Various Material Development Strategies for Suitable Catalysts of Photo Catalytic Water Splitting to Green Fuel H₂: A Critical Review

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Abstract
Fossil fuels are the most substantial & extensively used sources of energy for today’s world. Simultaneously, the unconscious exposure of toxic pollutants and green-house gases allied with fossil energy is not viable with contexture. Solar energy were treated as an auspicious source of energy from ancient age because of its richness & cleanness. But problem arises in its capture, storage, transformation, and distribution. That’s why scholars are trying to convert this renewable light energy to a user friendly and viable form of energy. By analyzing recent studies on H₂ fuel it is considered as most lucrative choice for clean and sustainable fuel with high calorific value & zero pollution. This review offers an overview of most recent advancement in development of photo-catalyst for solar water splitting which is treated as a promising Green-Harvesting technique among all H₂ generation techniques. Here we discussed about various catalyst development techniques especially about doping techniques, reactor design and light scattering/trapping systems. We found that among all doping is a promising technique and a lots of study have been done on this technique than others like as Heterojunction, Dye sensitzation, modification of surface or nanostructure formation. Hence we concluded with the decision that, more research are needed on heterojunction and nanostructure formation along with elemental doping.

Introduction
The high energy crisis, fossil fuels depletion & environment pollution becoming the major global challenges in recent and upcoming years.¹ Due to global warming & pollution issues, today’s world is searching for a sustainable, clean, and environment friendly alternatives. With a vast study on fuel and its negative impacts, scientists came to know that,
hydrogen fuel may be a solution for this crisis. \( \text{H}_2 \) is a fantastic energy conveyor with a high CV and clean property. As a bountiful element, \( \text{H}_2 \) appear in many substances in the earth, like seawater, biogas, freshwater and fossil fuels, etc. For the production of \( \text{H}_2 \) with zero or low impact on the environment, almost all Carbon-dioxide with other unwanted particulates should be separated when \( \text{H}_2 \) is produced from fossils.\(^2\) Till now, hydrogen is mainly synthesized via steam reforming method where \( \text{CO}_2 \) is formed simultaneously. And this \( \text{CO}_2 \) is the key concern for today’s environmentalists, as it is the major greenhouse agent. Photocatalytic water splitting may be a solution to these problems. Some other important sources of the hydrogen production process are Electrolysis, Thermochemical processes, Dark fermentation process, Thermolysis, Photo-fermentation or Bio-photolysis, Hybrid thermochemical cycles, and Photo-catalytic water splitting, etc. The electrical energy needed here is much less than the conventional methods. Zero GHG emission is possible here by using the clean source of energy like solar, geological, wind or nuclear.\(^4\) Heat recovered from another process (such as industrial boiler or heat exchanger) can also be effectively used to run this process.\(^5\) In high temperatures operating system, the process units must have met some definite requirements for effective \( \text{H}_2 \) production. Most recent objections of these types of the process can be enlisted as: (a) stable electrolytic reagent synthesis with low electronic and strong ionic conductivity; (b) porous, low cost and chemically static electrode development for high electronic conductivity and finally (c) mechanically stable engineering materials at high temperatures. Again, Hybrid thermo-chemical cycles which conduct at low temperature is more viable while comparing with the thermally driven water-splitting system. Electrical and thermal energies fulfill the outer energy demand of particular reactions as hybrid systems conducted at lower temperatures. A major advantage of these types of systems is that \( \text{H}_2 \) generation from low-grade energy sources. But the major findings of this technique are that bulk amount heat source is not available everywhere and artificially generation of heat is also costly. Here alleviate temperature degradation of catalyst is a major challenge, which retard the hydrogen production rate.

On the other hand, thermolysis is another significant way of electrolysis where \( \text{H}_2 \text{O} \) is split to \( \text{H}_2 \) and \( \text{O}_2 \) at elevated temperatures ranging between 973K to1273K. Basically this process is more effective than generally used room-temperature splitting process where efficiency increases with the increment of heat. The electrical energy needed here is much less than the conventional methods. Zero GHG emission is possible here by using the clean source of energy like solar, geological, wind or nuclear.\(^6\) Heat recovered from another process (such as industrial boiler or heat exchanger) can also be effectively used to run this process.\(^7\) In high temperatures operating system, the process units must have met some definite requirements for effective \( \text{H}_2 \) production. Most recent objections of these types of the process can be enlisted as: (a) stable electrolytic reagent synthesis with low electronic and strong ionic conductivity; (b) porous, low cost and chemically static electrode development for high electronic conductivity and finally (c) mechanically stable engineering materials at high temperatures. Again, Hybrid thermo-chemical cycles which conduct at low temperature is more viable while comparing with the thermally driven water-splitting system. Electrical and thermal energies fulfill the outer energy demand of particular reactions as hybrid systems conducted at lower temperatures. A major advantage of these types of systems is that \( \text{H}_2 \) generation from low-grade energy sources. But the major findings of this technique are that bulk amount heat source is not available everywhere and artificially generation of heat is also costly.

Bio-photolysis as well as photo-fermentation techniques are familiar as photon-based biochemical
H₂ generation from water. The main privilege of this technique is the capability to generate H₂ from H₂O in aqueous media at conditioned temperature & pressure. Here in the Bio photolysis processes light-sensitive micro-organisms are used as biological converters in a special bioreactor. Here Microalgae are most preferable among all microbes because they are culturable in suitable media. Cultured microalgae isolates have the capacity to produce H₂ in a closed system and they show high H₂ yields. The primary hydrogen generation reactions using photo-activated enzymes are the following:

\[ 6H_2O + 6CO_2 \xrightarrow{hv} C_6H_{12}O_6 + 6O_2 \]  
\[ C_6H_{12}O_6 + 6H_2O \xrightarrow{hv} 6CO_2 + 12H_2 \]

However, this process is demonstrated at laboratory scale only and piloting is not yet possible to support the industries at the commercial level. Again Dark fermentation is a fermentation process which defined as the transformation of biochemical energy of organic to different forms of energy in dark conditions (during the reduced supply of light). In this process biochemical energy available in organic matter used to obtain H₂ in absence of light. Bioreactors used in these types of fermentation are cheaper and simpler in comparison with photo-fermentation because this method does not need solar input processing. There are several other benefits of H₂ production by dark fermentation like, (1) H₂ production from organic waste and (2) stabilized & control in bio-waste for reducing potential danger of pollution. The dark fermentation process can be implemented in water treatment units for H₂ production from organic wastewater. H₂ production costs can be reduced by using inexpensive and readily available organic wastes (including wastewater). But the major disadvantage of this method is that the hydrogen production rate is very low and huge amount of reagents are required for continuous fermentation process which are non-recyclable.

From all available H₂ production the process discussed here photo-catalytic water splitting using sunlight has been widely believed as a promising process for green and environment-friendly hydrogen generation, where a chemical reaction occur while following with the alteration of Gibbs free energy (Eq. - 3).

\[ 2H_2O \rightarrow 2H_2 + O_2 \quad \Delta G^\circ = 237.0 \text{ KJ/mol} \]  

This type of Water Splitting has harmony with photosynthesis because both of them are uphill type. From this site, the water-splitting system can be evaluated as artificial photosynthesis. The utilization of green, inexhaustible and sustainable solar energy is an urgent need to avoid the greenhouse effects. A huge amount of research articles are circulating every year on solar energy transformation systems like photo-catalytic conversion of organic pollutants, hydrogen (H₂) gas production through photo-catalytic water splitting, photovoltaic cells, and dye-sensitized solar cells. Photo-electrochemical water splitting process by Fujishima & Honda in the year of 1972 is most variant of this technique. Following this way, till now H₂ production by Photocatalytic water splitting is considered as a promising technology for green energy revolution. 15-17 Titanium oxide, (g-C3N4) Graphitic-Carbon Nitride21-23 and (CdS) Cadmium Sulfide24-26 are three widely studied catalysts for water splitting in the last few decades. Among them, titanium oxide (TiO₂) is found to be more superior, and a benchmark photo-catalyst still now.27

![Energy levels](image)

Due to its photostability, efficiency, band edge, non-toxicity and sustainability it became a burning topic in this sector.20-34 The mechanism of Photocatalytic activity of TiO₂ based catalyst for water splitting are illustrated in Fig. 1.0. The overall water splitting reaction on a photo-catalyst comprised of the following half reactions:

\[ H_2O + hv + VB \rightarrow 2H^+ + \frac{1}{2}O_2 \]
2H⁺+2e⁻ +CB → H₂ ...(5)

Overall reaction: \( H₂O \rightarrow H₂ + \frac{1}{2}O₂ \) ...(6)

Herein, an overview of current development in photocatalyst, a comparison of different water splitting processes, various catalyst development techniques especially doping on composite matrix, its effect on hydrogen production and various types of doping technique are critically explained. Different techniques for catalyst development including doping, Heterojunction, Dye sensitization, etc. are explained here. A complete study on doping is discussed here from all of its aspects. The numerous factors that affect the photo-catalytic water splitting such as band gaps, morphology, temperature, light intensity, pH, oxygen vacancies, and activity of sacrificial reagents are then scrutinously discussed here. Additionally, the reactor phenomenon and their commendation to further modification for \( H₂ \) production are also explained here.

