

Chapter 1: Introduction

Exhausting fossil fuels and availability of clean water are the two major concerns that draw serious attention worldwide. With the rapid development of industries around the world like petrochemical, chemical, mining, pharmaceutical, microelectronic and semiconductor, the need for pure water as well as purification of contaminated water has increased. This ever growing industrialization also causes environmental imbalance of available natural resources of energy around us. To constructively combat the issue of depleting energy fuels and increasing pollutant waste, a constant search has been going on for a recent and advanced form of energy that is a safe, renewable, clean, cheap, and viable alternative to nuclear energy and fossil fuels. Lately, hydrogen has received substantial attentiveness as an energy carrier of next-generation. Over the past several decades, overall splitting of water using inexhaustible renewable source of sunlight energy has been studied as a potential solution of hydrogen generation as well as for purification of water or degradation of persisting organic pollutants.

There are two divergent approaches for achieving solar water splitting through semiconductor materials, namely photo catalytic (for decomposition of pollutants) and photo electrochemical (for generation of hydrogen) water splitting. The effectiveness of both the processes is highly dependent on the choice of materials being used for above mentioned field of applications. Therefore, it is very important to choose materials that satisfy the criteria or overall conditions of water splitting. The following section describes the materials that are being used in the present study.

1.1 Choice of materials in this work- ZnO and BiVO₄

The first ever report on water splitting using PEC was published by Fujishima and Honda using TiO₂ as photo-anode and a Pt cathode as counter electrode. At the photo electrode, light photon

excites the electrons in the VB which jumps into the CB of the material and oxidizes the water to O_2 . The electrons migrate to the Pt electrode through the external wire and reduce water to hydrogen at counter electrode. Since then ZnO has been explored extensively for photocatalytic and PEC applications since it shares many same properties as TiO_2 . ZnO is a direct and wide band gap semiconductor with large exciton binding energy of 60 meV at room temperature [1,2]. The optical, magnetic and electrical properties of ZnO draw much attention and can be modified or tailored by the use of ZnO in nanoscale [3]. ZnO is an eco-friendly and non-toxic material which makes it attractive and useful for a broad range of applications without posing any risk to animal and mankind [4]. Due to its extraordinary properties, it has been used widely for the application of decomposition and mineralization of organic and toxic pollutants. ZnO possesses the same band gap and comparable band edge positions as that of TiO_2 , its photo activity is anticipated to be similar to TiO_2 . In addition, ZnO is more economic than TiO_2 for water treatment operation at large scale [5]. ZnO has the ability to absorb more light and photons from the spectrum than other metal oxides, which adds a feather to its properties. However, it suffers from the major drawback of large band gap and photo corrosion. Therefore, it is more active in UV region and causes fast recombination of charge carriers which causes reduction in its photo catalytic activity [6]. ZnO is a wide band gap ($E_g = 3.35$ eV) semiconductor which satisfies the essential energy criteria for photochemical water splitting without any need of external bias. ZnO photoanodes are stable under sunlight illumination as well as in water [7]. However, ZnO suffers from the problem of ineffective utilization of sunlight for photo generation of charge carriers due to its wide band gap [8].

Monoclinic- $BiVO_4$ has well-suited band structure (valence band edge $\sim 2.5 V_{RHE}$) with band gap of 2.4 eV, that strongly favors water oxidation (photocurrent of ~ 6.2 mA/cm²) by photo-generated holes and visible light driven photo catalytic activity [9,10]. However, conduction band of $BiVO_4$ is slightly positive with respect to proton reduction potential, as a result electron lack sufficient reduction activities and easily combine with hole [11]. Additionally $BiVO_4$ suffers from poor charge transport due to low mobility and short life time of holes lead to a short diffusion length

[12]. In this direction, new strategy 'synergetic BiVO₄/ZnO photoanode' by sequentially forming BiVO₄ and ZnO dual layer photocatalyst is proposed and stated challenges are circumvented as BiVO₄ is a visible light driven photocatalyst and double layer morphology as well as electron transfer from BiVO₄ to ZnO, leads to improvement in charge separation. Favorable electron transfer from BiVO₄ (low CB edge material) to ZnO (high CB edge material) takes place via several phenomenon as reported in BiVO₄-ZnO and BiVO₄-TiO₂ systems [13,14]. Additionally, spike and overshoot features that reduce solar to hydrogen efficiency in ferrite and BiVO₄ based photoanodes [15-17] are circumvented in the present work by tuning BiVO₄ concentration in BiVO₄/ZnO photo anode. Thus, BiVO₄/ZnO photo anodes has (i) absorbance of sunlight in visible region (ii) effective charge separation leading to enhanced life time of charge carriers (iii) relevant VB and CB edge positions w.r.t. hydrogen and oxygen water oxidation potential and (iv) inert and stable photo anode. In the present study, photo electrochemical studies have been carried out on dual layered BiVO₄/ZnO photoanode that are tunable in terms of their solar to hydrogen efficiency (SHE) by varying the BiVO₄ concentration.

Synergetic formation of wideband gap zinc oxide based nanostructures and visible light driven monoclinic bismuth vanadate have the potential to overcome the challenges including energetic criteria, photo anode's stability and slow kinetics of light driven oxygen evolution reaction (OER) and hydrogen evolution reaction (HER), associated with low cost water splitting using solar energy in photo electrochemistry [14,18,19]. Therefore, composite blends the advantage of both the materials showing effective utilization of solar spectrum due to the presence of BiVO₄ and increased water redox efficiency due to wide band gap of ZnO.

ZnO and BiVO₄ based nanocomposites/ photoanodes are newly emerging materials in this area and are known to show enhanced photo catalysis and photo electrochemical activity as compared to their pristine counterparts. Not much work has been done in this direction, and this provides a large scope to explore this nanocomposite. Theoretical investigations based on potential of heterostructures to tune the electronic properties of the composite are still lacking [14,19,20].

Further in this study, pure ZnO/BiVO₄ system has been used to demonstrate PEC activity, without the use of any supportive charge transport medium or co-catalyst, in contrast to studies as reported earlier [14, 19]. Moreover, it is well known that the photoactivity of a material depends on a number of factors, including its synthesis process and output product morphology. We reported seed layer assisted synthesis of ZnO nanocrystals on ITO substrate followed by BiVO₄ deposition to form ZnO-BiVO₄ heterojunction system. This process of synthesis resulted in the new mechanism of improved photoactivity by shifting the band edge positions of ZnO and BiVO₄ at the interface such that to promote hopping of charge carriers from CB of BiVO₄ to CB of ZnO. The process results in abundance of charge carriers in the CB of ZnO. Also, since ZnO has a large band gap, charge separation energy of e-h pair in ZnO is sufficient for complete redox of water. Thus, BiVO₄ being visible light active is acting as a light sensitizer for UV active ZnO.

1.2 Brief on photocatalytic and photoelectrochemical properties of ZnO and BiVO₄

Materials like ZnO, which has high potential for good photo catalysts in UV region [21], has certain drawbacks owing to its large band gap (which mainly governs the phenomenon of photo catalysis) and thus it is important to tailor its electronic and optical properties (to modify the rate of chemical reaction). Construction of heterojunction by producing an interface between ZnO and another semiconductor material with unequal band gap is one such effective strategy. ZnO based heterostructures/composites [22-26] such as Au-ZnO, Pt-ZnO, ZnO/Ag/Mn₂O₃, Fe₂O₃/ZnFe₂O₄/ZnO, and AuPd/ZnO/RGO with improved electro-optic properties have been found to work well in the visible region of the solar spectrum than pure ZnO. ZnO has an edge over narrow band gap material in terms of its suitable band edge positions which are beneficial for complete splitting of water [27] into hydrogen and hydroxyl ions, but at the same time the latter are more adapted to solar spectrum and thus show improved response to visible spectrum region. Much explored Bismuth Vanadate has a suitable visible-light active narrow band gap for photo catalysis [28], but simultaneously suffers from inappropriate band edge position for reduction of water; rather, it is

suitable only for oxidation of water due to slightly positive conduction band edge than 0V, making it inefficient for complete redox of water [29,30].

Bismuth vanadate can be more useful when used as photo anode which has ability of water oxidation to O₂ in half reaction and CO₂ to other bio-products/ bio-fuels [31,32]. Monoclinic form of bismuth vanadate has found to be the most photocatalytically active. There are a few merits of BiVO₄ and which is why it is used as a suitable photo catalyst (i) high photon absorbance performance due to its narrow band gap of 2.4 eV for monoclinic scheelite structure corresponding to wavelength of 520 nm [33,34] (ii) its thermodynamic level is close to hydrogen, with its VB position negative enough with respect to water and CB around 0 V vs. RHE [33, 35-37] (iii) improved extraction and separation of electron-hole pairs as the estimated effective masses for holes and electrons is lower than similar semi-conductors (e.g. TiO₂ or In₂O₃) [33,36,37] (iv) BiVO₄ has non-toxic properties so preferred as photo anode material [33, 37].

Various methods have been adopted to optimize BiVO₄ as photo catalyst material to improve its O₂ evolution activity. Bare BiVO₄ usually have poor photo activity due to reasons like (i) slow transport of electron in the conduction band [33, 38] (ii) slow O₂ evolution kinetics and (iii) surface and bulk electron-hole recombination [39]. Therefore it is required to assist its activity in some sort. Doping, morphology control, composition tuning or coupling with wide band gap semiconductors to form composite structures or heterojunctions are some of the adopted methods.

