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Various Material Development Strategies for Suitable Catalysts of Photo Catalytic Water Splitting to Green Fuel H_2: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 H_2 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 H_2 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 sensitization, 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.

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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,

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hydrogen fuel may be a solution for this crisis. H_2 is a fantastic energy conveyer with a high CV and clean property. As a bountiful element, H_2 appear in many substances in the earth likely seawater, Biogas, freshwater and fossil fuels, etc. For the production of H_2 with zero or low impact on the environment, almost all Carbon-dioxide with other unwanted particulates should be separated when H_2 is produced from fossils.[2] Till now, hydrogen is mainly synthesized via steam reforming method where CO_2 is formed simultaneously. And this CO_2 is the key concern for today's environmentalists, as it is the major greenhouse agent. Photo-catalytic 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. For ultra-pure H_2 production, electrolysis is a more reliable, technically sound, and widely acceptable system. Electrolysis is a technique where direct current (DC) is used to drive the anion-spontaneous electrochemical reaction.[3] To run this technique, immaculate power hubs may be engaged like as solar-powered energy, geothermal based energy, biogas energy, wind-powered energy, ocean and others. The energy produced from nuclear energy sources may also be used for driving this process. Hydrogen produces in this technique is purer than any other technique, O_2 production was also high in this technique. But the major disadvantage of this technique is that a huge amount of electricity is needed to run the electrolysis technique and the initial set-up cost is expensive in amount. The major reaction involve with the electrolytic technique of water is generally written as:

$$2H_2O \rightarrow 2H_2 + O_2 \qquad E_0 = -1.229\ V$$

On the other hand, thermochemical processes are another convincing process for hydrogen production. The thermochemical system is the process which mainly driven by heat as its primary energy. This type of process for the production of hydrogen is considered as the viable process for the probable alternative of the previous one. Most alluring support from thermochemical production cycles is no requirement of catalysts or agents to drive the process reactions.[4] All chemicals, without water (main raw material), used here can be reused easily. Other mesmerizing support of these types of degradation process are: (a) H_2 and O_2 can be separate from mixture gas without membrane; (b) optimum energy requirement range of 327–927°C; & (c) less electrical power consumption. This requirement of power can be provided by concentric solar energy, the geothermal energy, biogas, nuclear electricity, and other sources.[5] But the challenges of this technique is that the bulk amount of heat supply source is not available in everywhere and artificially generation of heat is also costly. Here alleviate temperature degradation of catalyst is a major challenge, which retard the hydrogenproduction rate.

On the other hand, thermolysis is another significant way of electrolysis where H_2O is split to H_2 and 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 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 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 artificial generation of heat is also costly.

Bio-photolysis as well as photo-fermentation techniques are familiar as photon-based biochemical

H_2 generation from water. The main privilege of this technique is the capability to generate H_2 from H_2O in aqueous media at conditioned temperature & pressure.[8] 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.[9] Cultured microalgae isolates have the capacity to produce H_2 in a closed system and they show high H_2 yields. The primary hydrogen generation reactions using photo-activated enzymes are the following:

$$6H_2O + 6CO_2 \xrightarrow{hv} C_6H_{12}O_6 + 6O_2 \quad ...(1)$$

$$C_6H_{12}O_6 + 6H_2O \xrightarrow{hv} 6CO_2 + 12H_2 \quad ...(2)$$

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 H_2 in absence of light.[10] 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 H_2 production by dark fermentation like, (1) H_2 production from organic waste and (2) stabilized & control in bio-waste for reducing potential danger of pollution.[11] The dark fermentation process can be implemented in water treatment units for H_2 production from organic wastewater. H_2 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 H_2 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).[12]

$$2H_2O \rightarrow 2H_2+O_2 \qquad \Delta G°=237.0 \text{ KJ/mol} \quad ...(3)$$

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 (H_2) gas production through photo-catalytic water splitting, photovoltaic cells, and dye-sensitized solar cells.[13] Photo-electrochemical water splitting process by Fujishima & Honda in the year of 1972 is most variant of this technique.[14] Following this way, till now H_2 production by Photocatalytic water splitting is considered as a promising technology for green energy revolution.[15-17] (TiO_2) titanium oxide,[18-20] (g-C3N4) Graphitic-Carbon Nitride[21-23] and (CdS) Cadmium Sulfide[24-26] are three widely studied catalysts for water splitting in the last few decades. Among them, titanium oxide (TiO_2) is found to be more superior, and a benchmark photo-catalyst still now.[27]

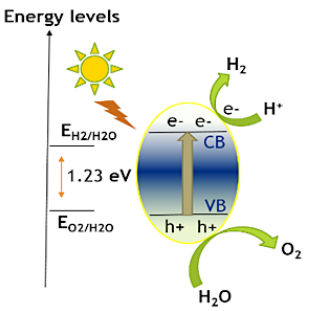


Fig.1: Photo-catalytic H_2 productionusing suitable semiconductor[28]

Due to its photostability, efficiency, band edge, non-toxicity and sustainity it became a burning topic in this sector.[29-34] The mechanism of Photocatalytic activity of TiO_2 based catalyst for water splitting are illustrated in Fig. 1.0.[35] The overall water splitting reaction on a photo-catalyst comprised of the following half reactions:

$$H_2O+hv+VB \rightarrow 2H^+ + ½O_2 \quad ...(4)$$

$2H^{+}+2e^{-}+CB \rightarrow H_2$ ...(5)

Overall reaction: $H_2O \rightarrow H_2+½O_2$ ...(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 H_2 production are also explained here.

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

Catalyst	Morphology	Synthesis method	Source of irradiation	H_2 generation rate	Ref.
Ag/TiO_2, Hg	nanoparticle	sol-gel	Vapor lamp (365 Nm)	910 mmol g1 h1	48
Ni/TiO_2, Pyrex	nanosheets	solid state reaction	F lamp, 100 W (365 Nm)	26,000 mmol g1 h1	49
Fe^{3+} ions doped and Ag deposited TiO_2	nanoparticle	solvothermal	UV light Source	515.45 µmol/h/g	50
Fe/TiO_2	Na	anodization	xe arc lamp	174.30 mmol g1 h1	51
Cu/TiO_2	nanotubes	anodization	300 W, xenon, lamp	28,700 mmol g1 h1	50
Au/TiO_2	Na	anodization	300 W, xe lamp	3550 mmol g1 h1	52
Cu/TiO_2	nanoparticle	commercial tio_2	125 W, Mercury Vapour lamp (High Pressure)	01–07 µmol/min	53
Pt or Au/TiO_2	nanotubes	anodization	Xe/Hg lamp (High Pressure)	.06 µmol/cm2/h	54
$Au/Ti_{0.9}O_2$	nanosheets	solid state reaction	xe lamp 300 W	6753.00 µmol/h/g	55
TiO_2/WO_3/Au	Na	electrospinning	Xe Arc lamp,300 W	270 µmol/h	52
rutile TiO_2	nanosheet	solvothermal	300 W, xenon lamp	22 mmol/g/h (5 h)	56
N/TiO_2, PdO & Pt loaded $NTiO_2$	nanoparticle	sol-gel	400 W, mercury lamp	55.0,544.0,772.0 µmol/h/g	48
SMK-TiO_2	nanoparticle	sol-gel	150 W Mercury lamp (Medium Pressure)	3.3 mmol/240 min	57
Co-moderated TiO_2	nanoparticle	commercial TiO_2	300 W, Xenon lamp	Nanoparticle	58
Ag-Fe/TiO_2	nanotubes Ti sheet (> 99% purity)	electrochemical	Xenon Lamp & Hg Llamp	Nanotubes Ti Sheet (> 99% Purity)	53
$Cu(OH)_2/TiO_2$	nanotube arrays	electrochemical anodization	300W, Xe lamp	Nanotube Arrays	59