### Table 1: Recent updates in photo-catalysts with different morphology and photocatalytic efficiency

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Morphology</th>
<th>Synthesis method</th>
<th>Source of irradiation</th>
<th>( H₂ ) generation rate</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag/TiO₂, Hg</td>
<td>nanoparticle</td>
<td>sol-gel</td>
<td>Vapor lamp (365 Nm)</td>
<td>910 mmol g⁻¹ h⁻¹</td>
<td>48</td>
</tr>
<tr>
<td>Ni/TiO₂, Pyrex</td>
<td>nanosheets</td>
<td>solid state reaction</td>
<td>F lamp, 100 W (365 Nm)</td>
<td>26,000 mmol g⁻¹ h⁻¹</td>
<td>49</td>
</tr>
<tr>
<td>Fe²⁺ ions doped and Ag deposited TiO₂</td>
<td>nanoparticle</td>
<td>solvothermal</td>
<td>UV light Source</td>
<td>515.45 µmol/h/g</td>
<td>50</td>
</tr>
<tr>
<td>Fe/ TiO₂</td>
<td>Na</td>
<td>anodization</td>
<td>xe arc lamp</td>
<td>174.30 mmol g⁻¹ h⁻¹</td>
<td>51</td>
</tr>
<tr>
<td>Cu/ TiO₂</td>
<td>nanotubes</td>
<td>anodization</td>
<td>300 W, xenon, lamp</td>
<td>28,700 mmol g⁻¹ h⁻¹</td>
<td>50</td>
</tr>
<tr>
<td>Au/ TiO₂</td>
<td>Na</td>
<td>anodization</td>
<td>300 W, xe lamp</td>
<td>3550 mmol g⁻¹ h⁻¹</td>
<td>52</td>
</tr>
<tr>
<td>Cu/ TiO₂</td>
<td>nanoparticle</td>
<td>commercial anodization</td>
<td>125 W, Mercury Vapour lamp (High Pressure)</td>
<td>01–07 µmol/min</td>
<td>53</td>
</tr>
<tr>
<td>Pt or Au/TiO₂</td>
<td>nanotubes</td>
<td>anodization</td>
<td>Xe/Hg lamp (High Pressure)</td>
<td>.06 µmol/cm²/h</td>
<td>54</td>
</tr>
<tr>
<td>Au/TiO₂</td>
<td>nanosheets</td>
<td>solid state reaction</td>
<td>xe lamp 300 W</td>
<td>6753.00 µmol/h/g</td>
<td>55</td>
</tr>
<tr>
<td>TiO₂/WO₃/Au rutile TiO₂</td>
<td>Na</td>
<td>electrospinning</td>
<td>Xe Arc lamp, 300 W</td>
<td>270 µmol/h</td>
<td>52</td>
</tr>
<tr>
<td>N/TiO₂, PdO &amp; Pt loaded NTiO₂</td>
<td>nanosheet</td>
<td>solvothermal</td>
<td>300 W, xenon lamp</td>
<td>22 mmol/g/h (5 h)</td>
<td>56</td>
</tr>
<tr>
<td>SMK-TiO₂</td>
<td>nanoparticle</td>
<td>sol-gel</td>
<td>400 W, mercury lamp</td>
<td>55.0,544.0,772.0 µmol/h/g</td>
<td>48</td>
</tr>
<tr>
<td>Co-moderated TiO₂</td>
<td>nanoparticle</td>
<td>commercial TiO₂</td>
<td>150 W Mercury lamp (Medium Pressure)</td>
<td>3.3 mmol/240 min</td>
<td>57</td>
</tr>
<tr>
<td>Ag-Fe/TiO₂</td>
<td>nanoparticle</td>
<td>electrochemical</td>
<td>300 W, Xenon lamp</td>
<td>Nanoparticle</td>
<td>58</td>
</tr>
<tr>
<td>Cu(OH)₂/TiO₂</td>
<td>nanotube arrays</td>
<td>electrochemical anodization</td>
<td>Xenon Lamp &amp; Hg Llamp</td>
<td>Nanotubes Ti Sheet (&gt; 99% Purity)</td>
<td>53</td>
</tr>
</tbody>
</table>

**Advancement In Photo-Catalyst Developments**

As per characteristics of elements throughout periodic table, a good number of semiconductors have shown the capability for photo-catalytic water splitting to produce hydrogen. The requirements for a photocatalyst to be viable on large scale usage...
Dye sensitization, Formation of Solid Solutions, such as Doping, Nanostructure, Heterojunction, Researcher heed their concentration on catalyst and organic substrate, which function as linking generation.

are excellent photo catalyst for photo catalytic H
catalyst named metal-organic frameworks or MOFs & large recombination rate.

still suffering from many drawbacks, for instance in splitting of water. Recent times g-C

Also, catalysts such as g-C$_3$N$_4$, oxides of graphene, graphene, nanotubes, and CQDs have been extensively investigated to develop their properties as they can exhibit better efficiency. Scientists are trying to develop the catalytic activity of photocatalysts through several techniques. Some of these are

Catalyst Development techniques

- Doping
- Heterojunction
- Dye sensitization
- Sensitization with noble metal loading
- Increasing Photo catalytically Active Area
- Modification of surface
- Nanostructure
- modification with Co-catalysts,

Doping
Among all of the stable and effective techniques for the development of catalysts, doping is the most effective and widely applied way to gear up catalyst's electronic activity as well as to accelerate the reaction surface. Non-metals and metals deposition onto the semiconductor surface enables supplying maximum active sites excellently for photo-catalytic hydrogen production. Besides, proper control of homogeneous distribution and metals particle size can supply sufficient active site resulting in maximum light transmittance. Catalyst modification induces
more charges due to the reduction of band gap, hence exciting more electrons for the production of hydrogen.\textsuperscript{61} TiO\textsubscript{2} is one of the prominent and pioneer catalyst with maximum efficiency from 1972 to now. Here, metal and non-metal doping of TiO\textsubscript{2}, elemental doping on titanium-based catalyst, doping on the various composite catalyst, such as g-C\textsubscript{3}N\textsubscript{4}, BiVO\textsubscript{4}, MoS\textsubscript{2}/Bi\textsubscript{2}S\textsubscript{3}, BiFeO\textsubscript{3} are discussed in a brief.

Doping

**Elemental Doping**

Doping deals with the replacement of an anion or cation within the surface of a substrate with some other agents (element) (Fig. 2a). Only an element of a similar charge and radius can be placed into a cation. The doping technique affects the band structure and decreases the band-gap by introducing a new forbidden level in the band. To choose the metal, its radius must match with the radius of the ion to be replaced. For example, in SrTiO\textsubscript{3} base lattice, Ti\textsuperscript{4+} (0.0605 nm) will be replaced by Ta\textsuperscript{5+} (0.064 nm) and Cr\textsuperscript{3+} (0.0615 nm) ions where F (0.133 nm) atom will replace by O\textsuperscript{2-} (0.140 nm).\textsuperscript{62}

![Fig. 2 : A 3-Dimensional representation for elemental doping on SrTiO\textsubscript{3}](image)

Doping with Single Element

Single-element doping is the replacement of single sites with one similar type of foreign element (fig. 2a). Although the sites are normally cation sites in the perovskite structure, such as A & B, but most replacement occurs at B site (fig. 2b). Different effects on PEC materials will occur for each doping entity because of the difference in the arrangements of valence shell electrons. Primarily, new donors or acceptors cause to form by doping in the forbidden band, resulting in the reduction in band gap. Currently, Cu doped CaTiO\textsubscript{3} shows an excellent result in H\textsubscript{2} production with a rate of 1447.8 mmol h\textsuperscript{-1} under irradiation of UV light.\textsuperscript{63} Here, table 02 exhibits the expected improved data obtained from photo catalyst while doping with a different single atoms with variable parameters. Results incur that the CaTiO\textsubscript{3} doping with Cu shows highest H\textsubscript{2} evolution rate of 1447.8 mmol h\textsuperscript{-1} with UV light.\textsuperscript{64} According to Shen P et al. SrTiO\textsubscript{3} catalyst, synthesized by polymerization method yield 47.00 mmol h\textsuperscript{-1} H\textsubscript{2} evolution rate under λ>420.0 nm & λ<800.0 nm light irradiation while doping with Rh metal atom.\textsuperscript{64} On the other hand according to the study of Sun X et al. Sr\textsubscript{2}TiO\textsubscript{4} exhibit maximum hydrogen evolution i.e. 97.7 mmol h\textsuperscript{-1} when doping with Cr under light.
irradiation of (λ>250 nm, visible). They developed this catalyst with Solid-state reactions mechanism and found highest output. Zou J-P et al., Yu H et al. get a regular output from SrTiO₃ catalyst while doping with Zn and Cr respectively under UV light irradiation. Zhang H et al. found that 1447.8 mmol h⁻¹ hydrogen evolution from catalyst while doping with Ca with Sol-gel method.

**Table 2: Outcome of doping with single element at perovskites (titanate-based) structure**

<table>
<thead>
<tr>
<th>No</th>
<th>Catalyst</th>
<th>Dopants</th>
<th>Method</th>
<th>Light source</th>
<th>H₂ generation rate</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>SrTiO₃</td>
<td>Rh</td>
<td>polymerizable complex, UV lamp</td>
<td>UV lamp</td>
<td>47.00 mmol h⁻¹</td>
<td>63</td>
</tr>
<tr>
<td>2</td>
<td>Ti₀.₉₈Cu₀.₀₂O₃</td>
<td>Ca</td>
<td>sol-gel</td>
<td>UV lamp</td>
<td>1447.80 mmol h⁻¹</td>
<td>65</td>
</tr>
<tr>
<td>3</td>
<td>Sr₂TiO₄</td>
<td>Cr</td>
<td>solid-state reactions</td>
<td>visible</td>
<td>97.70 mmol h⁻¹</td>
<td>66</td>
</tr>
<tr>
<td>4</td>
<td>Ba₉/₆TiO₃</td>
<td>Zn</td>
<td>sol-gel</td>
<td>UV lamp</td>
<td>2.90 mmol h⁻¹</td>
<td>66</td>
</tr>
<tr>
<td>5</td>
<td>Sr₂/₃TiO₃</td>
<td>Zn₁/₃</td>
<td>sol-gel</td>
<td>UV lamp</td>
<td>12.10 mmol h⁻¹</td>
<td>64</td>
</tr>
<tr>
<td>6</td>
<td>SrTiO₃</td>
<td>Cr</td>
<td>hydrothermal</td>
<td>visible and UV lamp</td>
<td>9.30 mmol g⁻¹ h⁻¹</td>
<td>67</td>
</tr>
</tbody>
</table>

**Doping with Double Element**

Here, replacement in the host material cause to happen with two types of foreign substrate at the same sites (B) or separate sites like X sites and A, B. Below in table 03, few effective cases listed through doping with the double element, along with the used parameters in experiments are shown. For example, on doping of cation with two elements, Sun et al. reported the increased hydrogen evolution rate to 211.4 mmol g⁻¹ h⁻¹ only with visible light (l > 415 nm) in SrTiO₃, Ta⁺⁺ and Cr³⁺ at Ti⁴⁺ sites compared to 97.7 mmol h⁻¹ H₂ evolution rate for doping of SrTiO₃ with Cr. High improvement, above two-fold, in case of Ta addition. Furthermore, the reported rate of H₂ evolution can be more accelerated if UV light source is included. On Co-doping, diffuse reflectance spectra revealed that Cr/Ta ions form a 3d donor level of Cr³⁺, above O 2p valence band. Yu et al. reported similar results, as in table 3, Yu H et al. shows. A study shows that the rate of hydrogen evolution in a double element doped SrTiO₃ was more about twice than that of mono element doped SrTiO₃, while fabricated through the same method. For B 2p electron, top valence band position was around 0.38 eV. But as Kang & Park reported the performance of composite catalyst material doped with double-element (15.4 mmol h⁻¹) was less than that of (Cr, Ta):SrTiO₃.(68). Results reveals that application of double doping in cation sites shows best outcomes than doping with only single element.

