**Review On Hydrogen Production via Photocatalytic Water Splitting**

Abhinav Pundir, Dr. Manoj Kumar\*

Department Of Chemistry, University Institute of Sciences,

Chandigarh University, Gharuan-140413, Mohali, Punjab, India

\*Corresponding author email- manoj.e12044@cumail.in

**ABSTRACT**

This review paper analyses techniques for separation of water via photocatalytic techniques for the synthesis of Hydrogen, utilizing different methods. Benefits and demerits of different techniques with specific features of photocatalytic hydrogen production are discussed in this paper. In the recent years (around 20-30 years), there has been critical advancement in water splitting photocatalysis, particularly in the fields of related physical and materials science. This article talks about ongoing improvements in hydrogen production through photocatalytic water splitting as World-Wide increase in temperature is turning into a major problem, hydrogen as an elective clean fuel has acquired significance. In this article we will learn about different recent techniques done in this specific field to break down various strategies for hydrogen production through photocatalytic water splitting, their benefits and weaknesses, future aspects and challenges also. Subsequent to having finished with this review article we will be able to decide the most solid, environment-pleasing and pocket-friendly techniques for supportable hydrogen production. Likewise, we will come to be aware of the new advancements done in this field alongside their future perspectives and challenges. Which is our principle point behind this review article.

Keywords- Hydrogen Production; Photocatalytic Water Splitting; Photocatalysts

**1. INTRODUCTION**

We are living in a continually growing and creating world which requires consistent inventory of energy to run the world. The worldwide energy request is persistently expanding over the past decades. Traditional petroleum products like coal, petrol, flammable gas, and so on, have been generally investigated to fulfill the energy needs[1]. In any case, the consuming of these powers discharge almost 7.8 billion metric huge loads of CO2 in climate not withstanding other impeding gases like CH4, SO2, NH3, and so on, which posture threatening effects for the biodiversity and living creatures because of an unnatural weather change and acid rains. Over 70% of CO2 radiated in the climate causes nursery effect[2]. It is hence understood that petroleum products, are getting exhausted due to their non-renewable nature, that’s why, it was important to save energy and investigate progressed sustainable power sources. It is also acknowledged that the only method of reducing the use of fossil fuels is to create renewable energy resources[3]. Hydro energy, wind energy and solar energy are examples of renewable energy supplies that can help to meet global energy concerns. This type of renewable energy not only gives sustainable sources of energy but also release fewer toxic chemicals in the environment[4]. It has already been observed that even the slightest usability of reusable energy is found to be better than the boundless variety of fossil fuels. These ideas have sparked interest in production of hydrogen energy that can potentially be used as a fuel in recent years. According to reports, the energy yield of H2 fuel is 2.75 times greater than that of hydrocarbon fuels[5]. It is indeed clear that H2 is a cleaner source of energy as it doesn't emit harmful chemicals like CO2. Hydrogen energy is utilized in various ways, such as petroleum refining industries, fat and oil hydrogenation and much more[6]. Automobiles which operate on H2 energy were found to be better in handling than that which run on gasoline. H2 can be generated through a number of traditional techniques, including hydrocarbon steam distillation, non-catalytic partial oxidation and water electrolysis. Biochemical processes such as bio-photolysis, dark fermentation, and artificial photosynthesis can also be used to synthesize H2[7]. Among the different processes for breaking down of water into Hydrogen and Oxygen, photocatalytic water separation is among the most reliable technique. This strategy is more cost-effective and easy to implement. Numerous photocatalysts have been documented in previous and recent researches[8]. Conventional photocatalysts such as TiO2, ZnO, and ZnS were examined in the literature in recent years, however, because of their huge energy gap (~3.2eV), those are presently getting replaced by photocatalysts of diverse properties[9].

Let us first get to know a little about a few terms that we are going to use in this review article.

**1.1 Photocatalysis:** Photocatalysis is a chemical reaction that occurs when a molecule comes into contact with photons having suitably high levels of energy, initiating free radicle mechanisms. Photocatalysis is a concept that describes the reactions involving the use of light and semiconductors.