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

involves high quantum yield; being inexpensive, earthly abundance, recyclable, nontoxicity, resistant to corrosion, and photo-stable; and also must have a long lifetime.[36] TiO_2, since Fujishima and Hondas study at 1972, has been regarded amongst the most preferable photo-catalysts for splitting water for its conveniences, e.g. being abundant, inexpensive, noncorrosive, photo-stable, and environmentally friendly.[14] Nevertheless, TiO_2 can use only UV light for H_2 evolution for its vast band-gap energy of 3.2 eV, separated electrons and holes in VB and CB of TiO_2 can swiftly recombine and release energy or useless photons that barricade its practical utilization for Photocatalytic H_2 generation using solar energy.[37] Solar energy utilization basically depends on the electromagnetic wavelength of radiation in which photocatalyst shows activeness. Within 400 nm, the conversion efficiency of solar energy does not reach beyond 2%.[38] Efficiency improves to 16% and 32% if the spectral wavelength reaches 600 and 800 nm respectively. Oxides other than TiO_2, e.g. Cu_2O, WO_3, Fe_2O_3, and $BiVO_4$, were also examined for photo-catalytic H_2 production, but their photo-catalytic efficiency for hydrogen evolution is still restricted by small amount of light-harvesting, large electron-hole recombination rates, and poor transportation of charge.[39] In times of $BiVO_4$, its edge position is inconvenient for HER. For Cu_2O, the efficiency solar to energy conversion is 18.0% theoretically, and it is vulnerable to auto-reduction in aqueous medium.[40] That's why it is very important to develop new photo-catalysts to use the visible range and near IR region wavelength. Metal-free and Earth-rich catalysts such as g-C_3N_4, graphene, oxide of graphene, carbon nano-tubes have been examined greatly owing to its possible cost minimization in the time of scaling up.[41] In recent times g-C_3N_4 based materials free from metal have gained popularity for application in splitting of water.[42] However, the catalyst g-C_3N_4 still suffering from many drawbacks, for instance insufficient surface morphology, reduced conductivity & large recombination rate.[43] Another significant catalyst named metal-organic frameworks or MOFs are excellent photo catalyst for photo catalytic H_2 generation.[44] MOFs are composed of inorganic ions and organic substrate, which function as linking point & as connectors, correspondingly.[45] At last Researcher heed their concentration on catalyst development by implementing different technique such as Doping, Nanostructure, Heterojunction, Dye sensitization, Formation of Solid Solutions, Sensitization with noble metal and Increasing Photo catalytically Active area etc.[46] Amid all of the technique applied Doping and Heterojunction is more striking.. Table 01 gives the recent update on catalysts with various morphology & photocatalytic H_2 production efficiency.[47]

Material (Catalyst) Development techniques

Most decisive characteristic of a photocatalyst are: its optimum band gap, surface morphology, crystal structure and stability under light irradiation.. TiO_2 based photocatalyst orAnatase TiO_2 is the photocatalyst mostly subjected to modification techniques to enhance H_2 production. Other oxides, e.g. g-C_3N_4, Cu_2O, WO_3, Fe_2O_3, and $BiVO_4$, were also studied for photo-catalytic H_2 production, rather their performance or efficiency for photocatalytic H_2 evolution is evaluated by some factors like, light harvesting time and rate, charge recombination, band edge and low charge transportation.[60] Also, catalysts such as g-C_3N_4, oxides of graphene, graphene, nanotubes, and CDQs have been extensively investigated to develop their properties as they can exhibit better efficiency.[61] Scientists are trying to develop the catalytic activity of photo-catalysts through several techniques. Some of these are

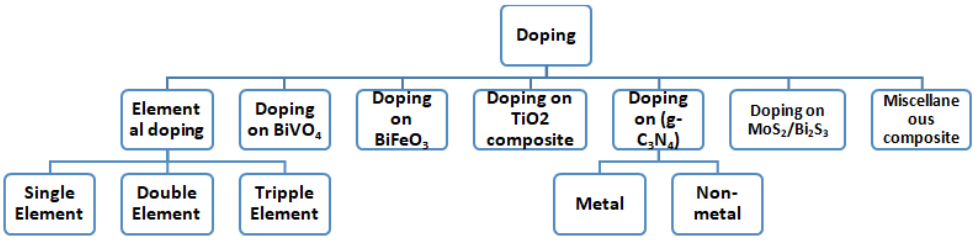
Catalyst Development techniques

- 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.[45] Catalyst modification induces

more charges due to the reduction of band gap, hence exciting more electrons for the production of hydrogen.[61] TiO_2 is one of the prominent and pioneer catalyst with maximum efficiency from 1972 to now. Here, metal and non-metal doping of TiO_2, elemental doping on titanium-based catalyst, doping on the various composite catalyst, such as g-C_3N_4, $BiVO_4$, MoS_2/Bi_2S_3, $BiFeO_3$ 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 $SrTiO_3$ base lattice, Ti^{4+} (0.0605 nm) will be replaced by Ta^{5+} (0.064 nm) and Cr^{3+} (0.0615 nm) ions where F (0.133 nm) atom will replace by O_2 (0.140 nm).[62]

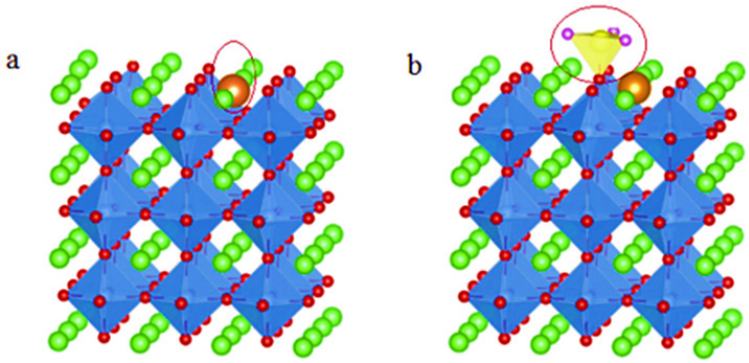


Fig. 2 : A 3-Dimensional representation for elemental doping on $SrTiO_3$[62]