**Table 3: Outcome of doping with double element at perovskites (titanate-based) structure**

<table>
<thead>
<tr>
<th>No</th>
<th>Catalyst</th>
<th>Dopants</th>
<th>Method</th>
<th>Light source</th>
<th>Rate of H₂ generation</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>SrTiO₃</td>
<td>Ta, Cr</td>
<td>spray pyrolysis</td>
<td>λ&gt;415 nm</td>
<td>211.4 mmol g⁻¹ h⁻¹</td>
<td>68</td>
</tr>
<tr>
<td>2</td>
<td>Sr0.9Bi0.1Ti0.9</td>
<td>Fe₀.₁O₃</td>
<td>solid state</td>
<td>λ &gt; 250 nm</td>
<td>185 mmol g⁻¹ h⁻¹</td>
<td>69</td>
</tr>
<tr>
<td>3</td>
<td>SrTiO₃</td>
<td>B, Cr</td>
<td>hydrothermal</td>
<td>visible &amp; UV</td>
<td>15.41 mmol g⁻¹ h⁻¹</td>
<td>67</td>
</tr>
<tr>
<td>4</td>
<td>CaTiO₃</td>
<td>La, Ag</td>
<td>sol-gel with ultrasound</td>
<td>visible &amp; UV</td>
<td>1064 mmol g⁻¹ h⁻¹</td>
<td>70</td>
</tr>
<tr>
<td>5</td>
<td>SrTiO₃</td>
<td>Al, Au</td>
<td>solid state</td>
<td>visible &amp; UV</td>
<td>348 mmol g⁻¹ h⁻¹</td>
<td>71</td>
</tr>
</tbody>
</table>
Doping with Triple Element
In doping with triple element, three dopant elements replace original host structure atoms, where two replace at A and B sites and the left other replaces O sites. Researchers doped anion to substitute O$_2$ with F for performing a research on material doped with double element in the same material as that used by Kang HW et al. in his work. Resultantly, for maintaining balance in charge, rest elements changed their charge in the initial structure. For instance, in case of SrTiO$_3$:Cr/Ta, when F ions substitute O$_2$ ions Rh$^{4+}$ & Ti$^{4+}$ reduces Rh$^{4+}$ respectively to Rh$^{3+}$ & Ti$^{3+}$ and it partially induces Rh$^{3+}$ and Ti$^{3+}$ formation, respectively from Rh$^{4+}$ & Ti$^{4+}$ in the sites B of the substrate, decreasing barrier towards the energy of activation and reducing stability.

### Table 4: Outcome of doping with tri-element at perovskites (titanate-based) structure

<table>
<thead>
<tr>
<th>No</th>
<th>Catalyst</th>
<th>Dopants</th>
<th>Fabrication Method</th>
<th>Wave Nature</th>
<th>Rate of H$_2$ generation</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>SrTiO$_3$</td>
<td>F/Ta/Rh</td>
<td>spray pyrolysis</td>
<td>visible</td>
<td>123.7 mmol g$^{-1}$ h$^{-1}$</td>
<td>71</td>
</tr>
<tr>
<td>2</td>
<td>SrTiO$_3$</td>
<td>Ta/F Cr</td>
<td>spray pyrolysis</td>
<td>visible</td>
<td>3887.5 mmol g$^{-1}$ h$^{-1}$</td>
<td>62</td>
</tr>
</tbody>
</table>

Here, charge distribution variation influences the band organization through making interactivity within electrons in a substrate. Also, F replacement in O$_2$ sites results in cation deficiency and cation deficiency are the root cause for the doping element to improve H$_2$ evolution in PEC. In a research by Kang HW et al. they noticed that catalyst SrTiO$_3$ yield 123.7 mmol g$^{-1}$ h$^{-1}$ H$_2$ while doping with tri–element such as (Rh/Ta/F). They synthesized the catalyst with Spray pyrolysis method and the light irradiation was 4% under visible range. At the same time in a separate investigation, by Kang HW et al. registered that 3887.9 mmol g$^{-1}$ h$^{-1}$ hydrogen was evaluated from SrTiO$_3$ catalyst while doping with Cr/Ta/F simultaneously. They also fabricate the catalyst matrix by spray pyrolysis method and conducted the reaction under visible light irradiation.

### Fig. 3: Metal doping on g-C$_3$N$_4$ based photo

**Doping on Photo-Catalysts based on Graphitic Carbon Nitride (G-C$_3$N$_4$)**

**Doping with Metal**
Recently Graphitic carbon nitride(g-C$_3$N$_4$), drawn a considerable concern as well as effectively investigated just as green, viable photo catalyst which results in a convenience e.g. metal-free, non-toxic semiconductor along with sensibility at the visible light range and narrow band gap, approximately, 2.7 eV. In addition, consisting with simple earth abundant element C & N, it is of low cost and also shows unique resistivity towards photo corrosion for the strength of covalent bonds shown by the atoms of carbon and nitride.
Also g-C$_3$N$_4$ shows exceptional photoluminescence (PL) characteristics, making it a quality co-catalyst for other semiconductor catalysts. But in practice, implementation of g-C$_3$N$_4$ as a photo-catalyst is limited, due to smaller specific surface area and high rate of recombination of photo induced charges. Ultimately, Doping is one of the effectual initiative for adjusting electronic formations of g-C$_3$N$_4$, and to stimulate the reaction surface to escalate photo-catalytic activity owing to the work function and Surface Plasmon Resonance effect according to the previous writings.

In the year 2014, Zhong Y et al. conduct Pt doping on photo-catalysts based on Graphitic carbon nitride (g-C$_3$N$_4$), under light irradiation of (300 W Xe lamp, l >420 nm) in Quartz reactor. They get hydrogen flow rate of 41.7 μmol·h$^{-1}$ which was not significant to continue further work. Further in 2015 prominent researcher Huang Z et al. and Ma L et al. again doped g-C$_3$N$_4$ photo catalyst with Pt. The final product was then led for photoreaction under light irradiation of 300 W Xe lamp, I >420 nm in Quartz reactor and Pyrex reactor respectively. Ma L et al. found 89.28 μmol·h$^{-1}$·g$^{-1}$ hydrogen production rate while Huang Z et al. found 261.8 μmol·h$^{-1}$·g$^{-1}$ in Quartz reactor. In 2018, Wang Y et al. doped potassium (K) on Graphitic carbon nitride (g-C$_3$N$_4$) based photo-catalysts. They found that, in Pyrex reactor under light irradiation condition of 300 W Xe lamp, I ¼ 400 nm, K doped g-C$_3$N$_4$ produce maximum 1337.2 μmol hydrogen at one hour. In the same year, another study of Liu M et al. shows maximum 4210.8 μmol·h$^{-1}$·g$^{-1}$ efficiency of Graphitic carbon nitride (g-C$_3$N$_4$) based , while doping with platinum (Pt). But in 2019, Chen D et al. found 79.00 μmol hydrogen by Mo doping on Graphitic carbon nitride (g-C$_3$N$_4$) based photo-catalyst.

<table>
<thead>
<tr>
<th>Year</th>
<th>Photocatalyst</th>
<th>Dopant (metal)</th>
<th>Reactor</th>
<th>Light Source</th>
<th>Efficiency μmol·h$^{-1}$·g$^{-1}$</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>2019</td>
<td>g-C$_3$N$_4$</td>
<td>Mo</td>
<td>Pyrex reactor(P)</td>
<td>Xe lamp, 300 W</td>
<td>790.0</td>
<td>81</td>
</tr>
<tr>
<td>2018</td>
<td>g-C$_3$N$_4$</td>
<td>Au</td>
<td>Pyrex reactor(P)</td>
<td>Xe lamp, 300 W</td>
<td>265.0</td>
<td>82</td>
</tr>
<tr>
<td>2018</td>
<td>g-C$_3$N$_4$</td>
<td>Cu</td>
<td>Pyrex reactor(P)</td>
<td>Xe lamp, 300 W, l &gt;430 nm</td>
<td>3020.0</td>
<td>83</td>
</tr>
<tr>
<td>2018</td>
<td>g-C$_3$N$_4$</td>
<td>Ni</td>
<td>Quartz reactor (Q)</td>
<td>Xe lamp, 300 W, l &gt;430 nm</td>
<td>529.10</td>
<td>84</td>
</tr>
<tr>
<td>2018</td>
<td>g-C$_3$N$_4$</td>
<td>Ni-P</td>
<td>Pyrex reactor(P)</td>
<td>Xe lamp, 350 W</td>
<td>937.00</td>
<td>85</td>
</tr>
<tr>
<td>2018</td>
<td>g-C$_3$N$_4$</td>
<td>Pt</td>
<td>Pyrex reactor (P)</td>
<td>Xe lamp,350 W</td>
<td>4210.80</td>
<td>86</td>
</tr>
<tr>
<td>2018</td>
<td>g-C$_3$N$_4$</td>
<td>K</td>
<td>Pyrex reactor (P)</td>
<td>Xe lamp, 300 W</td>
<td>1337.20</td>
<td>79</td>
</tr>
<tr>
<td>2017</td>
<td>g-C$_3$N$_4$</td>
<td>Co</td>
<td>Pyrex reactor(P)</td>
<td>Xe lamp, 300 W, l &gt;420 nm</td>
<td>280.00</td>
<td>86</td>
</tr>
<tr>
<td>2017</td>
<td>g-C$_3$N$_4$</td>
<td>Pt</td>
<td>Pyrex reactor(P)</td>
<td>Xe lamp, 300 W, l ¼ 400 nm</td>
<td>740.00</td>
<td>87</td>
</tr>
<tr>
<td>2015</td>
<td>g-C$_3$N$_4$</td>
<td>Pt</td>
<td>Quartz reactor(Q)</td>
<td>Xe lamp, 300 W, l &gt;420 nm</td>
<td>262.00</td>
<td>88</td>
</tr>
<tr>
<td>2015</td>
<td>g-C$_3$N$_4$</td>
<td>Pt</td>
<td>Pyrex reactor (P)</td>
<td>Xe lamp, 300 W</td>
<td>890.20</td>
<td>78</td>
</tr>
<tr>
<td>2014</td>
<td>g-C$_3$N$_4$</td>
<td>Pt</td>
<td>Quartz reactor (Q)</td>
<td>300 W,Xe lamp, l &gt;420 nm</td>
<td>420.00</td>
<td>77</td>
</tr>
</tbody>
</table>

**Non-Metal Doping**

Besides metal doping, doping with non-metals can effectively increase semiconductor’s photo-activity. In the modification of g-C$_3$N$_4$ polymers, doping with O, S, B & N; (the non-metal elements) shows excellent result while comparing with others. Its optical & electronic nature were effectively optimized for promoting photo-catalytic activity as a result of improved optical absorption process along with increased charge mobility. Hydrogen gas evolution performance should be enhanced as loading of various type of non-metal element that tunes the catalyst formation by reducing the band gap, inhibiting electron-hole pair recombination rate and stabilizing the catalyst. Zhou et al., during 2016, reported near 3.3 time’s higher hydrogen production than undoped g-C$_3$N$_4$ over modified N-doped g-C$_3$N$_4$, photo-catalyst (CN-20) with maximum reported hydrogen production was 64 mmol h$^{-1}$ (Fig. 6(a)). CN-20 catalyst was also documented for stability, as there was no notable decrease in the hydrogen production rate on repeated experiment under similar experimental situation used for four cycles (24 h), as Fig.6(b) reveals.
In another study by Chen et al. reported the 12 times higher enhanced photo-catalytic performance for sulfur loading than pristine g-C$_3$N$_4$ and long term stability for the water-splitting process, as it is documented in Fig. 6(c). This one resolved that S loading is able to efficaciously enhance the specific surface area, persuade the formation of nitrogen vacancy, retard photo produced electron-hole pair recombination rate and improve the visible range responsiveness of the catalyst. Similarly specified the non-metal Br doped g-C$_3$N$_4$, was also appeared having long-term stableness on visible range photo-catalytic activity for 20 h with highest hydrogen generation rate of around 48 mmol h$^{-1}$ as in the Fig. 6(d) showed. They also suggested that, the mechanism of reaction for water splitting using
Doping on BiVO₄ based Photo-catalysts: BiVO₄

Centenary of semiconductors are used for their Photo catalytic Properties, because it is impossible to fulfill all the conditions of photo catalytic water splitting by a particular element. Accordingly, element improvement stands the significant note for improving Photo catalytic water splitting act. In recent time, BiVO₄ takes excessive consideration as photo-anode substances for PEC water splitting, since certain modified BiVO₄ photo-anodes fulfill several essential necessities enlisted above. BiVO₄ is a n-type semiconductor photo catalyst with the maximum band gap energy of 2.4eV. Here, BiVO₄ engrosses sufficient amount of visible light spectrum and used as a stable, neutral, nontoxic, comparatively low-cost electrolyte.

