

Photocatalysts for Hydrogen Production via Photoelectrochemical Water Splitting - A Review

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Abstract

Hydrogen production is an urgent and efficient requirement in the recent era. Renewable energy is playing a vital role in the present scenario. The development of renewable source of alternative energy is in peak due to the high energy demand and more depletion of fossil fuels. Photoelectrochemical (PEC) water splitting is one of the best techniques for more efficient and economical hydrogen production. Enhancing the water splitting efficiency faces several obstacles due to energy losses associated with fast recombination of photogenerated charge carriers, electrode deterioration, and restricted light harvesting. This review focus on the recent developments or technologies in water splitting using PEC based nano-materials as well as different strategies to enhance hydrogen efficiency, with charge separation, co-catalysts doping, and light harvesting. The review concludes with a summary of this latest research field and its future outlook.

Keywords: Hydrogen production, photocatalysts and PEC water splitting.

Date of Submission: 18-08-2023

Date of acceptance: 03-09-2023

I. Introduction

Photoelectrochemical (PEC) water splitting is a propitious renewable energy technology for hydrogen generation for uses in the future hydrogen economy. PEC system use solar photons to generate a voltage in an electrolysis cell which is sufficient to electrolyze water, producing H₂ and O₂ gas. One major advantage of PEC system is that they involve relatively simple process steps as compare to other H₂ production systems. The primary challenges for PEC device are to develop materials with ample photovoltage to electrolyze water, to minimize the internal resistance losses, to have long lifetime (especially corrosion life), to maximize the photon utilization efficiencies, and to reduce the plant capital cost.

Directed Technologies Inc. (DTI) performed a technical economic assessment of the PEC hydrogen production system under contract. Four basic system configurations are chosen by the PEC Working Group to surround the technology spread of conceptual PEC production systems. The overall system designs and parameters, the costs of implementation, and the costs of the output hydrogen were determined for each of four conceptual systems. Each system is consisted of PEC reactor that generates H₂ and O₂, gas processing system that compresses and purifies the output gas stream, and additional equipment.

The first two of the four system configurations examined aqueous reactor beds containing colloidal suspensions of photovoltaic (PV) active nanoparticles, each nanoparticle are composed of appropriate layered PV materials to achieve adequate bandgap voltage to carry out electrolysis reaction. The third and fourth system configurations use the multi-layer planar PV cells in electrical contact with small electrolyte reservoir, and produce O₂ gas on the anode face and H₂ gas on the cathode face. They are positioned in fixed arrays facing the sun.

The researchers are highlighting their efforts more on investigating a clean and sustainable energy resource to cure out expected shortage of a non-renewable energy and to control the pollution. Renewable fuel, used in a vehicle, spacecraft propulsion, an aircraft and some electrical devices, is very favourable. Hydrogen is locked up in water, carbohydrate and other organic matter (1). Several methods for removing hydrogen from certain compounds have also been mentioned.

The splitting of water is a method of separating water into oxygen and hydrogen. Specific water splitting methods such as PEC, photocatalytic, radiolysis, photobiological and thermal decomposition have emerged (2, 3). A radiolysis produces nuclear waste as a by-product. The photobiological splitting of water is assisted by the bioreactor algae, switches from the production of oxygen (a natural photosynthesis) yielding low hydrogen production rate (4). Photoelectrochemical and photocatalytic splitting of water are the simplest, most effective and clean methods for producing hydrogen. The main downside to thermal decomposition is its low hydrogen yield and a high temperature requirement.

1.1 Basic mechanism associated with PEC water splitting

Honda and Fujishima developed the PEC water splitting system, which has a high efficiency and low cost (5, 26). The basic concept behind the PEC water splitting is the conversion of solar energy into hydrogen by applying an external bias on the photovoltaic materials immersed in an electrolyte containing the redox pair, of which one electrolyte is made of a semiconductor, exposed to light and therefore capable of absorbing light.

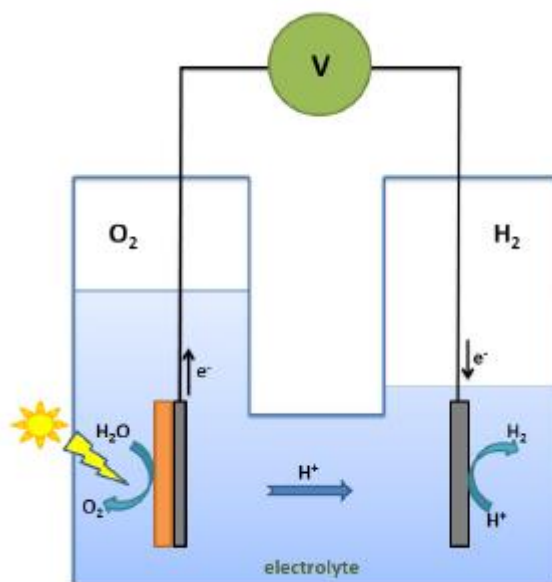


Fig. 1. A Photoelectrochemical cell representation (6)

Instead, electricity is used to electrolyse water. The semiconductors which have a specific character to serve as photocatalysts. Hence, in the presence of light it plays a key role in initiating the process of chemical reduction and oxidation. These photocatalyst electrodes capture light, which provides energy for the reactions, and an externally provided chemical / electrical bias gives the additional voltage required to complete the process. This bias overcomes the slow kinetics and gives PEC cell enough voltage to drive the reaction at a desired rate or current density. Photoelectrode with photon absorption, the electrons are excited and pairs of electron hole are produced through a redox reaction. So, hole (formed) can oxidize the molecule, and an electron can reduce from H^+ to H_2 (7-9). Energy level, where the probability of finding electron is half (i.e. Fermi Energy (E_f)), is important when reference electrode used to make measurements; also, it compare E_f of semiconductor with its own consistent Fermi level. In an intrinsic semiconductor, E_f will be exactly at centre band gap (i.e. between E_c (Conduction Energy) and E_v (Valence Energy)).

Depending upon the type of dopant E_f shifts towards or away from E_c , the equilibration takes place at the interface by shifting Fermi Level of the semiconductor to match with redox couple of the electrolyte. This results in the formation of a thin region of space charge layer which is close to the surface of semiconductor leading to band bending upwards/downwards, depending upon the type of semiconductor (n-type or p-type). So, there is strong dependency on the electronic properties of the photo-electrode to improve the water splitting efficiency. These photocatalyst electrodes capture light, which provides energy for the reactions, and an externally provided chemical/electrical bias gives the additional voltage required to complete the process. One of the efforts is the construction of hetero-structure photocatalysts (p-p/n-p/n-n junctions). This actually helps in the migration and the separation of charge carrier. Recombination of photo-generated carriers can be reduced with the help of heterojunction structure (10-12).

1.2 PEC PRINCIPLE

The PEC water splitting method works by turning light energy into electricity inside a tank with two (or three) electrodes immersed in an aqueous electrolyte, at least one of which is made of a light-exposed semiconductor that can absorb light. Then, this electricity is used for water electrolysis.

The photoelectrochemical (PEC) path to water splitting involves separating the oxidation and reduction processes into half-cell reactions (13).

Oxidation reaction: $2\text{H}_2\text{O} (\text{Light}) \rightarrow \text{O}_2 + 4\text{H}^+ + 4\text{e}^-$

$E^\circ = 1.23 \text{ V vs. SHE}$

(i)

Reduction reaction: $2\text{H}^+ + 2\text{e}^- (\text{Light}) \rightarrow \text{H}_2$

$E^\circ = 0.00 \text{ V vs. SHE}$

(ii)

Overall reaction: $2\text{H}_2\text{O} (\text{Light}) \rightarrow \text{O}_2 + 2\text{H}_2$

$\Delta E^\circ = -1.23 \text{ V}$

(iii)

In Equations (i) and (ii), the half-cell reactions with their corresponding standard reduction potential E° with respect to the standard-hydrogen-electrode (SHE) are shown. Equation (i) shows the overall reaction and its corresponding ΔE° . However, the negative ΔE° indicates that water splitting is not thermodynamically spontaneous process. So, for the reaction to proceed 1.23 V must be provided externally.

For that purpose, materials are necessary which upon the light absorption can drive water splitting reaction. The three fundamental requirements should be met by the system harvesting and converting solar energy to chemical energy:

- Photo-response of the system must perfectly match the solar spectrum.
- The photo-excited charges must be separated effectively to prevent recombination.
- Charges must have sufficient energy to carry out a desired chemical reactions like - water splitting.

The appropriate band gap for the PEC water splitting to be effective is 1.6-2.2 eV. The band edge position is correct in this range and greater mobility of the photo-charge carrier. It is possible to narrow the band gap by incorporating donor acceptors into semiconductors.

PEC water splitting can be done in two step process known as Z-scheme, which is like copying the natural photosynthesis. Here, in this system two different semiconductors are used for photo-excitation and reversible shuttle redox mediator (donor or acceptor pair).

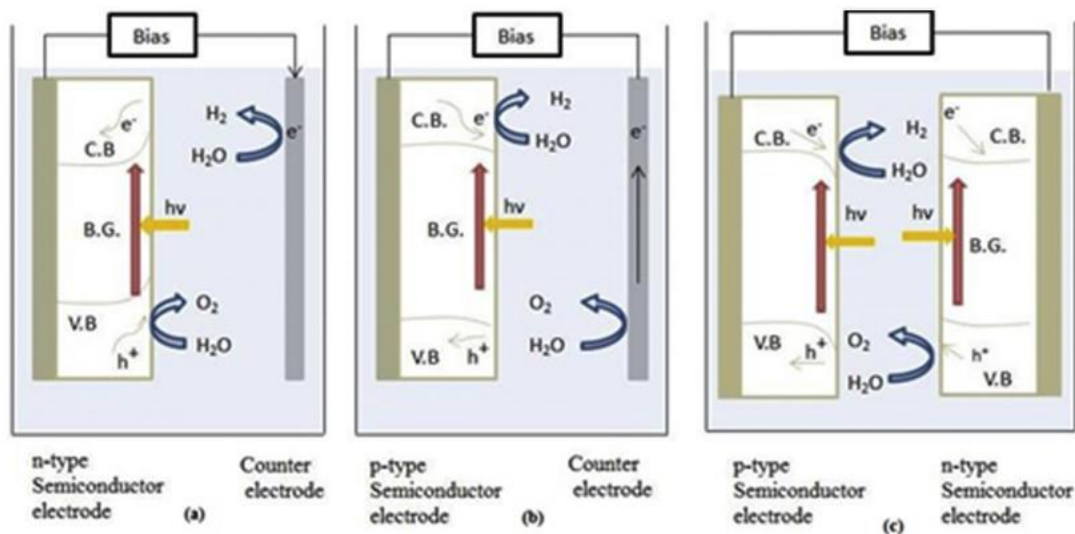
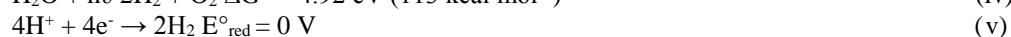
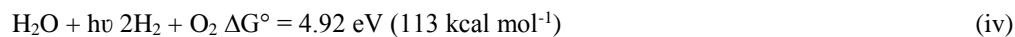


Fig.2. Z scheme of the PEC water splitting using n-type and p-type semiconductors (14).

Visible light can be more effectively utilized through the Z-scheme in comparison with the conventional one-step process. In this system, the hydrogen generation takes place via the reduction of protons by conduction-band electrons, where electron acceptor generated by the H₂ evolution photo-catalyst which is converted to its reduced form and the oxidation of donor electron by valence band holes. So, the water splitting achieved with phenomenon of redox pair cycle. Factors affecting this mechanism, structural and electronic properties of photocatalyst and the presence of co-catalyst (15). Through the Z-scheme movement of the photo-generated charge carriers enhancement in the photocatalytic activity is to be achieved (16).

However, n-type and p-type semiconductors are associated in the water splitting. Also, two different photo-electrodes can be merged, i.e. n-type and p-type semiconductors, hence oxidation and reduction can occur simultaneously and so can utilize the light energy more efficiently.

Photogenerated carrier recombination should be reduced as the efficiency of the PEC process improves. Charge carriers are created at the surface of nanoparticles due to their reduced size (i.e. enhanced surface to volume ratio), form, and controlled morphology, and hence water splitting occurs at the nanomaterial's surface. The Overall reaction involved in water splitting mechanism:



1.3 Efficiency calculations

To estimate PEC performance of the electrode with applied potential (E_{app}), the applied bias photon-to-current efficiency (ABPE) (η) can be evaluated as (17),

$$\eta(\%) = \frac{J_{\text{ph}}(1.23 - |E_{\text{app}} - E_{\text{ocp}}|)}{P} \times 100\% \quad (\text{vii})$$

Where, J_{ph} is photocurrent density (mA cm^{-2}), E_{ocp} is open circuit at which J_{ph} was measured, P is incident light power density (mW cm^{-2}).

Efficiency of PEC device can be evaluated by incident photon-current conversion efficiency (IPCE) (18),

$$\text{IPCE} = \frac{(1240 \times I_{\text{PH}})}{(\lambda \times P_{\text{light}})} \quad (\text{viii})$$

I_{PH} is the generated photo-current density (A/m^2), λ is incident light wavelength (nm), P_{light} is photon flux (W/m^2), and 1240 is unit correction factor. And, IPCE is the measure of photo-generated electrons collected per photon irradiated on PEC surface.

Fundamental factors that affect overall efficiency and performance of PEC water splitting are:

- i. The efficiencies of light absorption (η_{A})
- ii. The efficiencies of charge separation (η_{CS})
- iii. The efficiencies of charge transport (η_{CT})
- iv. The efficiencies of charge collection/reaction efficiency (η_{CR}).

So, solar-to-hydrogen (STH) conversion efficiency (η_{STH}) can be expressed as (19),

$$\eta_{\text{STH}} = \eta_{\text{A}} \times \eta_{\text{CS}} \times \eta_{\text{CT}} \times \eta_{\text{CR}} \quad (\text{ix})$$

Efficiency of STH greatly depends on optoelectronic properties of the anode. Optoelectronic properties depend upon the size, the shape and the morphology.

Nano-materials exhibits great impact in increasing STH efficiency due to its large surface to volume ratio.

Semiconductors with the high quantum efficiency (QE) produce hydrogen under visible light illumination.