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 $CaTiO_3$ shows an excellent result in H^2 production with a rate of 1447.8 mmol h^{-1} under irradiation of UV light.[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 $CaTiO_3$ doping with Cu shows highest H_2 evolution rate of 1447.8 mmol h1 with UV light.[64] According to Shen P *et al*. $SrTiO_3$ catalyst, synthesized by polymerization method yield 47.00 mmol h1 H_2 evolution rate under λ>420.0 nm & λ<800.0 nm light irradiation while doping with Rh metal atom.[64] On the other hand according to the study of Sun X *et al*. Sr_2TiO_4 exhibit maximum hydrogen evolution i.e. 97.7 mmol h1 when doping with Cr under light

irradiation of (λ>250 nm, visible).[65] 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 $SrTiO_3$ catalyst while doping with Zn and Cr respectively under UV light irradiation.[66, 67] They synthesized the catalyst matrix in Sol-gel method. However, a significant result was found by Zhang H *et al*. from the catalyst Ti0.98Cu0.0$_2$O$_3$ by Ca doping system under UV light irradiation. Zhang H *et al*. found that 1447.8 mmol h1 hydrogen evolution from catalyst while doping with Ca with Sol-gel method.[64]

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

Results obtained by single-element doping to titanate-based perovskites						
No	**Catalyst**	**Dopants**	**Method**	**Light source**	**H_2 generation rate**	**Ref.**
1	$SrTiO_3$	Rh	polymerizable complex,	UV lamp	47.00 mmol h1	63
2	$Ti_{0.98}Cu_{0.02}O_3$	Ca	sol-gel	UV lamp	1447.80 mmol h1	65
3	Sr_2TiO_4	Cr	solid-state reactions	visible	97.70 mmol h1	66
4	$Ba_{5/6/6}TiO_3$	Zn	sol-gel	UV lamp	2.90 mmol h1	66
5	$Sr_{2/3}TiO_3$	$Zn_{1/3}$	sol-gel	UV lamp	12.10 mmol h1	64
6	$SrTiO_3$	Cr	hydrothermal	visible and UV lamp	9.30 mmol g1 h1	67

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 g1 h1 only with visible light (l > 415 nm) in $SrTiO_3$, Ta^{5+} and Cr^{3+} at Ti^{4+} sites compared to 97.7 mmol h1 H_2 evolution rate for doping of $SrTiO_3$ with Cr. High improvement, above two-fold, in case of Ta addition.[65] Furthermore, the reported rate of H_2 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 Cr^{3+}, 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 $SrTiO_3$ was more about twice than that of mono element doped $SrTiO_3$, while fabricated through the same method. For B 2p electron, top valence band position was around 0.38 eV.[67] But as Kang & Parkreported the performance of composite catalyst material doped with double-element (15.4 mmol h1) was less than that of (Cr, Ta):$SrTiO_3$.(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

Outcomes of titanate-based perovskites listed through doping with double element						
No	**Catalyst**	**Dopants**	**Method**	**Light source**	**Rate of H_2 generation**	**Ref.**
1	$SrTiO_3$	Ta, Cr	spray pyrolysis	λ>415 nm	211.4 mmol g1 h1	68
2	Sr0.9Bi0.1Ti0.9	Fe0.1O3	solid state	λ > 250 nm	185mmol g1 h1	69
3	$SrTiO_3$	B, Cr	hydrothermal	visible & UV	15.41 mmol g1 h1	67
4	$CaTiO_3$	La, Ag	sol-gel with ultra-sonication	visible & UV	1064mmol g1 h1	70
5	$SrTiO_3$	Al, Au	solid state	visible & UV	348 mmol g1 h1	71

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 byKang 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+} & T^{4+} in the sites B of the substrate, decreasing barrier towards the energy of activation and reducing stability.[68]

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

Outcome of perovskites (titanate-based) listed through doping with tri-element						
No	**Catalyst**	**Dopants**	**Fabrication Method**	**Wave Nature**	**Rate of H_2 generation**	**Ref.**
1	$SrTiO_3$	F/Ta/Rh	spray pyrolysis	visible range	123.70 mmol g1 h1	[71]
2	$SrTiO_3$	Ta/F Cr	spray pyrolysis	visible range	3887.5 mmol g1 h1	[62]

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 g1 h1 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 g1 h1 hydrogen was evaluated from the$SrTiO_3$ 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.[71]

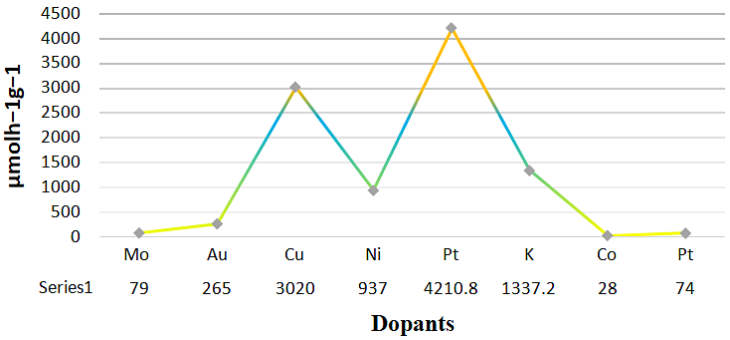


Fig. 3: Metal doping on g-C_3N_4 based photo

Doping on Photo-Catalysts based on Graphitic Carbon Nitride (G-C_3n_4)

Doping with Metal

Recently Graphitic carbon nitride(g-C_3N_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.[72] 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.[73]

Also g-C_3N_4 shows exceptional photoluminescence (PL) characteristics, making it unstable as quality co-catalyst for other semiconductor catalysts.[74] But in practice, implementation of g-C_3N_4 as photo catalyst is limited, due to smaller specific surface area and high rate of recombination of photo induced charges.[75] Ultimately, Doping is one of the effectual initiative for adjusting electronic formations of g-C_3N_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.[76]

