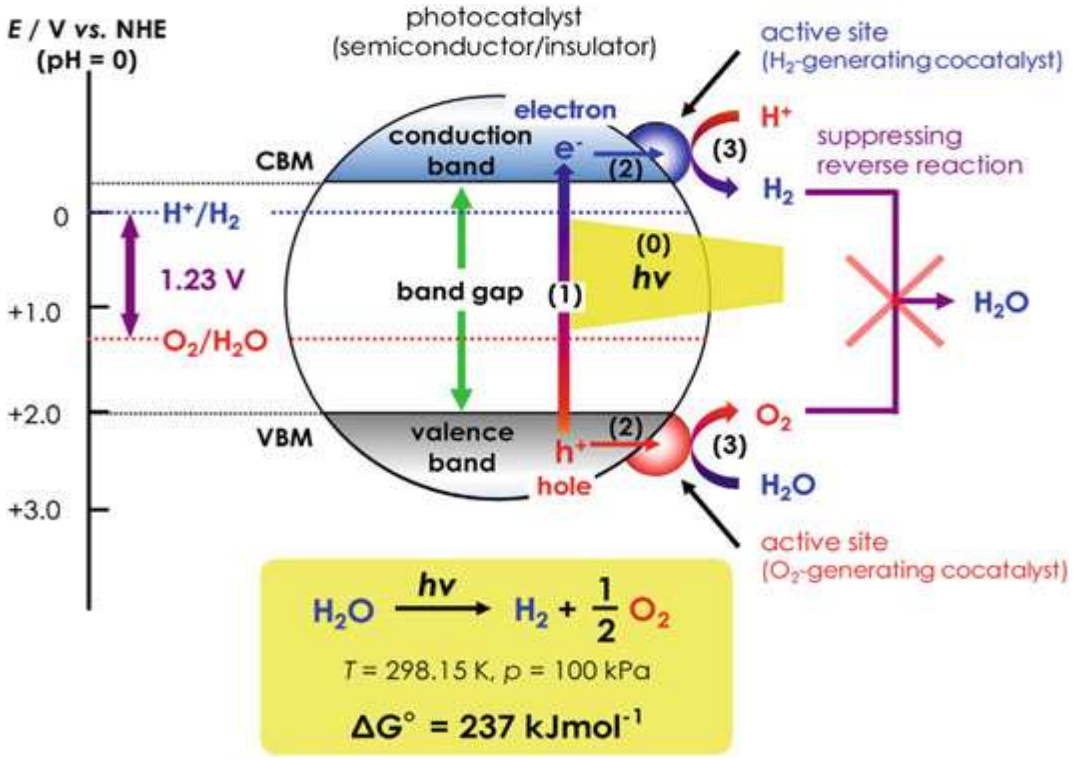


**Figure 1. Overall water splitting process in a single photocatalyst by photoexcitation: (0) Irradiation of light radiation (1) electron-hole pairs photo-excitation (2) movement of excited electrons on to the surface (3) The oxidation-reduction reaction at the surface.**

The thermodynamic requirementfor a photocatalyst is it should possess lesser bandgap energy of about 1.23 eV, with a valence band maximum(VBM) below the oxygen-evolution potentialand with a conduction band minimum (CBM) above the hydrogen-evolution potential.The water redox process can be speeded up if the electrons and holes have an additionalpotentialto overcome the potential barriers of the diffusion in addition to the mentioned thermodynamic condition. This kinetic energy requirement demands the photocatalyst's to possesses a minimum bandgap to ~1.83 eV[12].Thecrystallinity and few imperfections of photocatalystscan limit the electron-hole recombination and allow quick diffusion of the electrons, holes on to the surface[13].Co-catalysts are often requiredfor providing different sites for optimal hydrogen and oxygen evolution, as well as to reduce back reaction, as shown in Fig.1.A good photocatalyst, like any other catalysts, must be

chemically stable andalso offer photocorrosion resistance. The photocatalysts are to be made from earth-abundant materials in a eco-friendly methods[14].Nanomaterials possess high surfaceto volume ratio and a short distance for photoexcited electrons and holes to diffuse onto the surfaces and they also have the potential of producing solar hydrogen with high efficiency.