Controlling morphology and crystal structure brings positive change in the enhancement of dye degradation efficiency of BiVO₄ material. Various attempts with different morphologies have been explored. Obregan et al. [40] synthesized with BiVO₄ diverse morphologies and tested for its photo activity efficiency by changing preparation conditions such as precipitation agent and hydrothermal reaction time. It was found that morphology was in direct relationship with the efficiency of degradation of dye. Back and front side illumination creates the difference in photocurrent generation that explains the doping effect of semiconductor material. After front side illumination, holes rush towards the surface and generation of electron-hole pair near to electrolyte

interface takes place. During this, electrons move to counter electrode and then to conductive surface. Photocurrent generation is less in front end illumination indicating slow electron transition is a major drawback [33,41]. Study by Zhong et al. [39] shows that quantum efficiency (IPCE) and photocurrent density is higher in back side illumination for bare BiVO₄. But electron mobility is improved when BiVO₄ is doped with material like Tungsten (W).

1.3 Features of ZnO

1.3.1 Crystal structure

ZnO is commonly available in three well-defined crystal structures-wurtzite, rocksalt or cubic (zinc blende) structure. ZnO with rocksalt structure is quite rare and can be obtained under high pressures. ZnO wurtzite structure, of the three structures, is the most thermodynamically stable and common structure of ZnO [42,43]. It belongs to P6₃mc space group having a hexagonal wurtzite crystal at ambient temperature and pressure exhibiting a non-centrosymmetric structure, which renders ZnO to be pyroelectric and piezoelectric [44]. It is defined by two lattice parameters, 'a' and 'c', with values 0.3296 nm and 0.52065 nm, respectively [45]. Fig 1.1 shows the zinc blende, rocksalt and wurtzite unit cell structures of ZnO. It is observable that wurtzite ZnO is formed of hexagonally-arranged close-pack-atoms forming stacked layers along the c-axis [46]. Each Zn²⁺ sub lattice consists of four Zn²⁺ ions neighboured by four O²⁻ forming a tetrahedron coordination which induces piezoelectric effect in ZnO [47].

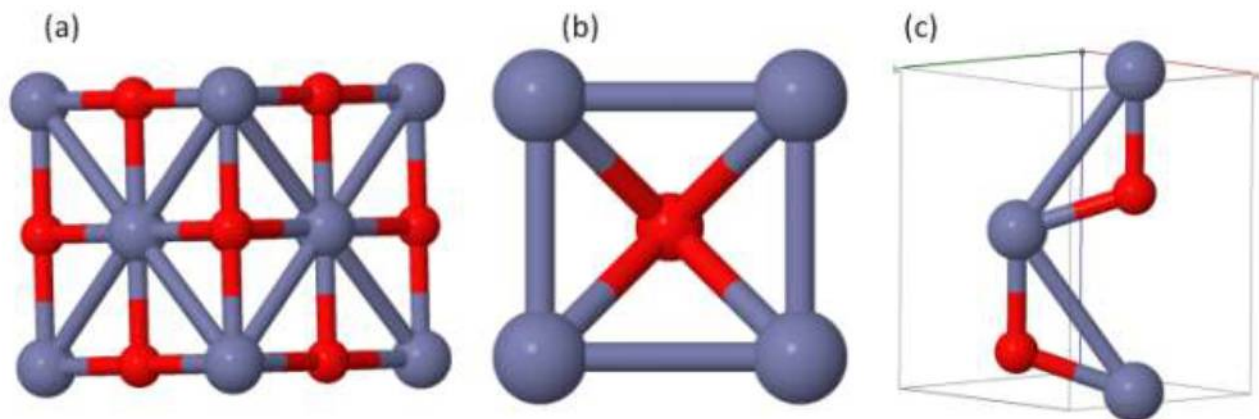


Figure 1.1 The (a) rocksalt (cubic), (b) zinc blende (cubic) and (c) wurtzite (hexagonal)

structures model of ZnO.

1.3.2 Electrical and optical properties

ZnO is n-type material (semiconductor) with direct band-gap of ~3.37 eV with good optical and electrical properties and high electrochemical stability [48,49]. Even under high energy radiation, ZnO remains very chemically and thermally stable. Besides large exciton binding energy at room temperature of 60 meV, it has high electron mobility, higher breakdown field strength and high breakdown voltages [48-51]. Table 1.1 presents the electrical and optical properties of single crystal wurtzite. With such excellent properties, ZnO has thus found large applications in areas of field emission devices and transparent conducting electrode for various types of opto-electronic devices. The recombination of charge carriers in ZnO produces UV light and hence are used for optoelectronics applications such as UV emitter which requires short wavelength [52].

Table 1.1 Optical and electrical properties of single crystal ZnO wurzite structure [53]

Property	Value
Energy band-gap (E_g)	3.2-3.7 eV (Direct)
Exciton binding energy	60 meV
Effective electron mass (M^*)	0.24-0.30 m_e
Effective hole mass (m_h^*)	0.45e-.60 m_e
Electron Hall mobility at 300 K for n-type (m_e)	200 $\text{cm}^2 \text{V}^{-1} \text{S}^{-1}$
Electron Hall mobility at 300 K for p-type	5-50 $\text{cm}^2 \text{V}^{-1} \text{S}^{-1}$
Refractive index (n_w, n_e)	2.008, 2.029
Intrinsic carrier concentration (n)	$<10^6 \text{cm}^{-3}$
Background carrier doping	n-type: $\sim 10^{20} \text{electron cm}^{-3}$ p-type: $\sim 10^{19} \text{holes cm}^{-3}$
Optical transmission, $T (1/\alpha)$	80-95%

1.3.3 Luminescence properties

Photoluminescence (PL) can be employed to characterize the luminescence characteristics of ZnO. The PL spectrum of ZnO consists of two main region, ultra violet and broad visible emission region [54,55]. The UV emission region is ascribed to the recombination of excited holes and electrons pairs. High UV emission region indicates high crystallinity of ZnO [56]. Various defects and impurities in the structure form the green band in the visible region. The presence of oxygen vacancies at the surface may recombine with the excited electrons and holes in the valance bands. This recombination relates to the presence of visible emission in the spectra and its increased intensity may relate to the large concentration of defects [57].

1.4 Features of BiVO₄

Bismuth vanadate is an n-type material and an inorganic compound. It is a bright yellow solid powder and may have a slight green tint with the formula BiVO₄. This section briefly discusses the useful properties of this material. General physical properties of BiVO₄ are mentioned in table below.

Table 1.2 General physical and structural properties of BiVO₄ [58]

Formula	BiVO ₄
Synonyms	Bismuth Orthovanadate; Bismuth Vanadate Vanadic acid, Bismuth salt
Colour and odour	Yellow, Very soft
Molecular weight (g/mol)	323.92
Melting point (°C)	934

Boiling point (°C)	1997
Solubility in water	Insoluble, soluble in strong acids
Structure	Monoclinic, tetragonal
Combustibility	Non-combustible
Stability	Stable under normal conditions
Density (g/cm ³) (g/mL)	6.95
Band gap (eV)	2.4 (m-BiVO ₄), 2.9 (t-BiVO ₄)
Specific gravity (gm/cc)	6.98
Crystal Structure	Monoclinic
Cell parameters (Å)	a = 5.195 b = 11.701 c = 5.092, β=90.38

1.4.1 Crystal structure

Most commercial pigments of bismuth vanadate are now based on pure bismuth vanadate with tetragonal (dreyerite) structure or monoclinic (clinobisvanite). Mainly it exists in three crystalline phases: tetragonal scheelite (dreyerite), monoclinic scheelite (clinobisvanite, distorted scheelite), and tetragonal zircon (pucherite) structure [59]. The monoclinic structure can be created by high temperature synthesis, while at lower temperatures tetragonal zircon-type structure is obtained. Monoclinic form can be reversibly transformed to tetragonal scheelite by heating it above 255°C [60]. Mechanical treatment of tetragonal structure such as grinding/mixing with mortar and pestle also irreversibly transforms to monoclinic form. Tetragonal BiVO₄ with around ~2.9 eV band gap is more active for UV absorption, while monoclinic scheelite BiVO₄, has a comparatively narrow band gap (around ~2.3 eV) which makes the material active in visible light and UV absorption. This advantage of monoclinic structure renders the material with lots of possibilities and potential as an active photo catalyst material. In both the cases of monoclinic and tetragonal BiVO₄, band

transition from O2p to V3d is associated with UV absorption of light, whereas visible light absorption is due to the transition from valence band formed by Bi6s or a hybrid orbital of Bi6s and O2p to conduction band of V3d [61]. Additionally, the dissociation efficiency of photo-induced holes and electrons increases due to the fact that Bi-O bond is distorted in monoclinic BiVO₄ [62].

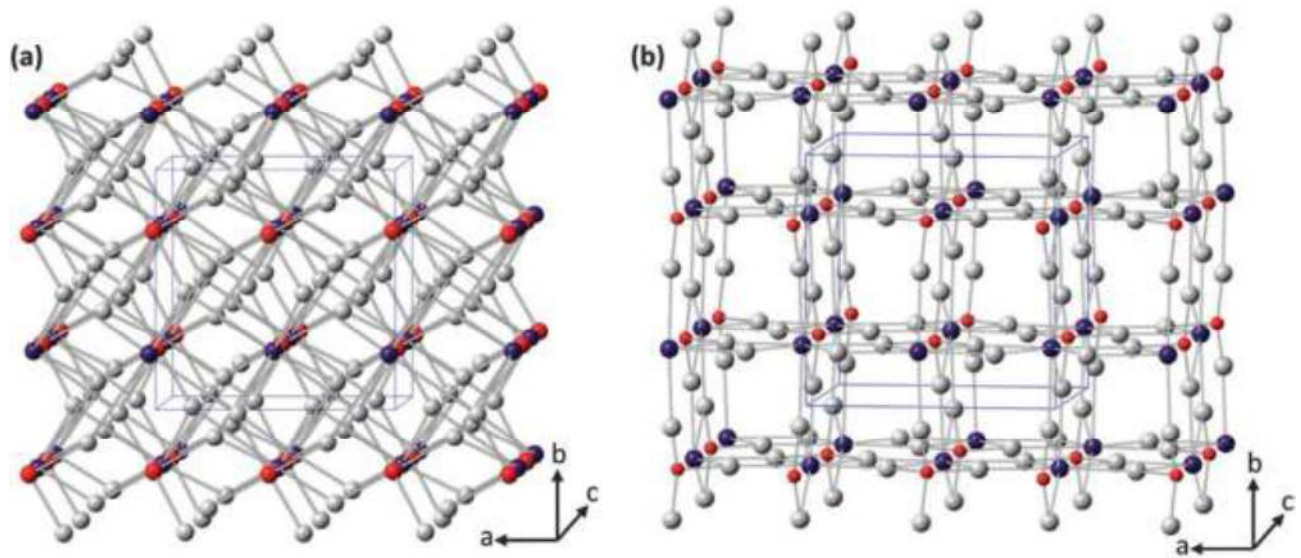


Figure 1.2 Crystal structure models of (a) scheelite and (b) zircon-type BiVO₄ [63].