Quantum efficiency can be calculated as (20),

$$\text{QE} = \frac{\text{number of reacted electrons}}{\text{number of incident photons}} \quad (\text{x})$$

$$\text{QE} = \frac{\text{number of evolved Hydrogen molecules}}{\text{number of incident photons}} \quad (\text{xi})$$

Using the technique of water splitting, H_2O reduction involves three sections; photoelectrochemical (PEC), photocatalytic (PC), and photovoltaic - photoelectrochemical (PV-PEC) systems. Photocatalytic system (PC) is an easiest, unembellished, adaptable and ascendable method for water splitting. Powdered photocatalyst are disseminated in H_2O , under light beam, for H_2O reduction. The advantage of photocatalysts is the water splitting in the homogeneous phase without any clean electrodes and directive emend. However, photocatalytic systems have different disadvantages that limit its usage for splitting of water (21). Dividing the hydrogen and oxygen instantly when formed is required, that absorbs extra energy, results less productivity of water reduction (22). The embellishment of photocatalytic system without the transfer of catalysts will radiate photo-stationary condition, where the forward and backward reactions contain similar rates, and water splitting cannot take place. Applying photocatalytic system with higher scale is challenging. To gain overall water splitting and the associated production of solar fuels, a complex device are required to successfully capture light from the sun, separate photogenerated charges, and catalyzes reduction reactions and oxidation reactions. The highest performing solar fuel devices rely on multi-component systems, which give interfaces that can be associated with more performance loss due to thermodynamics and kinetic considerations. PEC water splitting is one of the best techniques for more efficient and economical hydrogen production (22). Although, enhancing the solar water splitting efficiency suffering immeasurable difficulties, because of the energy loss with respect to rejoining of the photo-generated charged carrier, electrode abasement, and limiting the light gathering. Also, recent advanced applications and astounding advancement for photoelectrochemical water reduction with some favourable materials are considered.

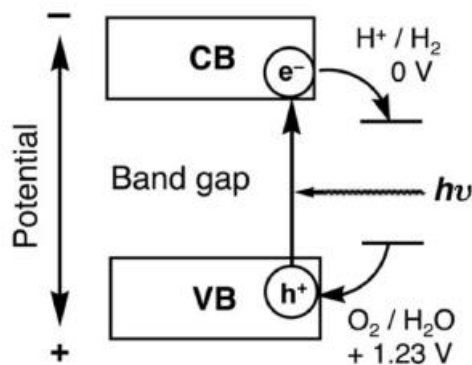


Fig. 3. Photocatalytic water splitting (23)

Basically, different ways have been used to convert the solar energy into a chemically stored form as H₂. The semiconductor-based PEC water splitting into H₂ and O₂ with sunlight as the energy input is one viable technique.

1.4 Photoelectrolysis

Photoelectrolysis is used for describing the semiconductor-based PEC water splitting. So, there are three approaches. Possible approaches are by using either photovoltaic cells (PV) or semiconductor-liquid junctions (SCLJ), or a combination of these two approaches (PV/ SCLJ). These various approaches will display single externally connected components in water splitting process. It is clear that more integrated architectures are needed for systems that convert solar energy into chemical energy, are cost effective, commercially feasible, and provide the performance required for practical applications.

1.4.1 Photovoltaic Approach

The photovoltaic-based approach is to combine a solar panel with an electrolyzer to form a single system that uses solar energy to generate electricity. An early report identified the use of multiple junction semiconductor structures when immersed in an electrolyte and exposed light to transform light energy into chemical energy (24).

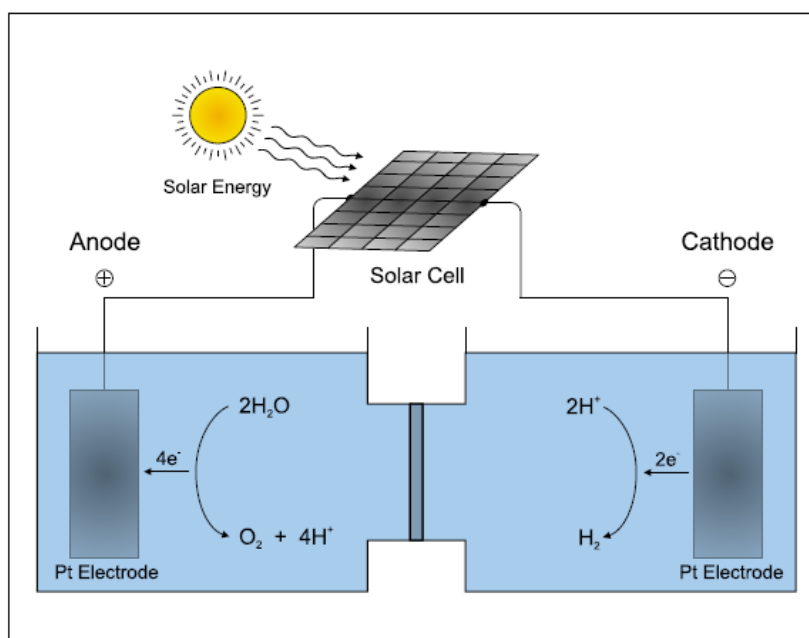


Fig. 4. A PV approach, where PV system is coupled with an electrolyser (6).

Semiconductor layers are connected in series, one after the other, in a single monolithic system capable of generating the water splitting power. These so called tandem cells or multi-junction cells are modified or connected to electrolytes producing H₂ and O₂ such as Pt and RuO₂-modified Pt, respectively acting as cathode

and anode. Such as, n-p GaInP₂/GaAs, multiple junction p-i-n amorphous Si and n-p Al_xGa_{1-x}As/Si, cells used for water photoelectrolysis.

A PV approach was used at high temperatures in solar-driven water electrolysis. The basic principle behind this is the reduction of the splitting potential of electrochemical water with rising temperature. Solar radiation is used by illumination photovoltaic cells as well as the heat source to allow water electrolysis to produce the required energy. This allows solar cells with smaller band gaps to push water cleavage from molten NaOH at sufficiently low temperatures (500°C).

1.4.2 Semiconductor–Liquid Junction Approach (SCLJ)

The water splitting potential is produced directly at the semiconductor-liquid interface for arrangements centered on semiconductor-liquid junctions. A semiconductor photoelectrode's ability to drive either water oxidation into O₂, or water reduction into H₂, or the entire water splitting reaction is determined by its band gap and the edges of the valence and conduction band position relative to the water redox reactions. In addition to the location of the edges of the unit, there are other criteria to be addressed in a SCLJ method for a material to be used for water splitting purposes. The semiconductor must be active over a broad spectral range and the material should effectively isolate the charges produced as light is absorbed. This, of course, also applies to the photovoltaic approach. In fact, the submerged semiconductor must be stable and free of corrosion in the electrolyte. For instance, TiO₂ is very stable in a wide range of pH, but due to its large bandgap it is active only in the UV zone. Also, WO₃ is only active in the solar spectrum's short wavelength range, but it is less stable in acidic media. Fe₂O₃ has a smaller band gap and absorbs the visible, but in acidic solutions it is also not very stable. Compounds such as CdTe or InP also have smaller band gaps that are better matched with the spectral distribution of sunlight entering the planet, but these materials either corrode or become inert when used in aqueous solution as photoelectrodes (25). These few examples and the ones mentioned below demonstrate that each semiconductor has its disadvantages. A large number of research efforts have been dedicated worldwide for several decades in the search for suitable semiconductors to be used for water oxidation, water reduction, as well as water splitting in semiconductor-liquid junctions. In 1972, sunlight-assisted electrolysis of water using crystalline TiO₂ photoelectrodes was first reported by Fujishima and Honda (26). The photoelectrochemical cell consisted of a photoanode of TiO₂ (rutile) and as a cathode of platinum. TiO₂ electrode illumination contributed to the development of O₂ on the photoanode and H₂ on the cathode.

With an increase in alkalinity in the TiO₂ photoanode compartment and acidity in the Pt cathode compartment, the quantum efficiency improved. This indicates that the 1.23 V thermodynamic potential needed for water splitting was significantly reduced due to the presence of a wide pH gradient between the compartments (about pH~13, chemical bias~0.77 V).

Using the SCLJ method, various semiconductors were investigated for water cleavage after the seminal work of Fujishima and Honda. Most materials with semiconductors were used to simultaneously accelerate water oxidation and water reduction.

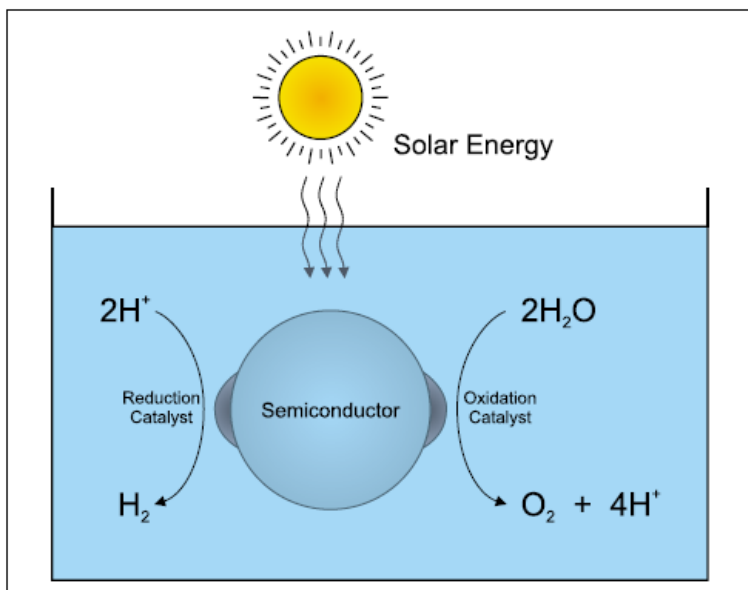


Fig. 5. SCLJ solution with a reduction catalyst and an oxidation catalyst armed with one semiconductor (25).

Undoped and Ni-doped In- TaO₄, InNbO₄, Ln₂Ti₂O₇ (Ln = La, Pr, Nd), MCo₁/3Nb₂/3O₃ (M = Ca, Sr, Ba), RbNdTa₂O₇, NaTaO₃ doped with La, La₃TaO₇ and La₃NbO₇, Y₂Ti₂O₇ and Gd₂Ti₂O₇, and H₂La₂/3Ta₂O₇ are examples of photocatalytic water divided by light irradiation. For all these compounds, when loaded with a reduction and/or oxidizing co-catalyst such as Pt, RuO₂, or NiO, the photocatalytic activity increases significantly. Recently, oxynitride (Ga_{1-x}Zn_x)(N_{1-x}O_x) modified with RuO₂ nanoparticles (27). and a mixed oxide of rhodium and chromium has been used as a photocatalyst for total water splitting with visible light into H₂ and O₂. A solid solution of zinc oxide and germanium nitride (Zn_{1+x}Ge)(N₂O_x) (x = 0.44) has also been shown to be an efficient photocatalyst for total water splitting under ultraviolet and visible light when adjusted by RuO₂ nanoparticles on the surface. Domen and coworkers have demonstrated that when equipped with RuO₂ as a co-catalyst, β-Ge₃N₄ exhibits its activity for the stoichiometric decomposition of water into H₂ and O₂ under ultraviolet irradiation. Improving the β-Ge₃N₄ crystallinity results in increased photoactivity and significantly reduces the release of N₂ due to photo-generated holes self-decomposition.

It is more promising to have a photoelectrolysis cell based on two illuminated semiconductor-liquid junctions. A n-type semiconductor is used for the production of O₂ and a p-type semiconductor for the synthesis of H₂. Each reaction can be dealt with at a time by splitting the cycles of oxidation and reduction into half-cell reactions. Therefore, two semiconductors with smaller band gaps can be used as each only needs to provide part of the capacity for water splitting. In the visible area of the solar spectrum, where the sun has a larger photon flux, the smaller band gap means more absorption. As a result, the theoretical maximum efficiency is significantly higher (25). The system is contingent on the efficient recombination of electrons formed in the n-type semiconductor (photoanode) with holes formed in the p-type semiconductor (photocathode) via back contact connections in both materials.

This is potentially only possible if the photocathode's valence band is positive (higher electrochemical potential) in comparison to the conduction band of photoanode. This means that careful selection of the two characteristics of the semiconductor electrode ensures that the energy required for water photoelectrolysis is obtained entirely from the illumination, removing the need to use energy from an external source. This means that careful selection of the two characteristics of the semiconductor electrode ensures that the energy required for water photoelectrolysis is obtained entirely from the illumination, removing the need to use energy from an external source. Through combining single crystal p-SiC and nanocrystalline n-TiO₂ water splitting was observed without the use of any external potential, although at low photocurrent density (0.05 mA / cm²) and low efficiency (0.06 percent) due to a high recombination of photogenerated electron-hole pairs (25). Photocatalytic splitting of water was reported under UV light irradiation with a composite of two semiconductors, Cr-doped Ba₂In₂O₅/In₂O₃. In the presence of a redox mediator, the powders of two separate semiconductor photocatalysts were also used to split water. In an aqueous solution with the IO₃⁻/I⁻ redox pair as mediator, Pt-loaded WO₃ and Pt-loaded SrTiO₃ (doped with Cr, Ta) were used for the O₂ and H₂ evolution. Water photoelectrolysis was also demonstrated using the same redox mediator using Pt-charged TaON for H₂ evolution and Pt-charged WO₃ for O₂ evolution.

In a PEC cell where the cathode was Zn doped p-GaP or p-Cu₂O, polycrystalline n-Fe₂O₃ photoanodes were examined. Spontaneous water splitting was documented under visible light illumination, although its process efficiency remained low. The photoelectrolysis cell had a different compartment for the anode Fe₂O₃ and the cathode in the latter experiment. The anode compartment had an alkaline electrolyte, while an acidic electrolyte was used for the cathode compartment. Consequently, due to the pH difference between the compartments (chemical bias), the thermodynamic (theoretical) voltage required to break water was significantly reduced. Using a polycrystalline Si composite with a doped TiO₂ thin film layer on top, a multi-junction cell arrangement like in photovoltaic devices was adopted for an SCLJ approach with two semiconductors. The doped TiO₂ absorbs the part of solar light in the short wavelength (blue light, λ < 500 nm). The long part of the wavelength is absorbed in the back by the polycrystalline Si layer. Upon light absorption, an electron is excited in two steps from a low TiO₂ valence band to a high Si conductive band lying, resulting in hydrogen evolution on the Pt counter electrode and oxygen evolution on the TiO₂ doped surface. Surface alkylation and metal nano-dot coating may solve the stability problem of silicon electrodes.

