

# Chapter 22

## Electrocatalytic and Photo-catalytic Water Splitting



Preeti Chaudhary and Pravin P. Ingole

**Abstract** In the present time where our renewable energy sources are depleting, and soot from industries and coal burning is making air poisonous to breathe, the need for a switch into a sustainable energy system has become a necessity. One fruitful solution to the problem is photo-electrochemical (PEC) water splitting. Implementing PEC for the power generation reduces the burden on fossil fuels for solar energy storage. The Sun being a natural and the most abundant energy source, a dilemma is how to most effectively capture that energy and store it but at the lowest cost; we would try to discuss this in the present chapter. Designing photo-electrocatalyst is one of the main challenge, keeping all the perspective of PEC in mind. Fabricating heterojunction using different functional and suitable material for PEC in a single catalyst enables to enlarge the area of light harvesting properties and enhancing water splitting efficiency by improving the photo-excited charge separation and increasing the chemical stability of the catalyst to make it viable. The chapter gives an overview on the designing of heterojunctions for enhancing PEC water splitting performance. Along with the heterojunction synthesis, recent progress in the heterojunction-based PEC system and the working mechanism behind the charge separation is also discussed in the chapter. The chapter also provides the future directions for PEC water splitting.

**Keywords** Photo-electrochemical water splitting · Photo-electrocatalysts · Heterojunctions · Charge transfer mechanism and kinetics

### 22.1 Introduction and Scope

Due to the rapidly growing energy demand and depletion of fossil fuels and sources of energy, the world in the present century is on the edge of energy crises. According to International Energy Outlook 2016 (IEO 2016) [1] report, total

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P. Chaudhary · P. P. Ingole (✉)  
Department of Chemistry, Indian Institute of Technology, Delhi, New Delhi 110016, India  
e-mail: [ppingole@chemistry.iitd.ac.in](mailto:ppingole@chemistry.iitd.ac.in)

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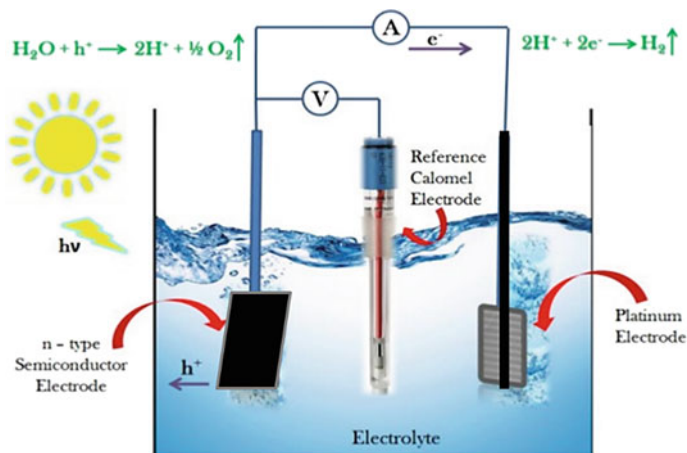
consumption of energy would increase from 549 quadrillion Btu in 2012 to 815 quadrillion Btu in 2040. It is the time to lay down the foundation of a sustainable society which would reduce the dependency on fossil fuels and also the amount of environmental pollution, because the depletion is leading to global climate change and environmental deterioration. Thus, it is the need of the time to increase the use of renewable energy sources as they are the fastest growing energy sources and are good replacement to fossil fuels.

Among the various sources of renewable energy such as solar, biomass, biofuel, geothermal, wind and tidal, the solar energy has gained a lot of attention as it is the largest and one of the most promising sources for sustainable development without having any compromise with the quality of environment. The energy from Sun is by far the largest natural resource as the Sun irradiating the surface of the Earth ( $1.3 \times 10^5$  TW) but a jump has been found in a global energy consumption ( $1.6 \times 10^1$  TW in 2010) [2]. Solar water splitting can be accomplished by three methods: photo-catalysis, photovoltaics and photo-electrochemical (PEC) water splitting. Photovoltaic electrolysis is high in both cost and efficiency, but the main quandary is between efficiency and cost. The cost problem can be sorted out by using photo-catalysis, but at the same time, the consumption of energy reduces the overall water splitting efficiency. PEC water splitting demonstrated for the first time by Fujishima and Honda [3] takes over the high potential efficiency up to >30% and is also cost effective. It efficiently converts solar energy to storable and transportable hydrogen fuel because of its potential high efficiency and other advantages of low cost and environmental friendliness. The solar energy conversion efficiency can be improved by solar water splitting techniques [4]. Thus, considering all the points, PEC came out to be an attractive and excellent technological solution to tackle the present environment and energy related issue.

In this chapter, nano-heterostructured materials are discussed for PEC cell application. Some of the nanostructure materials came out with multifunctional electrocatalytic activity. The following part presents brief introduction to PEC water splitting cells, PEC cell apparatus, PEC set up, reactions involved, thermodynamic and kinetic aspects, major breakthrough and advances in the field of PEC. The latter part covers the developed materials and their application in PEC cell followed by the future perspective effective in the field of PEC.

## 22.2 Concept of Photo-Electrochemical Water Splitting

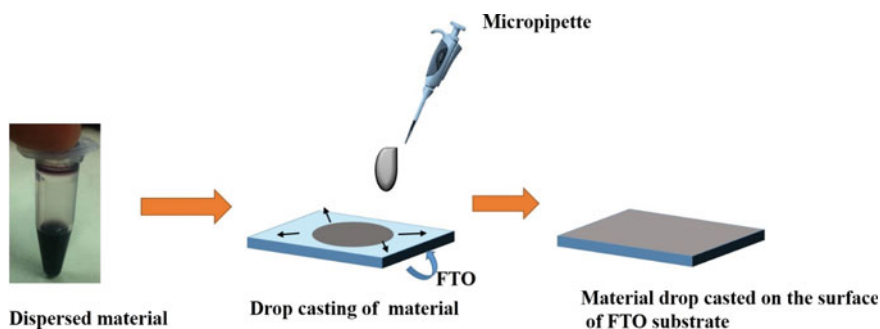
Photo-electrochemical water splitting, i.e. for the evolution of hydrogen and oxygen, being one of the effective techniques for the utilization of solar energy [5] has drawn great interest. A basic design for a PEC water splitting cell is such that it consists of two electrodes dipped in aqueous electrolyte as shown in Fig. 22.1. One is the working electrode (p-type or n-type semiconductor or a heterostructure) an active photo-electrode for the initiation of water splitting and another one is counter electrode, and water-based electrolyte. The third electrode is reference electrode;



**Fig. 22.1** Basic configuration of PEC cell consisting of three electrodes and an electrolyte. The reactions at anode and cathode are also shown

generally, Ag/AgCl/saturated KCl, Hg/HgO or saturated calomel electrode (SCE) is used that monitors the voltage applied on working electrode. For the working electrode to be illuminated with light, the PEC cell should consist of an optically transparent (quartz) window.

Construction of working electrode involves the drop casting (as shown in Fig. 22.2) of dispersed catalyst on the conductive side of the substrate. For making its connection feasible in PEC cell, thin copper wire is glued with the substrate using silver paste for electrical contact, and the corners and backside of the substrate were blocked using the epoxy resin. The free copper wire was sealed in glass tube to avoid its contact with electrolyte and assure that only the front side of electrodes comes in contact with the electrolyte otherwise the electrochemical reactions associated with Cu wire may interfere with the redox features from PEC water splitting.