In comparison with other common O₂ evolution photo catalyst like Fe₂O₃ and WO₃, BiVO₄ consumes a quite high CB (conduction band) energy (0.02 V vs. RHE). Therefore, the needless bias potential to elevate the photoelectrons upper the water reduction potential (0.0 V vs. RHE). However, the drawback is a very poor electrical conductivity with drippy water oxidation kinetics. Hence, several improvement techniques had undertaken for takeover the shortcomings of the BiVO₄ catalyst as a photo-anode and to magnify its photo catalytic water splitting properties. Doping is one of the significant steps of them. Bismuth vanadate is suffering from the problems of the transfer of electron. Therefore, doping in BiVO₄ can be a noble strategy to develop the electron transfer process in it and later photocurrent along with catalytic execution. In a research by Patil et al. informed that 2.00% of silver which is doping in uncontaminated BVO could rise its photocurrent density near about 3-fold as linked to an undoped BVO. In another work, Fang and his team presented that, the pure BVO Catalyst have less photocurrent density rather than Ag-BiVO₄ structure.

Table 7: The recent study of doping on BiVO₄ composite photo-catalyst

<table>
<thead>
<tr>
<th>Year</th>
<th>Photo catalyst</th>
<th>Dopant (metal)</th>
<th>Reactor Solution</th>
<th>Light Source</th>
<th>Efficiency µmol h⁻¹ cm⁻² h⁻¹</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>2018</td>
<td>BiVO₄</td>
<td>Nb-TiO₂</td>
<td>1.0M KCl at pH 9.2</td>
<td>AM1.5G illumination</td>
<td>80µmol h⁻¹ cm⁻² h⁻¹ 109</td>
<td></td>
</tr>
<tr>
<td>2018</td>
<td>BiVO₄</td>
<td>Bi₂S₃</td>
<td>Na₂S/Na₂SO₃</td>
<td>1000 W m⁻² (1 Sun).</td>
<td>417 µmol h⁻¹ cm⁻² h⁻¹ 106</td>
<td></td>
</tr>
<tr>
<td>2018</td>
<td>BiVO₄</td>
<td>Nb-TiO₂/W</td>
<td>0.50 M phosphate buffer</td>
<td>AM1.5G illumination</td>
<td>80 µmol h⁻¹ cm⁻² h⁻¹ 110</td>
<td></td>
</tr>
<tr>
<td>2017</td>
<td>BiVO₄</td>
<td>MDH</td>
<td>0.50 M phosphate buffer</td>
<td>AM1.5G illumination</td>
<td>21 µmol h⁻¹ cm⁻² h⁻¹ 111</td>
<td></td>
</tr>
<tr>
<td>2017</td>
<td>BiVO₄</td>
<td>3-Fe₂O₃</td>
<td>phosphate buffer solution</td>
<td>AM1.5G illumination</td>
<td>27.34 µmol h⁻¹ cm⁻² h⁻¹ 112</td>
<td></td>
</tr>
<tr>
<td>2016</td>
<td>BiVO₄</td>
<td>CDs</td>
<td>0.50 M phosphate buffer</td>
<td>300.0 W Xe-lamp</td>
<td>0.92 µmol h⁻¹ cm⁻² h⁻¹ 107</td>
<td></td>
</tr>
<tr>
<td>2016</td>
<td>BiVO₄</td>
<td>HDP</td>
<td>1.0 M KCl at pH 7</td>
<td>1.0 G sun illumination solar light, AM 1.50 G</td>
<td>121 µmol h⁻¹ cm⁻² h⁻¹ 107</td>
<td></td>
</tr>
<tr>
<td>2016</td>
<td>BiVO₄</td>
<td>WO₃-NRs</td>
<td>potassium phos -</td>
<td>102 µmol h⁻¹ cm⁻² h⁻¹ 105</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2014</td>
<td>BiVO₄</td>
<td>WO₃</td>
<td>0.9M K₂SO₄ (pH 7.0)</td>
<td>100 mW cm⁻², AM 1.50 G</td>
<td>75 µmol h⁻¹ cm⁻² h⁻¹ 105</td>
<td></td>
</tr>
<tr>
<td>2011</td>
<td>BiVO₄</td>
<td>RhO₂/Mo</td>
<td>- seawater</td>
<td>AM1.50 G solar light simulated AM 1.50 G sunlight</td>
<td>9 µmol h⁻¹ cm⁻² h⁻¹ 113</td>
<td></td>
</tr>
<tr>
<td>2011</td>
<td>BiVO₄</td>
<td>Mo</td>
<td>-</td>
<td>7 µmol h⁻¹ cm⁻² h⁻¹ 113</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Where Martin Rohloff et al. described that the photo catalytic water splitting routine of the Mo-doped BiVO₄ film photo-anodes are much better compared to their pure BiVO₄. The photocurrent densities for Mo-BVO go to 1.90 mA cm⁻² at 1.23V vs. RHE under solar light irradiation (100.00mW cm⁻²).
In a work, Diane K. Zhong et al. described that the photo-current densities of BiVO$_4$, after W doping were improved to 0.7 mA cm$^{-2}$ at 1.23 V vs. RHE under 1.0 sun light illumination (100.00mW cm$^{-2}$). Amongst surface modification techniques deposition of catalysts layers on the BiVO$_4$ surface, cobalt phosphate (Co-Pi) displayed the significant benefits of being effortlessly coconspirator with the BiVO$_4$ surface. The Co-Pi alteration is a modest and effective technique to produce an earth abundant water-oxidation electro-catalyst for developing photo catalytic water oxidation. Heritable 07 shows the recent study of doping on BiVO$_4$ composite photo catalyst.

### Table 8: Key findings in development of Photocatalytic activity of BiFeO$_3$ by doping with Gd$^{3+}$.\textsuperscript{114}

<table>
<thead>
<tr>
<th>Sl. No.</th>
<th>Catalyst</th>
<th>Doped Element</th>
<th>Preparation Method</th>
<th>Efficiency</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>01</td>
<td>BiFeO$_3$</td>
<td>nil</td>
<td>sol-gel synthesis</td>
<td>21.9 $\mu$mol cm$^{-2}$ h$^{-1}$</td>
<td>Yuxuan Yang, et. al., 2018</td>
</tr>
<tr>
<td>02</td>
<td>BiFeO$_3$</td>
<td>Gd$^{3+}$</td>
<td>sol-gel synthesis</td>
<td>67.6 $\mu$mol cm$^{-2}$ h$^{-1}$</td>
<td>Yuxuan Yang, et. al., 2018</td>
</tr>
</tbody>
</table>

**Doping on BiFeO$_3$ based Photo-Catalysts: by Gd$^{3+}$**

In a work, Yuxuan Yang et al. reported that, sol-gel synthesis along with photo-catalytic H$_2$ evolution of BiFeO$_3$ and Gd$^{3+}$ doped BiFeO$_3$. The results of this work exhibits increased photo-catalytic H$_2$ evolution due to Gd$^{3+}$ doping. The H$_2$ production rates are about 21.90 and 67.60 $\mu$mol cm$^{-2}$h$^{-1}$ for BiFeO$_3$ and Gd$^{3+}$ doped BiFeO$_3$, respectively. So, it is absolutely larger photocatalytic activity, the rate, more than three times of Gd$^{3+}$ doped BiFeO$_3$ than that for pristine BiFeO$_3$. So, Gd$^{3+}$ doping effects performance of BiFeO$_3$. Also, It is mentionable that for a particulate photo-catalyst the H$_2$ production ability depends on its different properties e.g. microstructure, crystallinity, electronic and optical etc.\textsuperscript{115}

### Table 9: The recent study of Doping on TiO$_2$ & TiO$_2$ based composite photocatalyst

<table>
<thead>
<tr>
<th>Year</th>
<th>Photocatalyst (metal)</th>
<th>Dopant</th>
<th>Reactant</th>
<th>Light Source</th>
<th>Efficiency $\mu$mol h$^{-1}$g$^{-1}$</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>2019</td>
<td>SrTiO$_3$</td>
<td>Al</td>
<td>Pure water</td>
<td>300.0 W, Xe Lamp</td>
<td>05.70</td>
<td>\textsuperscript{118}</td>
</tr>
<tr>
<td>2018</td>
<td>PCN-777</td>
<td>Pt</td>
<td>TEOA</td>
<td>300 W,</td>
<td>586.00</td>
<td>\textsuperscript{116}</td>
</tr>
<tr>
<td>2018</td>
<td>RP/TiO$_2$</td>
<td>Red-P</td>
<td>Methanol</td>
<td>350.0W, mercury Lamp</td>
<td>276.00</td>
<td>\textsuperscript{119}</td>
</tr>
<tr>
<td>2006</td>
<td>Sr3Ti2O7</td>
<td>NiOx</td>
<td>Pure water</td>
<td>Hg lamp,400–450.0 W</td>
<td>144.00</td>
<td>\textsuperscript{120}</td>
</tr>
<tr>
<td>2002</td>
<td>CaTiO$_3$</td>
<td>NiOx</td>
<td>Pure water</td>
<td>Xe lamp,400–450.0 W</td>
<td>30.00</td>
<td>\textsuperscript{121}</td>
</tr>
<tr>
<td>2002</td>
<td>Sr4Ti3O10</td>
<td>NiOx</td>
<td>Pure water</td>
<td>Xe lamp,400–450.0 W</td>
<td>170.00</td>
<td>\textsuperscript{122}</td>
</tr>
<tr>
<td>1998</td>
<td>B/Ti oxide</td>
<td>Pt</td>
<td>Pure water</td>
<td>Hg lamp,400–450.0 W</td>
<td>22.00</td>
<td>\textsuperscript{123}</td>
</tr>
<tr>
<td>1997</td>
<td>K2La2Ti3O10</td>
<td>NiOx</td>
<td>Pure water</td>
<td>Hg lamp,400–450.0 W</td>
<td>2186.00</td>
<td>\textsuperscript{124}</td>
</tr>
<tr>
<td>1997</td>
<td>TiO$_2$</td>
<td>Pt</td>
<td>Pure water</td>
<td>Xe lamp,400–450.0 W</td>
<td>568.00</td>
<td>\textsuperscript{125}</td>
</tr>
<tr>
<td>1995</td>
<td>TiO$_2$</td>
<td>Pt</td>
<td>Pure water</td>
<td>Hg lamp,400–450.0 W</td>
<td>106.00</td>
<td>\textsuperscript{126}</td>
</tr>
<tr>
<td>1987</td>
<td>TiO$_2$</td>
<td>NiOx</td>
<td>Pure water</td>
<td>Hg lamp,400–450.0 W</td>
<td>62.00</td>
<td>\textsuperscript{127}</td>
</tr>
<tr>
<td>1985</td>
<td>TiO$_2$</td>
<td>Rh</td>
<td>Pure water</td>
<td>Xe Lamp, 400–450.0 W</td>
<td>449.00</td>
<td>\textsuperscript{128}</td>
</tr>
<tr>
<td>1980</td>
<td>SrTiO$_3$</td>
<td>Rh</td>
<td>Pure water</td>
<td>Hg lamp, 400–450.0 W</td>
<td>27.00</td>
<td>\textsuperscript{129, 130}</td>
</tr>
<tr>
<td>1980</td>
<td>SrTiO$_3$</td>
<td>NiOx</td>
<td>Pure water</td>
<td>Hg lamp, 400–450.0 W</td>
<td>40.00</td>
<td>\textsuperscript{127, 131}</td>
</tr>
</tbody>
</table>
Doping On TiO$_2$ & TiO$_2$ Composite Photo-Catalyst