**1.2 Photocatalysts:** A photocatalyst is a material that remains unchanged during the chemical reaction, under the effects of light. They are used to absorb light to excite it to higher energy level and provide energy to make a chemical reaction occur. **ZnO,** **ZnS, CdS, SrO2, WO3**and **Fe-TiO2** etc. are some examples of photocatalysts.

**1.3 Photocatalytic Water Splitting:** In this review article we are going to review about research performed by various researchers in the area of photocatalytic breakdown of water for into hydrogen. Hydrogen as a sustainable energy will be a big treat looking at the alarming rate of fossil fuel usage .If the fossil fuels get to be used constantly like this, it will not take much time since the fossil energy will be completely extinguish and we will find ourselves in a catastrophic situation[10]. We all are too much dependent on fossil-based energy for our daily use that we can’t even imagine a single day without the energy consumption. Fossil energy is used everywhere in our day-to-day life. From lighting a small bulb to running a car, everything needs energy to operate. Also, the fossil-based energy is not only very expensive but is also very hazardous for the environment[11]. The harmful chemicals that are emitted on the combustion of fossil energy pollute the environment resulting in serious problems like air pollution, water pollution, effects of global warming, etc. Seeing so many drawbacks of fossil-based energy, the utility of any sustainable and harmless energy increase even more. We need energy which is not harmful to the environment as well as is easy to obtain in pretty good amount. This is where the need for hydrogen energy comes into action[12]. Hydrogen energy is a non-hazardous and easily manufactured form of energy as it costs less than that of fossil-based energy. There are many methods for generating hydrogen energy. One such way is via Photocatalytic water splitting. As water is present in a large amount on the Earth, this method proves to be a boon for generating hydrogen energy in large amount. In this article we are going to discuss about Photocatalytic water splitting via different types of photocatalysts[13].

Now that we got familiar to the terms like Photocatalysis, Photocatalysts and Photocatalytic water splitting, we can now proceed further with our analysis about using different types of photocatalysts.

**2.Discussion**

**2.1 Methods for Hydrogen Production**

Hydrogen is an easily accessible element that can be found in a wide range of natural materials, the main sources of which are freshwater and seawater. There are various methods to generate Hydrogen, such as, Electrolysis, Thermolysis, Photocatalysis, by using Photoelectrochemical cells, Photoelectrolysis, Biophotolysis and photofermentation, and Light-based Hydrogen production and Photocatalytic water splitting[14].