In the year 2014, Zhong Y *et al*. conduct Pt doping on photo-catalysts based on Graphitic carbon nitride (g-C_3N_4), under light irradiation of (300 W Xe lamp, I >420 nm) in Quartz reactor. They get hydrogen flow rate of 41.7 $\mu molh^{-1}g^{-1}$ which was not significant to continue further work. Further in 2015 prominent researcher Huang Z *et al* and Ma L *et al*. again dopedg-C3N4 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.[77,78] Ma L *et al*. found 89.28 $\mu molh^{-1}g^{-1}$ hydrogen production rate while Huang Z *et al*. found 261.8 $\mu molh^{-1}g^{-1}$ in Quartz reactor. In 2018, Wang Y *et al* doped potassium (K) on Graphitic carbon nitride (g-C_3N_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_3N_4 produce maximum 1337.2 µmol hydrogen at one hour.[79] In the same year, another study of Liu M *et al*. shows maximum 4210.8 $\mu molh^{-1}g^{-1}$ efficiency of Graphitic carbon nitride (g-C_3N_4) based ,while doping with platinum (Pt).[80] But in 2019, Chen D *et al*. found 79.00 µmol hydrogen by Mo doping on Graphitic carbon nitride (g-C_3N_4) based photo-catalyst.[81]

Table 5: Metal doped photo-catalysts based on g-C3N4 for H2 production

Year	Photocatalyst	Dopant (metal)	Reactor	Light Source	Efficiency $\mu molh^{-1}g^{-1}$	Ref.
2019	g-C_3N_4	Mo	Pyrex reactor(P)	Xe lamp, 300 W	790.0	81
2018	g-C_3N_4	Au	Pyrex reactor(P)	Xe lamp, 300 W	265.00	82
2018	g-C_3N_4	Cu	Pyrex reactor(P)	Xe lamp, 300 W, I >430 nm	3020.00	83
2018	g-C_3N_4	Ni	Quartz reactor (Q)	,Xe lamp, 300 W, I >430 nm	529.10	84
2018	g-C_3N_4	Ni-P	Pyrex reactor(P)	Xe lamp, 350 W	937.00	85
2018	g-C_3N_4	Pt	Pyrex reactor (P)	Xe lamp,350 W	4210.80	80
2018	g-C_3N_4	K	Pyrex reactor (P)	Xe lamp, 300 W I ¼ 420 nm	1337.20	79
2017	g-C_3N_4	Co	Pyrex reactor(P)	Xe lamp, 300 W, I > 420 nm	280.00	86
2017	g-C_3N_4	Pt	Pyrex reactor(P)	Xe lamp, 300 W, I ¼ 400 nm	740.00	87
2015	g-C_3N_4	Pt	Quartz reactor(Q)	Xe lamp, 300 W, I >420 nm	262.00	88
2015	g-C_3N_4	Pt	Pyrex reactor (P)	Xe lamp, 300 W I >400 nm	890.20	78
2014	g-C_3N_4	Pt	Quartz reactor (Q)	300 W,Xe lamp, I >420 nm	420.00	77

Non-Metal Doping

Besides metal doping, doping with non-metals can effectively increase semiconductor's photo-activity. In the modification of g-C_3N_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_3N_4 over modified N-doped g-C_3N_4 photo-catalyst (CN-20) with maximum reported hydrogen production was 64 mmol h-1 (Fig. 6(a)).[89] 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.

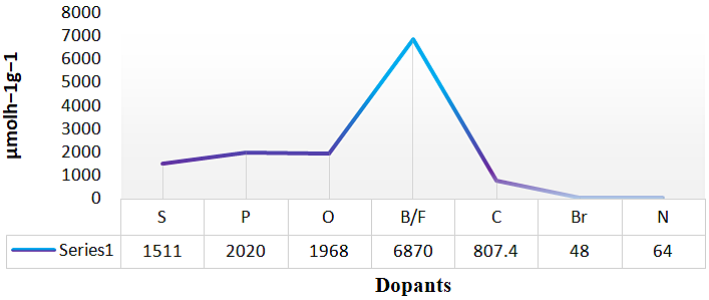


Fig. 4: Non-metal doping on g-C_3N_4 based photocatalyst

Table 6: The recent study of Non-metal loading on photocatalyst based on g-C_3N_4 for hydrogen generation

Year	Photocatalyst	Dopant (inorganic)	Reactor	Light Source	Efficiency µmolh^{-1}g^{-1}	Ref.
2019	g-C_3N_4	S	Pyrex reactor (P)	Xe lamp,300 W,λ = 420	1511.2	[92]
2019	g-C_3N_4	P	Pyrex reactor(P)	350 W, Xe arc lamp, λ > 420 nm	2020	[93]
2018	g-C_3N_4	O	Pyrex reactor(P)	300 W, Xelamp λ = 420	1968.00	[94]
2018	g-C_3N_4	B/F	Pyrex reactor(P)	Xe lamp, 300 W, λ> 420 nm	6870.00	[95]
2018	g-C_3N_4	S	Pyrex reactor(P)	Xe lamp, 300 W, λ> 420 nm	240.1	[84]
2018	g-C_3N_4	O	Pyrex reactor(P)	Xe lamp, 350 W,	1968.00	[94]
2017	g-C_3N_4	P	Pyrex reactor(P)	Xe lamp, 300 W, λ > 420 nm	570.00	[94]
2017	g-C_3N_4	C	Pyrex reactor(P)	Xe lamp, 300 W, λ> 420 nm	807.40	[96]
2016,	g-C_3N_4	Br	Pyrex reactor(P)	Xe lamp, 300 W, λ ¼ 400 nm	480.0	[91]
2016	g-C_3N_4	N	Quartz reactor(Q)	Xe lamp, 300 W, λ > 420 nm	640.0	[89]
2015	g-C_3N_4	C	Pyrex reactor(P)	Xe arc lamp, 350 W, λ >420 nm	540.0	[97]
2014	g-C_3N_4	C	Pyrex reactor(P)	Xe lamp ,Visible light, λ > 420 nm	700.0	[98]

In another study by Chen *et al*. reported the 12 times higher enhanced photo-catalytic performance for sulfur loading than pristine g-C_3N_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.[90] Similarly specified the non-metal Br doped g-C_3N_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

photo catalyst designed for CNBr as demonstrated in the Fig. 6(e).[91] Here, Table 7 demonstrates the cases for the non-metal doping on g-C_3N_4 aimed at water splitting using photo catalyst.