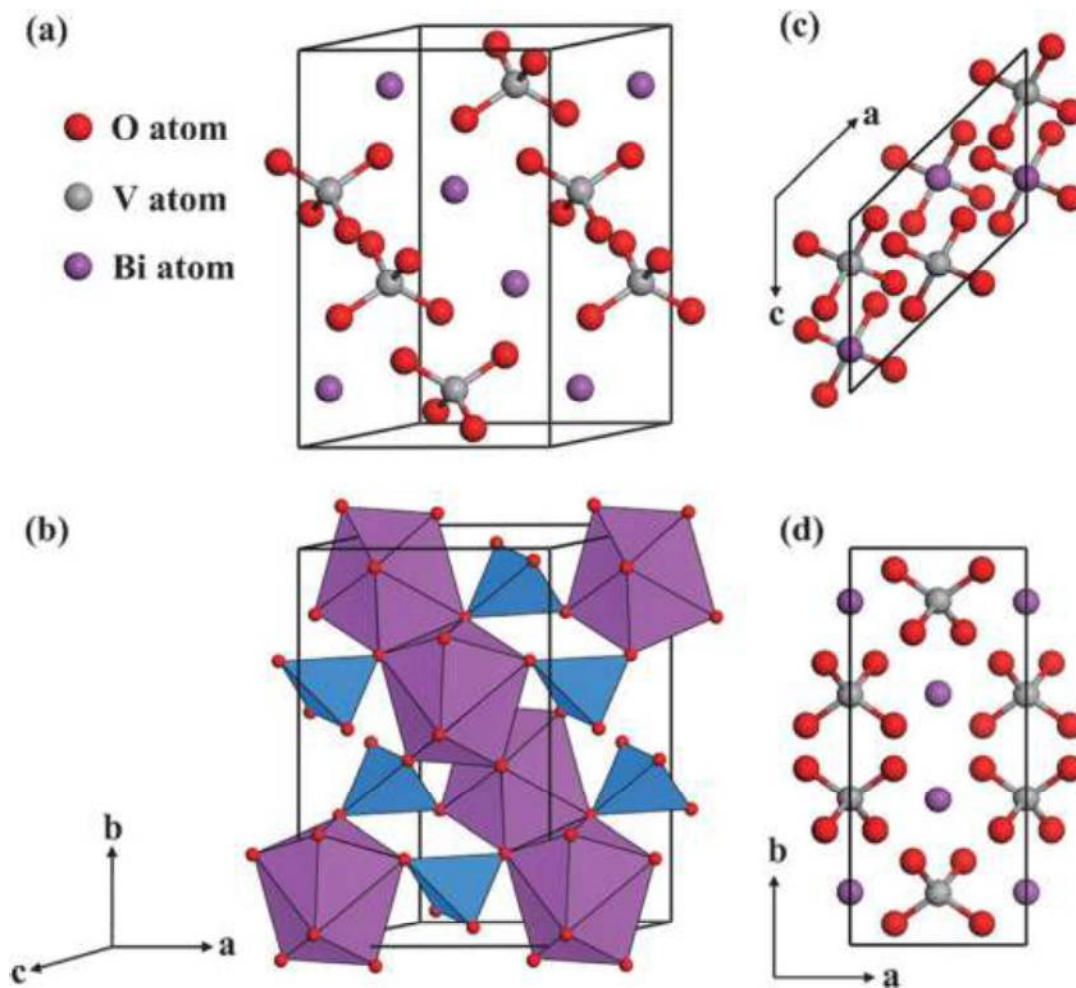


Figure 1.3 (a) Crystal structure of monoclinic clinobisvanite BiVO_4 ; (b) polyhedron structure representation; (c) top view and (d) side view [63].

1.4.2 Electronic structure and properties

To better understand the behaviour of different solid structures of BiVO_4 and their influence on photocatalytic and electronic properties, it is necessary to study their electronic structure theoretically. The calculations were performed using density functional theory (DFT) as implemented by Cambridge Serial Total Energy Package (CASTEP) code [64]. Unit cell structure of monoclinic BiVO_4 (Clinobisvanite) with the space group: $C2/c$ and point group $C62h$ is depicted in Fig 1.3. Basic unit structure of BiVO_4 consists of a BiO_8 polyhedron and VO_4 tetrahedron. Bi site is neighboured by eight oxygen atoms, and V site is encircled by four oxygen atoms. BiO_8 polyhedron is connected to VO_4 tetrahedron by sharing an apex oxygen atom. BiVO_4 exhibit the characteristics of a layered structure by arranging V and Bi atoms alternately along the

crystallographic axis [36]. In contrast to experimental band gap value, calculated GGA band gap with 2.02eV is about 0.28eV lower compared to former [11,65,66]. The conduction bands at bottom are mainly composed of anti-bonding states and the valence bands are primarily composed of O2p-Bi6p and O2p-V3d. The O2p orbital also pairs with the lone pair Bi6s orbital and originates filled anti bonding states near the Valence Band Maximum (VBM). Such pairing makes BiVO₄ a direct band gap material. Two types of bond lengths are present for V-O, and four types for Bi-O bond. The bond lengths of different types indicate that both BiO₈ polyhedra and VO₄ are slightly distorted [62].

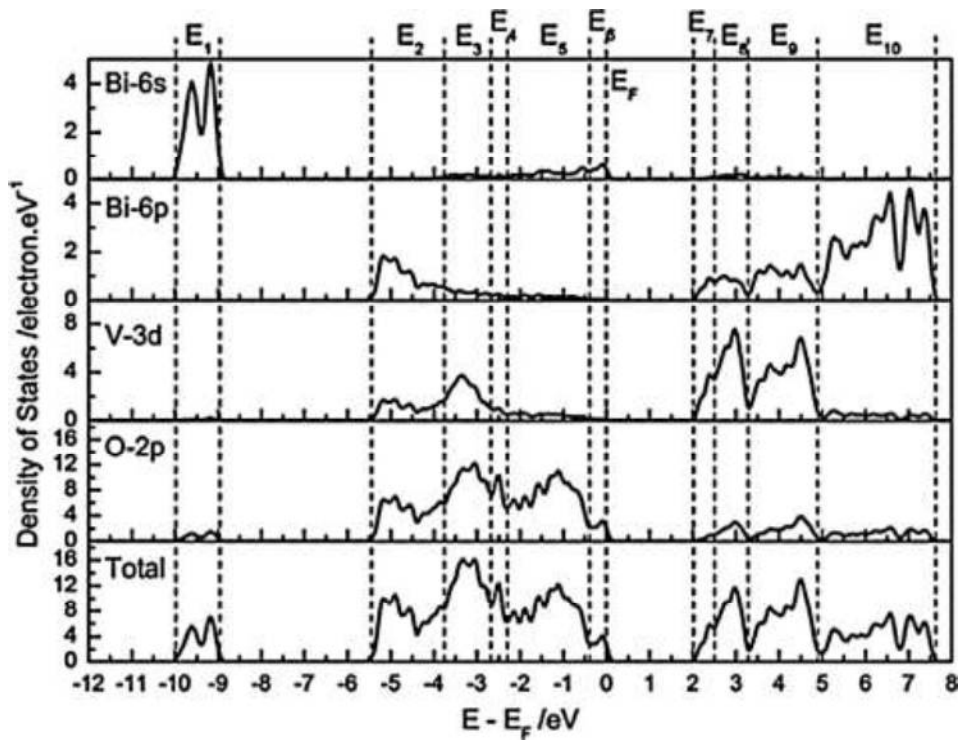


Figure 1.4 Total and local partial density of states of monoclinic clinobisvanite BiVO₄. The DOS is decomposed into the main electron states of each component [63].

This distortion disperses the VB upwards by enhancing the lone pair impact of Bi 6s states and thus reducing the band gap and making the material active in visible light. Bond length parameters for monoclinic BiVO₄ phase are given in Table 1.3.

Table 1.3 Bond length of monoclinic BiVO₄

Crystal system	Bond length (Å)	
	Bi-O	V-O
Monoclinic	2.354 x 2	1.69 x 2
	2.372 x 2	1.77 x 2
	2.515 x 2	
	2.628 x 2	1.72 x 4

1.4.3 Optical properties

Possessing a great ability for oxidation of water, BiVO₄ is an interesting material for solar fuel applications. Introduction of Bi cation into the metal-oxide structure helps achieving the hybridization of the O 2p and orbitals, which results in the upward shifting of the top of VB and thus reduction in the band gap of m-BiVO₄. In a report by Kudo et al. [34], they investigated the effect of calcination on monoclinic BiVO₄ powders synthesized by mixing of parental reactants at room temperature. They obtained a band gap of 2.4 eV, as compared to 2.9 eV found for tetragonal phase observed in the same study. Kubelka–Munk function is a well-known method for the estimation of optical band gap of semiconductor catalysts. The effect of annealing on the samples revealed that as the annealing temperature increases from 400°C to 600°C, the value of band gap gradually decreases from 2.53 to 2.47 eV [67]. Similarly, Thalluri et al. [68] synthesise monoclinic BiVO₄ by precipitation method and found that material band gap decreased (from 2.49 eV to 2.38 eV) with temperature of calcination (from 350°C to 800°C respectively). Zhao et al. [37], using DFT calculations, found that there exists a considerable optical anisotropy near the absorption edges in the monoclinic phase of BiVO₄ due to distorted crystal structure and special electronic structure. They demonstrated varying absorption coefficient along different spatial axis as a reason for this optical anisotropy. a- and c- axis exhibited a peak at 440 nm, whereas b- was located at about 330 nm. Moreover, same bonds were present along a- and c-axis, while different dipoles formed along

b-axis restricted the transition from top of valence band to bottom of conduction band. This is why controlling morphology to expose larger areas of (001) and (100) facets of crystal are a common technique to enhance the photo catalytic efficiency of BiVO₄.