**2.1.1 Photocatalytic Water Splitting Methods**

Photocatalytic water splitting technologies have generated a lot of curiosity in the most recent writing because they utilise two of the most accessible, pure, environmental, and regular energy sources that are currently available to us. This has led to the identification of photocatalytic hydrogen production as a potential replacement to address problems regarding non-renewable power sources, such as excessive use, inadequate savings, and detrimental environmental effects. [15]. The interaction uses sunlight-based energy to make hydrogen in a pristine manner with no indications of GHG emissions, therefore the benefits of photocatalytic separation of water in hydrogen and oxygen could be reported as both financial and natural benefits[16]. It is highly predicted that photons that are having energies larger than that of photo catalytic band holes will produce electron-opening matches to transform water into hydrogen. Photons having energies below the photocatalyst's band hole are unable to produce these electron-opening matchings and are therefore useless for producing hydrogen through photocatalysis. It is seen to be necessary having the choice to utilise the energy stored in the visible range component in order to utilise the sunlight-based range as effectively as possible[17]. Water can be easily split into H2 and O2 utilising photocatalytic water splitting by employing particles and incident sunlight. It is capable of producing a pure, limitless source of hydrogen without emitting GHG’s or harming the climate[18]. Several photocatalysts have undergone UV testing in the past, and were found to be having remarkable quantum efficiencies. However, these current photocatalysts frequently squander water splitting while doing so. The following factors must be present for a process to be successful: (i) an appropriate band hole to support the maximum amount of sun-based range use; (ii) an appropriate CB and valance band arrangement to carry out oxidisation as well as reduce responses of overall water splitting; (iii) strength in the redox climate; (iv) low cos of production and activity; (v) recyclability; (vi) abundance; (vii) erosion opposition; and (viii) suitability for huge Nanomaterials perform significantly better in photocatalytic water splitting and hydrogen creation, claims a review research[19], contrasted to photocatalysts with larger molecular sizes, Cui et al.[20]. Notwithstanding, photocatalytic execution basically relies upon the characterizations of the nanoparticles. Even while not all nanoscale photocatalysts are seen to be having great H2 production percentage, as compared to the respective micromaterials in comparative experimental setups, they do produce more hydrogen. A range of CdS crystal diameters between 1 and 5 nm was speculatively investigated. The results demonstrate that 2.5-nm CdS particles can be used to achieve the most notable hydrogen production rates. Particles measuring 1.5 nm in size exhibited terrible crystallinity, which had an impact on their absorption edge. The fundamental reactivity of photocatalytic water separation against permitted semiconductor nano-crystallites, molecule size and interfacial microstructural surrenders assume an essential role, was demonstrated by Deshpande and Gupta [21]. Yao et al. directed some trials of different sorts of photoreactors and detailed that for financially savy plan and reasonable huge scope implementation, detached blending can possibly offer a possibly suitable and modest generators. By using solvothermal and sol-gel approaches, compound photocatalysts with high crystallinity CdS nanowires capped with Nanocrystals have efficiently been developed. These substances are seen to be amazingly diverse to producing H2 from water consisting sulfide and sulfite particles as opening wastes under noticeably brighter light. The most notable hydrogen production yield and rates have been seen at a CdS/TiO2 ratio of 0.2.This design has demonstrated effective in control detachment because of the quick dissemination of photoelectrons produced by CdS with respect to TiO2. Nanostructured ZnO had shown unusual biological and chemical characteristics that makes it particularly important for photocatalytic water separation[22].ZnO is a consistent as well as, in comparison to previously described two-fold nanosized metal oxides, modest metal oxide, making it prominent photocatalyst alternative to be found in recent studies. Du et al's[23], focus was on the surface characteristics of ZnO containing photocatalysts along with the influence on reactivity and photocatalytic water separating action of ZnO on a surface-level. In his investigation of nanocrystalline photocatalysts including ZnO, CuO, and SrCO3, Kowsari [24] found out considerable impact of shape on a photocatalyst's ability to perform photocatalysis. By doping TiO2 based photocatalysts with C or N and S, Liu and Syu [25] evaluated an anticipated method to improve the optical reaction. Pt piling on TiO2 for photocatalytic hydrogen generation may be reduced or eliminated by mesoporous TiO2 nanomaterials. According to Kandiel et al. [26], hydrogen generation using Pt/TiO2 that is 0.2 weight percent and heated upto 450 °C, found to be quite greater than those produced using Pt/TiO2-P25 and Pt/TiO2 that is calcined at 350 °C. Additionally, metal oxides are most favourably found to be more interesting to work in recent times. One example is the combination of K4Nb6O17 by Yan et al. [27] as a photocatalyst. Sabio et al.[28] looked at and similarly reviewed the photocatalytic water-dividing activities of suspended KCa2Nb3O10 nanoscale and bulk particles. There has been significant research work going in order for the greater productivity and overall result of photocatalytic water splitting in the literature. The utmost target is to generate sun-generated energy and use incident photons more effectively. It is commonly known that a crucial requirement when synthesising novel photoactive materials is the thermodynamic behaviour of photocatalysts. In the literature, there are some examples of innovative photocatalysts that have been developed that are nano-structured materials with surfaces that are virtually entirely high-energy features. The models include extremely thin sheets and symmetric polyhedral particles[29].