1.4.3 Photovoltaic/Semiconductor-Liquid Junction Approach (PV / SCLJ)

A PV cell with a semiconductor in direct electrolyte contact is used in a PV / SCLJ method for overall water splitting. A reduction (photocathode) or an oxidation (photoanode) photocatalyst may combine the PV cell. The water division reaction requires a two-electron reduction process for the production of H₂ and a four-electron oxidation cycle for the portion containing O₂. The biggest challenge in achieving photocatalytic splitting of water is the water oxidation reaction, primarily because four oxidative equivalents have to be stored. Consequently, the most challenging aspect of PEC water splitting is effective oxygen production at a semiconducting photoanode.

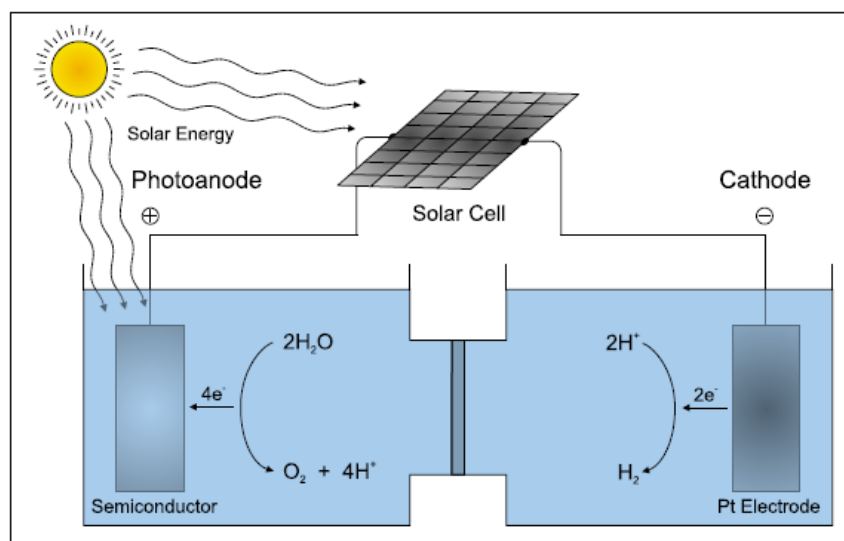


Fig. 6. PV/SCLJ approach with a Pt cathode and semiconductor photoanode (25).

A solar cell provides the additional bias for the evolution of hydrogen on a metallic cathode, resulting in a PV / SCLJ method for the overall division of energy. Nevertheless, numerous compounds were investigated for the H_2 evolution from water as reduction photocatalysts.

For water oxidation in O_2 (photoanode) and a p-type semiconductor for H^+ reduction in H_2 (photocathode), n-type semiconductor is used. The thermodynamic potential for water splitting is 1.23 V. Approximately 1.5 V must be produced by illumination to drive the reaction if over-potentials are considered. Also, n-type semiconductor is used for water oxidation in O_2 (photoanode) and a p-type semiconductor to minimize H^+ in H_2 (photocathode). The thermodynamic potential for splitting water is 1.23 V. When over potentials are considered, around 1.5 V must be generated by illumination to drive the reaction (25). A TiO_2 catalyst incorporated by CuO has been found to be an active photocatalyst to reduce H_2O under sacrificial conditions. The catalytic behavior originates from the photogeneration of excited electrons in semiconductors, TiO_2 and CuO conductive bands, resulting in the build-up of excess electrons in the conductive band of CuO .

Sacrificial agents have also been used with the same oxide semiconductor in separate water reduction and oxidation experiments. For $\text{Ln}_2\text{Ti}_2\text{S}_2\text{O}_5$ ($\text{Ln} =$ lanthanoid), MCrO_4 ($\text{M} = \text{Sr}, \text{Ba}$), $\text{Bi}_2\text{W}_2\text{O}_9$, Ag_2WO_4 , and AgBiW_2O_8 . H_2 production was recorded in the presence of sacrificial electron donors or production of O_2 when sacrificial electron acceptors were present in solution. For the evolution of O_2 from water, various compounds were investigated as photocatalysts for oxidation. Increased photochemical oxidation of water was observed with ruthenium complexes used as sensitizers adsorbed on clusters of RuO_2 , iridium oxide coupled with single centers of Cr in mesoporous silica or Bi_2MoO_6 in the presence of a sacrificial electron acceptor. Carbon- or nitrogen-doped TiO_2 , undoped, carbon-doped, or nitrogen-doped TiO_2 nanotubes, undoped or Mg-doped WO_3 , Ta-, Ti-, Al-, Si-, or Sn-doped Fe_2O_3 , Fe_2O_3 solid solutions, and BiVO_4 are all semiconductors capable of oxidizing water when an external potential is applied. Thin silver chloride layers also produce oxygen under UV / Vis illumination under appropriate conditions in aqueous solution. Experiments with gold, and silver sedimented colloids on AgCl layers as well as zeolite-modified AgCl photoanodes. Zeolite L monolayer as back support showed increased photoelectrochemical activity for water oxidation. For water photoelectrolysis, a PV / SCLJ method was used by connecting photoanodes with a nanocrystalline dye-sensitized TiO_2 solar cell in series tungsten trioxide (WO_3) or iron oxide (Fe_2O_3). The solar spectrum's short wavelength component is absorbed by the photoanode. Behind the transparent photoanode is mounted a nanocrystalline dye-sensitized TiO_2 solar cell capturing the solar spectrum's long wavelength portion. The second photosystem's photovoltage enables H_2 to be produced in a platinum cathode. In an integrated thin film system with an amorphous silicon-based PV cell and an effective catalyst film for hydrogen evolution, WO_3 was also used as a photoanode medium for oxygen evolution. In an acidic solution, the system demonstrated a stable solar to hydrogen conversion efficiency of approximately 3 percent. A triple amorphous Si solar cell coated with indium-tin-oxide (ITO) and attached to a Pt cathode also displayed the potential for water splitting. Conversion efficiencies were registered at around 5 percent, although the ITO layer's long-term stability was a concern. The photoanode must be protected from corrosion by, for example, a fluorinated tin oxide ($\text{SnO}_2: \text{F}$) layer. TiO_2 films prepared by anodic oxidation of titanium sheets were used in a PV / SCLJ system by combining the photoanode with a silicon-based PV cell and a Pt cathode. An AgCl photoanode was combined with a single junction of amorphous silicon solar cell attached to a platinum cathode. In the anodic portion, the AgCl layer and the platinum electrode were used in the cathodic part of a water photoelectrolysis system consisting of two separate

compartments linked by a salt bridge. The illumination of the AgCl photoanode as well as the amorphous Si solar cell contributed to the splitting of photoelectrochemical water into O₂ and H₂ (25).

Water splitting technology basically stores solar energy into the chemical bonds of diatomic hydrogen that to be used as a clean fuel without producing unwanted side reaction, by products or environmentally polluting compounds (28).

Table 1. Various semiconductors in photoelectrochemical cell reaction in water splitting process.

Semiconductor	Surface area (cm ²)	Electrolyte	Light source	Applied voltage (V)	Efficiency/ Hydrogen yield	Reference
TiO ₂	2	0.5 M H ₂ SO ₄ / 1N NaOH	UV light with intensity of 25mW/cm ²	-	60 μmol in 8 h	(29)
Vis-WO ₃ /vis-TiO ₂	2	0.025 M H ₂ SO ₄ / 0.05 M NaOH	UV light with intensity of 2.5mW/cm ²	-	39 μmol in 8 h	(30)
WSe ₂	0.0125	1 M KI+ 0.05 M I ₂	60 mW/cm ² tungsten lamp	-	ABPE = 17.1%	(31)
p-GaAs/n-GaAs/p-GaInP ₂	0.2	3M H ₂ SO ₄	150 W tungsten-halogen lamp	0.3	ABPE = 12.4%	(32)
AlGaAs/Si	0.22	1M HClO ₄	50 W tungsten-halogen lamp	-	ABPE = 18.3%	(33)
InGaP/GaAs/Ge	2	0.5 M H ₂ SO ₄ / 1 M NaOH	AM 1.5	-	440 μmol in 8 h	(34)
n-TiO ₂	0.2	5 M KOH	150 W Xe lamp	0.3	ABPE = 8.35%	(35)
n-TiO ₂	0.2	5 M KOH	150 W Xe lamp	0.6	ABPE = 1.08%	(35)
TiO ₂	1	Fe ³⁺ solution	500 W Xenon lamp	-	QE=10%	(26)
SrTiO ₃	0.25	9.5 M NaOH	Argon ion laser (351 nm)	-	QE=11%	(36)
SrTiO ₃	1.539	1M NaOH	150 W halogen lamp (340 nm)	0.5	QE=3.5%	(37)
p-type N-doped Ta ₂ O ₅	-	-	Visible light (λ ≥420 nm)	-	637.5 μmol/h/g _{catalyst}	(38)
CdS	-	-	300 W, Xe	-	500000.0 μmol/h/g _{catalyst}	(23)

Materials implemented in a device for sustainable hydrogen production are needed to be inexpensive, highly photoactive, chemically stable, environmentally sustainable, and have high solar-to-hydrogen conversion efficiency. As many semiconductor composites and nanostructures have been examined, thus no material satisfy all criteria of an implementable photocatalyst and many materials do not show required energy conversion efficiency.

Materials that showed high efficiency often depend on the ultraviolet portion of solar spectrum, which does not have enough energy for industrial utilization of PEC water splitting technologies. Focusing on the use of the visible spectrum is important for hydrogen production. The research includes recent advancements in the activity of visible light semiconductors, both platinum and non-platinum group materials, and advancements in the use of nanostructures for designing the next generation of catalysts. A challenge related with the catalysis is its photocorrosion, which lacks established protocols.

1.5 Photocatalysts for hydrogen production

Several photocatalysts for PEC water splitting have been researched over the past 30 years. Photoanode, responsible for oxygen evolution must have a band gap that is suitable for absorb wide range of spectrum and efficient charge collection and charge carriers' mobilities. In addition to that, the materials must be stable in aqueous solution, low cost and environmentally friendly. Water splitting photocathode are also p-type semiconductors and must produce the needed cathodic current to reduce water to hydrogen and need to have high stability in aqueous surroundings. The optimal photocathode material, demand to have the conduction band edge potential to be more negative than the hydrogen redox potential.

Table 2. Water splitting by photoelectrochemical-cell reaction with different photocatalysts.

Photocatalyst	Reaction solution	Light source (lamp)	Rate of H ₂ evolution (μmol h ⁻¹)	References
Pt/TiO ₂	2.17M Na ₂ CO ₃	400 W Hg	568	(39)
NiO/ K ₄ Nb ₆ O ₁₇	H ₂ O	450 W Hg	197	(40)
ZrO ₂	1.09M Na ₂ CO ₃	400 W Hg	75	(41)
NiO/Sr ₂ Nb ₂ O ₇	Distilled water	400 W Hg	36	(42)
Pt/ZrO ₂	0.94M NaHCO ₃	400 W Hg	61	(41)
(Ortho)BaTa ₂ O ₆	0.0005 M Ba(OH) ₂	400 W Hg	59	(43)
(Tetra)BaTa ₂ O ₆	Distilled water	400 W Hg	10	(43)
Pt/TiO ₂	2 M KBr	500 W Hg	1.3	(46)
Pt/SrTiO ₃ :RhWO ₃	2 mM FeCl ₂ /FeCl ₃	500 W halogen	1.6	(45)
Pt/SrTiO ₃ : Rh BiVO ₄	5mM FeCl ₂ /FeCl ₃	300 W Xe	0.8	(45)
Ni/Rb ₄ Nb ₆ O ₁₇	Distilled water	400 W Hg	451	(40)
Ni/K ₄ Nb ₆ O ₁₇	Distilled water	400 W Hg	197	(40)

Earlier studies of electrochemical light-based materials focused on semiconductors III, IV, and V. The p-type semiconductor, which includes sulphide and oxides, is currently receiving a lot of interest. Therefore, this review focuses on various types of photocatalyst materials.

1.5.1 Copper-based Photocatalysts

Copper based photocatalysts are extensively being developed to surpass material price and transport difficulties. The main constraint of copper based photocatalysts is that their activity is lower than compared to good photocatalysts, for which different preparation methods like- co-doping, surface treatments, specific morphology control, Z-schemes and are applied.

1.5.1.1 Cuprous oxide (Cu₂O)

Cu₂O, also known as copper(I) oxide, is a red-brown compound that is composed of copper and oxygen atoms. It is a semiconductor material, which means that it has properties between those of a conductor and an insulator. This property makes Cu₂O a valuable material in the field of electronics and photonics.

Cu₂O is commonly used as a photocatalyst, which is a material that can promote chemical reactions when exposed to light. This property makes it useful in applications such as water purification, air purification, and the production of hydrogen fuel.

Cu₂O is also used in solar cells. The semiconductor properties of Cu₂O make it an efficient material for converting sunlight into electrical energy. This technology is known as a "copper oxide solar cell" and is an alternative to traditional silicon-based solar cells. Cu₂O is also used in the production of electronic devices such as transistors and diodes. Its semiconductor properties make it a suitable material for these applications.

Cu₂O is a relatively low-cost material, making it an attractive option for commercial applications. It is also a relatively stable compound, which makes it a safe and reliable material for industrial use. However, there are several disadvantages associated with this material that can limit its effectiveness in certain applications.

One major disadvantage of Cu₂O is its low electrical conductivity. This means that it is not as efficient at conducting electricity as other materials, such as copper, which can limit its effectiveness in applications such as solar cells and sensors. Additionally, Cu₂O has a relatively high bandgap energy, which can make it less effective in absorbing light and converting it into electrical energy. Another disadvantage of Cu₂O is its sensitivity to environmental factors such as humidity and temperature. This can make it less reliable in certain applications, such as sensors, where stability is critical. Additionally, Cu₂O is also prone to corrosion, which can further limit its lifespan and effectiveness in certain applications.