Recently, Xi and Ye [69] also formed monoclinic BiVO₄ nanoplates with exposed (001) facets yielding an improved photo catalytic O₂ evolution. They related larger surface energy and higher hydrophilic capacity of this plane for this increase in activity.

1.5 Photoelectrochemical and photocatalytic approach of water splitting through solar energy

There are two divergent approaches for achieving solar water splitting through semiconductor materials, namely photo catalytic and photo electrochemical water splitting. In the photo catalytic approach, the photo catalyst material which is in the form of powder is dispersed with the water contained in a tank irradiated with sunlight (natural or artificial) directly towards it. This is a relatively simple method with fewer complexities involved. Many review papers summarize about this form of semiconductor photo catalysis involving water splitting using visible and UV source. However, the use of sacrificial agents to study the activity of O₂ evolution becomes necessary in this case. AgNO₃ is the most used e-scavenger, which often results in the quick deactivation of the semiconductor material during irradiation. Therefore, innovative reactor systems are used to accurately determine production rate of oxygen and study deactivation mechanisms which is a principle drawback for the practical implementation of this system. Moreover, H₂ and O₂ evolve together in such a system, which inflicts a technical problem. In the second approach of photo electrochemical (PEC) splitting of water, it utilizes a set of two or three electrode system where the photo catalyst material is made as one of the electrodes (anode and cathode) submerged into an electrolyte solution making it electrically connected to other two counter and reference electrodes. This system has some inherent advantages over powder photo catalysis system which renders this system as a preferred approach in future development of functioning devices.

1.5.1 Photo-electrochemical cell for hydrogen generation

Photo-electrochemical cell uses solar power to split water directly into hydrogen and oxygen thereby providing a basis for a clean, renewable production of hydrogen from solar light. They rely on a photoactive semiconductor material capable of harvesting and transforming solar energy into stored chemical fuel, i.e. hydrogen.

Key Benefits of PEC:

- Operates at low temperatures
- Sustainable and clean - using only water and solar energy
- No emissions

Figure 1.5 illustrates the simple arrangement of a photo electrochemical cell based on metal counter electrode and a single photo anode. More complicated set-ups may involve photo cathodes or more than one photo electrodes. Semiconductor material, main constituent of the photo electrochemical cell, converts the photons falling on it to electron and hole pairs. Due to the existing electric field inside the semiconductor, these electrons and holes are spatially separated from each other. The generated electrons are swept through the external wire or circuit towards the counter electrode where hydrogen gas is formed by reducing water. The holes travel towards the semiconductor/electrolyte interface and produce oxygen gas by oxidising water.

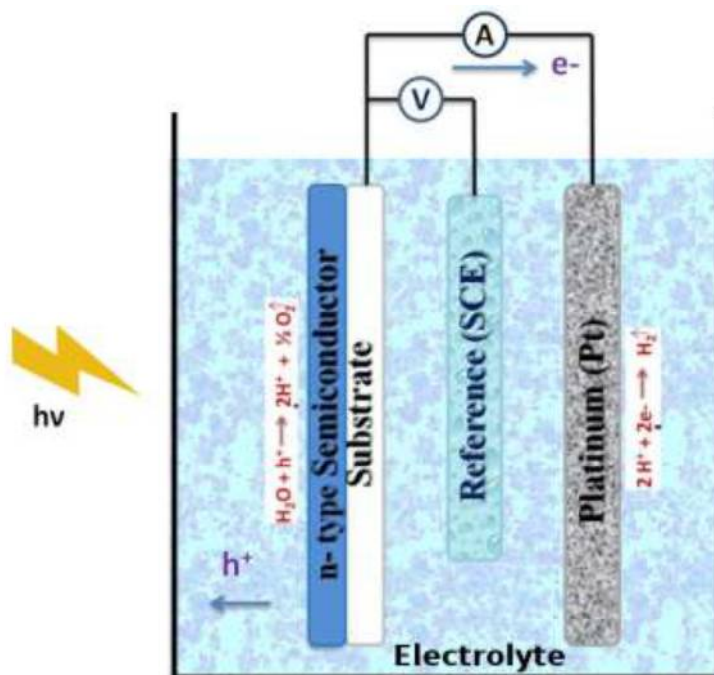


Figure 1.5: Photoelectrochemical based solar hydrogen production system

The reduction and oxidation reactions for an alkaline electrolyte can be written as-

By adding or subtracting the dissociation reaction of water into protons and hydroxyl ions, the appropriate reactions can be obtained for an acidic environment:

For overall water splitting reaction, Gibb's free energy change is given by the expression-

At standard concentrations (1 mol/L, 1 bar) and temperature (298 K), voltage of 1.229 V for the electrochemical cell corresponds to the change in Gibbs free energy i.e. +237 kJ/mol hydrogen. This indicates that water spitting reaction is thermodynamically favourable. And this is quite different in

photocatalytic dye degradation reaction in which change in Gibbs free energy is negative.

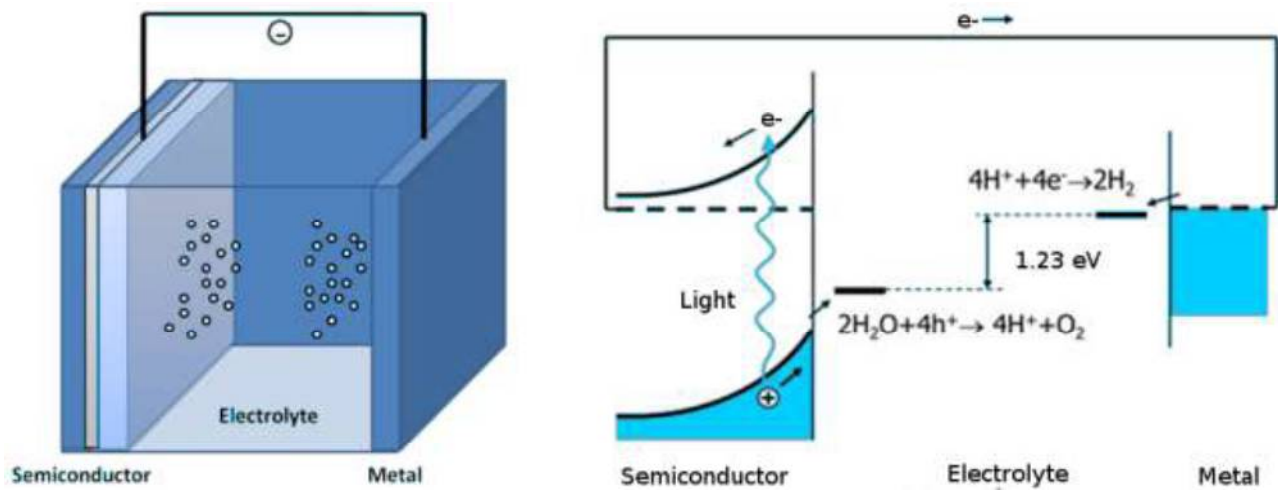


Fig. 1.6 Photoelectrochemical cell showing metal cathode and semiconducting photoanode & its energy diagram

1.5.1.1 Space Charges and Band Bending

Space charge or built-in electric field is one of the prime features of a semiconductor responsible for preventing recombination of generated hole and electron pair by providing their prolonged and efficient separation. The field is created by the movement of charges from the semiconductor bulk across its interface and therefore exists near the interface or surface of the semiconductor.

1.5.1.2 Origin of the Space Charge Layer

The origin of the space charge layer takes place when a semiconductor is brought in close contact with another semiconductor or a metal. When both the materials with dissimilar fermi levels or electrochemical potentials come in contact, transfer of charges takes place between the two until an equilibrium state is achieved.

Air contacts the metal oxide surface and water molecule (-OH) out of the air adsorbs at the surface of this metal. This leads to -OH surface termination and formation of electronic surface state. Free electrons occupy some energy level because this electronic state will have the energy level in conduction band. So there is a development of positive space charge as the donor is in bulk from where the free electrons came. This potential difference triggers the flow of charge till this

reaches the equilibrium state where no electron will flow. The energy level is around the middle level of the density of the surface of the state.

In a semiconductor there are other types of space charges as well which can be produced and they can form inversion layer. This layer can be formed if the number of adsorbed ions increases in a semiconductor where Fermi level goes beyond the middle of band gap. However, the formation of this inversion layer is quite uncommon. Deep depletion layers are more common in some materials where band gap is usually higher (than 2 eV) because of less number of minority carriers in photo electrode material. This is the case also in oxidation and reduction reactions where these minority charge carriers are consumed. If excessive amount of charge is adsorbed at the surface of a semiconductor then accumulation layer can be formed by the majority carriers which are moving freely and will store near to the surface to compensate the surface charge. In depletion layer, the ionized concentration of dopant restricts the charge density. Also the accumulation layer is much thinner than the depletion layer because effective density of state limits the electronic charge carrier concentration. Same procedure is there to measure the width of the deep depletion layer and normal depletion layer however it is hardly required to find out the thickness of accumulation and inversion layers. It is important to know that above mentioned layers can be formed by applying the potential to semiconductor photo electrodes.