**3. Ternary TiO2 Catalysts**

The three-step approach used to create ternary photocatalysts comprises of three separate elements or semiconductors with distinct functionalities. According to the literature, It is entirely possible to predict that ternary semiconductor composites will pave the way for heterojunction-driven electrical cycle driving and multi-photon excitation of photoactive materials using lower energy photons.As a result, it is possible to specifically photograph-excite limited electronic states in order to achieve higher selectivity [30]. Previously, Pt/TiO2-ZnO (Ti/Zn is found to be having value equal to 10) was shown to be a prominent photocatalyst for separation of water for H2 synthesis with the highest H2 producing percentage of 2150 mol h-1g-1 and reached the next level solidity by Xie et al. [31].  When the Pt/TiO2-ZnO material is lit, electrons may be transported to CB from VB on the TiO2-ZnO, and Pt nanoparticles serve as donors or acceptors to produce H2 as a result. Zhao et al. [32], in year 2016, came to the conclusion that CdS and AuNPs not only compensate for TiO2's shortage of UV light responsiveness, but also enhance it, and also improve the division of photo-generated charges. Whereas in the influence Ultra Violet radiation, the excited electrons of TiO2 were transported to the VB of CdS and reassemble through openings, while the excited electrons of CdS were transported to the CB of TiO2 through AuNPs. This exchange of photogenerated electrons is sped up by the AuNPs that exist between TiO2 and CdS. [33]

**4. Graphitic Carbon Nitride (g-C3N4) based Photocatalysts**

In the recent years Graphitic carbon nitride (g-C3N4) is getting too much consideration, furthermore, seriously concentrated as a maintainable photocatalyst as an aftereffect of its benefits, for example, non-harmful and sans metal semiconductor and responsiveness to noticeable radiation having restricted band hole (2.7 eV) [34]. In addition, it is very cost effective, basically comprises of earth-bountiful carbon and nitrogen, also have uncommon photograph consumption opposition because of solid covalent connections among carbon and nitride iotas[35]. The g-C3N4 additionally shows novel photoluminescence (PL) characteristics which were involved as decent co-photocatalyst of the semiconductor photocatalysts [36]. Tragically, the uses of g-C3N4 in photocatalysis is confined because of low unambiguous surface region and high recombination pace of photograph incited electron hole matches [37]. Be that as it may, the stacking of g-C3N4 with different semiconductors can help the photocatalytic execution that advances electron hole detachment, working on the particular surface region, furthermore, taking advantage of the light use capacity [38]. The promising furthermore, productive procedure is the coupling with other photograph catalysts which can fundamentally work on the detachment of electron hole pairs because of all around paired band structures [39].

**4.1 Heterojunction Semiconductor as Graphitic Carbon Nitride (g-C3N4) based Photocatalysts**

The photocatalytic activity of semiconductors based on g-C3N4 can be increased by adding semiconductor heterojunctions. It might alter the arrangement and banding of the inner electrical field. It can therefore work on the partition of spatial charges and enhance redox potential and response capacity [40]. The water oxidation process could also be accelerated by the heterojunction semiconductors [41]. TiO2, NiS, and CdS are the three semiconductors that are most frequently used with g-C3N4. Yin et al. [42] assumed that NiS2 nanoparticles formed on the g-C3N4 surface fundamentally improved the photocatalytic movement of g-C3N4 for H2 development under noteworthy illumination. The study discovered that 2 weight percent was the best stacking. NiS2 generates 4.06 mol of H2 every hour. The photogenerated electrons migrated from g-C3N4 to NiS2, despite the fact that NiS2 co-photocatalyst may efficiently limit the repetition of charge photogenerated and functions as a dynamic place for H2 creation. Ag2O/g-C3N4 was able to produce H2 at a rate that was much higher than that of pure g-C3N4, according to Wu et al’s research[43]. It is anticipated that Ag2O/g-C3N4 will have a beneficial synergistic effect on accelerating the partition of charge transporters, significantly enhancing the photocatalytic action and photostability.