One of the widely used p-type semiconductors is cuprous oxide in the application of solar water splitting. Cu₂O having band gap of 1.9-2.2 eV making it a perfect solar absorber, although photocorrosion is the greatest drawback of Cu₂O. It has good electrical conductivity, and favourable band edge position for reducing water, good carrier mobility, and ease of forming various nanostructures, morphologies and environment friendly constituent. By the latest researches, there are chances to avoid photocorrosion of cuprous oxide with the addition of passivation layer for semiconductor device Cu₂O. This coating avoids interaction between the layer of Cu₂O and the corresponding electrolyte (48).

Highly photoactive films are obtained by cathodic electro deposition using lactate stabilised copper sulphate precursor exhibiting a photocurrent density of -1 mA cm⁻² at -1 V vs RHE. It has a simple cubic

structure, it is a unit cell contains six atoms, the four Cu atoms in a face centred cubic lattice, the two oxygen atoms at tetrahedral site creating a body-centred cubic lattice enabling the four-fold co-ordination of oxygen atoms with copper atoms and linear coordination of copper atoms with oxygen atoms as nearest neighbours (Fig 7).

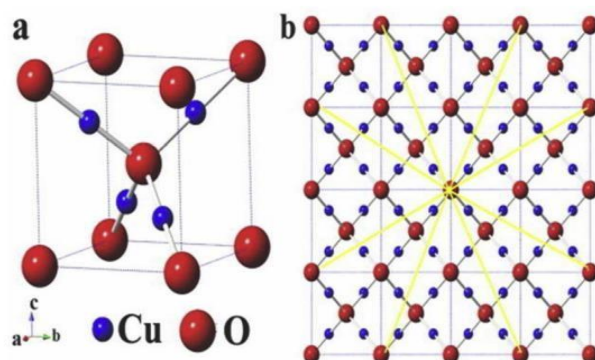


Figure : (a) Crystal structure of Cu₂O with blue balls being Cu atoms red balls being oxygen atoms and (b) 2D projection view of 64 Cu₂O unit cells. [Bagal, Indrajit V., et al. "Cu₂O as an emerging photocathode for solar water splitting-A status review." *International Journal of Hydrogen Energy* 44.39 (2019): 21351-21378]

Cu₂O can be utilized for PEC H₂ production because: i) it can absorb solar radiation in the range of 300-620 nm, which covers about 50% of the photons of the visible solar spectrum. ii) Fermi level positioning of Cu₂O suggests possibility of fabrication of efficient device for water splitting by coupling it with an n-type semiconductor electrode. iii) Cu₂O has a corresponding photocurrent of 14.7mA/cm² and theoretically Cu₂O can deliver solar light-to H₂ (STH) conversion efficiency of 18% for water splitting based on the AM 1.5 spectrums. iv) For a solar cell, Cu₂O has power conversion efficiency of about 20%. v) Cu₂O possesses desirable energy band positions and based on Mott-Schottky equation Cu₂O possess the flat band potential +0.7 V vs RHE.

To prevent photo-corrosion of Cu₂O photo electrode, different materials have been explored as protective layers, or as hetero junctions, or addition of a co-catalyst to favour the overall reaction kinetics and improve its stability. One such pioneer work has been reported by Paracchino et al. employing atomic layer deposition (ALD) technique to obtain (5×4 nm ZnO/0.17 nm Al₂O₃)/11 nm TiO₂ multilayer configuration that improved the photostability up to 78% [Paracchino, Adriana, et al. "Highly active oxide photocathode for photoelectrochemical water reduction." *Nature materials* 10.6 (2011): 456-461]. It was observed that the band bending between ZnO/TiO₂ and Cu₂O plays an adverse role for electron injection due to the n-type TiO₂ layer. Therefore, the addition of Pt as co-catalyst has been combined with the protective layer. The Cu₂O photocathodes have been developed by electrodeposition technique over transparent conducting fluorine-doped tin oxide (FTO) coated glass substrate using lactate stabilized copper sulphate precursor. Thin protective over layers of AZO and NiO_x have been used with the Cu₂O photocathode as a heterojunction to stabilize and prevent the direct contact of the photoelectrode with the electrolyte thus limiting the photo corrosion.

Hoang et al. reported a combination of graphene and amorphous non-stoichiometric MoS_x over Cu₂O as a protective layer that enhanced the photocatalytic activity and stability of pristine Cu₂O by many folds. Also, different co-catalysts, such as Graphene oxide (GO), Ag, Pt, RuO_x were integrated with Cu₂O or combined with the protective layers to further enhance the stability and photocatalytic performance. Heterojunction metal oxide was also reported where Al₂O₃ significantly improved the photocurrent density and stability of Cu₂O.

Overall, Cu₂O is a versatile and valuable material with a wide range of applications in the fields of electronics, photonics, and renewable energy. Its semiconductor properties, low cost, and stability make it an attractive option for commercial and industrial use.

1.5.1.2 Cupric Oxide (CuO)

CuO, also known as copper oxide, is a chemical compound composed of copper and oxygen. It is a dark red or black powder that is commonly used in a variety of industrial applications, such as ceramics, glass, and semiconductors. CuO is also used as a catalytic agent and in the production of pigments and fungicides.

One major advantage of Cu₂O is it has a high thermal conductivity, making it an effective heat sink material. It is commonly used in electronic devices and appliances to dissipate heat and prevent overheating. CuO has good electrical conductivity, making it useful in electronic and electrical applications. It is commonly used in semiconductors and in the production of electronic components such as transistors and diodes. CuO is highly stable in most chemical environments, making it suitable for use in harsh conditions. It is resistant to corrosion and oxidation, which makes it a suitable choice for applications in the chemical and metallurgical

industries. CuO is relatively non-toxic and safe to handle, making it suitable for use in consumer products such as ceramics and glass.

One major disadvantage of Cu₂O is it has a relatively low mechanical strength, making it susceptible to breaking and cracking under stress. This limits its use in applications where high mechanical strength is required. CuO is not very soluble in most solvents, making it difficult to dissolve and process in certain applications. This limits its use in certain chemical reactions and processes. CuO is toxic to aquatic life and can be harmful to the environment if not handled and disposed of properly. This makes it important to take precautions when using CuO in industrial applications.

Copper (II) oxide or cupric oxide is an inorganic nontoxic p-type semiconductor with the ideal narrow bandgap of 1.2 –1.7 eV. However, the small band gap give chance to cupric oxide to acquire much high photocurrent than that of cuprous oxide. The strong visible light absorption capability of this oxide makes it a largely promising material for solar water splitting compared to other photoactive metal oxides. Cupric oxide is one of the low- cost semiconductors that can be attained by the high amount of copper at earth crust or from the recovery operation of electronic wastes that contain a large amount of Cu wires scraps.

Due to the low symmetry of CuO, this material is supposed to have ferroelectric properties.

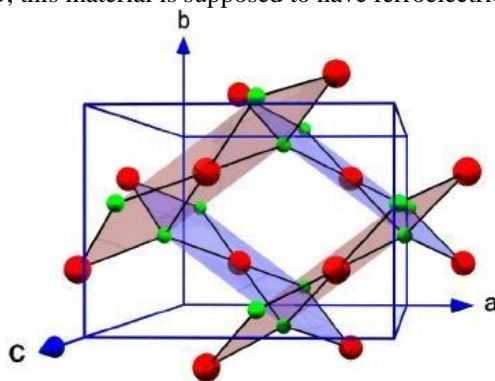


Figure 14: Structure of Cupric Oxide [Döring, G., et al. "Shake-up valence excitations in CuO by resonant inelastic x-ray scattering." *Physical review B* 70.8 (2004): 085115]

Besides, the exchange relation between Cu²⁺ ions via O²⁻ ions leads to a large but nearly constant paramagnetic susceptibility at low temperatures. Therefore, the giant magneto resistance, high thermal, and electrical characteristics of CuO have been pointed, which can be used in a wide range of organic – inorganic nanostructured composites. One of the advantages of CuO is the excellent variety of microstructures and the simplicity of synthesis of this material.

While cupric oxide as a photocatalyst for water splitting gained limited recognition as compared to cuprous oxide, as its conduction band is more positive than the conduction band of cuprous oxide (26). However, current researches on producing H₂ by cupric oxide with the composite light-emitting catalysts, results in the possibility of cuprous oxide for water splitting to give hydrogen (29, 36, 37).

Incorporating metallic elements into the CuO structure has a major influence on the morphology and stability of photoelectrodes in the electrolyte. Guo et al. fabricated CuO/Pd photocathode with bandgap energy of 1.56 eV and high PEC performance toward the hydrogen evolution reaction (HER) [Guo, Xin, et al. "CuO/Pd composite photocathodes for photoelectrochemical hydrogen evolution reaction." *international journal of hydrogen energy* 39.15 (2014): 7686-7696]. The electrodes were prepared by chemical to synthesize Cu nanoparticles, followed by the spin coating process on the FTO substrate. By further photo assisted electrodeposition of Pd nanoparticles, CuO/Pd photocathodes were formed with the highly enhanced photocatalytic stability of CuO.

Zhang et al. prepared Cu₂O/ CuO composite [Zhang, Zhonghai, and Peng Wang. "Highly stable copper oxide composite as an effective photocathode for water splitting via a facile electrochemical synthesis strategy." *Journal of Materials Chemistry* 22.6 (2012): 2456-2464]. The ultimate composite was composed of a protective thin film of CuO on the thin layer of Cu₂O. By comparing the stability of the prepared photocathode with that of the pristine Cu₂O electrode (30.1%), the composite electrode depicted enhanced stability of 74.4%. Compared to pristine CuO, the better photocurrent density and photostability of the Cu₂O/ CuO heterojunction is ascribed to the synergistic effect and enhanced crystallinity. As mentioned earlier, in Cu₂O/ CuO hybrid structure, the light-harvesting efficiency is improved. Furthermore, the electron – hole recombination rate falls and influenced an improvement in PEC water splitting activity. Also, the existence of nickel on the surface of Cu₂O/ CuO led to the rapid transfer of photogenerated electrons into the aqueous solution, as well as surface stabilization. Titanium dioxide (TiO₂) is another promising material to couple with CuO. A protective layer consisting of TiO₂ was placed in contact with the electrolyte to hinder the corrosion of CuO thin film. To

promote the performance, a CdS buffer layer between the CuO and TiO₂ formed the heterojunction. The ultimate attained system described high stability against the photo-corrosion with faradaic efficiencies close to 100%.

The synergetic photocatalytic effect of CuO and 2D materials heterojunctions similar as CuO/ 2D carbon material, CuO/ g-C₃N₄, and CuO/ dichalcogenides (TiO₂/ MoS₂) was found to be more efficient and offered better charge mobility at the proximity to the junction of the electrode/ electrolyte within the nanostructure. Thus, the heterojunctions are known to be responsible for decreasing the recombination rate of the photogenerated charge carriers.

Since photoinduced decomposition of CuO and Cu₂O photoelectrodes affect in photo-corrosion, therefore surface treatments or a thin layer of protective coatings can be an effective strategy to enhance the photostability. In this account, carbon-doped CuO dandelions / g-C₃N₄ photoelectrodes displayed an appreciable photostability and superior PEC performance, which retained ≈ 80 of its current density after 85 min, with high photocurrent density of ~ 2.85 mA cm⁻² at 0 V versus RHE [Siavash Moakhar, Roozbeh, et al. "Photoelectrochemical Water-Splitting Using CuO-Based Electrodes for Hydrogen Production: A Review." *Advanced Materials* 33.33 (2021): 2007285].

In conclusion, CuO has many useful properties that make it a versatile material for industrial applications. However, it also has some limitations that must be considered when using it. It is important to handle CuO with care and to use it in applications where its properties will be most beneficial.

1.5.1.3 CuWO₄

CuWO₄, also known as Copper Tungsten alloy, is a material that is commonly used in a variety of industrial and engineering applications. This material is known for its exceptional strength and durability, making it ideal for use in high-temperature and high-pressure environments.

One of the main advantages of CuWO₄ is its high thermal conductivity. This property allows for efficient heat dissipation, which is essential for applications that require high-temperature operations, such as in the aerospace and automotive industries. Additionally, CuWO₄ has excellent electrical conductivity, making it ideal for use in electronic components and electrical contacts. Another advantage of CuWO₄ is its high wear resistance. This material is resistant to abrasion and erosion, which makes it suitable for use in applications that require constant movement or contact, such as in machinery and equipment. Furthermore, CuWO₄ has a high melting point, which makes it ideal for use in high-temperature applications, such as in furnace linings and heat exchangers.

Despite its numerous advantages, CuWO₄ also has some disadvantages. One of the main disadvantages is its high cost. The production of CuWO₄ is a complex process that requires the use of expensive materials and equipment, which makes it more expensive than other materials. Additionally, CuWO₄ is relatively heavy and dense, which can make it challenging to use in applications that require lightweight materials.

One of the good photocatalysts among the various photo-active materials is Copper tungsten oxide (CuWO₄) having a band gap of 2.3 eV and n-type semiconductor for PEC process. This has been tested for various applications such as detector, optical sensor and laser. Because of its small band gap, it is much closer to ideal potential for PEC water splitting as favorable photoanode material. With it, single crystal of the material has a maximum conversion efficiency of 0.52% (61). CuWO₄ with PEC is significantly less owing to its poor absorption intensity and greater resistance to the shift of bulk load (61-64). Different methods such as surface functionalization and development of hetero-junction configurations greatly decrease some of the disadvantages of its PEC water splitting. Some findings show that transformation of the CuWO₄ photocatalyst surface with TiO₂ layered Au nanotubes can increase the effectiveness of PEC water splitting and raise the photocurrent water splitting from 0.03 to 0.1 mA / cm² (65). In fact, the combination of the CuWO₄ with WO₃, that produces a heterojunction photocatalyst, may improve the absorbing photon density and increase mobility (66, 67).

In conclusion, CuWO₄ is a versatile and durable material that is suitable for a wide range of industrial and engineering applications. However, its high cost and weight may be a disadvantage for some applications. Therefore, it is important to carefully consider the specific requirements of a project before deciding to use CuWO₄.