1.5.2 Photocatalysis

As mentioned above, catalytic water splitting into O_2 and H_2 is a typical “uphill reaction”, with Gibbs free energy ($G^\circ = 238 \text{ kJ mol}^{-1}$). The term photocatalysis is composed of combination of two words, photochemistry and catalysis. It implies that to initiate a chemical transformation, light and a catalyst are necessarily required. In other words, term photo catalysis can be described as “acceleration of a photoreaction in the presence of a catalyst”. This also defines and includes the term photosensitization which means a process of photochemical alteration in one chemical species occurring as a result of initial absorption of radiation by another chemical species called the photo

sensitizer. Based on the process of interaction between adsorbate and catalysts, reactions could be sensitized photoreaction or catalyzed photoreaction. In former, adsorbate is photo-excited first and then interacts with the ground state of the catalyst substrate while latter involves the photo-excitation of catalysts first and then interaction with the ground state adsorbate molecule. In most cases, semiconductor photo catalysis or semiconductor-sensitized photoreactions are referred as heterogeneous photo catalysis.

Photo catalysis is a rapidly emerging research area with ever growing demand in environment and energy related industries for various applications including purification and treatment of water [70, 71] and air [72-74], degradation of organic pollutants [75,76] and production of renewable fuels [77,78]. Organic pollutants in water such as waste dyes, surfactants and other harmful chemicals from industries are major threats to the environment and mankind. Photo catalysts, in the presence of light have the ability to produce reactive oxidising agents [79,80] which degrade the toxic organic materials and no waste residue is produced during this process [80,81]. Also, photo catalyst itself does not undergo any chemical reaction and thus can be used repeatedly resulting in simpler and cost effective setup [81]. Significant research efforts have been made to come up with new and superior photo catalyst materials, not only in terms of their dye degradation efficiency but at the same time for improved photo stability and reaction repeatability. Besides TiO₂ [81-83] and its composites as photo catalytically active materials; a large number of non- TiO₂ based materials (mostly metal oxides) [84-86] have been found to display strong photo catalytic response.

1.5.2.1. Semiconductor photocatalysis mechanism

In an ideal photo catalytic process, organic pollutants are mineralized into water (H₂O), carbon dioxide (CO₂) and mineral. The efficiency of a photo catalytic material for water splitting can be measured directly by the amount of pollutant degradation dispersed in solution under light irradiation. Different photo catalytic set-up configurations such as top radiation type and inner radiation type, and light sources such as Hg lamp and Xe lamp, are commonly used as artificial

source of light. The principle of mechanism for photo catalysis fundamentally remains the same as that of photo electrochemical cell. When light with sufficient energy falls on the photo catalyst, the charge carriers gets excited and jumps from VB to CB, get adsorbed on the pollutant surface such as dye and degrades the dye molecules by oxidising them. The amount of degradation gives efficiency of material.

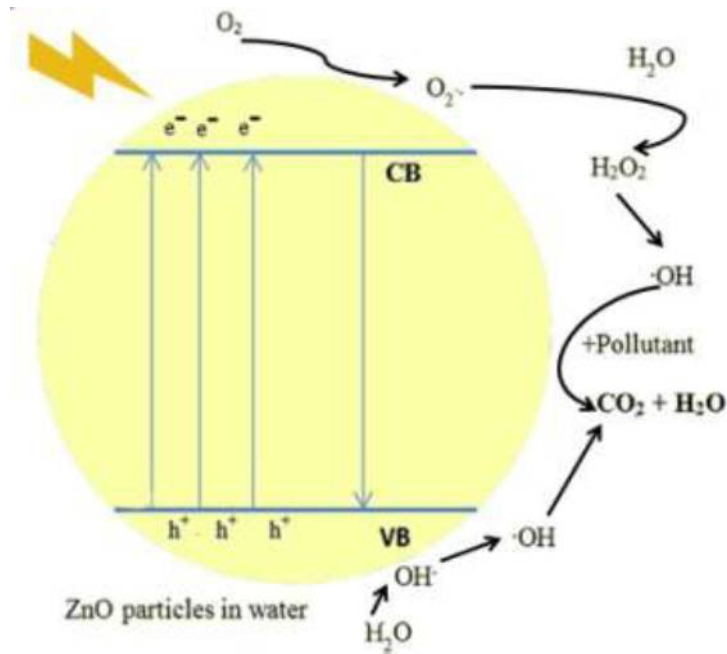


Figure 1.7: General mechanism of the photocatalysis

1.6 Issues in solar water splitting

In order to fully utilize a material for water splitting applications and improve the efficiency of PEC and photo catalysis, it is important for a semiconductor material to meet certain requirements.

Required condition for efficient overall water splitting for hydrogen and oxygen generation:

- 1) Photo–Electrode should have bottom of conduction band $< 0V$ for hydrogen generation.
- 2) Top of valence band should be > 1.23 for oxygen generation.
- 3) Band gap of around 2.45 (to efficiently utilize visible light spectrum).
- 4) Should have large surface to volume ratio in order to increase the area of contact with electrode.
- 5) Should be stable against corrosion in water.

6) Should be photo-stable.

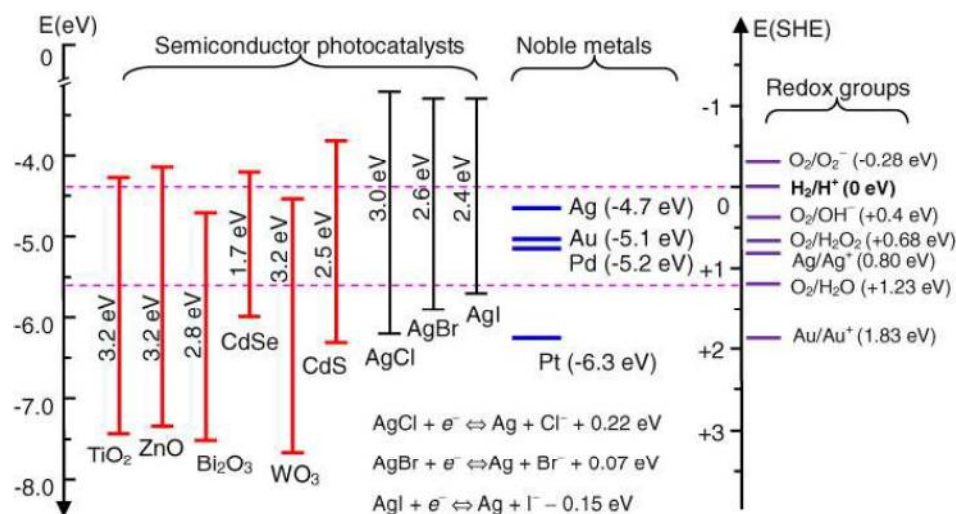


Figure 1.8: Band gap and edge position of various compounds

However, it is difficult for a material to exhibit and satisfy all the properties at the same time.

Some of the challenges encountered by materials are discussed below.

1.6.1 Material related issues

This section provides a brief overview of the materials requirement to be solar active viz. band gap, band edge potentials, chemical stability, photostability etc.

1.6.1.1 Band Gap

The band gap of the material determines the solar spectrum region in which it will absorb light. Fig 1.9 shows the complete solar spectrum of electromagnetic radiations. The region of visible light ranges from 400 nm to 700 nm. Below 400 nm the region extends to ultraviolet or UV while above 700nm, the region is known as infrared or IR region. The most explored and commercially used materials such as TiO_2 and ZnO have large band gaps of about 3.2 eV, thus their photo activity is limited to UV region of solar spectrum. But UV region occupies only 6% of the total spectrum range; therefore the aim is to bring down the activity of materials to visible light range as it

occupies almost 96% of the total electromagnetic spectrum. The ideal band gap for a semiconductor material for superior efficiency should range from 2.2 to 2.5 eV.

To dissociate water into its constituent atoms, oxygen and hydrogen, theoretically it requires a thermodynamic potential of 1.23 eV ($\Delta G = 237$ kJ/mol) since it's a highly endothermic reaction [87,88]. Taking into account various losses of energy (~ 0.8 eV) caused by recombination of photo-excited charge carriers, resistance of the electrical connections and electrodes and voltage losses at the contact, approximately around 1.8 eV of energy is needed for efficient overall splitting of water corresponding to a wavelength of visible light region. Therefore, to achieve water splitting with sufficiently fast reaction kinetics, minimum energy plus energy associated with losses has to be provided.