**Fig. 22.2** Steps involved in fabrication of working electrode for PEC water splitting

**Fig. 22.3** Basic principle of PEC water splitting cell representing the generation of electron and hole in the presence of light

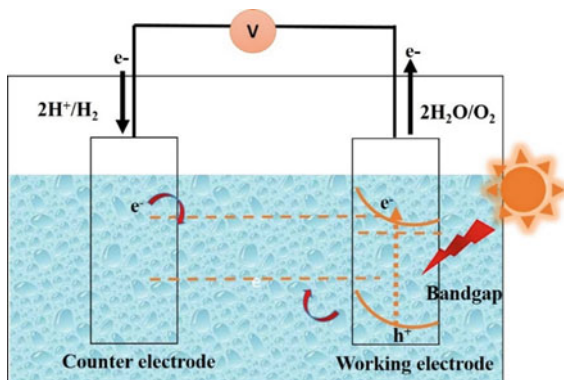
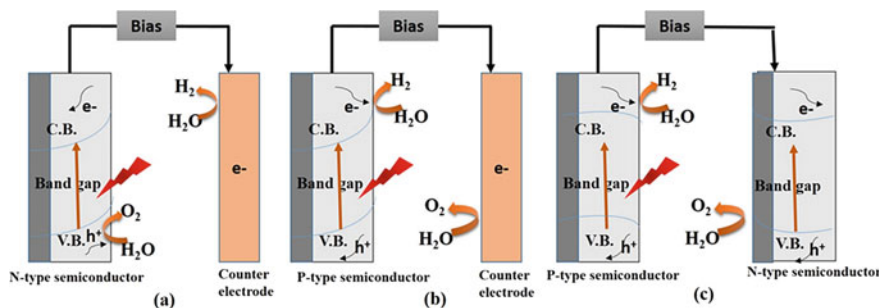


Figure 22.3 represents the basic principle of PEC water splitting. Under the illumination of light, electrons ( $e^-$ ) get excited from the valence band (VB) to the conduction band (CB) of a semiconductor photo-anode, where holes are left behind in the VB, thus generation of electron–hole pair takes place at photo-electrode.

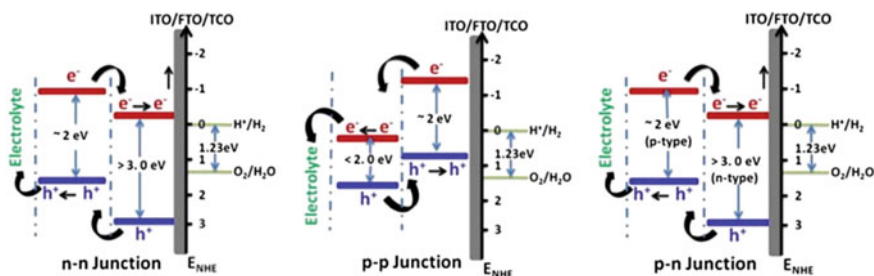
The generated electrons move to the counter electrode and are utilized for hydrogen evolution reaction (HER). The holes get transferred to the surface of working electrode and are involved in a process of oxygen evolution reaction (OER), the other half-reaction.

### Components of Photo-electrochemical (PEC) cell:

In all types of photo-electrochemical systems, the basic mechanism is same as that of generation of photo-excited electron–hole pair. The transfer of electrons at the interface continues until the Fermi level of the electrode and electrolyte are in the same position. In general, PEC cells are composed of a photo-electrode (photo-cathode or photo-anode) [6] with a counter electrode (as represented in Fig. 22.4) or in some cases, two photo-electrodes (photo-anode and photo-cathode) without external counter electrode. Using photo-anode as photo-electrode, the



**Fig. 22.4** Different types of photo-electrochemical cells, **a** counter electrode with photo-anode, **b** counter electrode with photo-cathode and **c** both photo-anode and photo-cathode without counter electrode. Reprinted with permission from Ref. [7]



**Fig. 22.5** Different types of heterojunctions with their band positions and water splitting charge transfer mechanisms. Reprinted with permission from Ref. [7]

transfer of electrons takes place to the counter electrode from the conduction band of a photo-anode. These electrons take part in HER whereas the holes left behind are utilized in the OER. In a p-type photo-cathode, OER takes place at the counter electrode and hydrogen generation occurs by utilizing electrons directly from the electrolyte. Moreover, the heterostructures between two semiconductors with varying electronic properties are also used. These are discussed below and depicted in Fig. 22.5.

### 1. n-n type:

Photo-anode constructed of heterojunction having both semiconductors of n-type, thus called n-n type [7]. In this heterostructure, semiconductors are chosen such that the conduction band position of semiconductor attached to the conductive layer should be lower than that of the conduction band position of the semiconductor lying on the electrolyte side. In the presence of light, photo-excited electrons travel to the counter electrode through external circuit for the reduction and the holes are accumulated on semiconductor electrode/electrolyte interface for water oxidation.

### 2. p-p type:

Here, a designed heterostructured photo-cathode has both the semiconductors of p-type. Photo-excited electrons are transferred directly to the semiconductor electrode/electrolyte interface and water is reduced to hydrogen. Figure 22.5 shows different types of heterojunctions with their band positions and charge transfer mechanism.

### 3. p-n type:

p-n type heterojunctions can be used either as photo-cathode or as a photo-anode. In both cases, holes and electrons move in opposite directions and an efficient charge separation takes place in comparison to single (n or p type) semiconductor electrode.

### Photo-electrode Materials:

TiO<sub>2</sub> was the first photo-anode material for PEC that was illustrated by Fujishima and Honda [8] in 1972. Then, Bard and co-workers illustrated the basics behind PEC cells using the materials like TiO<sub>2</sub>, Ni(OH)<sub>2</sub>, etc. But by the 2005, the number of published work on photo-electrochemical water splitting reflected the rapid interest of scientist in this field. Currently, the research on exploring more efficient semiconductor materials for PEC is still on. As TiO<sub>2</sub> is effective as a photo-catalyst only under the presence of UV light due to wider band gap of ca. 3.4 eV, scientists have tried to develop non-TiO<sub>2</sub> catalyst and had even succeeded in it by inventing some novel photo-catalysts such as  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>, ZnO, BiVO<sub>4</sub>, WO<sub>3</sub> and NiO. Other than metal oxides, their carbides, nitrides, sulphides, phosphides and selenides are also frequently indulged in PEC water splitting. Some semiconductors such as CuO and CdS show excellent light absorption but are not effective for driving water splitting due to their inappropriate band edge positions. Thus, the performance of a PEC cell depends mainly on the activity and features of the chosen semiconductor photo-electrode. There are a number of requirements related to material for effective PEC water splitting, and the most critical aspect among these is to design a catalyst for PEC water splitting. The material to be an ideal candidate for PEC activity should have some of the basic characteristics as discussed below.

### Suitable band gap and appropriate band edge positions:

The band gap of a material defines the light absorbing region for the photo-anode material. The lower band gap reflects the absorbance in wider light spectrum. The conduction and valence band edge positions should match with the electrochemical redox potentials for HER and OER, respectively, to drive the water splitting reactions and to maintain material stability. The water splitting reaction takes place at a potential difference of 1.23 eV, thus for a material to be useful for water splitting, it should have band gap energy greater than 1.23 eV. The band gap of the semiconductor should be greater than 1.23 eV for water oxidation. Some of the semiconductor materials with band gap values and band edge positions are shown in Fig. 22.6.