## 4.Nanomaterials for PEC water splitting

The photocatalysts having a larger bandgap are stable chemically and possess a greater photon-hydrogen quantum yield, but are unsuccessful at harvesting solar energy as they can absorb only the UV portion of the spectrum.Identifying a photocatalyst for optimal solar to hydrogen energy conversion is a challenge for the researchers[15].A few co-catalysts with the photocatalyst enhances the total water splitting, particularly under the visible light[16].This review encompasses the application of nanomaterials as photocatalysts for the generation of hydrogen throughwater splitting.

### 4.1. Titanium dioxide ($TiO_2$) based nanomaterials

TiO2 is the most commonly employed material for the generation of hydrogen by water spitting [17].As the bulk $TiO_2$ has a bandgap of 3.03eV 3.18 eV, it has a lower efficiency for the absorption of solar energy, but thelow cost and high stability makes it potentially useful for water splitting.Among $TiO_2$ nanomaterials, the $TiO_2$ nanotube is the most preferable option.Black $TiO_2$ nanoparticles were produced as an alternative to coating $TiO_2$ with a substance, and they demonstrate effective photocatalytic activities[18].The conversion efficiency of nanoscale $TiO_2$ can be significantly influenced by its size and shape.Nanostructured $TiO_2$ has recently played a vital role in enhancing the efficiency of absorbing the light and generation of hydrogen.

When comparing $TiO_2$ nanorods to nanowires, nanowires outperform nanorods[19], [20].With a rise in annealing temperature, cell performance improves[21].This occurs as a result of the creation of crystalline structures, which promotes charge transport.The morphology and structure of a $TiO_2$ nanotube can be varied by annealing as shown in Figure2.