**5. RuO2/La:NaTaO3 catalysts prepared by sol–gel method**

It should be noticed that the combination course other than the utilization of co-catalysts meaningfully affects the underlying highlights, electronic also, photocatalytic properties. On account, NaTaO3 arranged using sol-gel and aqueous strategy, the photocatalytic movement regarding H2 synthesis was worked on in correlation with the strong state arrangement. Exercises using sol-gel, aqueous, and strong state photocatalysts, separately, were found to use 12000, 4000, and 70 mol after 5 hours of UV irradiation [44]. Due to the likelihood of obtaining complexes having controlled primary elements and morphology, low molecule size, and high crystallinity, the sol-gel methodology is much likely to be pursuaive rather than strong state method regarding setup of semiconductor substances having greater surface area and higher photocatalytic movement related to water separation. [45]. Tri-ruthenium dodecarbonyl was impregnated with varied amounts as a RuO2 precursor before being added to NaTaO3 and La:NaTaO3 semiconductors using the sol-gel method. The main goal behind using La was to lessen the electrons' flexibility as well as to prevent electron-opening pair recombination [46], as well as to prevent NaTaO3 from crystallising [47] and promote the growth of NaTaO3 nanoparticles having much unambiguous region. While, quiet the opposite, if a co-catalyst is added to the semiconductor's outer layer, it will advance a second electron-trap and stop the rejoining of electrons [48]. The RuO2/La:NaTaO3 photocatalysts were fully represented using X-beam Diffraction, nitrogen assimilation, UV spectroscopy, scanning electron microscopy (SEM), and High Goal Transmission Electron Microscopy (HRTEM), and the photocatalytic effect on the water separation was assessed.

**6. Environmental bening carbon-based nanomaterials**

Numerous carbon compounds, such as graphene [49], carbon nanotubes (CNTs), and graphitic carbon nitride (g-C3N4) [50], were being employed for photocatalysts for water splitting. Due to qualities like primary dissimilarity, electrical and thermal conductivity, exceptional mechanical toughness, huge surface area, as well as particularly desirable permeable structure, above mentioned substances make a perfect fit for the desired application. [51]. It is possible to build beneficial organic or inorganic assemblages that can inherently promote the photocatalytic movement of carbon materials thanks to the permeable and highly desirable design of carbon materials. Carbon nanomaterials possess wide range of administrations, including those for photosensitizers, support materials, cocatalysts, semiconductors, and the capacity to confine the band hole as well as absorb and transport electrons. Due to their high surface area, carbon materials can increase the total number of retention sites [52] to store larger amount of H2, that can assist as a link for the purification and separation of water [53]. Additionally, by restricting the configuration of bunches between them, carbon materials can withstand the strength of the ornamented nanoparticles at the cost of strength. To enhance the photocatalytic performance of the semiconductors, semiconductor nanocrystals can be deposited onto the top layer of carbon-based materials [54]. Since H2 production is substantially lower when smooth carbon materials are employed without correction, the geometry of carbon materials can be altered to improve their applicability [55]. By creating deserts, building user interfaces, hosting practical gatherings, and, in addition, hybridising them with various semiconductors, it is possible to modify the properties of carbon nanomaterials.

**7. Conclusion**

The enhanced viability of photocatalytic water splitting for commercial H2 energy production is evaluated in this review paper. With poor STH efficiency (10 percent) and a high hydrogen cost (>2-4 $/kg), widely studied photocatalytic water splitting for H2 age did not show any commercially viable indicators for more than five years. Currently, the majority of studies are conducted in renowned research facilities. A few non-idealities could become more noticeable with an increase, which would worsen the subpar response outputs (STH proficiency or quantum yield). High STH proficiency is hampered by dynamic locations for water oxidation and charge recombination that may be generally identical for diverse photocatalysts. Even while research into cutting-edge materials is ongoing, the results are still far from mechanically encouraging. The thermodynamic barrier of 18 percent STH is insurmountable even after overcoming all other obstacles, as considerable water splitting is typically predicted to have an Eg of > 2.0 eV. The worst part is that even with the existence of a conciliation reagent, photon energy misfortunes during medium-to-medium travelling in photocatalytic water splitting are inescapable, respecting the best STH of just 3.32 percent. A further denial of the place of photocatalytic water splitting as a "real sunlight-based energy catching innovation" was made despite the fact that 30% STH was recognised in PV-innovation. In terms of cost, photocatalytic water splitting is less attractive than steam methane conversion, coal gasification, and thermochemical biomass conversion since that may result in a high hydrogen cost (10.36 $/kg). The increasing suitability of photocatalytic water splitting for commercial H2 energy production is assessed in this study.

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