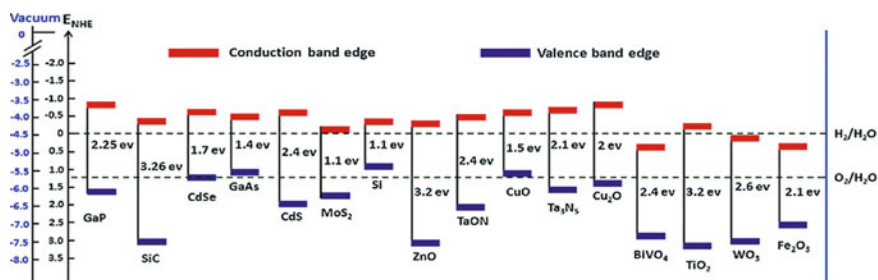


Fig. 22.6 Band gap values and band edge positions of some of the well-known semiconductors. Reprinted with permission from Ref. [7]

### Appropriate band edge positions:

Apart from having a perfect band gap for water splitting, appropriate valence and conduction band edge positions are a crucial requirement for water oxidation and reduction reactions of water. Figure 22.7 depicts the suitable band edge positions for water splitting. Conduction band minimum should hold a position at more negative energy than the redox position of  $\text{H}_2\text{O}/\text{O}_2$  level of water and its valence band maximum must be positioned at more positive than redox position of  $\text{H}_2\text{O}/\text{O}_2$ . The discussed positions of VBM and CBM ensure that the water splitting reaction is energetically favourable without bias voltage. Thus, to design an efficient catalyst for PEC, the knowledge of semiconductors electronic band structure parameters, viz. VBM and CBM positions especially relative to redox potential of  $\text{H}_2\text{O}/\text{O}_2$  is a scalable approach.

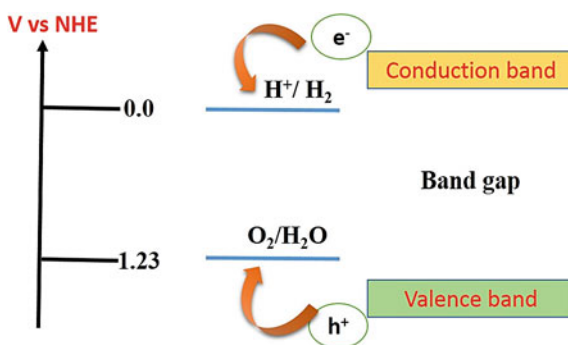
### High crystallinity and greater surface area:

Crystallinity and greater surface area are also an important parameter for the efficient PEC activity. The greater crystalline nature of the catalyst owes the ability to inhibit the photo-excited charge carriers. Improvement in crystallinity has the ability to repair the crystal defects. The presence of crystal defects decelerates the charge carrier recombination rate. Thus, with the improvement in crystallinity, these crystal defects get repaired up, lowering down the speed of charge carrier recombination. Another factor that triggers the activity of PEC catalyst is the higher surface area. Greater surface area creates more number of active sites that facilitate the semiconductors contact with reactant molecules/species or we can say that it provides the more opportunities for the catalyst activity to take place thus promoting the catalytic activity of water oxidation at a rapid rate. Thus, to prevent the recombination phenomenon for better charge separation and mobility, catalyst should possess high crystallinity and larger surface area.

### Stability:

Years long work has been done in the field of PEC but for making this technology to be up scaled, the stability is a key factor. Though there has been a significant number of publications in this field, the main focus has been put with various ideas

**Fig. 22.7** Ideal straddling condition of conduction and valence band edges of a semiconductor



in having the efficiency and stability of the catalyst especially for the cost effective materials. The stability of a material can be explained in various ways especially for PEC catalyst; stability in the presence of light, withstanding the reaction for a longer time and maintaining its identity even after completion of the reaction, the reusability of the material, and stability in different pH conditions. Electrochemical material has to be thermodynamically stable when in contact with the electrolyte and should be kinetically stable while being indulged in faradic reactions. Corrosion stability should also be taken into consideration that is after coming in contact or after keeping dipped in the electrolyte for long hour, the material should not be corroded or oxidized. Sometimes the dissolution of the certain material is also being noticed when applied potential is varied or while in contact with the electrolyte. Stability in the presence of light is also important for PEC study. It has been noticed many a times that the catalyst is stable electrochemically but once it is illuminated with the light either the dissolution or the decrement in the activity is observed. Another stability that is of prerequisite is stability in the varied pH electrolyte, that is the catalyst showing a good performance should be stable in acidic, basic and neutral medium.

After being aware of the necessity and the types of stability, the several steps have been implied for forming the stable semiconductors: (a) implementation of thin metallic film or layer that would even work as a catalyst and helps in forming the Schottky junctions and (b) sustain the stability even in the harsh conditions a few nanometer thick oxide layers are implemented that can easily tunnel the charge carriers. Oxide layer should be chosen such that it avoids the electrolyte permeability, possibility of cracks and reduction of pinholes. Thus, stability and sustainability are an important parameters for a catalyst to be applicable in industry.

#### **Low cost:**

It is important to keep in mind the abundance and cost of the material while designing the catalyst, especially for commercial application. The production of hydrogen by different techniques is compared [9] in Table 22.1 accompanied with their capital cost and the efficiencies. Thus, to bring the material in commercial application, the low cost is another critical consideration. Besides this, for the large-scale implementation, the materials should be non-toxic.

#### **PEC mechanism:**

Increasing interest to store solar energy in the form of alcohols and hydrogen inspires the photo-oxidation of water. It is generally followed by two methods as represented in Fig. 22.8: one is natural photosynthesis, that represents the approach in the direction of hydrogen production, and another is water splitting. PEC splitting of water is an artificial photosynthesis mechanism. It is an uphill reaction, thus requires an external bias as photo-voltage to drive water splitting reaction. This generates an interest in the generation of charge carriers for the two half reactions.



**Table 22.1** Comparison of the installed capital cost and production cost for different hydrogen production technologies

Production technology	Efficiency (%)	Installed capital cost	Production cost
Steam methane reforming (SMR)	80	\$138.9 Million	6.73 \$/GJ
Partial oxidation (POX)	89	\$307.1 Million	12.02 \$/GJ
Gasification of coal	48	\$490.5 Million	16.89 \$/GJ
Electrolysis grid power	95	\$331.3 Million	23.49 \$/GJ
Electrolysis PV power	95	\$389.2 Million <sup>3</sup>	53.73 \$/GJ
Electrolysis solar thermal power	95	\$360.3 Million <sup>3</sup>	38.61 \$/GJ

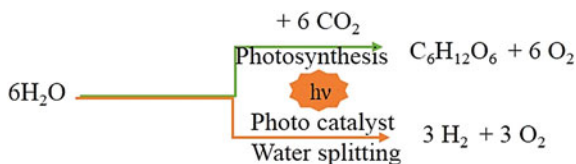
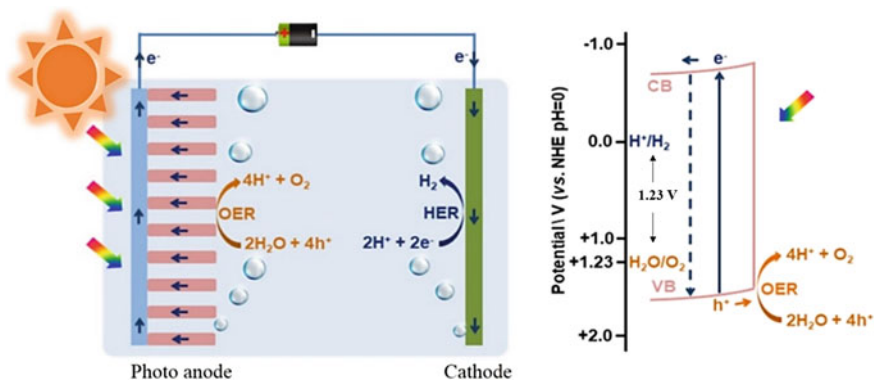
**Fig. 22.8** Representation of two complimentary reaction of water splitting into their respective constituents**Photo-anode as a Photo-electrode:**

Figure 22.9 represents the PEC water splitting mechanism based on photo-anode as a photo-electrode. In the presence of light, electrons get excited from the valence band (VB) of the photo-anode to the conduction band (CB), and holes remain behind in the VB. On the application of external bias, the upward bending of CB and VB at the interface takes place. At the interface in a direction from photo-electrode to electrolyte, an electric field is built up due to which the separated photo-generated holes migrate towards electrolyte and electrons stays back in the photo-anode. These electrons transferred to the conductive substrate through the nanostructured material which further gets conducted to the cathode surface where they reduce the protons for the generation of hydrogen gas. In this scenario, the holes which are left behind in the VB of the photo-anode travel from within the surface and oxidizes water for oxygen production. Some photo-generated holes and electrons which fail to reach the photo-electrode surface during transfer process get recombine and neutralize.