Doping on $BiVO_4$ based Photo-catalysts:$BiVO_4$

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, $BiVO_4$ takes excessive consideration as photo-anode substances for PEC water splitting, since certain modified $BiVO_4$ photo-anodes fulfill several essential necessities enlisted above.[99-101] $BiVO_4$ is a n-type semiconductor photo catalyst with the maximum band gap energy of 2.4eV. Here, $BiVO_4$ engrosses sufficient amount of visible light spectrum and used as a stable, neutral, nontoxic, comparatively low-cost electrolyte.[102-104] In comparison with other common O_2 evolution photo catalyst like Fe_2O_3 and WO_3, $BiVO_4$ 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 $BiVO_4$ 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 $BiVO_4$ 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-$BiVO_4$ structure.[105]

Table 7: The recent study of doping on $BiVO_4$ compositephoto-catalyst

Year	Photo catalyst	Dopant (metal)	Reactor Solution	Light Source	Efficiency $\mu molh^{-1}cm^{-2}h^{-1}$	Ref.
2018	$BiVO_4$	Nb-TiO_2	1.0M KCl at P^H 9.2	AM1.5Gillumination	80μmolh−1cm−2h^{-1}	109
2018	$BiVO_4$	Bi2S3	Na2S/Na2SO3	1000 W m−2 (1 Sun).	417 μmolh−1cm^{-2} h^{-1}	106
2018	$BiVO_4$	Nb-TiO2/W	0.50 M phosphate buffer	AM1.50G illumination	80 μmolh−1$cm^{-2}h^{-1}$	110
2017	$BiVO_4$	MDH	0.50 M phosphate buffer	AM1.50 G illumination	21 μmolh−1cm^{-2} h^{-1}	111
2017	$BiVO_4$	3-Fe2O3	phosphate buffer solution	AM1.50 G illumination	27.34 μmolh−1cm^{-2} h^{-1}	112
2016	$BiVO_4$	CDs	0.50 M phosphate buffer	300.0 W Xe-lamp	0.92 μmolh−1cm^{-2} h^{-1}	107
2016	$BiVO_4$	HDP	1.0M KCl at pH	1.0 G sun illumination	121 μmolh−1cm^{-2} h^{-1}	107
2016	$BiVO_4$	WO3-NRs	potassium phos -phate(pH =7)	solar light, AM 1.50 G	102 μmolh−1cm^{-2} h^{-1}	105
2014	$BiVO_4$	WO3 /(W; Mo)	0.5M K_2SO_4 (pH 7.0)	100mWcm−2 , AM 1.50 G,	75 μmolh−1cm^{-2} h^{-1}	105
2011	$BiVO_4$	RhO2/Mo	-	AM1.50 G solar light	9 μmolh−1cm^{-2} h^{-1}	113
2011	$BiVO_4$	Mo	seawater	simulated AM 1.50 G sunlight	7 μmolh−1cm^{-2} h^{-1}	113

Where Martin Rohloff *et al*. described that the photo catalytic water splitting routine of the Mo-doped $BiVO_4$ film photo-anodes are much better compared to their pure $BiVO_4$. 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}).[106] 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.[107] The modification of surface of $BiVO_4$ semiconductor with W-doped and Mo-doped, are increased the photocurrent densities to 1.25 and 4.6 mA cm^{-2} at 1.23 V vs. RHE under illumination of 1.0 sun light, respectively.[103, 108] Heretable 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+}.[114]

Sl. No.	Catalyst	Doped Element	Preparation Method	Efficiency	Ref.
01	$BiFeO_3$	nil	sol-gel synthesis	21.9 μmolcm^{-2} h^{-1}	Yuxuan Yang, *et. al.,* 2018
02	$BiFeO_3$	Gd^{3+}	sol-gel synthesis	67.6 μmolcm^{-2} h^{-1}	Yuxuan Yang, *et. al.,* 2018

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 67.60μmol $cm^{-2}h^{-1}$ 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 $BiFeO_3$.[114] 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.[115]

Table 9: The recent study of Doping on TiO_2 & TiO_2 based composite photocatalyst

Year	Photocatalyst	Dopant (metal)	Reactant	Light Source Solution	Efficiency μmolh^{-1}g^{-1}	Ref.
2019	SrTiO3	Al	Pure water	300.0 W, Xe Lamp	05.70	118
2018	PCN-777	Pt	TEOA	300 W,	586.00	116
2018	RP/TiO2	Red-P	Methanol	350.0W, mercury Lamp	276.00	119
2006	Sr3Ti2O7	NiOx	Pure water	Hg lamp,400–450.0 W	144.00	120
2002	CaTiO3	NiOx	Pure water	Xe lamp,400–450.0 W	30.00	121
2002	Sr4Ti3O10	NiOx	Pure water	Xe lamp,400–450.0 W	170.00	122
1998	B/Ti oxide	Pt	Pure water	Hg lamp,400–450.0 W	22.00	123
1997	K2La2Ti3O10	NiOx	Pure water	Hg lamp,400–450.0 W	2186.00	124
1997	TiO2	Pt	Pure water	Xe lamp,400–450.0 W	568.00	125
1995	TiO2	Pt	Pure water	Hg lamp,400–450.0 W	106.00	126
1987	TiO2	NiOx	Pure water	Hg lamp,400–450.0 W	62.00	127
1985	TiO2	Rh	Pure water	Xe Lamp, 400–450.0 W	449.00	128
1980	SrTiO3	Rh	Pure water	Hg lamp, 400–450.0 W	27.00	129, 130
1980	SrTiO3	NiOx	Pure water	Hg lamp, 400–450.0 W	40.00	127, 131

Doping On Tio_2 & Tio_2 Composite Photo-Catalyst

TiO_2 & TiO_2 composite photocatalyst is the best, efficient, and cost-effective catalyst for photo-catalytic 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/RhCrOx/$SrTiO_3$: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 $\mu molh^{-1}g^{-1}$ 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 RhCrOx/$SrTiO_3$: 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_2S_3 Photocatalyst

In a study, W. P. Cathie Lee fabricated a flower-like Copper-doped molybdenum disulfide/bismuth sulfide (Cu-MoS_2/Bi_2S_3) photo-catalyst. The sample photo-catalysts with differing quantity of Cu were utilized in the photo-catalytic water splitting for H_2 production under simulated sunlight irradiation. The photo-catalysts 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]

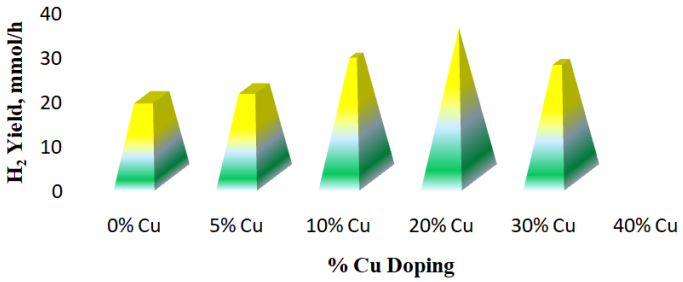


Fig. 5: Variation of Hydrogen production rate from variable Cu doping on Na_2S/Na_2SO_3 mixture illuminated under simulated sunlight over the duration of 6.0 h