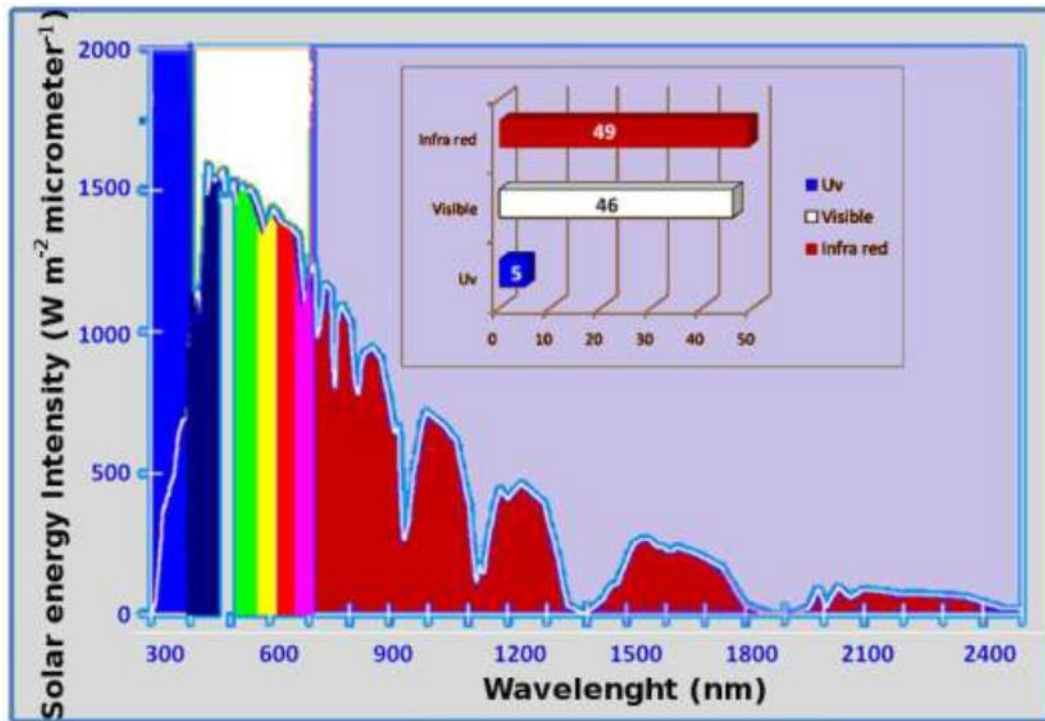


Figure 1.9: Intensity Vs wavelength plot of solar spectrum under 1.5 AM condition

1.6.1.2 Band edge potentials

Besides band gap, the band edge potentials i.e. conduction and valence band positions play a very crucial role in deciding the photo catalytic and photo electrochemical property of a semiconductor material. For efficient transfer process of charge carriers between electrolyte and semiconductor in

PEC or from VB to CB in photo catalysis, the CB energy of the material must be more positive than the reduction $E_{\text{red}}(\text{H}_2/\text{H}^+)$ and while VB energy must be more negative than the oxidation $E_{\text{ox}}(\text{OH}^-/\text{O}_2)$ of water [89]. Simultaneous oxidation and reduction of water remains a challenge for most materials. Non-oxide semiconductors act as good reducing agents but lack oxidation of water due to unsuitable position of band edge. On the other hand, most oxide semiconductors have the ability to oxidise but not reduce water.

1.6.1.3 Resistance

Good corrosion resistance and low electrical resistance are one of the key factors considered for high performance in water splitting [88,90]. With the mobility of electrons in the semiconductor, electrical resistance is reduced and electron transfer efficiency enhances. Basically, by the minimizing the amount of resistance between the substrate and the material, conversion efficiency could be improved.

The major sources of energy losses derive from the ohmic resistances of the internal and external circuits of the PEC include:

- electrolyte
- electrodes
- electrical connections
- electrical leads (wires)

To achieve maximum efficiency, above mentioned causes of losses should be minimised.

1.6.1.4 Stability

The photo electrode stability against photo-corrosion is another severe issue that needs to be taken care of while designing a photo catalyst or photo anode as a photo-unstable material may limit the usefulness of that photo-active material. Many metal-oxide semiconductors such as GaAs, Si, CdS, GaP suffers from this issue by either forming a thin oxide film or by getting dissolved. This

prevents the efficient transfer of electron charges across the electrolyte/ semiconductor interface [91]. Almost all metal oxide photo anodes lack thermodynamic stability that causes the generated holes to oxidise the semiconductor. However, photo-corrosion may be inhibited, if the charge transfer kinetics across the interface (oxidation of water) is quicker than the rate of decomposition at the anode although it may remain as a side reaction. For example, TiO_2 and SnO_2 show better stability than ZnO upon illumination in aqueous environments over a wide range of pH values and applied potentials. Wide band gap semiconductor metal oxides have a general trend of being stable against photo-corrosion, while non-oxide semiconductors or small-band gap metal oxide are not.

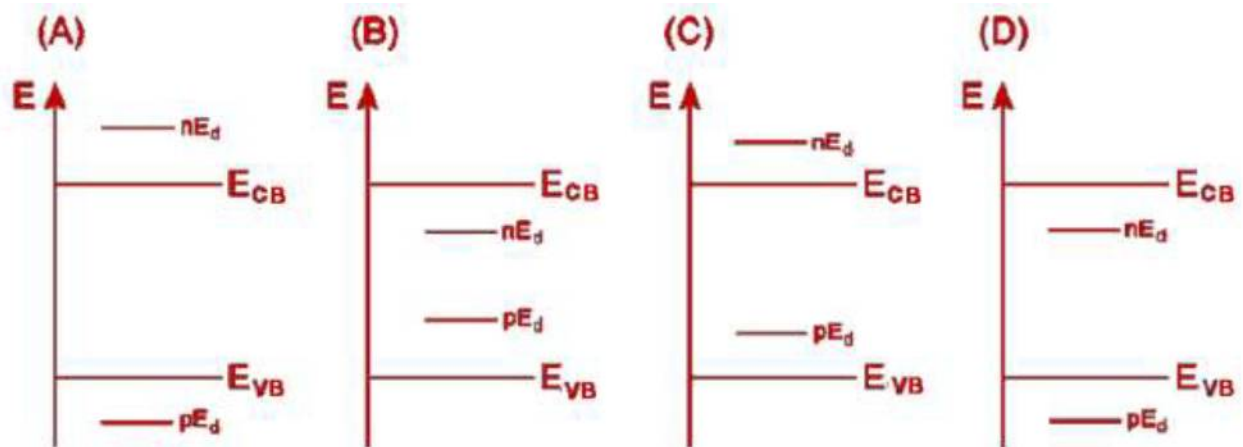


Figure 1.10: Conditions for semiconductor stability in electrolyte (A) stable, (B) unstable, (C) stability against cathodic decomposition, (D) stable against anodic decomposition; where E_d is decomposition potential

1.7 Targets to be achieved in solar water splitting

We are at the peak of the oil age but at the beginning of the hydrogen age. Photo electrochemical cells and photo catalysis offer a favourable method of hydrogen production and organic pollutant degradation respectively driven directly by solar energy.

However research is needed to overcome its certain limitations-

- **Stability-** Oxides are the most photochemically stable semiconductors in aqueous solution, but they suffer from either having small or too large band gaps which results in

inefficient visible light absorption, or they exhibit poor characteristics like low photostability.

- Efficient Band gap energy - For efficient solar energy absorption, band gap of the semiconductor for PEC applications should be around 2.2 eV. Small band gap will lead to inefficient water splitting and too large band leads to inefficient solar spectrum utilization.
- materials inefficiency
- challenge is to identify semiconductors robustness in splitting of water
- responsive to a wide portion of spectrum of the solar radiation i.e. visible spectrum
- should withstand photo corrosion
- development of high-performance materials

Closing this gap will lead to the development of efficient and cheap systems for production of hydrogen directly from solar energy and therefore directly address, not only the conversion, but also the storage issues.

1.8 Strategies to improve photo activity of material

1.8.1 Changing chemical composition

Chemical composition or crystal structure can be changed by doping the material with a suitable anion or/and cation. This can bring the materials band gap towards visible light of solar spectrum. Cation doping can lead to reduction in band gap resulting in formation of discrete levels within the band gap acting as trap levels. Doping with certain cationic elements like Indium adds energy levels to the CB of semiconductor, thereby reducing the amount of light energy needed to become activated and helps in improving the photo activity of the material. Anionic dopants like S or N helps in the creation of new valence band without affecting the position of conduction band. Now the transfer of charge may take place from the newly formed VB to CB needing lesser amount of quanta of photons to do so. Thus, structural modification via doping is an effectual and simple

strategy to improve the material's photo efficiency as the introduction of foreign atoms into the parent's lattice brings in positive changes in the structure beneficial for tuning materials electronic properties which facilitates the better electron-hole charge separation and enhancing the visible light absorption [92].

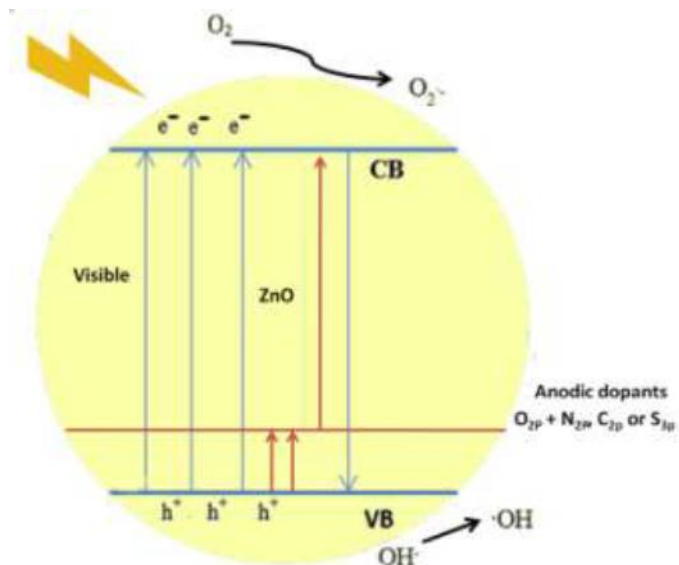


Figure 1.11: Photocatalytic process of ZnO with anodic dopants decorated on surface.

1.8.2 Altering Physical properties

Physical properties like crystallinity and surface area can be refined to enhance the photo catalytic activity of the material. Nanometer sized photo catalysts can be prepared by hydrothermal/solvothermal synthesis, sol-gel synthesis, polyol-mediated route, gel combustion route etc. Calcination of these nanoparticles at appropriate temperature makes nanocrystalline semiconductors having a reasonably high surface area.

1.8.3 Minimizing the recombination of charge carriers

Use of co-catalysts or coupled semiconductors can improve the activity of the photocatalyst. Construction of heterojunction by producing interface between ZnO and another semiconductor material with unequal band gap is an effective strategy. When two semiconductors of unequal band

gap or energy band potentials combine to form a composite, the charge transfer between the two plays an important role. Photo generated electrons can migrate from material whose CB potential lies at higher potential to another material whose CB edge lies at lower potential. This process reduces the recombination rate of the excited charge carriers. Noble metals like Pt also helps in increasing the lifetime of the carriers as noble metals act as a sink for electrons which increases the separation rate of photo generated charge carriers. Therefore, composite blends the advantage of both the materials showing effective utilisation of solar spectrum [92].