**Photo-cathode as a Photo-electrode:**

Prerequisite for the photo-cathode is that it should be a p-type semiconductor as represented in Fig. 22.10. When the p-type semiconductor is irradiated by light, electrons get excited from the VB to the CB leaving holes behind in the VB. At the interface of the electrolyte and photo-cathode, a downward bending of the VB and CB occurs which directs the electric field from electrolyte to the photo-cathode. In this case, electrons in the CB of photo-cathode travels to the surface of electrode for the HER and holes to the anode for the OER. As similar to the photo-anode, in



**Fig. 22.9** Representation of PEC water splitting mechanism using photo-anode as a photo-electrode. Modified image adapted from Ref. [9]

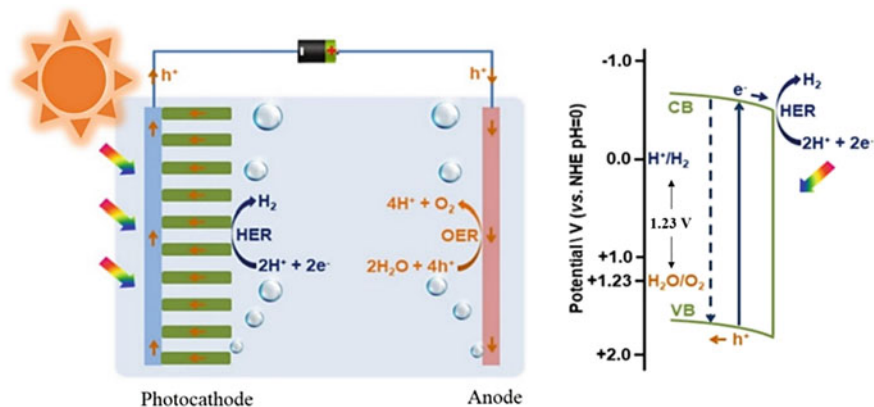
photo-cathode, neutralization of the left behind electrons and holes takes place (Fig. 22.11).

### Fundamental steps involved in photo-electrochemical water splitting:

PEC water splitting involves multiple steps as discussed below.

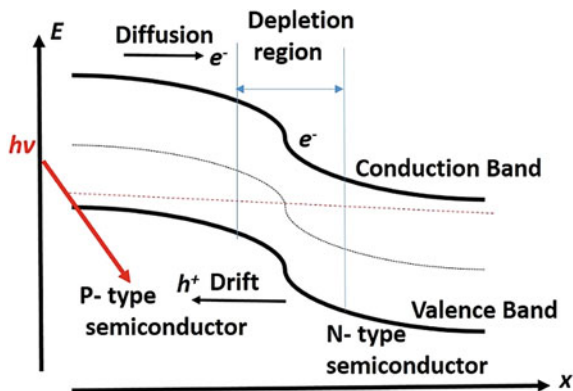
#### (a) Light-matter interaction

When the material is confronted to light, the light can be absorbed, reflected or transmitted depending on the media used. Generally, shortened propagation distance in the electrolyte media is profitable to avoid some of the necessary losses. When the light strikes the semiconductor, photons get absorbed if the



**Fig. 22.10** Representation of PEC water splitting mechanism using photo-cathode as a photo-electrode. Modified image adapted from Ref. [9] with permission

**Fig. 22.11** Energy band diagram for p–n junction presenting generation of photo-electrons and their movement



band gap energy of the semiconductor is lower than the energy of photon. Absorbed energy is conducted to the electrons in the VB thus leading to the generation of electron–hole pair [11].

(b) **Photo-generation of charge:**

Electronic states of the atoms combine to form valence band and conduction band in the semiconductor that are apart by a band gap called forbidden gap. If a material absorbs the photon from the incident light, the electrons get excited to the conduction band and vacancies are created in the valence band, called as holes. The kind of the majority charge carriers generated is either free electrons or holes and determines the nature of semiconductor whether n or p-type. Position of Fermi level also contributes to the opto-electronic properties of the materials. In the n-type semiconductor, the position of Fermi level is near to conduction band and majority charge carriers are electrons, but in the p-type semiconductor, the majority carriers are holes and the Fermi level is next to the valence band.

(c) **Separation of charge and transport:**

After the generation of charge carriers, the next crucial point is to avoid their recombination because due to this recombination, the free electrons and holes are not available for the further reactions. The separation of charges can be carried out in two ways either by external potential or by an internal potential. External potential can be applied via electrochemical instrument but many a times internal built-in potential is required to overcome the recombination. There are many ways for creating a built-in electric fields.

- p-n heterojunction:

p-n heterojunction is formed by bringing in contact the p-type and n-type semiconductor which are of totally different character. Due to the different nature of two materials, the diffusion of charges takes place thus forming a

space charge layer on the junction of electrode and electrolyte which gives rise to the strong internal electric field.

- Schottky junction:

Equilibration of the free electrons at Fermi level takes place thus leading to the bending of the valence and conduction band edges when in contact with metals.

- Semiconductor–liquid junction:
- Formation of the Helmholtz double layer takes place at semiconductor–liquid junction. Again, an equilibration of Fermi level would result into bending of band edges.
- Catalysis:

Catalyst also plays a crucial role in the efficiency of the water splitting reaction. Catalyst promotes the reaction in many ways like via providing alternate pathways, lowering the barrier of activation energy, etc. After the generation of charge carriers, the electrons/holes move to the surface for electrochemical reaction.

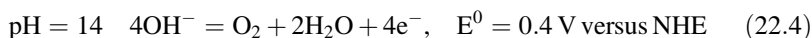
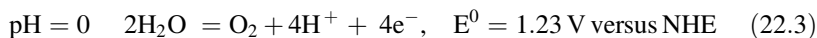
- Water splitting:

Water splitting drives two half reactions, HER and OER. The complete water splitting reaction requires a thermodynamic potential of 1.23 V. The variation in this potential value can be explained by the Nernst equation. The variation in potential value is also seen with the change in solution pH.

HER:



OER:



To drive these reactions effectively, we need overpotentials called  $\eta_{\text{HER}}$  and  $\eta_{\text{OER}}$ . The value of this overpotential that requires for water splitting decided by many factor like the electrocatalyst and pH value of the electrolyte. [12].

(f) **Photo-electrochemical Water Splitting:**

In PEC water splitting, generation of electron–hole pair takes place which are separated by the external or internal electric fields. Helmholtz double layer is formed at the interface due to the diffusion of charges, and Fermi level

equilibration also takes place. Further continuing the process, the band bending also takes place which maintains the electric neutrality. The separation of the electron-hole pairs takes place due to the built-in electric field.