TiO$_2$ & TiO$_2$ composite photocatalyst is the best, efficient, and cost-effective catalyst for photocatalytic water splitting. Since 1972 enormous scientists or researchers work on it. The TiO$_2$ & TiO$_2$ composite photocatalyst could be further stabilized by the deposition of various metal and non-metal elements on its surface to increase catalytic activity. According to Hang Liu et al. the photocatalyst Pt/PCN-777 exhibits excellent H$_2$ production rate of 586 mmolcm$^{-2}$ h$^{-1}$ in the presence of the TEOA reagent as a sacrificial agent under 300.0 W xenon lamp.$^{116}$ The most important is that, this composite is recyclable under the normal catalytic conditions. A prominent researcher Y. Goto et al. processed a TiO$_2$/CoOOH/RhCrO$_x$/SrTiO$_3$:Al photocatalyst into a 5.0 *5.0 cm sheets & the sustainability of the substance was tested by a panel-type photo reactor with water depth 1.5 mm by simulated light and ambient pressure.$^{117}$ The water splitting rate of these sheets are 5.7 μmol·h$^{-1}$·g$^{-1}$ and H$_2$ generation efficiency is 0.4% at the initial duration of irradiation.

Where according to Hao Lyu et al the AQY of the resulting RhCrO$_x$/SrTiO$_3$: Al at the time of overall water splintering was measured to be 54.0% at 360.00 nm, which consistent with the ancestral work.$^{118}$

Doping (Copper) on MoS$_2$/Bi$_2$S$_3$ Photocatalyst

In a study, W. P. Cathie Lee fabricated a flower-like Copper-doped molybdenum disulfide/bismuth sulfide (Cu-MoS$_2$/Bi$_2$S$_3$) photo-catalyst. The sample photocatalysts with differing quantity of Cu were utilized in the photo-catalytic water splitting for H$_2$ production under simulated sunlight irradiation. The photocatalysts demonstrated high Photocatalytic activity with a most favorable Cu loading of 20.0mol%, reaching a total hydrogen evolution of 32.4 mmol/h on reaction for 6 hours(Fig: 5.0). The Copper doped samples showed increased performance rising about 1.4 times of non-doped samples. The reaction time taken by the different samples are also shown in (Fig: 5-2) respectively.$^{132}$

Fig. 5: Variation of Hydrogen production rate from variable Cu doping on Na$_2$S/Na$_2$SO$_3$ mixture illuminated under simulated sunlight over the duration of 6.0 h

Fig. 6: Some images from FE-SEM of MoS$_2$/Bi$_2$S$_3$, (a) Undoped (b) 5.0mol% (c) 10.0mol% (d) 20.0mol% (e) 30.0mol% (f) 40.0mol%$^{132}$
The crystal structure and surface morphology info of synthesized photo-catalyst were inspected by W. P. Cathie Lee using TEM and FE-SEM. The standard structure of non-doped MoS₂/B₂S₃ is demonstrated in Fig. 2(a), where MoS₂ have been seen to cover surface of Bi₂S₃, growing on it. In each of six images, crumpled MoS₂ nano sheets is found to accumulate onto Bi₂S₃ surface, producing a flower-type frame. Upon copper (Cu) doping MoS₂/B₂S₃, no notable alteration on samples surfaces were noticed (Fig. 2(b) & (c)). Still, at greater Copper loading to 20.0mol%, on the surface the grown MoS₂ sheets were larger enough to be visible and distinguishable (Fig. 2(d)). But on increasing Copper(Cu) to 40.0mol%, the distinct Bi₂S₃ discoids' not formed, rather some Bi₂S₃ noticed to be in rod form (indicated as yellow in Fig. 2(f)) where MoS₂ sheets were in a arbitrary form. Doping on Miscellaneous Composite Photo-Catalyst Deposition of a foreign particle onto the semiconductor surface can supply maximum active surface for excellent Photo-catalytic H₂ production. There are many more option with semiconducting properties for Photocatalytic water splitting. Among them K₆La₃Ti₅O₁₅, possesses a perovskite structure is one of a unique catalyst photo catalysis. H₂ evolving happens on NiOx co-catalyst where O₂ evolves from hydrated interlayer. Various niobate, titanate and tantalite photo-catalysts with perovskite structure been reported from the period of K₆La₃Ti₅O₁₅ photocatalyst was designed. Sr₂Ti₂O₇ and Sr₃Ti₂O₇ photo-catalysts have perovskite slabs of SrTiO₃, La₂Ti₂O₇, La₂Ti₂O₇:Ba, KLaZr₀.₃Tio₇,O₃ and La₄CaTi₅O₁₇, photocatalysts with perovskite structure which give a maximum quantum yield. Na₂Ti₆O₁₃ and BaTi₄O₉ with a holo-tube type structure is also a unique photo-catalysts. On the other side Catalyst KTiNbO₅ shows activity when it prepared through a polymerizable complex composite system. In a study by S. Ikeda et al. they found that K₆La₃Ti₅O₁₅ yield 2186μmol Hydrogen in 0.1M KOH solution. They used NiOx as dopant and the irradiated light intensity was 400 to 450 W mercury lamp with quartz cell. On the other hand in the year 2006 get 2390μmol Hydrogen from a quartz cell using K₃Ta₃B₂O₁₂ as a catalyst and Pure water Reactant Solution. Table 10 shows a brief summary of recent study on miscellaneous catalyst for Photocatalytic water splitting process.

Table 10: Some study of doping on miscellaneous composite photo-catalyst

<table>
<thead>
<tr>
<th>Year</th>
<th>Photocatalyst</th>
<th>Dopant (metal)</th>
<th>Reactant Solution</th>
<th>Light Source</th>
<th>Efficiency μmol h⁻¹ g⁻¹</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>2008</td>
<td>LiCa₂Ta₃O₁₀</td>
<td>NiOx</td>
<td>Pure water</td>
<td>Hg–Q lamp</td>
<td>59.00</td>
<td>136</td>
</tr>
<tr>
<td>2007</td>
<td>CeO₂: Sr</td>
<td>RuO₂</td>
<td>Pure water</td>
<td>Hg–Q lamp</td>
<td>110</td>
<td>122</td>
</tr>
<tr>
<td>2006</td>
<td>Na₂Ta₂O₆</td>
<td>NiO</td>
<td>Pure water</td>
<td>Hg–Q lamp</td>
<td>391</td>
<td>137</td>
</tr>
<tr>
<td>2006</td>
<td>K₃Ta₃B₂O₁₂</td>
<td>None</td>
<td>Pure water</td>
<td>Hg–Q lamp</td>
<td>2390</td>
<td>138</td>
</tr>
<tr>
<td>2005</td>
<td>Cs₂Nb₄O₁₁</td>
<td>NiOx</td>
<td>Pure water</td>
<td>Hg lamp, 400–450 W</td>
<td>1700</td>
<td>139</td>
</tr>
<tr>
<td>2005</td>
<td>NaCa₂Nb₃O₁₀</td>
<td>RuO₂</td>
<td>Pure water</td>
<td>Hg–Q lamp</td>
<td>118</td>
<td>140</td>
</tr>
<tr>
<td>2005</td>
<td>Sr₅Ta₄O₁₅</td>
<td>NiO</td>
<td>Pure water</td>
<td>Hg–Q</td>
<td>1194</td>
<td>141</td>
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<tr>
<td>2005</td>
<td>Ba₅Ta₄O₁₅</td>
<td>NiO</td>
<td>Pure water</td>
<td>Hg–Q</td>
<td>2080</td>
<td>142,144</td>
</tr>
<tr>
<td>2004</td>
<td>Y₂Ti₂O₇</td>
<td>NiOx</td>
<td>Pure water</td>
<td>Hg lamp</td>
<td>850</td>
<td>143,144</td>
</tr>
<tr>
<td>2004</td>
<td>La₃Nb₇</td>
<td>NiOx</td>
<td>Pure water</td>
<td>Hg lamp, 400–450 W</td>
<td>35</td>
<td>142</td>
</tr>
<tr>
<td>2003</td>
<td>KaLaZr₀.₃Ti₀.₇O₄</td>
<td>NiOx</td>
<td>Pure water</td>
<td>Hg lamp, 400–450 W</td>
<td>230</td>
<td>145</td>
</tr>
<tr>
<td>2000</td>
<td>K₂Pt₅O₁₅</td>
<td>NiO</td>
<td>Pure water</td>
<td>Hg–Q</td>
<td>1550</td>
<td>146</td>
</tr>
<tr>
<td>1997</td>
<td>Rb₂La₂Ti₃O₁₀</td>
<td>NiOx</td>
<td>0.1M KOH</td>
<td>Hg lamp, 400–450 W</td>
<td>2186</td>
<td>148</td>
</tr>
<tr>
<td>1997</td>
<td>K₂La₂Ti₃O₁₀</td>
<td>NiOx</td>
<td>Pure water</td>
<td>Hg–Q</td>
<td>60</td>
<td>149</td>
</tr>
</tbody>
</table>

Heterojunction
The heterojunction is the interface that takes place between two layers or sectors of varying crystalline semiconductors. These semiconducting materials have a different band gaps as contrary to a homo junction. Many reviews have shown that various
semiconductors can be coupled with BiVO₄ for favorable result. The formation of successful hetero junction has been reported between BiVO₄ and WO₃, SnO₂, FeO₃, Fe₂O₃, CuWO₄, and CdS. Kim et al. showed that hetero type dual photo-anodes, HDP, of BiVO₄/α-Fe₂O₃, reports also implies largely increased photocurrent on HDP of BiVO₄/α-Fe₂O₃, SnO₂, nearly 80μmolcm⁻²h⁻¹ by Savio et al. On the other hand, the Fe₂O₃/BiVO₄ photo-anode containing 3 spin coated films demonstrated 1.63mA/cm² photocurrent density at 1.23V vs. RHE, reported by Xia et al. that is nearly 2.2 times higher in comparison to pure BiVO₄ photo-anode, submerged in 0.1M KH₂PO₄ (pH 7) electrolytic solution beneath AM1.5G sun light. Rates of hydrogen production for Fe₂O₃/BiVO₄ has been around 28μmolcm⁻²h⁻¹, quite larger in comparison to BiVO₄ photo-anode. A BiVO₄/CuWO₄ heterojunction electrodes made by Pilli et al. via spray accumulation method was reported two times photocurrent density to pristine BVO at 1.0V vs. Ag/AgCl in 1.0M Na₂SO₄ electrolytic solution at pH 7. In contrary to pristine BVO, BiVO₄/WO₃ largely enhanced the IPCE, Incidence of Photon to Current Efficiency, from 9.3% to 31% as reported by Grimes et al. referred it to the phenomenon of enhanced electron migration towards WO₃ from BiVO₄. Also, as reported by Savio et al., BiVO₄ and ZnO pairing generate a significant, 2 mA/cm² at 1.23V vs. RHE, photocurrent density in observable radiation range. Similarly, four times amplified photo current of BiVO₄/TiO₂, pairing of BiVO₄ and TiO₂, has been reported by Kimura et al., contrary to pristine BiVO₄ on 100mWcm⁻² brightness, and they ascribed it to the formational alterations of BiVO₄ which improved electron transferring throughout the junction.