1.9 Importance of splitting of water for PEC application for hydrogen generation

Mobility (transport of people and goods) is a socio-economic reality and need for which is bound to grow in the coming years. Modes of transport should be safe, economic and reasonably environmental friendly. Hydrogen could be ideal as a synthetic energy carrier for transport sector as its gravimetric energy density is very high, abundantly available in combined form on the earth and its oxidation product (water) does not contribute to greenhouse gas emissions. However, its sustainable production from renewable resources economically, on-board storage to provide desirable driving range, usage in durable energy conversion devices and development of infrastructure for its delivery remain significant challenges. Almost any energy source can be used to produce hydrogen. Presently, non-renewable sources dominate hydrogen production processes but the need of the hour is to develop and promote the share of renewable sources for hydrogen production to make it completely sustainable. Hydrogen may be used as a fuel for almost any application, where fossil fuels are used presently and would offer immediate benefits over the conventional fuels, if produced from renewable sources. For achieving a successful "hydrogen economy" in the near future, the technical and economic challenges associated with hydrogen must be addressed quickly. Finding feasible solutions to different challenges may take some time but

technological breakthrough by way of on-going efforts do promise hydrogen as the ultimate solution for meeting our future energy needs for the transport sector.

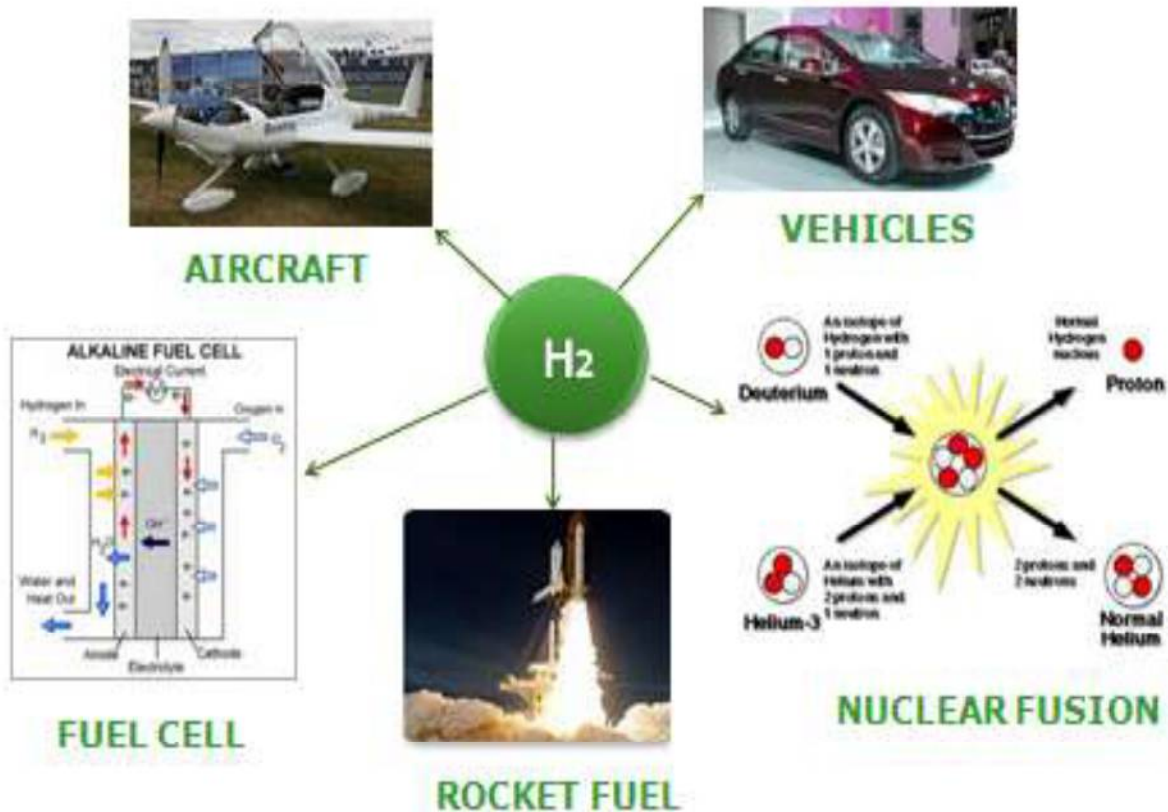
1.9.1 Applications of hydrogen

Recent literature [93-98] focuses on the applications of hydrogen covering every sphere of human being's activity-be it industrial, transport, domestic or space. Hydrogen is mainly used in petroleum refineries [99,100], ammonia/fertiliser production [101,102] and, to a lesser extent for metal refining such as nickel, tungsten, molybdenum, copper, zinc, uranium and lead and amounts to consumption of more than 60 million metric tonnes worldwide [103,104]. Hydrogen may be used as fuel in almost any application where fossil fuels are used presently-particularly for motorising the vehicles which would offer immediate benefits in terms of reduced pollution and cleaner environment [95,105,106]. Currently hydrogen is being used for synthesis of ammonia and other nitrogenised fertilizers, refining and desulphurization (hydrogenation reactions, hydrodesulphurization); hydrogenation of hazardous wastes (dioxins, PCBs); chemical plants, food preparation; synthesis of methanol, ethanol, dimethyl ether (DME); alternative fuels synthesis by Fischer-Tropsch (FT) process; gas to liquid (GTL) synthesis technology; rocket fuel; IC engine fuel; high temperature industrial furnaces fuel [107]. Balat et.al has put forward a small report on the world hydrogen consumption, for the production of ammonia, chemical and its use in photochemistry. Out of the total 500 Billion cubic meters (Bcm) of hydrogen ammonia production consumes 250Bcm followed by production of other chemical products which consume 65Bcm, and petro chemistry consume 185Bcm of hydrogen, accounting for 50%, 13% and 37% respectively [96,107].

Jain reports various application of hydrogen for future such as for electricity generation, as cooking fuel, fuel for automobiles and jet planes, industrial applications, fuel for hydrogen village and for meeting all our domestic energy requirements [93].

Hydrogen finds various prospective energy uses from powering vehicles in a non-polluting manner, heating homes & offices to fuelling aircrafts. On one hand, the use of hydrogen in running

city buses, powering mining equipment's are few examples of mobile applications that have advanced to demonstration levels and on the other its use in home generators and large electrical



generating systems signifies promising utilization in stationary applications. Hydrogen is a potential

Fig 1.12 Various applications of hydrogen energy in diverse fields

fuel having many advantages over its conventional counterparts. However, a widespread and practical use will definitely call for measures for sustainable distribution from the producer to the end-user, more support facilities, fuelling stations and many other new concept and technologies.

1.9.2 Problem Statement

Energy production for growing needs and associated environmental challenges are twin issues of paramount interest that require our serious attention in the 21st century [108]. The global primary energy demand was estimated to be 13.371 billion tonnes of oil equivalent (btoe) in 2012 by International Energy Agency and is projected to reach 18.30 btoe in 2035 in current policies scenario representing a growth rate of 1.37% [109]. To satisfy the world's growing appetite for

energy and keep our planet healthy, at least 10 TW (terawatt) of carbon-free power generating capacity has to be created by 2050 [110]. The dramatic increase in the international price of petroleum in the recent years, the finite nature of fossil fuels, growing concerns relating to adverse environmental impact associated with increasing use of fossil fuels on greenhouse gas emissions, and health and safety considerations are forcing the search for new energy sources and develop alternative ways of powering the world's growing population of motor vehicles [111]. Energy related global CO₂ emissions were estimated to be 30.4 gigatonnes (Gt) in 2010 [112].

At present, a large portion (about 65%) of the world energy demand is met by the liquid and gaseous fossil fuels (i.e., petroleum and natural gas), because of their widespread availability and convenience of use, with petroleum oil being the largest primary fuel contributing a share of more than one third in the global primary energy mix and more than 92% of transport energy demand and balance being provided by natural gas (5%) and electricity 3% [113,114]. However, world's fossil fuel production is expected to peak soon, and thereafter begin to decrease. While some energy experts estimate that about half the world's oil production is consumed by road vehicles, the International Energy Agency (IEA) estimates that about 77% of global transport oil demand in 2010 was on account of road transport and the respective shares of biofuel, gas and electricity in transport sector was estimated to be 39%, 3%, 1% respectively in 2010 [113,115]. By 2050, the global energy demand is projected to be double or triple and oil and gas supply is unlikely to meet the demand.

The constantly increasing number of automobiles raises environmental concerns, such as exhaust emission and global warming, and accounts for some 18% of primary energy use and some 17% of global CO₂ emissions [116]. Local air pollution (particulate matter, ozone), climate change, congestion, land use, accidents, and noise are particular concerns in this respect. Local air pollution, especially from road transport, is quickly becoming a major issue for urban air quality, particularly in the world's growing megacities. The consumption of fossil fuels is responsible for the increase in the CO₂ in the atmosphere of approximately 3×10^{12} kg/year, a major contributor of global warming [117,118].

Fossil fuels are depleting gradually and there is an increase in the price of petroleum. Emissions from the fuels cause adverse environmental impact. Large portion of the world energy demand is met by the liquid and gaseous fossil fuels. So there is a need to conserve our natural resources for future generations. Renewable energy resources such as wind, solar, bio-energy, and geothermal are capable of meeting a significant energy need. This demands use of cleaner alternative fuels that are sustainable such as hydrogen without producing CO₂, the leading cause of global climate change.