## 22.3 Experimental Methodology

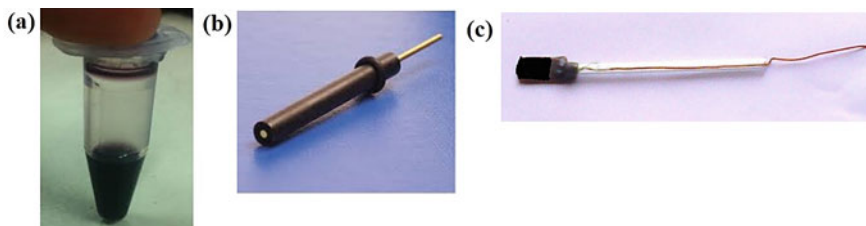
### Electrode fabrication:

The designing of proper electrodes has an important role in electrochemical measurements. Powdered material is dispersed in suitable solvent as shown in Fig. 22.12a and then drop casted on the working electrode surface. For HER study, the glassy carbon electrode as represented in Fig. 22.12b is used as the working electrode (in general). The dispersed material is drop casted on the glassy carbon surface and dried under the lamp for further use. For PEC study, a smooth film of the dispersed material is drop casted on ITO/FTO either manually or by using spin coating. For the electrical contacts, these substrates are connected by a copper wire using a silver paste. The uncovered conducting substrate is covered by the epoxy resin.

For the study of PEC measurements, the prepared electrodes are dipped in electrolyte in electrochemical cell. The cell constitutes of three electrodes: working electrode, counter electrode and reference electrode, all together dipped in an electrolyte. Quartz allows the light to reach the working electrode. After all the connections, WE is confronted to light and PEC study is done.

### Cyclic Voltammetry:

Cyclic voltammetry is an electrochemical technique that helps in studying the redox property of an analyte and is also used for studying the qualitative information about the catalyst, like electrochemical response of the catalysts, catalytic activity of the catalyst, etc. This technique finds an important application in OER, HER and oxygen reduction reaction (ORR). All these cyclic voltammetry studies are done under the varied potential window. In cyclic voltammetry study, a fix potential window is decided with fixed initial and final potential points. We apply the

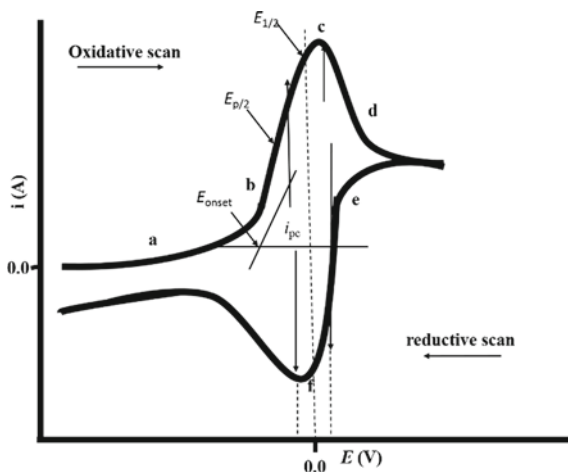


**Fig. 22.12** a Sample dispersion ready for drop cast, b fabricated working electrode for HER and c fabricated working electrode for PEC

potential and study the current feature with respect to the potential. Thus, we plot a current recorded at the working electrode versus applied potential.

In the cyclic voltammetry study, we get a redox peak for the ions/molecules present in the analyte as well adsorbed on the electrode surface depending upon the nature of the analyte under study. The materials' oxidation and reduction potential can be found. In cyclic voltammetry, we study both the forward (positive) and backward scan (negative). In a way, we can say that it is the cyclic study, ends up at the point where it has been started. We can carry out the cyclic voltammetry study either by as single or multiple cycle. A reversible cyclic voltammetry is represented in Fig. 22.13 describing the various parts labelled. In the given figure, scan starts at the  $-0.4$  V and sweep in a forward direction. Portion (a) of the fig represents the initial potential region where the potential is not sufficient for the redox process to take place and the observed current is due to the non-Faradaic processes. Part (b) shows the next step where the onset of oxidation has started and the current increases exponentially with the increasing voltage. This process is studied when the analyte is within the diffuse double layer near the electrode. The current reaches a maximum point (c), an anodic peak current ( $i_{pa}$ ) for oxidation. After this, the current starts decreasing as the analyte has almost depleted and the diffuse double layer increases in size. In the portion (d), the current starts decreasing exponentially as the current is limited by the mass transport. The potential is scanned in a more positive direction till the point steady state is reached and further increase in potential has no effect on the current. In the next step (e), the scan reverses to the negative potential and the reductive scan continues until the oxidized analyte which has accumulated on the electrode can be reduced. The last portion (f) is labelled for the cathodic peak current ( $i_{pc}$ ) scans in opposite direction at the cathodic current peak ( $E_{pc}$ ). The obtained peak current for the anodic and cathodic should be reversed in sign and equal in magnitude, provided we are studying the reversible process.

**Fig. 22.13** Pictorial representation of CV curve for a reversible electron transfer system



**Linear Sweep Voltammetry (LSV):**

LSV is a voltammetry technique similar to cyclic voltammetry except that the scanning of the potential takes place in a single direction. The potential is varied at a constant rate and the current is produced by the electrode as a function of applied potential. The increased current is recorded which flows between the working and counter electrode.

**Chronoamperometry:**

The electrochemical stability of the catalyst is recorded using the chronoamperometry at a particular potential. In this technique, current is recorded as a function of potential. Before running the chronoamperometry, cyclic voltammetry scans are run to find out the fixed potential for the study of chronoamperometry. In chronoamperometry, fixed area electrodes are used to study the electrode processes. This technique is used for the analysis of diffusion coefficient of the electroactive species and for mechanistic investigations of the electrode process. The relation between the current and time is explained by the Cottrell equation [13].

$$i(t) = \frac{nFACD^{1/2}}{\pi^{1/2}t^{1/2}} = kt^{-1/2} \quad (22.5)$$

The current versus  $t^{-1/2}$  gives a straight line and their slope provides the diffusion coefficient ( $D$ ), surface area ( $A$ ) and concentration of the species.

**Transient Photocurrent:**

Transient photocurrent study is employed to study the time-dependent extraction of charges in the presence of light and functioning of current with time in the presence and absence of light. To further study about the photo-generated electron-hole pairs response v/s time, the transient photocurrent is studied. When a semiconductor film is exposed to light, the photo-generation of charges takes place. These charges are extracted on the electrodes resulting in a current as photocurrent. Photocurrent curves are recorded for certain number of ON-OFF cycles under white light illumination (i.e. under light chopping). During repeated ON-OFF irradiation cycles, the reproducible current responses are recorded. A prompt and reproducible photocurrent under each illumination is observed and quickly returns to zero when the irradiation was interrupted, the photocurrent rapidly dropped to almost zero (steady-state value), and reverted to the original value once light was switched on back again. Greater value of photocurrent for a material is regarded as a best candidate. This also notifies the efficient charge separation and longer life span.

**Mott-Schottky:**

Mott-Schottky (M-S) analysis is an important tool to study semiconductor heterostructure behaviour, properties and to gain the idea about the fundamental mechanism for comparative PEC performance including the onset and increment in photocurrent density. It is the measurement of interfacial capacitance of electrode

with voltage. Two important parameters, flat band potential and the charge carrier density of the semiconductor material, can be calculated from Mott–Schottky plot. The n-type and p-type nature of the material is verified by the nature of the slope of M-S plot. If the slope is positive, it is n-type, and if the slope is negative, it is p-type semiconductor. When no band bending takes place even after the application of the voltage is called flat band potential, this flat band potential can be obtained from the Mott–Schottky equation.

$$\frac{1}{C^2} = \left( \frac{2}{q \epsilon \epsilon_0 N_d} \right) \left( V_{\text{app}} - V_{\text{fb}} - \frac{kT}{q} \right) \quad (22.6)$$

The Mott–Schottky curves ( $1/C^2$  vs electrode potential, where  $C$  is the space charge layer capacitance) were plotted to estimate the donor density ( $N_d$ ), flat band potential ( $V_{\text{fb}}$ ) and depletion layer width of thin films. Here,  $e$  is the electronic charge,  $\epsilon$  is the dielectric constant of the semiconductor,  $\epsilon_0$  is the permittivity of the vacuum,  $V_{\text{app}}$  is the applied potential,  $q$  is the electric charge and  $kT/q$  is the temperature-dependent term. We can obtain flat band potential extrapolating linear plot at  $1/C^2 = 0$ .