**Dye-Sensitization**

For HOMO and LUMO states being reconfigurable on anchorage of various ligands, dye sensitization is considered an effective way to improve the visible range response of photocatalyst for hydrogen generation. Broad usage for dye sensitization is to set visible light to transform energy. Some of the dyes are possible to be utilized in solar cells and Photo-catalytic methods, which have redox property and which are sensitive to visible light.

On illumination of visible light, electrons from excited dyes can be infused to the conduction band of semiconductors, causing initiation of photo catalytic actions as described in Fig.- 7. Some dyes such as safranine O/EDTA, T/EDTA, are susceptible to take in visible light to generate reducing agents electrons which have enough strength to generate H₂ even without semiconductors. But it is very little H₂ generation rate by dyes without semiconductors. Dhanalakshmi et al. carried out a parametric research to study the effect of applying 2b as a dye sensitizer on Photocatalytic H₂ generation from H₂O, under visible light irradiation.

![Fig. 7: Schematic representation of dye sensitizer action mechanism](image)

Dhanalakshmi et al. observed improved H₂ generation rate under visible range radiation due to adsorption of dye molecules to the TiO₂ on parametric research studying the influence of applying 2b as a dye sensitizer on Photocatalyst based H₂ generation from H₂O. Splitting process. Gurunathan et al. noticed influence of various dyes, for example, EDTA, during H₂ generation for SnO₂ photocatalyst using or not using sacrificial agents. Having band gap 3.5 eV and, SnO₂ was unable to be activated on visible irradiation. On dye sensitization, SnO₂ was capable of H₂ generation on visible range irradiation. As observed, overall order of efficiency for dyes for improving rate of H₂ generation is as following: Eosin blue>Rose Bengal>Ru(bpy) 32+>RhodamineB>Ac riflavin>Fluorescein. By analyzing the phusico-chemical properties of these dyes, a effective conclusion could be dawn. Like as Rhodamine pose a longer absorption range maxima including more negative potential (−545V) than conduction range (−34V) of SnO₂. But the problem is that it does not improve the H₂ production rate significantly.
Sensitization with Noble Metal

Noble or precious metals, comprising Pt, Pd, Au, Ni, Rh, Cu & Ag, proved very efficient to improve photocatalytic activity of TiO$_2$. For these noble metals, Fermi levels are lesser in comparison to TiO$_2$ and another similar photocatalyst. The photogenerated electrons transfers towards metal particles from conducting band of photocatalyst, depositing, while holes stay on the Valance Band of the photocatalyst. This decreases the possible rebinding of electron and hole greatly, leading to effective separation and stronger photo-catalytic reaction.172 The prominent researcher Anpo & Takeuchi accustomed ESR, signals to observe transferring of an electron from photo-catalyst towards Pt. Increased Ti$^{3+}$ signals were observed on increasing irradiation duration and Pt loading decreased the of Ti$^{3+}$ quantity. This investigation shows electron shifting towards Pt particles from TiO$_2$ (Titanium dioxide). With electron deposition on particles, Fermi levels of the noble metals switch closer to the Conduction Band within TiO$_2$ photo-catalyst leading energy levels towards more negative(-ve) direction which is effectual for splitting water, producing $\text{H}_2$.173-175 Small size metal particle accumulation cause huge shifting of Fermi level on negative (+ve) direction on surface of TiO$_2$ catalyst.175 Electrons deposited on the metal particles can move towards $\text{H}^+$ upon the surface, adsorbed, and subsequently reduce $\text{H}^+$ to form $\text{H}_2$. Hence, noble metals having satisfactory work function able to assist in transferring electron, resulting in increased photo-catalytic activity.176 Bamwenda et al. compared $\text{H}_2$ generation from water-ethanol solution using TiO$_2$ photo-catalyst loaded with two different metals, Au and Pt. they also examined variant methods for depositing metal particle, for example, deposition–precipitation, photo deposition & impregnation method.176 They observed that Pt loaded TiO$_2$ better operated than Au loaded TiO$_2$. On the other hand, Au loading arranged by photo deposition operated better among other methods. Changing could be attributed to improved contact in the photo deposition system between TiO$_2$ active sites and metal particles. But, the preparation system was hardly influencing in case of Pt-loaded TiO$_2$.177 Among others Sakthivel et al. observed good loading in experiment for photo oxidation of acid green 16 treatment with TiO$_2$ photocatalyst loaded with Pt, Au & Pd. As written above, photon absorption by TiO$_2$ can be hampered by too much deposition of metal particles and also it may lead to formation of centers for charge recombination, resulting in less efficiency.177

<table>
<thead>
<tr>
<th>Sl. No.</th>
<th>Dye</th>
<th>Class</th>
<th>$\lambda_{\text{max}}$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>01</td>
<td>Thionine (TH+)</td>
<td>Thiazin</td>
<td>596</td>
</tr>
<tr>
<td>02</td>
<td>Toluidine blue</td>
<td>Thiazin</td>
<td>630</td>
</tr>
<tr>
<td>03</td>
<td>Methylene blue (MB)</td>
<td>Thiazin</td>
<td>665</td>
</tr>
<tr>
<td>04</td>
<td>Eosin</td>
<td>Xanthen</td>
<td>514</td>
</tr>
<tr>
<td>05</td>
<td>Azure B</td>
<td>Thiazin</td>
<td>647</td>
</tr>
<tr>
<td>06</td>
<td>Azure A</td>
<td>Xanthen</td>
<td>535</td>
</tr>
<tr>
<td>07</td>
<td>Azure C</td>
<td>Thiazin</td>
<td>620</td>
</tr>
<tr>
<td>08</td>
<td>Phenosafranin (PSF)</td>
<td>Phenazin</td>
<td>520</td>
</tr>
<tr>
<td>09</td>
<td>Saf-O/SO</td>
<td>Phenazin</td>
<td>521</td>
</tr>
<tr>
<td>10</td>
<td>Saf-T/ST</td>
<td>Phenazin</td>
<td>524</td>
</tr>
<tr>
<td>11</td>
<td>Neutral red (NR)</td>
<td>Phenazin</td>
<td>534</td>
</tr>
<tr>
<td>12</td>
<td>Neutral red (NR)</td>
<td>Phenazin</td>
<td>534</td>
</tr>
<tr>
<td>13</td>
<td>Fluorescein</td>
<td>Xanthen</td>
<td>490</td>
</tr>
<tr>
<td>14</td>
<td>Erythrosin B</td>
<td>Xanthen</td>
<td>525</td>
</tr>
<tr>
<td>15</td>
<td>Dye</td>
<td>Xanthen</td>
<td>530</td>
</tr>
</tbody>
</table>

Table 11: Absorption wavelength maxima $\lambda_{\text{max}}$(nm) dyes$^{169}$


Increasing Photo Catalytically Active Area

Photo catalytically active field in a photocatalyst is a necessary factor that readily impacts \( \text{H}_2 \) generation rates. So, it was a concern to apply methods for enhancing photo catalytically active area. Two ordinary but efficient ways exist for enhancing the specific surface area. The first way is building uniform nanoparticle-containing thick surfaces and incorporating second material (nanowires, nano cells, nanoparticles, etc.) covering primary photocatalyst exterior is the second way. CdS nanorods as well as nanowire highly active photocatalyst for hydrogen generation can be produced through solvothermal & hydrothermal methods. Also, ultrasonic mediating precipitation, two-step aqueous route, and some additional ways can be effectively used to synthesis mesoporous (CdS) Nanoparticle.\(^{44}\)

Modification of Surface with Graphene and other Carbonaceous Material

At present, Surface moderation of the photo-catalyst is performed with carbonaceous materials such as graphene, graphene quantum dot (GQDs)s, carbon nano dots, carbon nanotubes (CNTs) and fullerenes (\( C_{60} \)) for improving \( \text{H}_2 \) generation in UV, UV-VM, and visible range area has drawn more remark because of the expanded visible-light absorption range and enhanced charge transfer:\(^{44}\) Graphene exhibits excellent electron mobility (200,000 cm\(^2\) V\(^{-1}\) s\(^{-1}\)), substantial surface area specific (2630 m\(^2\) g\(^{-1}\)), superior conductivity, electrical & thermal, and good chemical and physical stableness. Also, it is handily achievable from graphite bulk through mechanical, chemical, and thermal ways.\(^{175, 179}\) Zhang et al. pointed out the synthesis of graphene / TiO\(_2\) Nano composites and the improved photo catalytic hydrogen production through splitting of water, as well as observed that the photo catalytic performance of graphene / TiO\(_2\) Nano composites rely on rGO ratio and calcination process.\(^{180}\) In another work of Li et al., graphene quantum dot (GQD)/ TiO\(_2\) composite co-doped with sulfur and nitrogen (S.N-GQD/TiO\(_2\) photocatalyst) showed much improved performance than pristine TiO\(_2\) caused by improved visible radiation absorbance and efficient dissolution and transferring of photo generated charge.\(^{181}\) Fan et al. systematically conducted an inspection on reduction method influence on the hydrogen production performance of the Nano composite TiO\(_2\)/RGO, and observed that Nano composite produced through hydrothermal method showed the best performance in \( \text{H}_2 \) generation activity on UV-Vis light radiation.\(^{182}\) Also, Fan et al. observed that graphene quantum dot anchored TiO\(_2\) showed improved photo catalytic hydrogen generation performance on using methanol solution because of graphene quantum dots (GQD) operating as effective reservoirs for electron and fantastic photo sensitizer’s for Titanium dioxide.\(^{183}\)

Formation of Solid Solutions

A Solid solution production for compressing band-gap of semiconductors is a proper way to enhance efficiency for visible light absorption and utilization. Solid solution of ZnS and AgInS\(_2\), (AgIn) \( x \)Zn\(_{1-x}\) S\(_2\) consisting of a compressed band-gap exhibited high visible-light photo-catalytic hydrogen production activities from aqueous S\(^{2-}\) and SO\(_4^{2-}\) solutions for sacrificial purpose. On AgInS\(_2\) ratio increment to ZnS, the light absorbance of (AgIn) \( x \)Zn\(_{1-x}\)S\(_2\) solid solutions transferred to larger wavelengths because the photo-physical, photo-catalytic activities of (AgIn) \( x \)Zn\(_{1-x}\)S\(_2\) solid solutions were dependent upon the structure changing for band position variation.\(^{44}\) In addition, easily produced solid solutions from same crystal formation ZnS and CdS, ZnS-CdS photocatalyst are fantastically responsive towards visible-light for hydrogen generation.\(^{184}\)

Reactor Design & Development

A chemical reactor is an enclosed system in which chemical changes are takes place. The scheme/model of a chemical reactor deals with multiplex aspects of chemical engineering. Chemical engineers design a reactor to maximize the efficiency for the given reaction. Reactor modeling is a significant part in photo-catalytic water splitting systems as well as hydrogen production plants.