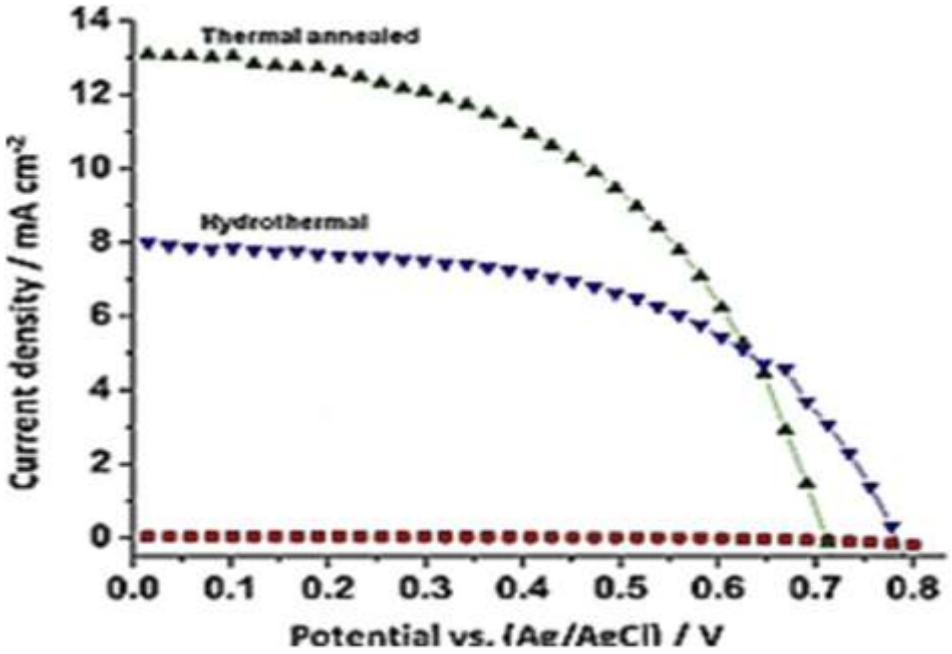


**Figure 2. – I-V curves for TiO2 nanotube before and after different annealing treatments**[21].

### 4.2. Niobium pentoxide($Nb_2O_5$) based nanomaterials

The bandgap of $Nb_2O_5$ is around 3.4 eV, making it an n-type semiconductor[22].Bulk $Nb_2O_5$ is incapable of decomposing pure water to produce hydrogen,however with the co-catalysts such as Pt,NiO and CuO, mesoporous $Nb_2O_5$ exhibits outstanding photocatalytic activity for the generation of hydrogen.The photocatalytic enhancement of mesoporous $Nb_2O_5$ is caused by two factors:For ion exchange, mesoporous $Nb_2O_5$ has a greater pore volume and surface area than the bulk $Nb_2O_5$;The pore walls of mesoporous $Nb_2O_5$ are likewise very thin, reducing the carrier migration distance[23].The rates of hydrogen evolution are 1405, 800, and 510 μmol $h^{-1}g^{-1}$, respectively[24].The photocatalytic activity of Pt modified mesoporous $Nb_2O_5$ is 20 times higher than that of bulk $Nb_2O_5$[23].The rate of electrons and holesrecombination in mesoporous $Nb_2O_5$ is substantially lower than in bulk $Nb_2O_5$, which is thought to be the most likely reason.These compounds, however, are unable to induce total water splitting.

### 4.3. Zinc oxide (ZnO) based nanomaterials

Water splitting with ZnO nanoparticles has been extensively investigated[25], [26]. It has a comparable energy band structure to $TiO_2$ (bandgap energy 3.3 eV) and optoelectronic characteristics. Because of its low photocatalytic quantum efficiency and the ability for absorbing the visible light is low and it shows a lower photocatalytic activity[25]. At ambient temperature, ZnO has a band gap energy of 3.37 eV and a high exciton binding energy of 60 meV. They have a higher electron mobility potential, chemically stable, and are very transparent. The shape, electrolyte interactions, and defect density all influence

hydrogen production. on defect density, electrolyte interactions, and morphology, Nanostructures should adapt their essential properties using deposition procedures and annealing to maximise the generation.

### 4.4. Metal Nitride and Oxynitride based nanomaterials

Water splitting is also possible with metal nitrides like GaN, $Ge_3N_4$, and $Ta_3N_5$, as well as oxynitrides of metals like TaON and solid solutions of (N1-xOx)(Ga1-xZnx)[27], [28] The valence band of metal oxynitrides has hybridised N2p and O2p orbitals[29]. Hybridized orbitals, such as Ge 4s4p orbitals, make up the conduction band. Metal nitrides have a large bandgap, but it is narrower than metal oxides due to its electronic configuration. The water splitting isaided by metal nitrides. $Ta_3N_5$ can, for example, catalyse the breakdown of water into hydrogen and oxygen when exposed to visible light with a wavelength less than 600 nm[30]. As oxygen posesses a electronegativity greaterthan nitrogen, the oxynitridesof metal possess a broader bandgap than metal nitrides, whereas TaON has a bandgap of roughly 2.4eV and a light absorption edge of 520 nm[31]. The solid solution (Ga1-xZnx)(N1-xOx) has a narrow bandgap ranging between 2.4–2.8 eV, permitting visible light absorption[32]. For total water splitting, the average apparent quantum yield of this solid solution in the 300–480 nm region is roughly 0.14 percent[33]. Irradiation under the visible light ranging between 400–475 nm, the stoichiometric dissociation of water into hydrogen and oxygen is also achieved utilising InGaN nanowire arrays having an apparent quantum yield of about 12.3% in neutral solution[34].

### 4.5. Bismuth vanadate ($BiVO_4$) based nanomaterials

Thehigh absorption capacity and band gap energy of $BiVO_4$ nanoparticle has engrossedits application for water splitting[35], [36]. $BiVO_4$ nanoparticle is an ideal photoanode for the water splitting due to its stability, band gap energy andwell-polished band edge even in acidic mediums. $BiVO_4$ thin films with photocurrent density of 0.8 $mA/cm^2$ at an applied potential of 1.9 V vs RHE can bemade via electrostatic spray pyrolysis at a cheap cost and with flexibility[37]. Doping can be used to boost photocurrent density even further. $BiVO_4$ thin films that have been doped can perform twice as well as those that have not been doped.

### 4.6. Other Newly Developed Nanomaterials

#### 4.6.1.Hybrid nanomaterials

Wide band gap semiconductors like $TiO_2$ and ZnO have made significant progress in achieving a wider photoresponse range and improving water splitting efficiency. Combining semiconductors with other elements or chemicals to create hybrid semiconductor nanomaterials (HSNs) is one of the most promising solutions. In these instances, HSNs not only absorb light more efficiently, but they also prevent photogenerated electrons and holes from recombinating, As a result, as compared to pure semiconductors, they perform significantly better in water splitting. Doping semiconductor nanostructures with metal ions like iron and copper is one way to change their characteristics[38] or non-metal species such as silicon,phosphorous,carbon and sulphur.But thermal instability, a rise in carrier-recombination centres, and the need for an expensive ion-implantation facility have all been reported in HSNs with metal-ion doping[39].