1.5.1.4 CuFeO₂

CuFeO₂, also known as copper iron oxide, is a type of compound that has been widely studied for its potential applications in various fields such as electronics, energy storage, and catalysis. This material has a unique combination of physical and chemical properties that make it an attractive option for different applications. However, like any other material, CuFeO₂ also has its own set of advantages and disadvantages. CuFeO₂ has a high electrical conductivity, making it suitable for use in electronic devices such as solar cells and sensors. CuFeO₂ has a high thermal stability, meaning it can withstand high temperatures without degrading. This property makes it a good option for use in catalytic applications. CuFeO₂ has magnetic properties, which

can be useful in magnetic data storage applications. CuFeO_2 is an environmentally friendly material, as it is made of non-toxic and abundant elements. CuFeO_2 is a relatively low-cost material, making it accessible to a wide range of applications.

Some of the disadvantages of CuFeO_2 are like CuFeO_2 has low photocatalytic activity, which limits its use in photocatalytic applications. CuFeO_2 is difficult to synthesize, as it requires high temperatures and specific conditions to form. CuFeO_2 has limited applications due to its unique combination of properties. It is not suitable for all types of applications. CuFeO_2 has low optical properties, which can limit its use in optical applications. CuFeO_2 is not very chemically stable, which can limit its use in certain applications such as catalysts.

CuFeO_2 seems to have ABO_2 -type semiconductor material having a band gap of 1.5–1.6 eV and also contains a maximum amount of visible light. In relation with its minimal band gap, CuFeO_2 is a surface rich material with high onset potential and enhanced sustainability in aqueous solution (68). Although, due to poor charge transfer, limit its performance for the photoelectrochemical water splitting process. Latest researches have shown that manufacturing processes which included the photocatalyst treatment with hybrid microwave annealing have improved the efficiency and durability of the photoelectrode which is going to make CuFeO_2 desirable for the PEC water splitting. The photocurrent activity of CuFeO_2 holds enhancement after adjusting with electrocatalyst such as a nickel-iron (NiFe) and a reduced graphene oxide.

In conclusion, CuFeO_2 is a promising material that has many potential applications, but it also has its own set of limitations. Further research is needed to fully understand the properties of this material and how to optimize its use in different applications.

1.5.1.5 CuInS₂

CuInS_2 , also known as copper indium sulfide, is a type of semiconductor material that has been gaining popularity in the field of solar energy. This material is known for its high efficiency in converting sunlight into electricity, making it an attractive option for solar panel manufacturers.

One major advantage of CuInS_2 is it has a high absorption coefficient, which means it can absorb a large amount of sunlight and convert it into electricity. This makes it an efficient material for solar panels. CuInS_2 is relatively inexpensive to produce, making it a cost-effective option for solar panel manufacturers. CuInS_2 is a stable material that does not degrade over time, which means that solar panels made with this material will have a long lifespan. CuInS_2 can be easily processed into thin films, making it suitable for use in solar cells.

Disadvantages of CuInS_2 can be described as CuInS_2 is not as widely available as other semiconductor materials, which can make it difficult to obtain in large quantities. The process of producing CuInS_2 is complex, which can make it difficult to produce in large quantities. CuInS_2 is a fragile material that can be easily damaged if not handled properly. CuInS_2 has a low thermal stability, which means it can be damaged by high temperatures.

One of the photocatalysts among the various photo-active materials is Copper indium disulphide (CuInS_2) for PEC water splitting process. Because of the direct bandgap (i.e. 1.5 eV) and large absorption coefficient (i.e. 10^5 cm^{-1}) in visible spectral range, CuInS_2 is used in thin film solar cells. Even so the photocatalyst is environmentally acceptable, still the fabrication of CuInS_2 thin film is much costly (152). The assembly methods like chemical deposition, majorly spray pyrolysis, gives a result to this problem as we do coating on large area of thin film. Spray pyrolysis with lower temperature (i.e. 150–200°C) results in CuInS_2 thin film with low cost and workable substrates.

Overall, CuInS_2 is a promising material for solar energy applications due to its high efficiency and low cost. However, its limited availability and complex processing make it a challenging material to work with. Additionally, its fragility and low thermal stability can also be a concern. Despite these challenges, researchers and manufacturers continue to investigate and develop new ways to improve the use of CuInS_2 in solar energy applications.

1.5.1.6 CuGaS₂

Copper Gallium Disulphide (CuGaS_2) is a compound material that belongs to the chalcopyrite family. It is a wide bandgap semiconductor material, which makes it an attractive material for high-temperature and high-frequency electronics applications.

One of the advantage of copper gallium disulphide is it has a high thermal stability, making it ideal for high-temperature electronics applications. Copper gallium disulphide has high electron mobility and high breakdown field, which makes it ideal for high-frequency electronics applications. CuGaS_2 is highly resistant to corrosion and is a stable material in harsh environments. Copper gallium disulphide is a non-toxic material and does not produce harmful gases, making it environmentally friendly.

However, there are some disadvantages to using copper gallium disulphide as well, like CuGaS_2 has a low bandgap energy, which limits its applications in the optoelectronics field. Copper gallium disulphide is an

expensive material, which makes it difficult to use in large-scale applications. The supply of copper gallium disulphide is limited, which makes it difficult to obtain in large quantities.

One of the less used photocatalysts in solar cell than CuInS₂ among the various photo-active materials is Copper gallium disulphide (CuGaS₂) having a wide band gap of 2.4 eV. Whilst, the photocatalysts have conduction band at negative potential than that of CuInS₂ photocatalyst that builds to be a suitable photocatalyst for photoelectrochemical water splitting (153). Latest researches depict that the doped CuGaS₂ film with co-catalyst Ti and Zn inflate the properties of Cu-Ga photocathode film.

In conclusion, copper gallium disulphide has unique properties that make it an attractive material for high-temperature and high-frequency electronics applications, but it also has some disadvantages that must be considered before using it in specific applications.

1.5.2 Zinc-based Photocatalysts

Many research people are working on enhancing the zinc based photocatalysts. The promising photocatalysts based on the latest volume of literature and the attributed photo-activity are obtained as follows.

1.5.2.1 Zinc Oxide (ZnO)

Zinc oxide (ZnO) is a widely used material in the semiconductor and optoelectronic industries due to its unique properties such as high electron mobility, wide bandgap, and high transparency in the visible region. However, like any other material, ZnO also has its advantages and disadvantages.

One of the advantage of ZnO is it has a high electron mobility, which makes it suitable for use in electronic devices such as field-effect transistors, solar cells, and light-emitting diodes (LEDs). ZnO has a wide bandgap of 3.37 eV, which makes it an ideal material for use in high-power electronic devices such as solar cells and LEDs. ZnO is highly transparent in the visible region, which makes it suitable for use in optoelectronic devices such as LCDs and OLEDs. ZnO is highly chemically stable, which makes it suitable for use in harsh environments such as high temperatures and high humidity. ZnO is a relatively low-cost material, which makes it a suitable choice for many applications.

Disadvantage of ZnO can be described as ZnO has a high thermal conductivity, which can lead to thermal stress in electronic devices. ZnO has a low mechanical strength, which can lead to mechanical stress in electronic devices. ZnO has a limited range of doping, which can limit the performance of electronic devices. ZnO has a lack of p-type doping, which can limit the performance of electronic devices. ZnO has a low electron mobility, which can limit the performance of electronic devices.

ZnO nanomaterials, with a direct bandgap of 3.37 eV and a high mobility of 210 cm² V⁻¹ s⁻¹, have played an indispensable role in such solar-to-chemical energy conversion system (72,73). Zinc oxide is considered promising due to their high electron mobility, large exciton binding energy, earth abundance, and environmental friendliness. The generation of hydrogen depends on the morphology, the interactions of electrolytes and the number of defects (74-76).

However, the wide bandgap of zinc oxide of 3.37 eV limits its absorption to the UV range, which accounts for only ≈5% of the solar radiation reaching the earth. ZnO nanorod array (NA) consisted of many single vertically aligned single-crystal ZnO nanorods fabricated through an extremely facile and cost-efficient hydrothermal technique is highly promising as a PEC photoelectrode material for more elaborate changes. Research indicates that by regulating the properties of ZnO, the ability to extract energy could be improved by a thermal evaporation method with a photocurrent of ~0.4 mA / cm²; the potential implemented is 0.8V Ag / AgCl (77, 78).

In a particular ZnO-based PEC photoanode, four main problems basically need to be considered in sequence: a) charge recombination inside bulk ZnO, b) recombination of charge carriers at the surface and interface, c) small charge extraction efficiency, and d) small surface reaction kinetics. In order to effectively increase the water oxidation reaction kinetics that seriously bounds the PEC efficiency, various electrocatalysts in different forms have been integrated on the surface of ZnO-based photoelectrodes.

A highly crystalline InN nanopyramid array with different facets was coated on a ZnO surface as an active catalyst. Based on calculations, the nonpolar face shows excellent catalytic activity, which effectively increases the PEC performance. Moreover, the built-in electric field in the ZnO/InN structure enhances the transport of photogenerated carriers, specifically holes to InN and electrons to the Pt cathode.

In conclusion, ZnO has many advantages such as high electron mobility, wide bandgap, and high transparency in the visible region. However, its disadvantages such as high thermal conductivity, low mechanical strength, limited range of doping, lack of p-type doping, and low electron mobility must be considered when selecting this material for specific applications.

1.5.2.2 ZnS

Zinc sulfide (ZnS) is a compound that is composed of zinc and sulphur atoms. It is a semiconductor material that has a wide range of applications in the fields of optics, electronics, and photonics.

One of the advantages of ZnS is it ZnS is a highly efficient scintillator material, which means it can convert high-energy radiation into visible light. This property makes it useful in applications such as radiation detection and imaging. ZnS has a wide bandgap (3.6 eV), which makes it useful in electronic devices such as LEDs and solar cells. ZnS is an inexpensive and abundant material, making it a cost-effective option for many applications. ZnS is a stable material that is resistant to corrosion and has a high melting point (1810 °C).

One of the disadvantages of ZnO is its property of relatively poor electrical conductor, which limits its use in certain electronic applications. ZnS is not a good thermal conductor, which can be a disadvantage in applications where heat dissipation is important. ZnS is not a very strong material and can be brittle, which can make it difficult to work with in some applications. ZnS can be highly toxic when inhaled, and proper safety precautions must be taken when handling it (80-82).

One of the good eligible photocatalysts among the various photo-active materials for PEC water splitting is Zinc sulphide (ZnS) because of the ability, the elimination of mobile light-excited charged transporter, and utmost conduction band potential, enabling the fast transfer of the electrons. Meanwhile, ZnS with the active sites producing H₂ without deposition of expensive charge transfer co-catalyst such as Pt or RuO₂. Because of its large band gap of 3.6 eV (approximately), ZnS functioning in photocatalysis is restricted, showing refined ZnS to be more active in UV irradiation range (84, 85). Hence, the Investigations have been performed to increase the light absorption quality of ZnS photocatalyst. It reports that ZnS injecting with transition metal complexes such as Ni, Cu and Sn strengthened the generation of Hydrogen in visible light irradiation (86-88). Defect engineering, which enhances the total efficiency of ZnS, is a further method to dope. Nevertheless, the variation of the manufacturing environment may lead towards the defected states in ZnS films which modify the visible-light absorption, the charge separation, and the photocurrent until 1.6 mA/cm² (89).

Overall, ZnS has many advantages and is widely used in a variety of applications due to its unique properties. However, it does have some limitations, and proper safety precautions must be taken when working with it.

1.5.2.3 Zinc Selenide (ZnSe)

Zinc Selenide (ZnSe) is a compound of zinc and selenium, and is commonly used as a material for optical windows, lenses, and coatings in various applications such as infrared spectroscopy, laser systems, and thermal imaging.

One of the advantages of ZnSe is it has a high transmission rate in the infrared region, making it an ideal material for infrared spectroscopy and thermal imaging applications. ZnSe has a high thermal stability, making it suitable for use in high-temperature environments. ZnSe has low absorption in the infrared region, making it an ideal material for laser systems and other applications where low absorption is required. ZnSe is a hard and brittle material, making it suitable for use in applications where high mechanical strength is required.

Major disadvantage of ZnSe is relatively expensive compared to other materials used in optical applications, making it less cost-effective for some applications. ZnSe is brittle, making it more susceptible to breaking or cracking during processing or handling. ZnSe is not as widely available as other materials used in optical applications, making it harder to obtain for some applications. ZnSe can be difficult to process and shape due to its brittle nature, which can limit its use in some applications.

ZnSe is well known n- type of II – IV semiconducting material having wide band gap energy of 2.7 eV at room temperature. ZnSe is a stable and affordable semiconductor which enables absorption of near-UV and some visible light. The conduction band (CB) is located at around -1.1 Vvs. NHE (pH 0), giving ample driving force for the reduction of aqueous protons. ZnSe is a stable and affordable semiconductor which enables absorption of near-UV and some visible light. The conduction band (CB) is located at about -1.1 V vs. NHE (pH 0), supplying ample driving force for the reduction of aqueous protons. Despite these favorable properties, ZnSe has gotten unusually little attention for solar energy production.

It's efficiently utilized in red, blue and green light emitting diodes, photovoltaics, laser screens, thin films transistor and photoelectrochemical cells. In photoelectrochemical cells (PEC), the usage is formed of the interface which forms on mere dipping the semiconductor into electrolyte solution and the liquid junction potential barrier can be effortlessly established.

Hence the ZnSe is utilized as window layer for thin film heterojunction solar cells. though it has been used as a buffer layer in chalcogenide based thin film solar cells as well. Fe doped ZnSe based nanostructures are fabricated employing distinct techniques like, electrodeposition, hydrothermal, thermo diffusion method, and spray pyrolysis.