### 22.3.1 *Strategies for Modifying Semiconductor for Enhanced Photocurrent and Stability*

PEC water splitting makes the best use of semiconductor properties such as excited electron–hole pair, their separation and charge transfer due to them. But, in most of the cases, even after the well-aligned positions of valence band/conduction band edges for HER and OER, the kinetics of the reactions results out to be sluggish. The enhancement for the kinetics accounts for the overpotential. Hence, to enhance the PEC activity at the lower overpotential, the various strategies are being taken into account such as band gap engineering via doping, nanostructuring, making heterojunctions, usage of co-catalyst and surface passivation.

#### **Doping:**

The practical efficiency of the catalyst sometimes comes out to be lesser than the theoretical value because of some factors such as short hole diffusion length, poor conductivity and slow kinetics. Among the various strategies, doping is an effective approach to improve the efficiency of a PEC semiconductor catalyst as it tailors the electronic and optical properties. Insertion of a heteroatom with diverse atomic radii and varied electronic configuration into a semiconductor lattice proved to be a most exportable approach. Since years, various metal and non-metal elements such as Cr, Ti, Sn, S, P and N have been doped in the semiconductor to improve the overall PEC activity. The effect of doping: (1) increases the range of light absorption, (2) increases the concentration of charge carriers, thus improving the electrical



conductivity, (3) acts as an electron traps thus facilitating the separation of electron hole, (4) The inclusion of the foreign element by in situ doping also alters the morphology of the semiconductor.

When a doping is done in a semiconductor, the formation of intermediate band states takes place which efficiently harvests the solar light and thus enhances the PEC activity. Doping strategies enhance the optical and electrical properties even for small band gap semiconductors [14, 15] specially in metal oxide due to polar-on-hopping conduction mechanism (charge carriers in metal oxides tends to localize as small polar-on) [16]. Non-metal dopants like B, C, N, P, S and halogen lead to improved photo-activity and better charge transport properties. Using metal ions as a dopant such as  $\text{Fe}^{3+}$ ,  $\text{V}^{4+}$ ,  $\text{Mo}^{5+}$  in wider band gap semiconductors such as  $\text{TiO}_2$  leads to enhancement in photo-electrochemical performances. Metal doping leads to a donor or acceptor energy level in a semiconductor band gap, which leads to extension of the range of absorption. It can be seen from Fig. 22.14 that the acceptor level or the donor level can effectively shorten the semiconductor band gap so that it can effectively absorb and utilize the visible light.

Generally, neither very low level of doping can sufficiently increase the conductivity nor too high level increases the efficiency. An adequate amount of doping alters the optical and electrical properties, mobility, diffusion length, and charge carrier concentration thus resulting in increased photocurrent, and shifts in onset potential is also observed due to alteration of band gap. Given below is Table 22.2 that shows the comparison of variant dopants with current value achieved.

### Nanostructuring:

Nanostructuring of materials represents an effective strategy to reach the goal of efficient PEC. One-dimensional (1 D) nanostructures such as nanowires, nanotubes and nanorods enhance photo-electrochemical activity as compared to corresponding planar structures. Discovery of carbon nanotube with variety of interesting properties motivated the research focus in the field of nanostructured materials. Among the various nanotube materials, titanium dioxide nanotube arrays are of particular

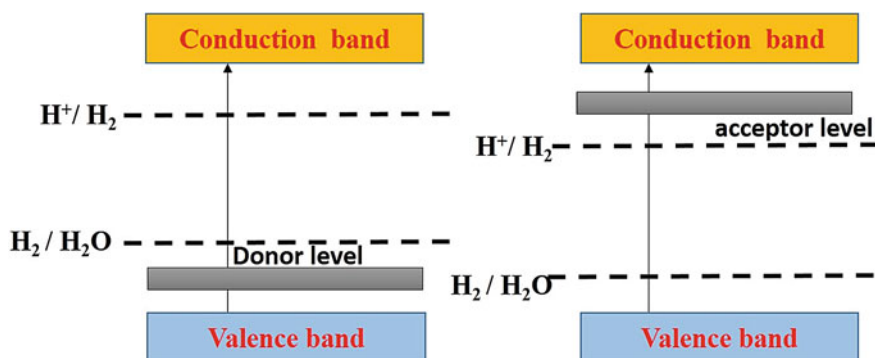


Fig. 22.14 Schematic representing the donor and acceptor level due to the metal doping

**Table 22.2** Table showing the comparison of various dopants with achieved current density value in a particular electrolyte using AM 1.5 light source and a potential of 1.23 V versus RHE

S.N.	Base material	Dopant	Electrolyte used	Current density	Ref.
1.	Fe <sub>2</sub> O <sub>3</sub>	La	1 M KOH	0.11 mA/cm <sup>2</sup>	[17]
2.	CN <sub>x</sub>	Ni	0.1 M KOH	75.6 μA/cm <sup>2</sup>	[18]
3.	g-C <sub>3</sub> N <sub>4</sub>	B	0.1 M Na <sub>2</sub> SO <sub>4</sub>	103.2 μA/cm <sup>2</sup>	[19]
4.	BiVO <sub>4</sub>	Mo	0.5 M Na <sub>2</sub> SO <sub>4</sub>	4.98 mA/cm <sup>2</sup>	[20]
5.	WO <sub>3</sub>	Bi	1 M NaOH	1.511 mA/cm <sup>2</sup>	[21]
6.	Fe <sub>2</sub> O <sub>3</sub>	S	1 M NaOH	1.44 mA/cm <sup>2</sup>	[22]
7.	Fe <sub>2</sub> O <sub>3</sub>	Sn, Zr	1 M NaOH	1.34 mA/cm <sup>2</sup>	[23]
8.	Fe <sub>2</sub> O <sub>3</sub>	Mn	1 M NaOH	1.60 mA/cm <sup>2</sup>	[24]
9.	Fe <sub>2</sub> O <sub>3</sub>	Si	1 M NaOH	1.45 mA/cm <sup>2</sup>	[25]
10.	Fe <sub>2</sub> O <sub>3</sub>	Ti	0.1 M KOH	0.42 mA/cm <sup>2</sup>	[26]
11.	Fe <sub>2</sub> O <sub>3</sub>	Sn	0.1 M KOH	1 mA/cm <sup>2</sup>	[27]

interest. Moreover, the branched or dendritic-shaped nanostructure semiconductor grown vertically on the substrate proves to be more efficient for PEC [17]. Vertically aligned nanostructure materials provides a large surface area thus enabling the greater amount of photo-generated charge carriers to diffuse in the electrode–electrolyte interface thus preventing the charge recombination and supporting charge separation. Nanostructures could also reduce the surface light reflection thus increasing the light absorption efficiency.