Factors to be consider for reactor design

- Geometrical set-up of the reactor
- Source of radiation (Natural or artificial)
- Catalyst (Slurry or hold in support)
- Sacrificial agents (CH\(_3\)OH, Waste Water, etc.)
- Light source position (35 - 45\(^{0}\) angle, Concentric)
- Sacrificial agents
- Irradiation time
- Shelf-life
Photo-Reactor Design
The photo-reactor is any chamber or vessel where reaction between the photo-catalyst and reactants takes place with the presence of photon (light) and Sacrificial reagents (where needed). Different types of reactor based on UV and visible light irradiation has been shown in Fig: 8. \(^{28}\) The photo-catalyst and light source are the main constituents of photo-reactor. For better photo-catalytic performance, an ideal photo-reactor must have uniform light distribution.\(^{185}\) Tactics of operation and phase are important factors which determine the types of photo-reactor. Here Table-12 demonstrates the benefits and drawbacks of different photo-reactors. Table-12 summarized the benefits and drawbacks of different types of photo-reactor.

Batch-type Photo Reactor
The batch type reactor is the primary photo reactor in reactor types. Here Fig: 9.0 exhibits a batch type photo reactor for the catalytic hydrogen evolution from water. This types of the batch reactor are consist of a catalysts bed, reaction vessel, cooling water system, Quartz windows, light source, evacuation system, sample collection system, and gas detection device.\(^{28}\) The water jacket around the reactor circulates water continuously to control the reactor and reaction temperature at a particular range. Light source will emit rays along the quartz windows.

Continuous Annular Photo-Reactors
Continuous annular photo-reactors are composed of a ring shaped reactor with a light source located in the center. The inert N\(_2\) environment is maintained into the reactor, to isolate the system from the surroundings. A constant flow of Ar gas bubble is provided through the reaction slurry to keep the suspension homogeneous. To analyze, a portion of the produced hydrogen gas is inserted to a gas valve of gas chromatography (GC). The benefit of continuous annular photo-reactors is to enhance the liquid-gas interfacial area, which simplifies the release of H\(_2\) from the photo-catalyst surface. One of the major drawbacks of these types of the reactor is, more photon can be received by the interior of the annular reactor than that of the exterior.

Photo Catalytic Membrane Reactor
Photo catalytic membrane reactor (PMRs) is effective for sustainable production of hydrogen by suppressing the reversed reaction between O\(_2\) and H\(_2\). Pure hydrogen can be obtained in a single step without further purification. In the case of PMRs design, photo-catalyst and metal loading, the mechanical resistance, permeability, membrane morphology are important factors to be considered and needed to get excellent efficiency of catalytic membrane system while in hydrogen evolution. There are various types of PMRs for hydrogen evolution, such as H-type Photo-catalytic
reactor (HPR), membrane electrode photo-catalyst assembly (MEPA), membrane twin reactor (MTR), and polymer membrane electrode assembly (PMEA).28

**Optical Fiber and Honeycomb Reactors**
Generally Optical fibers, made of silica, are used to transmit light from one end to another end of the fibers. Light is split into two parts by the variation of refractive index between the quartz core and the semiconductor, such as TiO$_2$, coating during hitting the internal surface of the fiber.28 Some portion of the light is transmitted and reflected through the fiber, while the rest fraction excites and penetrates the titanium layer on the interface. Thus, photo-reactions occur through the formation of electron-hole pair. As a result, optical fibers are utilized to radiate the light properly in the interior of a photo-reactor.187 Light is passed through the fibers core by forming a cover which is lower refractive index that captures light beam in the core through total internal reflection.188 Formerly, H$_2$ production rate was increased through photo catalytic water splitting using optical fiber coated with SiO$_2$ and TiO$_2$.189 There are several benefits of optical fibers such as: It has higher efficiency enlighten the interior of reactor uniformly and it causes higher interactions between irradiations and catalyst surface.

**Monolith Reactor**
It is a multifunctional reactor which is integrated with separation and heat exchanger. The designs of a monolith reactor are uniform sets with a parallel line that can be constructed into various configurations (sizes and shapes). Application of monolith reactor having a narrow path with larger light beam interaction surface area (SA) can enhance the transformation and product rates.190 Because of its excellent properties the Ceramic monolithic reactor formations shows an attractive choice to commonly designed catalyst nubbles or powders. Monoliths has several advantages over typical catalyst powders or nubbles, such as: improved weight transfer rate, good coating adhesion, better porosity, minimal pressure fall, better thermal and mechanical strength.191 Current improvement in photo (light) technology exhibited that, when compared with other commercial reactors, the monolith reactors have several benefits over them. In 2017, splitting of water for hydrogen evaluation with sacrificial agent, ethanol, in a monolith photo-reactor has been tested by Gaudillere et al.192 According to Tahir Met al., the quantum efficiency (QE) in micro-channel monolith reactor gave much higher (0.10%) than deal with cell type reactor (0.0005%).193 In another analysis performed by Tahir Met al. they used/applied photo catalyst NiOeIn$_2$O$_3$/TiO$_2$ which showed superior performance in the batch type monolith photo reactor than considering cell type reactor under identical conditions of reaction with efficiency of 14.13 times higher.194

Fig. 10: The pictorial representation of an optical fiber honeycomb reactor185

Fig. 11: The pictorial representation of a photo-reactor (large scale) for photo-catalytic reactions with an immobilized photo-catalyst196
**Particulate Photo Catalytic Reactor**

Particulate photo catalyst reactor systems are narrated here having some facilities in case of designing cost and scale-up potential as compared with photo electrochemical and photovoltaic systems.\(^{195}\) However, the development of photo catalytic water splitting set up even to the one to one meter scale has rarely been published, although the ultimate demand of fabricating plants tens of square kilometers.\(^{186}\) Elsewhere, the power generation through photovoltaic system have been installed and commercialized in an extend phase. This indicates a non-stop challenge to the application of photo-catalytic splitting of water as a way of production of solar fuel.

Formerly, photo-catalytic water splitting has been studied in flask-type reactors using suspensions of photo-catalyst powders on the small-scale. Nevertheless, the disadvantage in the development of suspension systems can be guessed from the deficiency of big-scale displays of water splitting by sunlight overall with noticeable values of STH. Honestly, this an attempt is annoying on big scales for various factors.\(^{186}\) Firstly, it is challenging to lessen the costs of reactor, such as huge water is required. For example, 1 cm depth, water quantity in a reactor increases in values of 10 kg one square meter and reactors seem to be larger and high cost. This is not be feasible on a big scale production process assuming that the highest cost allowed for the complete hydrogen production systems is about US$102 m\(^{-2}\), as mentioned earlier.\(^{196}\) Secondly, there is a tendency of the particulate photo-catalysts to precipitate to the basement of the reactor if not the reactor is positioned perfectly. They do not receive incident light effectively too. Tubular shaped reactors combined with a CPC (compound parabolic concentrator) have been experimented for big scale industrial operation of photo-catalytic hydrogen evolution reactions (HER) in the availability of sacrificial reagents (SR).\(^{197}\) In the research done by Jing et al., CPCs contain the highest half incident beam angle of 14°, length of 0.4 m, and whole arm of 1.5 m, and pyrex reactor tubes 1.6 m in length were used. However, as particulate photo-catalytic reactor is scalable and it has low operation and maintenance cost, it is more effective than others.

### Table 12: The benefits and drawbacks of different types of photo-reactors

<table>
<thead>
<tr>
<th>Reactor Type</th>
<th>Findings</th>
<th>Drawbacks</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Slurry reactor</td>
<td>• Can be operated in fixed bed mode or continuous flow patterns</td>
<td>• Continuous stirring causes the additional cost</td>
<td>28, 185</td>
</tr>
<tr>
<td></td>
<td>• Combination of gas-liquid-solid phase</td>
<td>• Active contact surface for reaction is low</td>
<td></td>
</tr>
<tr>
<td>Fluidized reactor</td>
<td>• High photo-catalytic activity</td>
<td>• Abrasion of particles and attrition of the catalyst may causes erosion in reactor difficult to separate from mixture</td>
<td>188, 198</td>
</tr>
<tr>
<td></td>
<td>• Efficient rate of heat and matter transfer by vigorous excitation of solid</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Optical reactor</td>
<td>• Surface area is larger</td>
<td>• Deactivation catalyst at high temperature</td>
<td>188</td>
</tr>
<tr>
<td></td>
<td>• Efficiency of light utilization is higher</td>
<td>• Maximum reactor volume cannot be applying Uniform coating of fibers is complex</td>
<td></td>
</tr>
<tr>
<td>Monolith reactor</td>
<td>• Ratio of surface to volume is higher</td>
<td>• Light efficiency is low</td>
<td>188, 198, 199</td>
</tr>
<tr>
<td></td>
<td>• Pressure drop is low</td>
<td>• Catalyst adhesion on wall is lower</td>
<td></td>
</tr>
<tr>
<td></td>
<td>• Flow rate is higher</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fixed bed reactor</td>
<td>• large Surface area</td>
<td>• low Light efficiency</td>
<td>188, 198, 199</td>
</tr>
<tr>
<td></td>
<td>• minimum reaction period</td>
<td>• lower adhesion</td>
<td></td>
</tr>
<tr>
<td></td>
<td>• Lower Operating cost</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Particulate photo-catalyst reactor</td>
<td>• Minimal fabrication cost</td>
<td>• reactors tend to be bulky</td>
<td>186</td>
</tr>
<tr>
<td></td>
<td>• High scale up potential</td>
<td>• water is required in large volumes</td>
<td></td>
</tr>
<tr>
<td></td>
<td>• Operating cost is lower</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Process Parameters for Photo Catalytic Reaction

- Light intensity or Irradiation of light
- Temperature effect
- PH effect
- Reactor design
- Oxygen vacancies
- Presence of Sacrificial agents
- Miscellaneous factors affect

Light Intensity

The higher hydrogen production rate is linearly related to light irradiation. The effectiveness of photo catalytic splitting of water can be improved with the rise in light intensity generating power more than the threshold level of activation. Two regions are available related to the photo-catalytic reaction related to the UV photon flux. One region is for laboratory research fluxes which are 25 mW cm-2. Compare to the reaction of recombination the hole electron couple is consumed quicker in a chemical reaction. During the half-order region, the intensity remains higher, the recombination rate is a major factor and creates less change on the rate of the change the reaction process. The change of the value of the reaction rate is related to the wavelength which appears following the catalyst spectrum of the adsorption with a minimum reading level with respect to the band potential energy. In the year 2013, Baniasadi et al announced that the rate of hydrogen generation from Zinc-Sulfide (ZnS), increased by 20% with rise in intensity range of light from 90 to 100 mW cm-2. In another research work report by Leon and Tambago, indicated that the hydrogen (H₂) production increased using Cd0.4Zn0.6S while the intensity of light was increased.