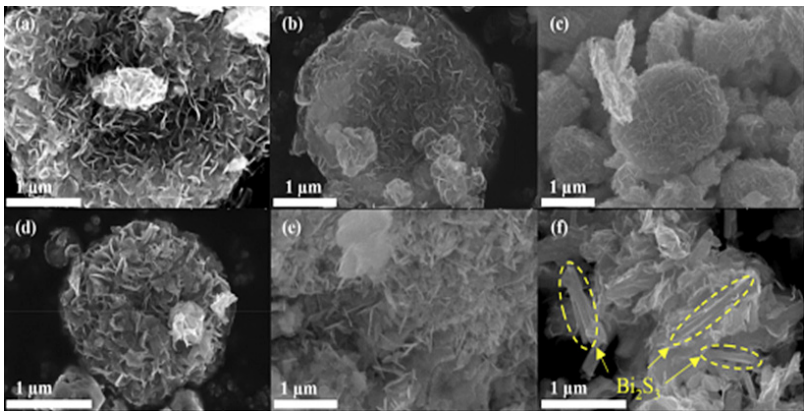


Fig. 6: Some images from FE-SEM of MoS_2/Bi_2S_3, (a) Undoped (b) 5.0mol% (c) 10.0mol% (d) 20.0mol% (e) 30.0mol% (f) 40.0mol%[132]

The crystal structure and surface morphology info of synthesized photo-catalyst were inspected by W. P. Cathie Lee using TEM and FE-SEM.[132] The standard structure of non-doped MoS_2/B_2S_3 is demonstrated in Fig. 2(a), where MoS_2 have been seen to cover surface of Bi_2S_3, growing on it.[133] In each of six images, crumpled MoS_2 nano sheets is found to accumulate onto Bi_2S_3 surface, producing a flower-type frame.[134] Upon copper (Cu) doping MoS_2/Bi_2S_3, 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 MoS_2 sheets were larger enough to be visible and distinguishable (Fig. 2(d)).[132] But on increasing Copper(Cu) to 40.0mol%, the distinct Bi_2S_3 discoid's not formed, rather some Bi_2S_3 noticed to be in rod form (indicated as yellow in Fig. 2(f)) where MoS_2 sheets were in a arbitrary form.[132]

Doping on Miscellaneous Composite Photo-Catalyst

Deposition of a foreign particle onto the semiconductor surface can supply maximum active surface for excellent Photo-catalytic H_2 production. There are many more option with semiconducting properties for Photocatalytic water splitting. Among them $K_2La_2Ti_3O_{10}$, possesses a perovskite structure is one of a unique catalyst photo catalysis.[135] H_2 evolving happens on NiOx co-catalyst where O_2 evolves from hydrated interlayer. Various niobate, titanate and tantalite photo-catalysts with perovskite structure been reported from the period of $K_2La_2Ti_3O_{10}$ photocatalyst was designed. $Sr_3Ti_2O_7$ and $Sr_4Ti_3O_{10}$ photo-catalysts have perovskite slabs of $SrTiO_3$. $La_2Ti_2O_7$, $La_2Ti_2O_7$:Ba, $KLaZr0._3Ti0._7O_4$ and $La_4CaTi_5O_{17}$ photocatalysts with perovskite structure which give a maximum quantum yield. $Na_2Ti_6O_{13}$ and $BaTi_4O_9$ with a holo-tube type structure is also a unique photo-catalysts. On the other side Catalyst $KTiNbO_5$ shows activity when it prepared through a polymerizable complex composite system. In a study by S. Ikeda *et al*. they found that $K_2La_2Ti_3O_{10}$ yield 2186μmol Hydrogen in 0.1M KOH solution.[124] 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 $K_3Ta_3B_2O_{12}$ 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.[136]

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

Year	Photocatalyst	Dopant (metal)	Reactant Solution	Light Source	Efficiency $\mu molh^{-1}g^{-1}$	Ref.
2008	LiCa2Ta3O10	NiOx	Pure water	Hg–Q lamp	59.00	136
2007	CeO2:Sr	RuO2	Pure water	Hg–Q lamp	110	122
2006	Na2Ta2O6	NiO	Pure water	Hg–Q lamp	391	137
2006	K3Ta3B2O12	None	Pure water	Hg–Q lamp	2390	138
2005	Cs2Nb4O11	NiOx	Pure water	Hg lamp, 400–450 W	1700	139
2005	NaCa2Nb3O10	RuO2	Pure water	Hg–Q lamp	118	140
2005	Sr5Ta4O15	NiO	Pure water	Hg–Q	1194	141
2005	Ba5Ta4O15	NiO	Pure water	Hg–Q	2080	120
2004	Y2Ti2O7	NiOx	Pure water	Hg lamp	850	142-144
2004	La3NbO7	NiOx	Pure water	Hg lamp, 400–450 W	35	142
2003	KaLaZr0.3Ti0.7O4	NiOx	Pure water	Hg lamp, 400–450 W	230	145
2000	K2PrTa5O15	NiO	Pure water	Hg–Q	1550	146
1997	Rb2La2Ti3O10	NiOx	0.1 M RbOH	Hg–Q	869	147
1997	K2La2Ti3O10	NiOx	0.1M KOH	Hg lamp, 400–450 W	2186	148
1996	KTaO3	Ni	Pure water	Hg–Q	60	148, 149

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 $BiVO_4$ for favorable result. The formation of successful hetero junction has been reported between $BiVO_4$ and WO_3,[150-152] SnO_2,[153, 154] Fe_2O_3,[155, 156] $CuWO_4$,[157] and CdS,[158, 159] Kim *et al*.showed that hetero type dual photo-anodes, HDP, of $BiVO_4$ & a-αFe_2O_3.[156] Reports also implies largely increased photocurrent on HDP of $BiVO_4$/αFe_2O_3 becoming permanent. 7 $mAcm^{-2}$ photocurrent at 1.23V vs. RHE has been reported below 1 solar radiation making subsequent hydrogen production for $BiVO_4$/αFe_2O_3 nearly 80$\mu molcm^{-1}h^{-1}$ by Savioet *et al*. On the other hand, the Fe_2O_3/$BiVO_4$ photo-anode containing 3 spin coated films demonstrated 1.63$mAcm^{-2}$ photocurrent density at 1.23V vs. RHE, reported by Xia *et al*. that is nearly 2.2 times higher in comparison to pure $BiVO_4$ photo-anode, submerged in 0.1M KH_2PO_4 (pH 7) electrolytic solution beneath AM1.5G sun light.[155] Rates of hydrogen production for Fe_2O_3/$BiVO_4$ has been around 28$\mu molcm-2h^{-1}$, quite larger in comparison to $BiVO_4$ photo-anode. A $BiVO_4$/$CuWO_4$ 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 Na_2SO_4 electrolytic solution at pH 7.[157] In contrary to pristine BVO, $BiVO_4$/WO_3 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 WO_3 from $BiVO_4$.[160] Also, as reported by Savio *et al*., $BiVO_4$ and ZnO pairing generate a significant, 2 mA/cm^2 at 1.23V vs. RHE, photocurrent density in observable radiation range.[161] Similarly, four times amplified photo current of $BiVO_4$/TiO_2, pairing of $BiVO_4$ and TiO_2, has been reported by Kimura *et al*., contrary to pristine $BiVO_4$ on 100$mWcm^{-2}$ brightness , and they ascribed it to the formational alterations of $BiVO_4$ which improved electron transferring throughout the junction.[162]