The 2D nanostructures have greater surface area, and also their small thickness reduces the travelling distance for the photo-generated holes to reach to the surface. Among them, NiO as a 2D nanostructured material is particularly the most promising one because of its appropriate valence band edge positions for the OER [29] and other examples are ZnO nanorods, TiO<sub>2</sub> nanotubes [30] and nanoflowers [31]. Similarly, nanostructured branched or dendritic [32] semiconductors are also proved effective for water splitting.

Some of the nanostructured materials with current density in different electrolyte are discussed in Table 22.3. Nanostructured materials have low charge carrier recombination as small radial dimension enables a greater fraction of photo-generated minority carriers to diffuse to the electrode–electrolyte interface; due to the direct growth of the photoactive material over the substrate, an electron transfer between the material and substrate is improved. The nanostructuring of the semiconductors also enhances the visible light absorption extent. Some types of nanostructures are being compared in a Table 22.4 with different features and current density value.

### Surface Passivation

OER is a slow kinetic reaction but the passivation of the surface has proved out to be an effective strategy to reduce the energy barrier for water splitting and thus

**Table 22.3** Table showing the comparison of nanostructure catalyst with achieved current density value in a particular electrolyte using AM 1.5 light source at a given applied potential

S. N.	Nanostructured catalyst	Electrolyte	Potential, V versus RHE	Current density (mA/cm <sup>2</sup> )	Ref.
1.	TiO <sub>2</sub> nanotubes	1 M KOH	1.23	0.90	[29]
2.	TiO nanotubes array	1 M KOH	1.23	0.065	[30]
3.	TiO nanotubes array with other semiconductors	1 M KOH	1.23	1.5	[31]
4.	Hydrogen-treated TiO <sub>2</sub> Nanowire	1 M NaOH	0.40	1.9	[32]
5.	Ni/Si-doped TiO <sub>2</sub> nanostructure	1 M KOH	1.23	2.28	[33]
6.	PtO/ZnO nanowires	0.2 M Na <sub>2</sub> SO <sub>4</sub>	1.23	2.3	[34]
7.	CuO nanowires	1 M Na <sub>2</sub> SO <sub>4</sub>	-0.30	1.4	[35]
8.	Cu <sub>2</sub> O nanowire	0.5 M Na <sub>2</sub> SO <sub>4</sub>	0.00	10	[36]

lowering the onset potential. Initially, the passivating layers were mainly employed to overcome corrosion and increase the photochemical stability. Some semiconductors have large surface area for water oxidation, but this needs to be compensated with greater overpotential or external application of bias. Surface passivation came out as a strategy to reduce the large overpotential for catalytic activity of water oxidation or reduction. In other words, suppressing the overpotential for catalytic activity also helps in preventing the self-oxidation and reduction thus improving the stability.

Table 22.5 summarizes surface passivation approach to enhance the water oxidation. Grazel et al. reported surface modification of hematite with IrO<sub>x</sub> to attain the PEC current value of 3 mA/cm<sup>2</sup> [53]. Some mixed transition metal oxides are also investigated such as NiO and NiFeO<sub>x</sub> which lead to a cathodic shift in onset potential. Generally, a passivating layer is a surface layer that inhibits the consumption of photo-generated charges by the side reactions and thus increases the Faradic efficiency and voltage. The designing of passivating layers has paved a greater interest as it prevents charge transfer inhibition and can be easily incorporated onto a high surface area nanostructure. A few examples of surface passivating OER catalyst are Ni(OH)<sub>2</sub>, FeOOH and NiOOH.

### Surface Plasmon Resonance (SPR):

Combination of surface plasmon with exciton such as Ag [29] and Au [54] decorating on the surface of hematite is studied to help in water splitting activity. Generally, surface plasmons are studied as the conduction electrons oscillations of the conductive material. Metal nanoparticles being irradiated by the incident light

**Table 22.4** Table showing the comparison of nanostructure catalyst with achieved current density value with different synthesis method

S. N.	Morphology	Features	Synthesis method	J (mA/cm <sup>2</sup> )	Ref.
1.	Bulk	Dense, high e-h recombination and high photon absorption	Electrodeposition	No photo-response	[37]
2.	Dendrites	Dense, poor light absorption, long electron path and high e-h recombination	Electrodeposition	0.018	[38]
3.	Nanoparticles	More surface area than bulk, long electron path and low electrode/ electrolyte interaction	Anodization	0.05	[39]
4.	Mesoporous	More surface area than bulk and higher electrode/ electrolyte interaction than nanoparticles	Colloidal Synthesis	1.1	[40]
5.	Nanowires	Strong anisotropic conductivity and low grain boundaries	Hydrothermal	1.24	[41]
6.		Nanowalls of 5–6 nm thick and high aspect ratio	Sono-electroanodization	1.41	[42]
7.	Nanocones	Large surface area and enhanced light trapping	Template-assisted ultrasonic spray pyrolysis	2.42	[43]

The current density is measured at 1.23 V versus RHE

generate electric field at the surface of nanoparticles. Photo-anodes decorated with plasmonic metals increase the light absorption. Plasmonic nanoparticles show the interaction with photons via excitation of surface plasmon resonance. By using

**Table 22.5** Table showing the comparison of surface passivation layer with achieved current density value, onset values and with different synthesis ways

S. N.	Passivation layer	$E_{\text{Onset}}$ shift (mV)	$E_{\text{Onset}}$ , V versus RHE	Electrolyte	Synthesis method	Ref.
1.	IrO <sub>2</sub>	200	0.80	1 M NaOH	Controlled potential electroflocculation	[44]
2.	Co-Pi	100	0.60	1 M KOH and 0.2 M KCl supporting	Photo-electrodeposition	[45]
3.	Co-Pi	170	0.90	1 M NaOH	Photo-electrodeposition	[46]
4.	Ni(OH) <sub>2</sub>	300	0.80	1 M KOH	ALD	[47]
5.	Co <sub>3</sub> O <sub>4</sub>	40	0.66	1 M NaOH	In situ hydrothermal	[48]
6.	Al <sub>2</sub> O <sub>3</sub>	100	0.80	1 M NaOH	ALD	[49]
7.	TiO <sub>2</sub>	100	0.88	1 M NaOH	ALD	[50]
8.	Ga <sub>2</sub> O <sub>3</sub>	220	0.80	1 M NaOH	Chemical bath deposition	[51]

different composition, size and shape of plasmonic nanostructures, we can design the catalyst that can enhance the light absorption to the full solar spectrum. So far, several mechanisms are being studied to improve the PEC water splitting such as plasmon resonance energy transfer (PRET), plasmon induced heating, hot electron transfer and photon scattering and reflection reduction at the interface [55].

### Quantum dot Sensitization:

Quantum dot (QD) sensitization is an efficient tool for effective PEC due to following reasons:

- (i) Extend the material absorption from UV visible to NIR region.
- (ii) Tuning of the band gap across the absorption spectra.
- (iii) Resistance to photo-bleaching.
- (iv) Generation of excitons and energy transfer-assisted charge collection.

Working with metal oxide/QD facilitates charge separation and inhibits recombination via generating a potential difference at the interface. Further, Table 22.6 represents the summary of quantum dot sensitization with photocurrent densities.