![Graph: Comparison of photo-catalysts for hydrogen (H₂) generation under irradiation of solar Light for TNS (titanium nano sheet), TNT (titanium nano tube) and TNR (titanium nano rod).]

Table 13: Temperature effect on H₂ production rate

<table>
<thead>
<tr>
<th>Sl. No.</th>
<th>Temperature°C</th>
<th>H₂ production rate</th>
<th>Catalyst</th>
</tr>
</thead>
<tbody>
<tr>
<td>01</td>
<td>30°C</td>
<td>59.00 mol/g.s</td>
<td>Pt/TiO₂</td>
</tr>
<tr>
<td>02</td>
<td>40°C</td>
<td>92.00 mol/g.s</td>
<td>Pt/TiO₂</td>
</tr>
<tr>
<td>03</td>
<td>50°C</td>
<td>370.00 mol/g.s</td>
<td>Pt/TiO₂</td>
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</table>

Temperature Effect

The photo-catalytic behavior of catalyst material is introduced by temperature, since electron and hole generation is not related to it directly. But, the temperature has a crucial role to improve desorption of hydrogen gas (H₂) from the surface area of the considering catalyst to accelerate the effect of photo catalyst. It is thermodynamically established that, temperature ameliorates the reaction process in maximum cases. The rate of change of applied temperature differs according to the change of catalyst. The photo-catalytic activity could be increased by the adjustment of the factor. The hydrogen (H₂) production becomes slower when the value of the temperature goes down. In this process desorption limits the reaction mechanism. The higher valance electron in the valance band will be transferred to higher energy levels during high-temperature conditions. The electron and hole generation will initiate oxidation & reduction reaction.
Paucity of oxygen can be produced by applying water-splitting process, an electron is generated throughout the reaction process. A significant organic species is needed for the proton reforming. It is recommended to generate hydrogen in a strongly acidic solution rather than in a basic solution (pH>7). Similarly, the band gap potential shift also depends on pH value. In a CuOx/TiO2 catalytic medium with basic medium (pH 10) hydrogen production is maximum. The atom copper Cu (I) shows unstable behavior in TiO2 based acidic medium. In the visible light TiO2 part of the catalyst, Si/CdS/TiO2/ Pt is unstable in a strong base or acidic reaction. The optimum pH value of a photo-catalytic reaction for better hydrogen production rate in CuAlO2/TiO2 catalyst surface is 11.2 The catalyst Pt/r-TiO2 has the ability to produce hydrogen up to 56.6mmol in a pH condition at 5.5 during 4h of operation from pH value 12 to 2.0 (211). The hydrogen generation is 1200mmol g−1 h−1 in NiO/TiO2 catalyst in a pH condition 6.6. So the hydrogen generation is directly depends on the accurately pH reading of the reaction where the best pH reading is about zero [0.00] charge value.212 In an acidic solution of methanol-water the photosensitized TiO2/RuO2-MV2+ catalyst can generate enough hydrogen (H2).213 The reduction reaction of hydrogen from H+ to H2 can be increased when more protons are present on the surface of the regarding catalyst in an acidic solution (pH<7). The hydrogen generation is rapid in the acidic solution than in the basic solution.203 So in a photo-catalytic reaction the hydrogen production is better in the acidic solution.

Oxygen Vacancy
Oxygen vacancy is a significant factor to enhance H2 production as well as the ionic longevity increase. Paucity of oxygen can be produced by applying metal oxides with the process of catalyst synthesis, decreasing value and mixture.214 When the titanium-oxide (TiO2) is used as the titanium ion and oxygen gap are created at the same time. More titanium ions are produced because of the increasing oxygen gap. As a result, there is a situation of titanium defects, amorphous surface area disorder, and finally relative oxygen gap. This oxygen gap indirectly related to electron stability because of the absence of oxygen ion. Whereas, the regular lattice of the oxygen atom was taken by electrons, and the local state was formed by oxygen vacancies and Ti3+. Then, the VB holes of TiO2 were generated and the electrons excited to the CB of TiO2. At CB, the H+ reduce to H2 through a reduction reaction.215 So hydrogen gas generation without the recombination of the electron-hole and the amelioration of the charge longevity is the main aim to be achieved.

Reagent for Sacrificial Behavior
By introducing organic species in the reaction process the efficiency of the photo-catalyst can be improved. For example Methanol, Ethanol, phenol, and Glycerol can act as reaction agents which will be sacrificial. Relative to the water molecule, organic species behaves like a hole which will be a scavenger.216 Photo-catalysis process is one of the major way of sustainable hydrogen production. Now the effect of the sacrificial agents in the way of hydrogen production must be fruitful. This hydrogen production can be accelerated using alcohol. This process is also known as photo-reforming. Because alcohol helps semiconductor in oxidation and reduction reaction. The activity order of sacrificial reagents is, Glycerol > Ethylene glycol > Methanol > Ethanol.217 The hydrogen gas generation is a dependable factor with respect to the alpha hydrogen. Glycerol has a unique structure with five alpha hydrogen which is major than glycol, methanol and ethanol. On the other hand hydrogen generation is also have a relation with the concentration of alpha hydrogen and concentration of the agents.218

Figure:-13 exhibits the outcome rate of hydrogen with the increment of methanol percentage and reaction time. It shows that at 5%methanol concentration the value hydrogen production rate is optimum. But further concentration rise does not help further in hydrogen production. The reason behind it may be the saturation of catalyst surface. When the surface
area of the photo-catalyst goes to a saturated level then the hydrogen production does not rise further. So only a certain level of hydrogen production rate can be maintain from all the arrangement.

**Fig.13 : The photo-catalysts comparison for hydrogen generation in the irradiation of solar Light for TNS, TNT and TNR**

**Table 16:A Summary of numerous sacrificial reagents used in photo-catalytic H\textsubscript{2} production process**

<table>
<thead>
<tr>
<th>Year</th>
<th>Feed</th>
<th>Catalyst</th>
<th>Reactor/Parameter</th>
<th>Efficiency</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>2019</td>
<td>10 % ethanol -water</td>
<td>.05 g TiO2/MMT</td>
<td>Slurry reactor 40 W Xe lamp</td>
<td>methanol &gt;ethylene glycol &gt; ethanol &gt;&gt; propanol &gt;Glycerol</td>
<td>219</td>
</tr>
<tr>
<td>2017</td>
<td>15% glycerol -water</td>
<td>85 mg</td>
<td>Pyrex reactor 130 W Hg lamp</td>
<td>Pt&gt;Pd&gt;Au glycerol &gt; Propan-2-ol</td>
<td>220</td>
</tr>
<tr>
<td>2016</td>
<td>25 % n-propanol -water</td>
<td>50 mg 0.5 % RuO\textsubscript{2}@TiO\textsubscript{2}</td>
<td>Glass reactor Medium pressure</td>
<td>MeOH &gt; t-BuOH &gt; n-BuOH, PrOH&gt; n-EtOH</td>
<td>221</td>
</tr>
<tr>
<td>2015</td>
<td>15% 2-propanol -water</td>
<td>0.065 g &amp;1 wt% Pd</td>
<td>Tubular reactor UV (375 nm, 10 mW cm-2)</td>
<td>Pd&gt; Pt z Au. methanol &gt;2- ethanol &gt;propanol &gt;t-tert-butanol ethylene &gt; anhydrous glycol &gt;Methanol</td>
<td>222</td>
</tr>
<tr>
<td>2015</td>
<td>5% methanol -water</td>
<td>450 mL water solution,</td>
<td>Quartz reactor system 250 W Xe arc lamp, 30C under atmospheric pressure</td>
<td></td>
<td>223</td>
</tr>
<tr>
<td>2015</td>
<td>5% glycol -water</td>
<td>6.5 mg 1.5 wt% Au/P25</td>
<td>Tubular reactor SB-100P/F lamp (100 W, 265 nm)</td>
<td>Au/P25 &gt; Au/brookite&gt; Au/anatase</td>
<td>217</td>
</tr>
</tbody>
</table>

**Conclusions**

In comparison with cleanness and high calorific value Hydrogen is now a burning issue for today’s energy regulatory authorities rather than other fuels like fossil, wind, solar, or another renewable. However, in nature H\textsubscript{2} is not available in free form (i.e. atomic state). Among various H\textsubscript{2} production process low-cost H\textsubscript{2} is available from fossil i.e. petrochemicals, but the main question that arises here is the sustainability of this process. To ensure affordable and clean energy (SDG Goal-7) Sunlight to Hydrogen or STH is the best solution. While comparing with other traditional fuels H\textsubscript{2} is a Future dominating fuel with its best transportation, storage, transmission, and cleanness. Photo catalysis is the best way to achieve maximum STH conversion with less set-up and reagent cost. However, there are still so many technical drawbacks in catalytic
water splitting as this technique still not mature enough. Several researchers are trying to develop this process from the different technical corners like catalyst development, process parameter optimization, reactor design, etc. Some other catalyst development techniques like Sensitization with noble metal loading, Increasing Photo catalytically Active Area, modification of Surface with graphene and other Carbonaceous material, Formation of Solid Solutions, and Modification of Photo-catalysts with Co-catalysts are also studied to develop Photocatalytic efficiency of catalysts. Among all techniques doping, Heterojunction and Dye sensitization shed a light on development techniques for efficient catalyst synthesis. Within this three-technique, the development of doping in the different catalysts is the most promising one. Doping in the catalyst surface may extend its photonic response from the UV region to the visible length of electromagnetic radiation by forming an impure energy band. However, there is still a lot to work on the photocatalytic water splitting process for better understanding and smooth future of this process.

**Highlights**

- Photo-catalytic water splitting is a promising Green-Harvesting technique among all H₂ generation methods
- Doping, Heterojunction and Dye sensitization shed a light on development strategies
- Elemental doping exhibit’s maximum efficiency while doping with rare earth metals

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**Conflict of Interest**

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