ZnO ZnSe nanonail array was fabricated via a two sequential hydrothermal synthetic route. In this synthetic procedure, ZnO nanorod array was first grown on a fluorine- doped tin oxide (FTO) substrate by

utilizing a seed-mediated growth approach via hydrothermal method (Fig. 15). The fabricated ZnO/ZnSe nanonail array electrode has the highest charge separation rate, highest electron injection efficiency, and highest chemical stability. The photocurrent density of the ZnO/ZnSe nanonail array heterostructure reaches 1.01 mA/cm² at

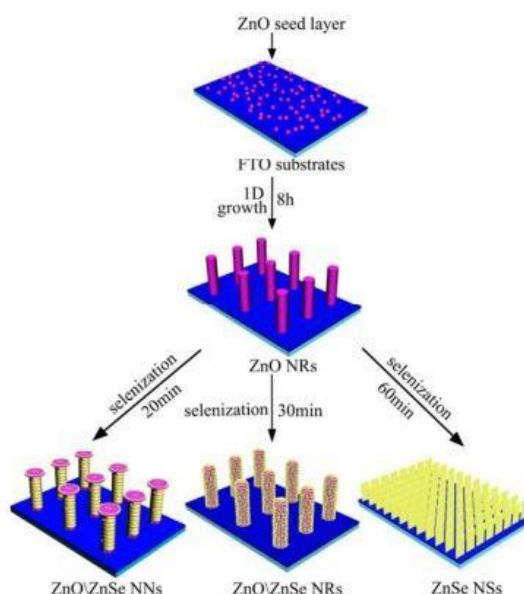


Figure 15: Schematic image of the growth process of the ZnO/ZnSe heteronanostructure arrays on FTO substrate [Wang, Liyang, et al. "In situ formation of a ZnO/ZnSe nanonail array as a photoelectrode for enhanced photoelectrochemical water oxidation performance." *Nanoscale* 8.17 (2016): 9366-9375]

an applied potential of 0.1 V (vs Ag/ AgCl), which is highly improved than that of the ZnO/ZnSe nanorod array (0.71 mA/cm²), the pristine ZnO nanorod array (0.39 mA/cm²), and the ZnSe (0.21 mA/cm²), denoting its meaningful visible light driven activities for photoelectrochemical (PEC) water oxidation. This special morphology of nail-capped nanorods might be significant for providing a better insight of the correlation between them.

Overall, ZnSe is a versatile material that offers many benefits for optical applications, such as high transmission, high thermal stability, and low absorption. However, it also has some limitations, such as high cost, brittleness, and limited availability and processing capabilities.

1.5.3 Iron-based Photocatalysts

We have used iron based photocatalysts to enhance its cost and the transport problems. Mainly different preparation methods such as- Z scheme, surface treatments and specific morphology control are in routine for iron based photocatalysts.

1.5.3.1 LaFeO₃

LaFeO₃, or Lanthanum Iron Oxide, is a material that has gained attention in recent years due to its potential as a cathode material in solid oxide fuel cells (SOFCs). SOFCs are a type of fuel cell that converts chemical energy from a fuel, such as natural gas or hydrogen, into electrical energy through an electrochemical reaction.

Advantage of LaFeO₃ can be described as it has a high conductivity for both electrons and ions, which is important for the efficient operation of a fuel cell. LaFeO₃ is relatively stable at high temperatures, which is important for the long-term operation of a fuel cell. LaFeO₃ can be synthesized from inexpensive precursors, which makes it more cost-effective than other cathode materials.

One of the disadvantages of LaFeO₃ is the electrocatalytic activity of LaFeO₃ is lower than other cathode materials, which means that more LaFeO₃ is needed to achieve the same level of performance. The electronic conductivity of LaFeO₃ is lower than other cathode materials, which can lead to a decrease in overall cell performance. LaFeO₃ has a low thermal expansion coefficient, which can lead to cracking and damage to the cell over time.

One of the good photocatalysts among the various photo-active materials is a perovskite oxide like LaFeO₃ i.e. used in splitting the water through photoelectrochemical method because they are more efficient and stable inside water. A preferred catalyst to be used for water splitting is LaFeO₃ with ABO₃ perovskite structure due to the strong stability of LaFeO₃ and the small band gap energy. Latest effort shows that the efficiency of

LaFeO₃ as a photocathode can be improved via doping it with metals of 2+ oxidation state same as that of Fe³⁺, such as Zn²⁺ and Mg²⁺. These doping agents show changes in electrical properties of the photocatalyst that increases the PEC results of LaFeO₃ (144-148).

Overall, LaFeO₃ has been shown to have a lot of potential as a cathode material in SOFCs due to its high conductivity and stability, but it also has some significant disadvantages such as low electrocatalytic activity and electronic conductivity.

1.5.3.2 CaFe₂O₄

CaFe₂O₄, also known as iron oxide-based spinel, is a type of inorganic compound that has gained attention in recent years due to its potential applications in various fields such as energy storage, catalysis, and environmental protection.

One of the advantages of CaFe₂O₄ is it has a high thermal and chemical stability, making it suitable for use in high-temperature and corrosive environments. The spinel structure of CaFe₂O₄ allows for a high surface area, which is beneficial for applications such as catalysis and adsorption. CaFe₂O₄ is relatively inexpensive to produce, making it a cost-effective option for many applications. CaFe₂O₄ has been found to have potential applications in various fields such as energy storage, catalysis, and environmental protection.

Disadvantages of CaFe₂O₄ can be listed as it has poor electrical conductivity, which can limit its use in certain applications such as battery electrodes. The precursors for CaFe₂O₄ synthesis are not widely available, making it difficult to produce on a large scale. CaFe₂O₄ has limited solubility in most solvents, which can make it difficult to work with in certain applications.

One of the good photocatalysts among the various photo-active materials is Calcium iron Oxide (CaFe₂O₄) which is p-type semiconductor preferred for water splitting process, having a band gap of 1.9 eV with certain valance band edges and conduction of +1.3 and -0.6 V vs. RHE, respectively. As the bad charge dissociation and less charge carrier strength of CaFe₂O₄, the photo-retaliation is low. Whilst, CaFe₂O₄ with doping of metal like Au and CuO results in more photocurrent response because of improved absorption wavelength (149-151).

In conclusion, CaFe₂O₄ has several advantages such as high stability, high surface area, and low cost, making it a promising material for various applications. However, its poor conductivity and limited availability of precursors and solubility can present challenges in some applications.

1.5.4 Phosphide-based Photocatalysts

Many researchers and scientists are working on the enhancing the zinc based photocatalysts. Some capable photocatalysts on the basis of current advancements and the ascribed photo-activity are attained in this review analysis.

1.5.4.1 GaP

GaP (Gallium Phosphide) is a semiconductor material that has gained popularity in the electronics industry due to its unique properties and potential for various applications. GaP is a binary compound of gallium and phosphorous, and it has a wide bandgap of 2.26 eV, which makes it suitable for high-power and high-frequency electronic devices.

One of the advantages of GaP is it has a high breakdown voltage of around 5.5V, which makes it suitable for high-voltage applications such as power electronics and high-voltage switching. GaP has a high thermal conductivity of around 60 W/mK, which makes it an excellent material for thermal management in high-power electronic devices. GaP has a high electron mobility, which makes it suitable for high-frequency applications such as microwave and millimeter-wave devices. The wide bandgap of GaP makes it an excellent material for optoelectronic applications such as light-emitting diodes (LEDs) and laser diodes. GaP is a relatively low-cost semiconductor material compared to other materials such as GaN, making it more accessible for commercial applications.

Disadvantages of GaP can be listed as it has a limited operating temperature range of around 150°C, which makes it less suitable for high-temperature applications. Although GaP has a high electron mobility, it is still lower than other semiconductor materials such as GaN, which limits its performance in high-frequency applications. GaP is sensitive to moisture and oxygen, which makes it vulnerable to chemical degradation and limits its lifetime in harsh environments. GaP can only be grown using a limited number of methods, such as metalorganic chemical vapor deposition (MOCVD), which limits its scalability for commercial applications.

In conclusion, GaP is a semiconductor material with unique properties that make it suitable for high-power and high-frequency electronic devices. However, its limited operating temperature, low electron mobility, poor chemical stability, and limited growth methods are some of the drawbacks that need to be considered when using GaP in electronic devices. Despite these disadvantages, GaP is a promising material that has the potential to be used in various applications, such as power electronics, high-frequency devices, and optoelectronics.

Gallium phosphide (GaP) can also be used as a photocatalyst in solar water splitting process. It has 2.2–2.3 eV indirect band gap and band edges beyond the reduction potential of hydrogen making it an appropriate photocatalyst in PEC process. The n-type semiconductor forms of GaP are unstable in water, where p-type semiconductor forms of GaP are more stable for long interval of time in the electrolyte in cathodic conditions. In spite of the broad bandgap of GaP photocatalyst, however it does not exhibit the contemplated photocurrent (154).

Gallium phosphide has employments in optical systems. Its static dielectric constant is 11.1 at room temperature. Its refractive index varies between ~ 3.2 and 5.0 across the visible range, which is high than in maximum other semiconducting materials. In its transparent range, its index is high than nearly any other transparent material, including gemstones akin to diamond, or non-oxide lenses similar as zinc sulphide.

The gallium phosphide (GaP) compound possesses the cubic zinc blend structure. Where each atom is at the centre of the regular tetrahedron, at the four corners of which lie atoms of the different type. The unit cell of the cubic zinc blend structure is identical as the diamond form except that the two different kinds of the atom occupy alternate position in the lattice.

Despite the wide band gap of GaP, still it doesn't display the expected photocurrent. Recent probing shows that the influence of the interface structure region between the semiconductor and the electrolyte, depositing of Pt particle on the top of GaP notable increase the efficiency of PEC cell.

Latest related studies depict the impact of the interface structure zone between photocatalyst and electrolyte, the deposition of Pt molecules on the uppermost layer of photocatalyst raise the efficiency of the PEC setup.

1.5.4.2 Indium Phosphide (InP)

InP (Indium Phosphide) is a semiconductor material that has been widely used in the field of optoelectronics and telecommunications. InP has several advantages and disadvantages that make it a suitable or unsuitable choice for certain applications.

One of the advantages of InP is it has a high electron mobility, which means that electrons can move quickly through the material. This is an important property for electronic devices such as transistors and integrated circuits. InP has a high optical gain, which means that it can amplify light signals. This property makes InP suitable for optical amplifiers, which are used in telecommunications systems. InP has a low absorption loss, which means that it does not absorb a lot of light. This property makes InP suitable for optical waveguides, which are used in telecommunications systems. InP has a high thermal conductivity, which means that it can dissipate heat quickly. This property is important for electronic devices that generate a lot of heat.

Disadvantages of InP is its relatively expensive material compared to other semiconductor materials. This can make it less suitable for certain applications. InP is not as widely available as other semiconductor materials. This can make it difficult to find the right suppliers and manufacturers. InP is a relatively difficult material to process. It requires special equipment and expertise, which can make it less suitable for certain applications. InP has a high electron effective mass, which means that electrons are heavier than in other semiconductor materials. This can make it less suitable for certain applications that require fast switching speeds.

InP exhibits a band gap of 1.35 eV, describing near-optimal absorptivity of the solar spectrum. Nevertheless, the high cost of InP limits its marketable processibility as a photoelectrode for water splitting (78, 93-95).

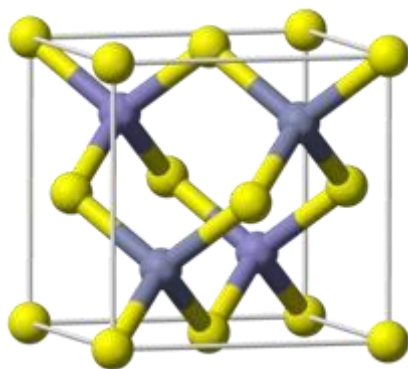


Figure : Cubic Unit cell of the GaP Structure [65]

But the authors claimed that the performance of InP- based photoelectrodes was restricted by severe photocorrosion. Thus, amorphous TiO₂ has been employed as a surface passivation layer to isolate InP photoelectrode from the electrolyte. One should similarly note that the large valence band offset between TiO₂

and these metal phosphides can result in an energy barrier for holes reaching the surface, decreasing the recombination at the surface.

It's worth mentioning that Hannappel and co-workers have developed an effective tandem cell based on group II–IV materials. The tandem structure consists of a GaInP n–p top cell ($E_g = 1.78$ eV) and GaInAs n–i–p bottom cell ($E_g = 1.26$ eV) with Rh electrocatalysts deposited onto the surface (May, Matthias M., et al. "Efficient direct solar-to-hydrogen conversion by in situ interface transformation of a tandem structure." *Nature Communications* 6.1 (2015): 1-7). The as-prepared tandem device yields a STH of 14% and 17% for unbiased and potentiostatically supported water splitting, respectively, which is the current standard efficiency for a tandem PEC device. Since, conduction band edge of the photocatalyst is slightly up than water reduction potential, therefore, InP tends to be a preferable photocathode in PEC process. However, photocorrosion is major drawback of InP photocatalyst in acidic medium (96), but we can raise the efficiency and stability of InP electrode with protective layer of TiO_2 catalyst. Even with its efficiency, cost effectiveness of bulk materials and fabrication process, InP restricts its expandable applications (97, 98).

In conclusion, InP has several advantages and disadvantages that need to be considered when choosing it as a material for electronic devices. Its high electron mobility, high optical gain, low absorption loss, and high thermal conductivity make it suitable for optoelectronics and telecommunications systems. However, its high cost, limited availability, difficult processing, and high electron effective mass make it less suitable for certain applications.

1.5.5 Sulphide-based Photocatalysts

Sulphide based photocatalysts are majorly enhanced to beat transportation hitches and semiconductor cost. These photocatalysts have diverse preparation methods such as surface treatments, co-doping and specific morphology control.

1.5.5.1 Cadmium Sulfide (CdS)

Cadmium sulfide (CdS) is a semiconductor material that has been widely used in various applications, including photovoltaics, light-emitting diodes (LEDs), and sensors. The material has several advantages and disadvantages that should be considered when deciding whether or not to use it in a specific application.

One of the advantages of CdS is it has a high absorption coefficient, which means that it can absorb a large amount of light. This makes it an ideal material for photovoltaic cells and LEDs. CdS is relatively inexpensive to produce, making it an attractive option for many applications. CdS has a wide bandgap of 2.4 eV, which means that it can be used in applications that require high-energy photons, such as LEDs. CdS is a good conductor of electricity, making it an ideal material for sensors and other electronic devices.

One of the disadvantages of CdS is it is made from cadmium, which is a toxic heavy metal. This can be a concern for both the workers who produce the material and the environment. CdS is not as stable as some other semiconductor materials, and it can degrade over time. This can be a problem for applications that require long-term stability. CdS has poor thermal conductivity, which means that it does not dissipate heat well. This can be a problem for applications that generate a lot of heat. CdS has a limited range of applications, and it may not be suitable for certain types of devices.