### 4.6.2. Plasmonic nanomaterials

Plasmonic nanoparticles are frequently employed to adorn semiconductor photocatalysts. This improves the light scattering,absorption or the transfer of resonance energy which intern improvesits efficiency for the conversion of solar energy[40], [41]. Commonly used plasmonic nanoparticles include noble metals Ag, Cu and Au[40]. Plasmonic nanomaterials, like semiconductor photocatalysts, have recently been shown togenerate electrons by absorb light. The water splitting is achieved by linking plasmonic nanoparticles with the cocatalysts for the evolution of hydrogen and oxygen. [42].

### 4.6.3 Sensitized nanostructures

The domains of photo-electrochemistry,photocatalysis and photovoltaics utilise the dyes to sensitise semiconductors for enhancing the absorption of solar light[43], [44].The Dye sensitization improves thephoto-electrochemical reactions by increasing absorption of visible-light and photoconversion in various studies[44].As shown in Figure3, the dye molecules not only act as a visible-light sensitizer, but also works as an effective stabiliser and a molecular bridge to connect water oxidation catalyst $IrO_2H_20$ nanoparticles.

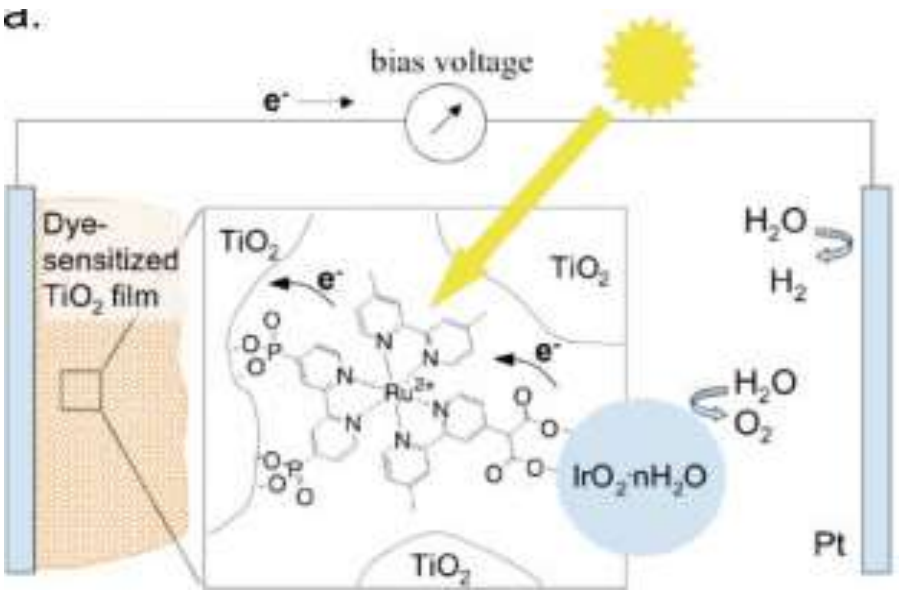


**Figure 3. Schematic of the water splitting dye sensitized solar cell.**

This one-of-a-kind nanostructure has the potential to boost light absorption while also facilitating the water oxidation reaction. The photoresponse of the sensitised $TiO_2$ film was better than that of the unsensitized $TiO_2$ film but the bleaching of dyes limits the photocurrent densities of these dye-sensitized devices.

## 5. CONCLUSION

Along with constant research in the field of renewable energy technologies,larger attempts to develop nanomaterials in the area of hydrogen generation and utilization has been achieved.The paper provided an overview on the methods involved in hydrogen generation,principal of PEC cells and nanomaterials for PEC water splitting.Although there many challenges including efficiency,stability,nanomaterials still have the potential to provide low-cost, clean renewable energy solutions in the future.Possible solution includes using advanced nanostructures with improved property.

## Acknowledgments

The authors would like to thank Rashtreeya Vidyalaya College of Engineering, Bengaluru, for providing the facilities required to write this review article.

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