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.[163-165]

On illumination of visible light, electrons from excited dyes can be infused to the conduction band of semiconductors, causing inauguration 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 H_2 even without semiconductors.[166] But it is very little H_2 generation rate by dyes without semiconductors.[164] Dhanalakshmi *et al*. carried out a parametric research to study the effect of applying 2þ as a dye sensitizer on Photocatalytic H_2 generation from H_2O, under visible light irradiation.[167]

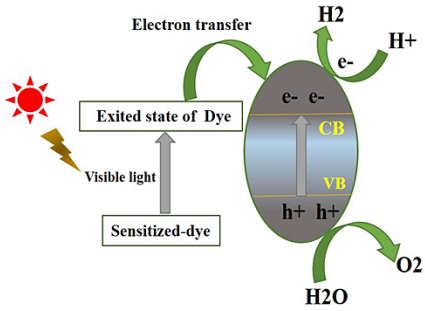


Fig. 7: Schematic representation of dye sensitizer action mechanism

Dhanalakshmi *et al*. observed improved H_2 generation rate under visible range radiation due to adsorption of dye molecules to the TiO_2 on parametric research studying the influence of applying 2þ as a dye sensitizer on Photocatalyst based H_2 generation from H_2O. Splitting process.[163] Gurunathan *et al*. noticed influence of various dyes, for example, EDTA, during H_2 generation for SnO_2 photocatalyst using or not using sacrificial agents. Having band gap 3.5 eV and, SnO_2 was unable to be activated on visible irradiation.[168] On dye sensitization, SnO_2 was capable of H_2 generation on visible range irradiation. As observed, overall order of efficiency for dyes for improving rate of H_2 generation is as following: Eosin blue>Rose Bengal>Ru(bpy) 32+>RhodamineB>Ac riflavin>Fluorescein.[167] By analyzing the phusico-chemical properties ot these dyes, a effective conclusion could be dawn.[527] Like as Rhodamine pose a longer absorption range maxima including more negative potential (.545V) than conduction range (.34V) of SnO_2(167). But the problem is that it does not improve the H_2 production rate significantly.

Table 11: Absorption wavelength maxima λmax(nm) dyes[169]

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

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.[170, 171] 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 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.[173] Electrons deposited on the metal particles can move towards H^+ upon the surface, adsorbed, and subsequently reduce H^+ to form 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 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.[167]

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]

Increasing Photo Catalytically Active Area

Photo catalytically active field in a photocatalyst is a necessary factor that readily impacts 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 (GQD)s, carbon nano dots, carbon nanotubes (CNTs) and fullerenes (C_{60}) for improving 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 m2 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.[178, 179] Zhang *et al*. pointed out the synthesis of grapheme /TiO2Nano composites and the improved photo catalytic hydrogen production through splitting of water, as well as observed that the photo catalytic performance of grapheme /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 H_2 generation activity on UV-Vis light radiation.[182] Also, Fan el al. observed that grapheme 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) $xZn_2(1-x)S_2$ consisting of a compressed band-gap exhibited high visible-light photo-catalytic hydrogen production activities from aqueous S^{2-} and SO_3^{2-} solutions for sacrificial purpose.On $AgInS_2$ ratio increment to ZnS, the light absorbance of (AgIn) $xZn_2(1-x)S_2$ solid solutions transferred to larger wavelengths because the photo-physical, photo-catalytic activities of (AgIn) $xZn_2(1-x)S_2$ 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_3OH, 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, 186] 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.

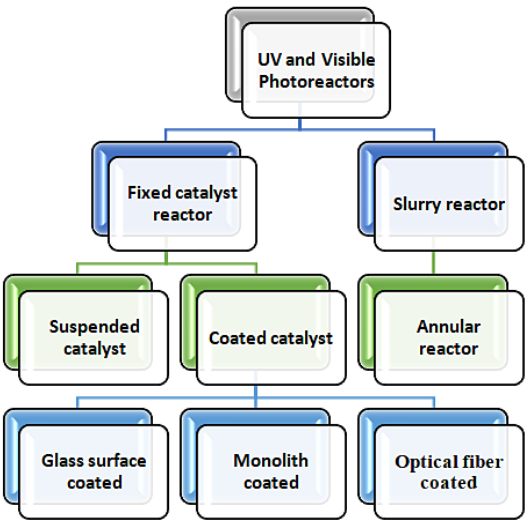


Fig.8: Types of photo-reactors for visible and UV light photo-catalytic to produce hydrogen[28]

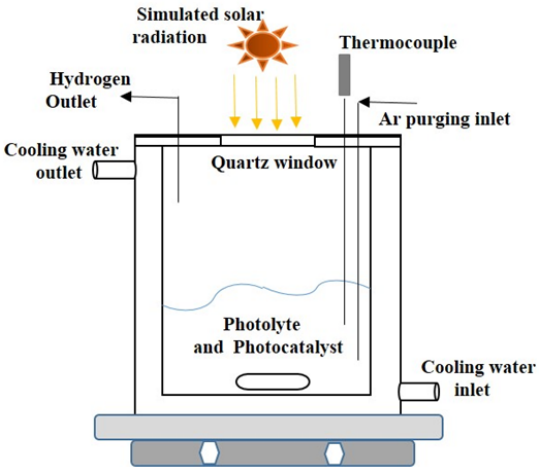


Fig. 9: Pictorial representation of a typical photo reactor built with stainless steel vessel and quartz oxeye[28]

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 M*et 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 M*et al*. they used/applied photo catalyst $NiOeIn_2O_3/TiO_2$ 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]

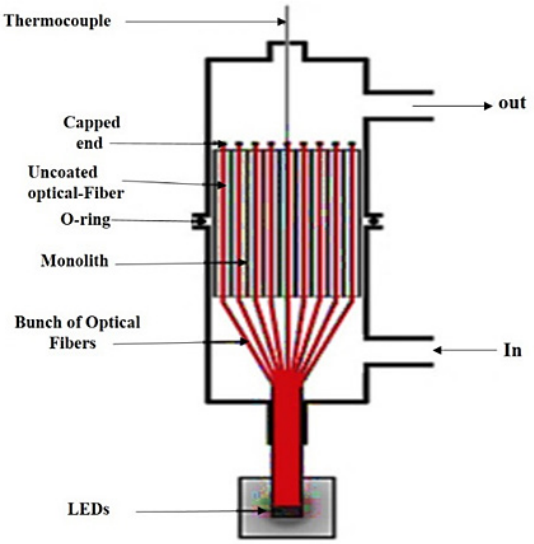


Fig. 10: The pictorial representation of an optical fiber honeycomb reactor[185]