Overall, CdS is a versatile and cost-effective semiconductor material that has many advantages, but also some limitations. Careful consideration of the specific requirements of an application should be made before deciding whether or not to use CdS.

Cadmium sulfide (CdS), as a typical II–VI chalcogenide n-type semiconductor, has currently been extensively explored as a typical photoanode for solar driven water splitting due to the easy preparation, suitable 2.4 eV wide band gap compound semiconductor that behaves like n-type material (99, 100) and superior light absorption ($\lambda < 516$ nm). While the photocurrent behavior of CdS is ineffective, as the photogenerated charges, holes and electrons are not gradually isolated and shifted (100-102). CdS electrodes are one of the most thoroughly studied binary compound semiconductors for photocatalysis, photonics, photovoltaics, and optoelectronics employments. However, the poor photogenerated electron-hole pairs separation and serious photocorrosion have impeded its further application (103). The recent research indicates the development of CdS 2-dimensional-nanostructure, that provides certain improvements, such as the decrease of the scattering limit, which improves the carrier collection quality and the storage of incident light (104).

An increasingly number of modified techniques have been developed to address the aforementioned problems to enhance the PEC water splitting performance of CdS photoelectrode, such as decorating with noble metal, ion doping, constructing heterostructures and so on, among which the heterostructure photoelectrodes linking with distinct semiconductors have been proved as a feasible method to effectively separate the photogenerated carriers of CdS photoelectrode. Although heterojunctions play an effective role in broadening the visible response and enhancing carrier separation, it is still an urgent task to search a suitable heterojunction for the conduction band (CB) and valence band (VB) level.

Overall, CdS is a versatile and cost-effective semiconductor material that has many advantages, but also some limitations. Careful consideration of the specific requirements of an application should be made before deciding whether or not to use CdS.

1.5.5.2 MoS₂

MoS₂, also known as molybdenum disulfide, is a two-dimensional material with unique electronic and mechanical properties. It is a compound of molybdenum and sulfur atoms arranged in a layered structure, similar to graphene. Due to its unique properties, MoS₂ has been gaining attention in the field of material science and has been researched extensively for its potential applications in various industries.

One of the most notable properties of MoS₂ is its high mechanical strength. It is known to have a high Young's modulus and tensile strength, making it a strong and durable material. This makes MoS₂ a potential candidate for use in aerospace and automotive applications, where high strength and durability are essential.

Another key property of MoS₂ is its electronic properties. MoS₂ is a semiconductor material, which means it can conduct electricity but not as well as a metal. This makes MoS₂ a potential candidate for use in electronic devices such as transistors and solar cells. The material has a large bandgap, which makes it suitable for use in optoelectronic devices such as light-emitting diodes (LEDs) and photodetectors. MoS₂ has also been explored as a potential material for use in batteries, as it has a high capacity for lithium storage.

MoS₂ is also known for its excellent thermal conductivity. This property makes it a suitable material for use in thermal management applications, such as thermal interface materials and heat sinks. The high thermal conductivity of MoS₂ also makes it a potential material for use in high-power electronic devices, where heat dissipation is a critical issue.

In conclusion, MoS₂ is a unique two-dimensional material that has gained attention in the field of material science due to its excellent mechanical, electronic, and thermal properties. Its high strength, electronic properties, and thermal conductivity make it a potential candidate for use in various applications, including aerospace and automotive, electronics, optoelectronics, and thermal management.

1.5.6 Titanium Dioxide (TiO₂)

Titanium dioxide, also known as TiO₂, is a naturally occurring mineral that is widely used in various industrial and commercial applications. The most common form of TiO₂ is anatase, which is a white, powdery substance that has a high refractive index and is highly photocatalytic.

TiO₂ is used in a wide range of industries, including paint and coatings, plastics, ceramics, and paper. In the paint and coatings industry, TiO₂ is used as a whitening agent and a UV absorber, which helps to protect the paint from fading and chalking. In the plastics industry, TiO₂ is used as a whitening agent and a UV stabilizer, which helps to protect the plastic from breaking down due to UV exposure. In the ceramics industry, TiO₂ is used as a glaze and a whitening agent, which helps to improve the appearance and durability of the ceramic product. In the paper industry, TiO₂ is used as a whitening agent and a brightness enhancing agent, which helps to improve the appearance and readability of the paper.

In addition to its industrial uses, TiO₂ is also used in a wide range of consumer products, including sunscreens, cosmetics, and food products. In sunscreens, TiO₂ is used as a physical sunscreen, which helps to protect the skin from UV radiation. In cosmetics, TiO₂ is used as a whitening agent and a pigment, which helps to improve the appearance of the product. In food products, TiO₂ is used as a whitening agent and a colorant, which helps to improve the appearance and consistency of the product.

Despite its many uses, TiO₂ is also a potential health concern. Inhaling high levels of TiO₂ dust can cause lung inflammation and lung cancer. Therefore, it is important for workers handling TiO₂ to take the necessary precautions to protect their health.

Overall, TiO₂ is a versatile and widely used mineral that has many industrial and commercial applications. Its high refractive index and photocatalytic properties make it useful in many industries, while its whitening and UV protection properties make it useful in many consumer products.

PEC water splitting involves the use of sunlight to split water molecules into hydrogen and oxygen, with the goal of producing clean and renewable hydrogen fuel. TiO₂ is a key component in this process due to its unique properties, including its ability to absorb a wide range of wavelengths of light and its high electron mobility.

TiO₂ can be used in PEC water splitting in two main ways: as a photoanode or a photocathode. A photoanode is the electrode that absorbs light and generates electrons, while a photocathode is the electrode that receives electrons and generates hydrogen gas. TiO₂ can be used as a photoanode in PEC water splitting by absorbing light and generating electrons, which can then be used to reduce water to hydrogen. In this process, TiO₂ is typically coated on a semiconductor material, such as silicon, to improve its efficiency.

Alternatively, TiO₂ can be used as a photocathode in PEC water splitting by absorbing light and generating oxygen gas. This process is typically carried out in a two-electrode system, where TiO₂ is coated on

one electrode and a metal, such as platinum, is coated on the other electrode. In this system, the TiO_2 absorbs light and generates electrons, which are then used to oxidize water to oxygen.

TiO_2 based photoelectrodes for water splitting have been intensively researched since 1972, due to numerous favourable properties, similar as being composing of earth-abundant, nontoxic elements as well as being photochemically stable under either strongly acidic or strongly basic environment. Still, due to its wide band-gap (3.2 eV for anatase (Fig. 10) and 3.0 eV for the rutile phase), only 5% of the solar spectrum (generally UV light) can be absorbed, which leads to a really low maximum theoretical STH efficiency ($Z = 1.3\%$ for anatase and 2.2% for rutile TiO_2). This is identified as a photoanode with UV irradiation by Honda and Fujishima in 1972 for the first PEC water splitting (11, 16, 17, 26, 52). Since of its stability in aqueous solution, photoelectrodes (e.g. Cu_2O , Si, InP, etc.) which are unstable in water have been added as defense layers. However, the applications of TiO_2 photoanode in PEC water splitting are limited because of the large band gap (137).

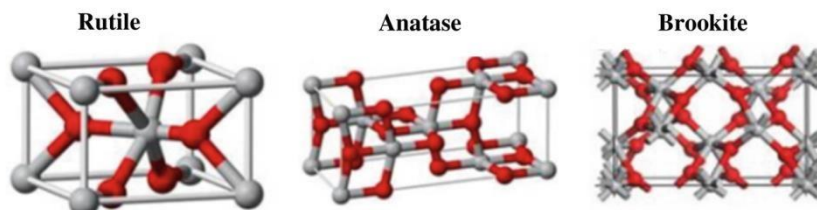


Figure : Crystal structure of TiO_2 [6]

TiO_2 photocatalyst requires pure water to achieve water splitting for hydrogen production due to the rapid recombination of photogenerated CB electrons and VB holes. In order to improve electron-hole separation and achieve high quantum efficiency, sacrificial reagents or electron donors can be added to photo-generated VB holes. In any case, the weakness of this procedure is the need to persistently add electron contributors to support the response since they will be consumed during photocatalytic response. Li and co. when organic pollutants acting as electron donors, such as formaldehyde, oxalic acid, and formic acid, were incorporated into the reaction system, improved photocatalytic hydrogen production was reported. The organic pollutants were said to decompose in a way that was consistent with the hydrogen product. Carbonate mariners were added to improve photocatalytic hydrogen product by suppressing its backward reaction to form water [Li, Yuexiang, Gongxuan Lu, and Shuben Li] in addition to the use of sacrificial agents. In-situ infrared spectroscopy is used to monitor donor adsorption and photocatalyze the production of hydrogen from electron donors in single and mixed systems." 52.5 *Chemosphere* (2003): 843-850]. The backward reaction of photocatalytic hydrogen to water was found to be suppressed by the addition of carbonate salts, thereby enhancing hydrogen production. Sayama and co. Sayama, Kazuhiro, and Hironori Arakawa reported that the stoichiometric photocatalytic decomposition of water into H_2 and O_2 was largely effective when carbonate salts were added to Pt-loaded TiO_2 suspensions. Effect of adding carbonate salt to the Pt- TiO_2 catalyst on the photocatalytic decomposition of liquid water." *Faraday Transactions* 93.8 of the *Journal of the Chemical Society* (1997): 1647-1654]. During the reaction, it was discovered that the Pt-loaded TiO_2 photocatalyst was coated in a variety of carbonate species. These carbonate species aid in the photoabsorption of oxygen on the TiO_2 and effectively repress the back reaction of water splitting into water.

Bamwenda and co prepared TiO_2 photocatalysts loaded with Au and Pt for the production of hydrogen through deposition, precipitation, impregnation, photodeposition, and colloidal mixing processes. [Bamwenda, Gratian R., et al.] found that synthesis methods and metal loadings have a significant impact on H_2 production. Hydrogen production aided by photosynthesis from a water-ethanol solution: a comparison of Au- TiO_2 and Pt- TiO_2 's activities." *A Issue of the Journal of Photochemistry and Photobiology*: 1995: *Chemistry* 89.2: 177-189]. The trapping of photogenerated electrons, reduction of protons, formation/desorption of hydrogen, and promotion of the activity of the photocatalyst by Surface plasma resonance are all functions that Au and Pt play on TiO_2 . SPR is defined as the collective motions of conduction electrons induced by light irradiation. Depending on the used excitation light source, the deposited gold nanoparticles serve as both light harvesters, injecting electrons into the conduction band of TiO_2 , and catalytic sites for gas generation.

The metal ion doping technique, in which a small amount of metal ions is incorporated into the crystal lattice of the photocatalyst, is the most common method for modifying the bandgap of the catalyst. Choi and co. systematically investigated the photoactivity of 21 transitional and rare earth metal ions doped into TiO_2 [Choi, Wonyong, Andreas Termin, and Michael R. Hoffmann]. Metal ion dopants' function in quantum-sized TiO_2 : correlation between charge carrier recombination dynamics and photoreactivity." 98.51, 2002, *The Journal of Physical Chemistry*: 1366913679]. It was established that TiO_2 's photoresponse could be enhanced into a visible-light spectrum by doping it with metal ions. Impurity energy levels in the TiO_2 bandgap are created as metal ions are incorporated into the lattice. For more precise charge transfer, photocatalysts should have metal

ions doped near their surface. Photocatalytic reactions will suffer as a result of metal ions acting as recombination centers when deep doping is used. Photocatalytic activity induced by visible light may be enhanced by these metal dopings.

There aren't many studies in the literature on the use of anion doping to boost photocatalytic activity under visible light, making it a novel strategy. Anion doping (N, F, C, S, etc.) in TiO₂ translucent could move its photocatalytic reaction into apparent light range. Anions, in contrast to metal ions (cations), are better at amplifying photocatalytic activity because they are less likely to form recombination centers. Bandgap narrowing occurs when non-metals like S and N are doped, expanding the valence band's range.

Lately, Mao et al. developed a new strategy to synthesise a disordered nanophase TiO₂ by assimilating a dopant through the hydrogenation of TiO₂ nanocrystals; the as-prepared hydrogenated TiO₂ exhibits a black colour, corresponding to a band-gap energy of 1.0 eV rather than 3.30 eV typically found for pure TiO₂, promising a much high solar-to-fuel conversion efficiency [Chen, Xiaobo, et al. "Increasing solar absorption for photocatalysis with black hydrogenated titanium dioxide nanocrystals." *Science* 331.6018 (2011): 746-750].

Specific approaches have been employed to improve light absorption and charged carries TiO₂ transport, such as cocatalyst doping (e.g., Co and Ag) (75, 92, 14, 105-107). For example, N-modified TiO₂ photoanode, which was synthesized in NH₃ atmosphere through nitridization of hydrothermally produced TiO₂ nanowires, obtained a band gap of 2.4 eV (108). Heat-treated and chemical-reduction TiO₂ nanoparticles show increased photocatalytic properties with 2.0 mA / cm² photocurrent at 1.23 V (109).

Overall, TiO₂ is a versatile and efficient photocatalyst for PEC water splitting due to its ability to absorb a wide range of wavelengths of light and its high electron mobility. Its use in PEC water splitting can lead to the production of clean and renewable hydrogen fuel, making it an important component in the quest for sustainable energy solutions.

1.5.7 Tungsten Oxide (WO₃)

WO₃, also known as tungsten trioxide, is a chemical compound composed of tungsten and oxygen. It is a common component in various industrial and technological applications due to its unique properties such as high electrical conductivity, high refractive index, and high transparency in the visible and ultraviolet regions of the electromagnetic spectrum. However, like all materials, WO₃ has its advantages and disadvantages.

One of the advantages of WO₃ is it has a high electrical conductivity, making it an ideal component in electronic devices such as transistors, diodes, and solar cells. WO₃ has a high refractive index, making it useful in optical applications such as coatings and lenses. WO₃ is transparent in the visible and ultraviolet regions of the electromagnetic spectrum, making it useful in optical applications such as coatings and lenses. WO₃ is considered to be a low toxicity material, making it safe to use in various industrial and technological applications. WO₃ is a durable and stable material, making it suitable for long-term use in various applications.