### Controlling surface states and electronic structure:

To minimize the superficial electronic states, the trap states play an important role in solving the problems of inefficient charge separation thus enhancing PEC efficiency. This can be done if we control the synthesis and post-synthesis treatments

**Table 22.6** Table showing the summary of quantum dot sensitization with photocurrent densities

S. N.	Semiconductor	Sensitizer	Morphology	Photocurrent density (mA/cm <sup>2</sup> )	Ref.
1.	TiO <sub>2</sub>	PbS/CdS with Al <sub>2</sub> O <sub>3</sub> over coating	Nanotube array	5.19 at - 0.25 V versus SCE IPCE	[55]
2.	TiO <sub>2</sub>	PbS	Nanofilm	1.9 at 0 V versus SCE	[56]
3.	BaSnO <sub>3</sub>	CdS	NWs	4.8 at 0 V versus SCE	[57]
4.	$\alpha$ -Fe <sub>2</sub> O <sub>3</sub>	CdSe	Nanoporous film	0.55 at 1.0 V versus SCE	[58]
5.	N-doped ZnO	CdTe	NWs array	0.46 at 0.5 V versus Ag/AgCl	[59]
6.	ZnO	CdS and CdSe modified with IrO <sub>x</sub>	NWs on silicon microwires	1.64 at 0 V versus Ag/AgCl	[60]
7.	ZnO	CdSe	Nanotubes	5.10 at 0 V versus SCE	[61]
8.	ZnO	CdSe	Nanorods	2.48 at 0 V versus SCE	[62]
9.	WO <sub>3</sub>	PbS	Nanoflower	1.8 at 1 V versus Ag/AgCl	[63]

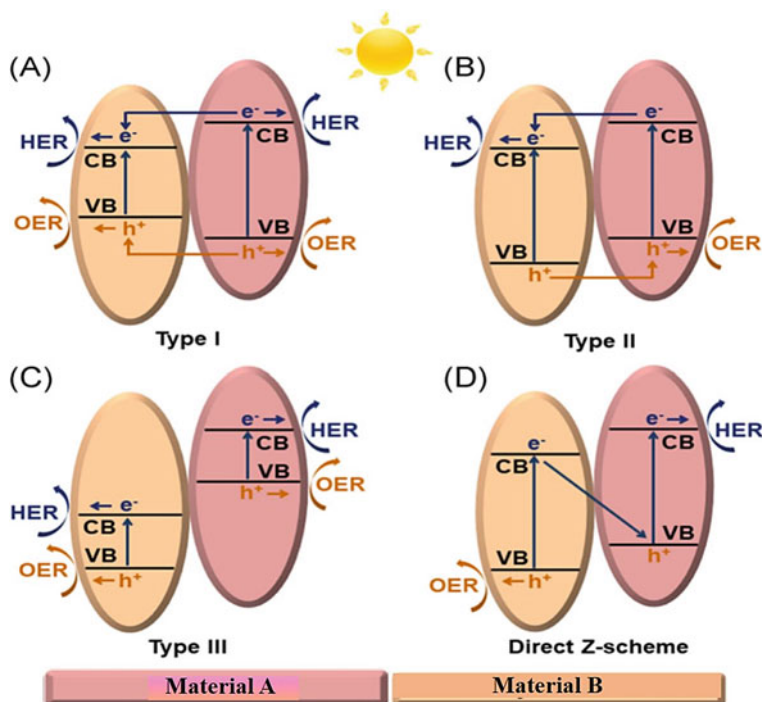
or if we incorporate other metals on the surface of the semiconductor which can both fill the traps and acts as an OER catalyst.

### Heterostructure:

Enhancement in the PEC performance can be achieved by analysing the charge transfer process at the interface. Different junctions or interfaces among the different materials or with electrolyte enable the charge separation. This practice paved a new pathway for the designing of heterostructures. This approach allows the varied suitable properties from participating semiconductor and overcoming a single photo-catalysts' drawback such as limited absorption range and the electron hole recombination. Heterostructure of the functional materials is designed such as that the energy levels of the materials have matched or overlapped band structures. This overlapping of the band structures facilitates the charge migration from one material to another and thus enhancing the oxidation and reduction ability.

### Types of heterostructure on the basis of band alignment:

Generally, for the study of photo-generated charge separation, there are mainly four types heterojunctions named as type I, type II, type III and Z-scheme as described in Fig. 22.15. Among these structures, type II and Z-scheme play the most important



**Fig. 22.15** Band alignment and charge transfer mechanism of (A) type I, (B) type II, (C) type III, and (D) direct Z-scheme. VB is valence band; CB is conduction band; HER is hydrogen evolution reaction; OER is oxygen evolution reaction. Modified image [8] adapted from Ref. [9]

role in preventing the recombination of photo-generated electrons/holes, as will be discussed below.

### Type I:

In type I heterojunction, the VB and CB of the material A are within the band gap region of material B. When the hybrid is irradiated by the incident light, the holes and electrons are transferred from material B to material A in a single direction. This one-way movement of electrons and holes is also facilitated due to more negative CB and more positive VB of material B than that of material A.

### Type II:

In this type of heterostructure, the band edge positions of material A and material B are staggered between them such that the VB position of material A is more positive than B and the CB position of material B is more negative than that of material A, thus the electrons and holes flow in opposite directions. When the heterostructure is exposed to light, the electrons get transferred from B to A and holes from A to B.

This kind of double charge transfer plays significant role in charge separation and thus improving the PEC activity.

### **Type III:**

In this type of heterostructure, the difference between the VB and CB edges is larger. The VB and CB of material A and B do not overlap with each other; as a result, they require a higher driving force for charge transfer. When the hybrid is excited by light, the photo-generated electrons from material A combine with the holes of material B, thus the holes from material A and electrons from material B are free to participate in the oxidation and reduction process of water, respectively.

### **Z-type:**

Though the type II alignment is quite effective for charge separation, it is limited by its drawback of reducing the redox ability of the photo-electrodes. The transfer of electrons from the CB of material A to the CB of material B and the flow of holes from the VB of material A to the less positive VB of material B reduce the redox ability of the photo-electrodes. To overcome this shortcoming, direct Z-scheme heterojunction has been reported. In this scheme, the electrons from the CB of material A combine directly with the holes in the VB of material B. Thus, the oxidation of water occurs in material A, and the left behind electrons in the material B contributes to water reduction.

### **Carbon nitride and metal oxide-based Heterojunction:**

Among the carbon-based semiconductors, graphitic carbon nitride ( $g\text{-C}_3\text{N}_4$ ) semiconductor with a suitable band gap of 2.7 eV is one of the most important catalysts for PEC reactions. Many efforts have been done to enhance its activity among which coupling with other semiconductors has proven to be an effective approach. Choosing the other semiconductor with  $g\text{-C}_3\text{N}_4$ , metal oxides came out with a fruit full strategy. Suitable band gap, low cost, ease of synthesis and low electric resistance make them the potential candidate for PEC. Further, the improvement of optical properties and charge separation is sort out via heterojunction [64]. Due to the suitable alignment of the  $g\text{-C}_3\text{N}_4$  and metal oxide, their heterostructures were designed and have proved out to be the best candidates. Graphitic carbon nitride selectively forms type (II) heterojunctions, thus a better charge separation is achieved in the heterostructure.

## **22.4 Summary and Future Outlook**

PEC water splitting has proved in itself to be the unique way for utilizing solar energy conversion into fuels. Since the pioneered time, a keen attention has been paid for the designing of efficient and active photo-anode. However, even after the many efforts, the photo-anode suffers from various intrinsic limitations which result in charge recombination and sluggish water oxidation kinetics. Still, a long way has



to go to achieve the benchmark in this field. In this chapter, we have discussed different aspects for a material to be an active photo-anode and the different modification strategies in the semiconductor to make them more reliable and efficient for PEC. These strategies include the modification of the surface by different methods and intrinsically. Among all the strategies described above, the formation of heterostructure has proved to be the most efficient. Especially, the type II and Z-type heterostructured has gained a great fame in the field of PEC due to the efficiently active approach for charge separation. These type of heterostructure can be formed between the two metal oxide semiconductors. Due to the suitable alignment of the  $g\text{-C}_3\text{N}_4$  and metal oxide, their heterostructures were also designed and are proved out to be one of the best candidates.

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