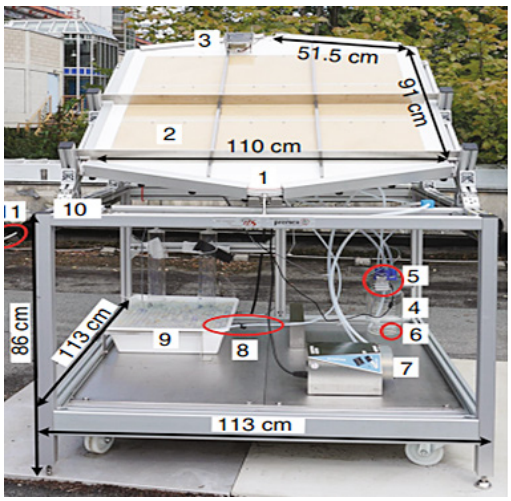


Fig. 11: The pictorial representation of a photo-reactor (large scale) for photo-catalytic reactions with an immobilized photo-catalyst[186]

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

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

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.[200, 201] 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.[202] 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.[203] In another research work report by Leon and Tambago, indicated that the hydrogen (H_2) production increased using Cd0.4Zn0.6S while the intensity of light was increased.[204]

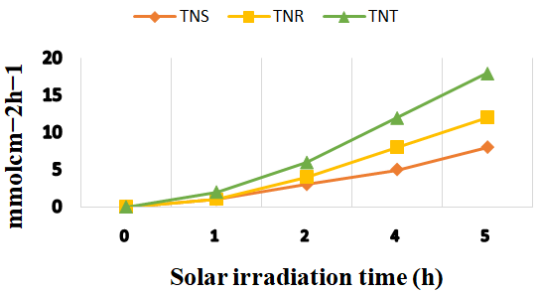


Fig .12: The comparison ofphoto-catalysts for hydrogen (H_2) generationunder irradiation of solar Light for TNS (titanium nano sheet), TNT (titanium nano tube) and TNR (titanium nano rod).[205]

Table 13: Temperature effect on H2 production rate

Sl. No.	Temperatuire^{0}C	H2 production rate	Catalyst
01	30^{0}C	59.00 mol/g.s	Pt/TiO2
02	40^{0}C	92.00 mol/g.s	Pt/TiO2
03	50^{0}C	370.00 mol/g.s	Pt/TiO2

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 (H_2) 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 (H_2) 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

respectively with charge carrier recombination.[202] In 30ºC, 40ºC, 50ºC the hydrogen gas generation was 59, 92 & 370 mol/g.s respectively.[206] Hydrogen generation increased from 4.71 mmol g1 to 15.18 mmol g1 after introducing a temperature rise from 45ºC to 55ºC.[207] In a photocatalytic study it was found that the optimum temperature of this process should be 60ºC to 80ºC.[208]

pH Effect

The hydrogen (H_2) generation from water splitting depends on the concentration of the proton which indicates the pH of the regarding solution. In the 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.[20] In a CuOx/TiO_2 catalytic medium with basic medium (pH 10) hydrogen production is maximum. The atom copper Cu (I) shows unstable behavior in TiO_2 based acidic medium. In the visible light TiO_2 part of the catalyst, Si/CdS/TiO_2/Pt is unstable in a strong base or acidic reaction.[209] The optimum pH value of a photo-catalytic reaction for better hydrogen production rate in $CuAlO_2$/TiO_2 catalyst surface is 11.[210] The catalyst Pt/r-TiO_2 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/TiO.[2] catalyst in a pH condition 6.6.So the hydrogen generation is directly depends on the according 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 TiO_2/RuO_2-MV^{2+} catalyst can generate enough hydrogen (H_2).[213] The reduction reaction of hydrogen from H+ to H_2 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 H_2 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 (TiO_2) 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 Ti^{3+}. Then, the VB holes of TiO_2 were generated and the electrons excited to the CB of TiO_2. At CB, the H^+ reduce to H_2 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 ismajor than glycol, methanol and ethanol. On the other hand hydrogen generation is also have a relationwith 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 at5%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.

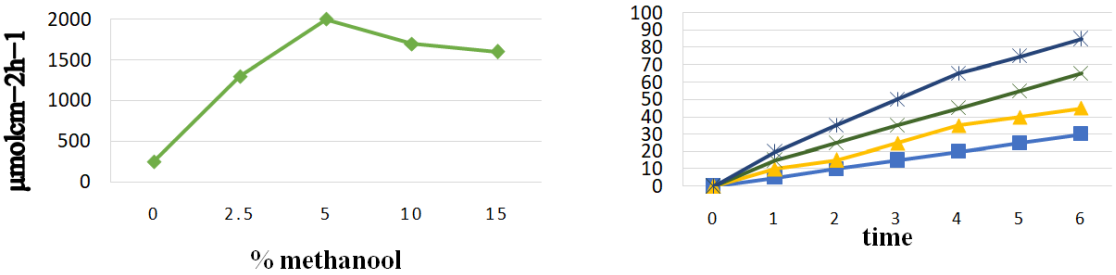


Fig.13 : The photo-catalysts comparison for hydrogen generation in the irradiation of solar Light for TNS, TNT and TNR[205]

Table 16:A Summary of numerous sacrificial reagents used in photo-catalytic H_2 production process

Year	Feed	Catalyst	Reactor/Parameter	Efficiency	Ref.
2019	10 % ethanol -water	.05 g TiO2/MMT Quartz flask	Slurry ractor 40 W Xe lamp	methanol >ethylene glycol > ethanol >> propanol >Glycerol	219
2017	15% glycerol -water	85 mg 0.5 wt% Pt//TiO2	Pyrex reactor 130 W Hg lamp Medium pressure	Pt >Pd> Au glycerol > Propan-2-ol	220
2016	25 % n-propanol -water	50 mg 0.5 % RuO_2@TiO_2	Glass reactor UV light Temperature at 25C	MeOH> t-BuOH > n-BuOH, PrOH> n-EtOH	221
2015	15% 2-propanol -water	0.065 g &1 wt% Pd	Tubular reactor UV (375 nm, 10 mW cm-2)	Pd> Pt z Au. methanol > 2- ethanol >propanol >tert-butanol	222
2015	5% methanol -water	450 mL water solution,	Quartz reactor system 250 W Xe arc lamp, 30C under atmospheric pressure	ethylene > anhydrous glycol >Methanol	223
2015	5 % glycol -water	6.5 mg 1.5 wt% Au/P25	Tubular reactor SB-100P/F lamp (100 W, 265 nm)	Au/P25 > Au/brookite> Au/anatase	217

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_2 is not available in free form (i.e. atomic state). Among various H_2 production process low-cost H_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_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 H_2 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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