Major disadvantages of WO₃ can be discussed as it can be expensive to produce, which can increase the cost of the end product. WO₃ is not as readily available as other materials, which can make it difficult to find for certain applications. WO₃ can be sensitive to temperature changes, which can affect its performance in certain applications. WO₃ is a brittle material, which can make it susceptible to breaking or cracking under certain conditions. WO₃ is not a flexible material, which can limit its use in certain applications.

However, the advantages of WO₃ outweigh its disadvantages, making it a valuable component in various industrial and technological applications (93, 94).

One of the good photocatalysts among the various photo-active materials is Tungsten oxide (WO₃), and it is most researched semiconductor as compared to their other metallic nanoparticles as a photoanode for the PEC water split. WO₃ is n-type semiconductor and has an apparent 2.5–2.8 eV band range that can capture approximately 12 per cent of the solar spectrum (14, 93). WO₃ in acidic medium is non-corrosive, cheap, and has good stability. This material can however consume a small portion of visible light and the reason is its wide band gap (54, 169). WO₃ have high crystallinity, porosity, the ability of capturing 12% of the solar illumination, moderate hole diffusion length, good chemical stability and easy and cheap preparation methods.

Due to the load resistance imposed on the substratum, the photocurrent density depends on the substratum and the temperature of the procedure. The effect can be attributed as temperature function. The density of the photocurrent increases as the temperature increases. At a higher temperature, there is a transition from crystalline to amorphous state and there is also a large recombination of charging carriers that leads to a reduction in photocurrent density and affects electrode stability (90). WO₃ nanoflakes with hierarchical architecture improved photoelectrochemical activity due to the multiple light dispersion that facilitates better light absorption and the exposure of active sites resulted in increased interfacial load transfer.

Furthermore, the conductive band is very small (0.3 V vs RHE) correlated with the redox potential of hydrogen evolution reaction (96) Such research shows that hydrothermal treatment could have a substantial effect on the shape of the modulated electrode and indicate a much higher enhancement of WO₃ photoelectrode (97, 98).

In conclusion, WO_3 has a number of advantages such as high electrical conductivity, high refractive index, and high transparency, but it also has some disadvantages such as high cost, limited availability, and fragility.

1.5.8.1 TaON

TaON, also known as tantalum oxide nitride, is a material that is commonly used in the semiconductor industry. It is a compound of tantalum, oxygen, and nitrogen, and is known for its high thermal stability and excellent electrical properties.

Advantage of TaON is known for its high thermal stability, which means that it can withstand high temperatures without degrading. This makes it ideal for use in high-temperature applications such as in the semiconductor industry. TaON has excellent electrical properties, including high dielectric constant, low dielectric loss, and high breakdown voltage. This makes it ideal for use in electronic devices such as capacitors and transistors. TaON has a low leakage current, which means that it can maintain a stable voltage even under high temperatures. This makes it ideal for use in electronic devices that require a stable voltage. TaON is highly resistant to wear, which means that it can withstand high levels of mechanical stress without degrading. This makes it ideal for use in applications where wear resistance is important.

Some disadvantages of TaON can be discussed as it is a relatively expensive material, which can make it cost-prohibitive for some applications. TaON is not widely available, which can make it difficult to obtain for some applications. The synthesis of TaON can be complex and requires specialized equipment, which can make it difficult to produce on a large scale.

One of the good photocatalysts among the various photo-active materials is Tantalum oxynitride (TaON) having 2.5 eV band gap and n-type semiconductor, with good solar water splitting capacity (110-112). TaON also have 34% quantum efficiency (113). TaON shows appropriate configuration of its conduction band and valance band edges with respect, OH^-/O_2 oxidation potential and H^+/H_2 reduction potential, produces hydrogen and oxygen. However, configuration (activity) for hydrogen produced is lesser than that for oxygen evolution, which is considered to be negative for H_2 production. As TaON result in poor equilibrium, the N 2p energy levels are included in the energy level. New study suggests that the catalytic efficiency of TaON for hydrogen production can also be strengthened by photodeposition with worthy nanoparticle like Ru (115).

In conclusion, TaON is a material that is known for its high thermal stability and excellent electrical properties. However, it is also relatively expensive and not widely available, which can make it difficult to use in some applications. Despite these disadvantages, TaON is a valuable material for the semiconductor industry due to its high thermal stability and excellent electrical properties.

1.5.8.2 Ta₃N₅

Ta₃N₅, also known as titanium nitride, is a type of ceramic material that has a variety of industrial and commercial applications. It is known for its exceptional hardness, high wear resistance, and excellent thermal stability. However, like any material, Ta₃N₅ also has its advantages and disadvantages.

Advantage of Ta₃N₅ is its incredibly hard property. This makes it highly resistant to wear and abrasion, making it ideal for applications such as cutting tools, wear parts, and coatings. Ta₃N₅ has a high thermal stability, making it suitable for high temperature applications. It can withstand temperatures up to 600°C without losing its properties. Ta₃N₅ is resistant to most acids and alkalis, making it suitable for applications in harsh chemical environments. Ta₃N₅ has a low friction coefficient, making it suitable for applications where low friction is required, such as bearings and gears. Ta₃N₅ is biocompatible, making it suitable for use in medical implants and devices.

Disadvantages of Ta₃N₅ can be discussed as it is relatively expensive to produce, making it less suitable for large-scale or mass production applications. Ta₃N₅ is a brittle material, making it susceptible to cracking or breaking under high impact or stress. Ta₃N₅ is difficult to machine due to its hardness, making it challenging to produce complex or detailed parts. Ta₃N₅ is not widely available, making it difficult to source in some regions.

Tantalum nitride (Ta₃N₅) actually have small band gap (2.1 eV) and less stability. Ta₃N₅ with conduction band lies at ca. -0.4 V vs. RHE, and valance band lies at ca. +1.6 V vs. RHE, perhaps make it to acquire unaided solar sourced water splitting (122-126). Consequently, Ta₃N₅ will separate unrestrained water as a single photocatalyst having highest solar Solar to Hydrogen efficiency of approximately 15% (126, 128). However, Ta₃N₅ is suffering from a lack of charge transfer, limited photocurrent performance and terrible energy absorption (129, 131). Methodologies generally used in the study have been intended to enhance Ta₃N₅ photocatalyst in PEC process, like morphology control and nanostructuring (132, 133). Ta₃N₅ photoanode with 1 dimensional configuration, like nanotubes and nanorods, are identified. This 1-dimensional nanomaterial provides new transfer of charge to a solid-liquid interface in absence of recombination and high absorption of light intensity. $\text{Co}(\text{OH})_x$ co-catalyst alteration of Ta₃N₅ nanoparticles provides 2.8 mA/cm² at 1.23 SV vs RHE consistent photocurrent density.

In conclusion, Ta₃N₅ is an excellent material for a variety of industrial and commercial applications due to its exceptional hardness, high wear resistance, and excellent thermal stability. However, its high cost, brittleness, and difficulty to machine make it less suitable for certain applications. Additionally, its limited availability can make sourcing the material difficult. Careful consideration of the advantages and disadvantages of Ta₃N₅ is essential when selecting a material for a specific application (117, 134-136).

1.5.9 BiVO₄

Bismuth vanadate, also known as bismuth(III) vanadate, is a chemical compound with the formula BiVO₄. It is a yellowish-green powder that is highly insoluble in water and is commonly used as a photocatalyst and a pigment.

Bismuth vanadate has a unique crystal structure known as tetragonal, which allows it to absorb light in the visible range and makes it an ideal material for photocatalysis. Photocatalysis is a process in which a material absorbs light and generates electron-hole pairs, which can then be used to catalyze chemical reactions. Bismuth vanadate has been extensively studied for its photocatalytic properties and has been found to be effective in a wide range of applications, including air purification, water purification, and organic synthesis (155).

Bismuth vanadate also has potential applications in the field of solar energy. Its ability to absorb light in the visible range makes it an ideal material for solar cells and it has been studied as a potential alternative to silicon-based solar cells. In addition, bismuth vanadate has been found to be effective in the photoelectrochemical splitting of water into hydrogen and oxygen, which is a key step in the production of hydrogen fuel.

As a pigment, bismuth vanadate is used in a wide range of applications, including ceramics, glass, and paint. It is known for its bright yellow color and is often used as a substitute for lead-based pigments.

One of the good n-type semiconductor photocatalysts among the various photo-active materials is Bismuth vanadate (BiVO₄) that comes out as a component that can be used for water separation. BiVO₄ does have 2.4 eV band gap and it can accommodate a considerable part of the visible spectrum (91, 105, 116). As its suitable conduction band position which is very near to the H₂ evolution potential, with relatively less onset potential for O₂ evolution (106, 107). Even in acidic aqueous solution, the well-polished edge of the band, moderate band gap energy and stability make BiVO₄ nanoparticle suitable for use as a photoanode for the use of water splitting.

Low cost and flexible BiVO₄ thin films can be prepared with a photocurrent density of up to 0.8 mA / cm² at an applied potential of 1.9 V versus RHE by means of electrostatic spray pyrolysis. Although, BiVO₄ has low photocurrent efficiency in solar radiation, slow charge transfer, fast electron-hole recombination, and its low water oxidation kinetics (108, 109, 118). To neglect these drawbacks, several methods have been applied like construction of heterojunction structure, doping, and morphology control (119, 120). Significant milestone was made with the use of BiVO₄ / SnO₂ / WO₃ triple-layer double-heterojunction photocatalyst by spin coating that raised PEC photocurrent to 3.1 mA / cm² at 1.23 V vs RHE (121).

In conclusion, bismuth vanadate is a versatile material with a wide range of applications in fields such as photocatalysis, solar energy, and pigments. Its unique crystal structure and ability to absorb light in the visible range make it an attractive material for research and development.

1.5.10 NiO

NiO, or nickel oxide, is a chemical compound made up of nickel and oxygen atoms. It is a yellow or brown powder that is often used as a pigment in ceramics and glass, as well as in electronics and batteries.

One of the main advantages of NiO is its high electrical conductivity. When used as a cathode material in lithium-ion batteries, it can greatly improve the performance and efficiency of the battery. In addition, NiO has a high melting point and good thermal stability, making it a useful material for high-temperature applications.

Another advantage of NiO is its use as a catalyst. NiO is an active catalytic material that can be used to promote chemical reactions in various industrial processes, such as the production of chemicals and fuels.

However, NiO also has some disadvantages. One of the main disadvantages is that it is not very stable in acidic environments, and can easily be dissolved by strong acids. Additionally, NiO can be toxic when inhaled in large quantities, and so proper safety measures must be taken when handling it.

One of the semi-transparent p-type semiconductor is Nickel oxide, having 3.6–4.0 eV band gap which possess more concentration, less resistance, a high hole mobility, and a low lattice discord with ZnO, which are commendatory for forming the p-n heterojunction (31, 137-139). But on other side, the photocurrents developed by Nickel oxide photomaterial are truly lesser as the low potential of its valence band (0.3V vs RHE). Although, sensitizing Nickel oxide photocatalyst having the quantum dots which acquires more photocurrent and photopotential (31, 32, 140).

Overall, NiO is a versatile and useful material with many advantages, but it also has some disadvantages that must be considered when using it.

1.5.11 Si

One of the photocatalysts among the various photo-active materials is Silicon (Si) for PEC water splitting process. Moreover due to its narrow band gap (1.1 eV) (141, 142), the photocatalyst is one of the promising photoelectrodes for water splitting process because of its natural abundance, environmental friendly and ability for the high-scale production (143-146).

Silicon has a diamond Cubic structure with a lattice parameter of 0.543 nm. The nearest neighbour distance is 0.235 nm. The diamond cubic structure has an FCC lattice with a basis of two Silicon atoms.

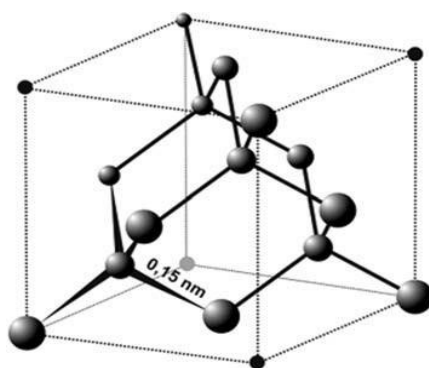


Fig. : Structure of Silicon [Nshingabigwi, Emmanuel Korawinga. Cross-section Transmission Electron Microscopy of Radiation Damage in Diamond. Diss. University of the Witwatersrand, 2006]

Practically the use of Silicon catalyst as photocathode in water splitting process was restricted because of the instability of Si in water. Still, different ways have been developed for protecting Si surface from corrosion by using protective layers (i.e. ALD of TiO₂, Al₂O₃, and more catalyst layers) to make Si electrodes to give more stable PEC water splitting performance in the different aqueous environments (96, 147-151). The recent researches showed the deposition of Si semiconductor with strontium titanate (SrTiO₃) as a protective layer with 35 mA/cm² photocurrent density and high stability (145).

II. Conclusion

Systems need to be cost-effective, economically viable, turning solar light into chemical fuel, and they should meet the performance needed for medium and large-scale applications. The products used should also be secure and plentiful in the environment.

These three water photoelectrolysis methods have their advantages and disadvantage that are inherent in the technique itself and/or the semiconductors used. The PEC cell consists of a photocathode and an anode, or a photoanode and a cathode, respectively, depending on the reaction at the semiconductor-liquid junction, which is either hydrogen or oxygen evolution.

The biggest challenge in achieving photocatalytic water splitting is the water oxidation reaction. Consequently, the most challenging aspect of PEC water splitting is efficient oxygen production at a semiconducting photoanode. Various research groups around the world have set project goals to create an effective photoanode semiconductor for the production of oxygen.

In research pursuit, a remarkable increase can be seen as a big achievement in the solar hydrogen production in the last decade by PEC water splitting process.

- In this review, we have discussed about the basic principle of water splitting and fundamental mechanisms of the process.
- We have scrutinized the basic engineering approach of hydrogen production by PEC water splitting process.
- We have discussed about various semiconducting materials such as p-type, n-type, nitride and oxides that have been successfully developed as a photocathode and photoanode electrodes for hydrogen production.
- The study of different parameters, like – temperature, pressure, concentration, band gap etc., can be done which affects the efficiency of solar-to-hydrogen (STH) and the generation of hydrogen in the PEC water splitting.
- The study different analytical tools to identify the characteristics of catalyst in the PEC water splitting.

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