The major problem is the fact, that a large amount (approximately 98%) of the CO₂ on earth is dissolved in the water of the oceans (7.5x10¹⁴kg C in the atmosphere, 4.1x10¹⁶ kg C in the oceans). About 2x10¹² kg C per year dissolves in the water of the ocean. The solubility of carbon dioxide decreases with the increasing temperature of water by approximately 3%/K. If the average temperature of the oceans increases, the carbon dioxide solubility equilibrium between atmosphere and ocean shifts towards the atmosphere and leads to a reduction in the CO₂ flux into the ocean and therefore, to an additional increase of the greenhouse gas in the atmosphere [119].

To resolve the problems of increasing fuel requirement and containing emissions associated with road transport there is an urgent need to find out solutions for use of energy in vehicles. The principal options are demand-side measures, development and use of more efficient vehicles and use of cleaner alternative fuels that are sustainable like bio-diesel, CNG and hydrogen [118]. Bio-diesel, a substitute to petroleum-diesel is derived from vegetable oils, animal fats, and used waste cooking oil including triglycerides. Significant efforts are being made globally for liquid bio fuel production from vegetable oils and *Jatropha curcas* L (JCL), which has attracted a lot of attention of investors, policy makers and clean development mechanism project developers in this regard. The oil produced by this crop can be easily converted to liquid bio-fuel [120]. Additionally, the press cake can be used as a fertilizer and the organic waste products can be digested to produce biogas. But bio-fuels alone cannot solve the dual problem of meeting a growing fuel demand for transport sector and reducing emissions.

CNG is another alternative automotive fuel that is being used in many countries. Of all the alternatives, CNG achieves the greatest reduction of 20–25% in vehicle emissions of CO₂ excluding hydrogen and electricity [118]. To further reduce the emissions from CNG, hydrogen can be blended with CNG. The alternatives to petrol and diesel exhibit some kind of constraints and drawbacks. No other fuel is expected to be as easy and cheap to produce and handle as petrol and diesel. While petrol and diesel can be produced from crude oil with high conversion efficiencies, the production of any alternative fuel will generally involve higher conversion losses. Moreover, the gaseous fuels are relatively difficult to handle and require a new distribution and refuelling infrastructure. Energy carriers like hydrogen and electricity even require new elements of drive-train like fuel cells and batteries.

Among the possible alternatives, hydrogen looks promising for transport applications on three counts: GHG emissions reduction, energy security and reduction of local air pollution. The breakthroughs in fuel cell technology in the late 1990's and its use in the internal combustion engines without incurring major investments are the main reasons behind the growing interest in hydrogen especially for transport application. Hydrogen is emission-free at the point of final use and thus avoids the transport-induced emissions of both CO₂ and air pollutants. This is also where fuel cells can make the significant impact by way of their high conversion efficiencies compared to the internal combustion engine [114].

According to the report put forward by the European Commission in 2003 and the US Department of Energy in 2004 [111], in many countries hydrogen is considered as an important alternative energy vector and fuel cell as a key technology for meeting energy needs in the stationary power, transportation, industrial and residential sectors on sustainable basis. In the present review, applications of hydrogen, its production methods, properties as a transportation fuel with environmental and safety aspects, its storage and delivery are discussed in different sections.

Hydrogen differs from conventional fuels-

- Hydrogen is non-toxic

- Hydrogen is colorless, tasteless and odorless.
- Hydrogen is highly combustible
- It will not contaminate groundwater
- Hydrogen is not a pollutant.

1.9.3 Production of hydrogen

To many countries in the world, hydrogen is the second most important form of energy source next to electricity. Hydrogen can be produced from a variety of feedstock. These include reformation of fossil resources, such as natural gas, oil and coal, as well as renewable resources, such as biomass and also by water splitting either through electrolysis using electricity generated by renewable energy sources (e.g. sunlight, wind, wave or hydro-power) or directly by photo-catalysis. A variety of processes can be used, including chemical, biological, electrolytic, photolytic and thermo-chemical for its production [121-124]. A detailed overview of various hydrogen production technologies has been reported by Holladay et al. [94]. The common hydrogen production methods include:

Table 1.4 Annual hydrogen production shares by different sources [96]

Source	Bcm/ yr	Share (%)
Natural gas	240	48
Oil	150	30
Coal	90	18
Electrolysis	20	4
Total	500	100

1.9.3.1 Steam methane reforming

Steam methane reforming (SMR) is a process by which natural gas or methane containing streams, such as biogas or landfill gas, is reacted with steam in the presence of a catalyst to produce hydrogen and carbon dioxide. According to US DOE (2010) when starting with natural gas, SMR is

approximately 72% efficient in producing hydrogen on a lower heating value basis [125]. SMR produces a hydrogen rich gas that is typically of the order of 70-75% hydrogen on a dry mass basis, along with smaller amounts of methane (2-6%), carbon monoxide (7-10%), and carbon dioxide (6-14%). About half of the global supply of hydrogen is produced by reforming natural gas [126,127]. Presently, this is the most commonly used method for hydrogen production in view of its favourable economics [95,97]. The reforming of natural gas, however, is not an attractive production route for a sustainable and mature hydrogen economy, because the order-of magnitude increase in demand would deplete the finite natural gas reserves and coupled to it the concentration of gas reserves in a relatively few regions of the world could lead to geopolitical tension and unstable supplies. Consequently, the purpose of achieving energy security, one of the objectives of hydrogen economy would get defeated. Environmental impact is also a major concern, as reforming natural gas to hydrogen produces as much pollution and CO₂ as burning the natural gas directly [128].

1.9.3.2 Auto-thermal Reforming of Oil

Partial Oxidation (POX) is an alternative to SMR and is generally preferred with higher hydrocarbons or if pure oxygen is available. With lower product concentration of hydrogen, this process offers lower efficiency in comparison to SMR but offers rapid dynamic response and compactness [129]. POX can be performed with or without catalyst. Catalytic Partial Oxidation (CPOX) can be carried out at relatively lower temperature than 1300-1500°C used in POX [130,131]. Auto-thermal Reforming (ATR) adds steam to CPOX. It consists of a thermal zone where POX or CPOX is used to generate the heat needed to drive the downstream steam reformation reactions in a catalytic zone. The heat from the POX negates the need for an external heat source, simplifying the system and decreasing the start-up time. A significant advantage for this process over SMR is that it can be stopped and started very rapidly while producing a larger amount of hydrogen than POX alone. For ATR to operate properly both the oxygen to fuel ratio and

the steam to carbon ratio must be properly controlled at all times in order to control the reaction temperature and product gas composition while preventing coke formation [94].

1.9.3.3 Gasification of coal and other hydrocarbons

In the POX process, also known more generally as “gasification,” hydrogen can be produced from a range of hydrocarbon fuels, including coal, heavy residual oils, and other low-value refinery products. The hydrocarbon fuel is reacted with oxygen in a less than stoichiometric ratio, yielding a mixture of carbon monoxide and hydrogen at 1200 to 1350°C [132]. Gasification (coal, petroleum coke, and gasification and reforming of heavy oil) also dominates hydrogen production along with steam methane reforming [97,133].

1.9.3.4 Electrolysis of water

Electrolysis is the process by which water molecules are split directly into hydrogen and oxygen molecules using electricity and an electrolyser device. The two most common types of electrolysers are alkaline (use a potassium hydroxide electrolyte) and PEM (use a solid polymer membrane electrolyte). Hydrogen can be produced via electrolysis of water from any electrical source, including utility grid power, solar photovoltaic (PV), wind power, hydropower, or nuclear power. Electrolysis is currently done at a wide range of scales, from a few kW to up to several MW. The electrolysis reaction produces pure oxygen as a by-product along with pure hydrogen [134]. In contrast, a photo electrochemical (PEC) water-splitting process is a zero emission process and uses free solar energy to split water in a single step without converting solar energy into electricity firstly and then use it in an electrolyser to split water. However, PEC systems are currently under development and are not commercially available.

Although water electrolysis has been known for around 200 years [135,136] and has the advantage of producing extremely pure hydrogen, its applications are often limited to small scale and unique situations where access to large scale hydrogen production plants is not possible or economical, such as marine, rockets, spacecraft's, electronic industry and food industry as well as medical applications [97,137,138]. Mustafa Balat reported natural gas to be the major source of

hydrogen production accounting 48% of the total share, oil being the second with 30% followed by coal with 18% and electrolysis contributing 4% of the total share [96].

Besides electrolysis, there could be other possible variants of breaking of water into H₂ and O₂. This includes methods such as photo-catalysis and bio-photolysis use of renewable energy i.e. sunlight. Photo-electrolysis of water is the process whereby a light source is used to break water directly into oxygen and hydrogen. Systems based on such processes offer great potential for reduction of cost of electrolytic hydrogen. Hydrogen production via photo-biological method consists of two steps: photosynthesis and hydrogen production catalysed by hydrogenase in, for example, cyanobacteria and green algae.

1.9.3.5 Hydrogen from Biomass

Biomass conversion technologies can be divided into thermo-chemical and biochemical processes. Thermo-chemical processes obtain higher reaction rates as they can be operated at higher temperatures and, therefore, tend to be less expensive. They involve either gasification or pyrolysis (heating biomass in the absence of oxygen) to produce a hydrogen-rich stream of gas known as “syngas” (a blend of hydrogen and carbon monoxide). They can utilize a broad range of biomass types. Gasification of biomass has been identified as a possible method for producing large quantities of renewable hydrogen in efficient manner, wherever it is beneficial to exploit biomass resources and thereby reducing dependence on insecure fossil energy sources [111,133]. Several processes available to make hydrogen from biomass can yield other useful products/by-products such as adhesives, carbon black, activated carbon, polymers, fertilizers, ethanol, various acids, Fischer-Tropsch diesel fuel, waxes, and methanol.

1.9.3.6 Nuclear energy

Various nuclear energy based hydrogen production methods employing either thermal energy or electricity are possible, which include splitting of water using various thermo-chemical processes such as the sulphur-iodine cycle, electrolysis of water using nuclear power, and high-temperature electrolysis that would use nuclear system waste heat to lower the electricity required for

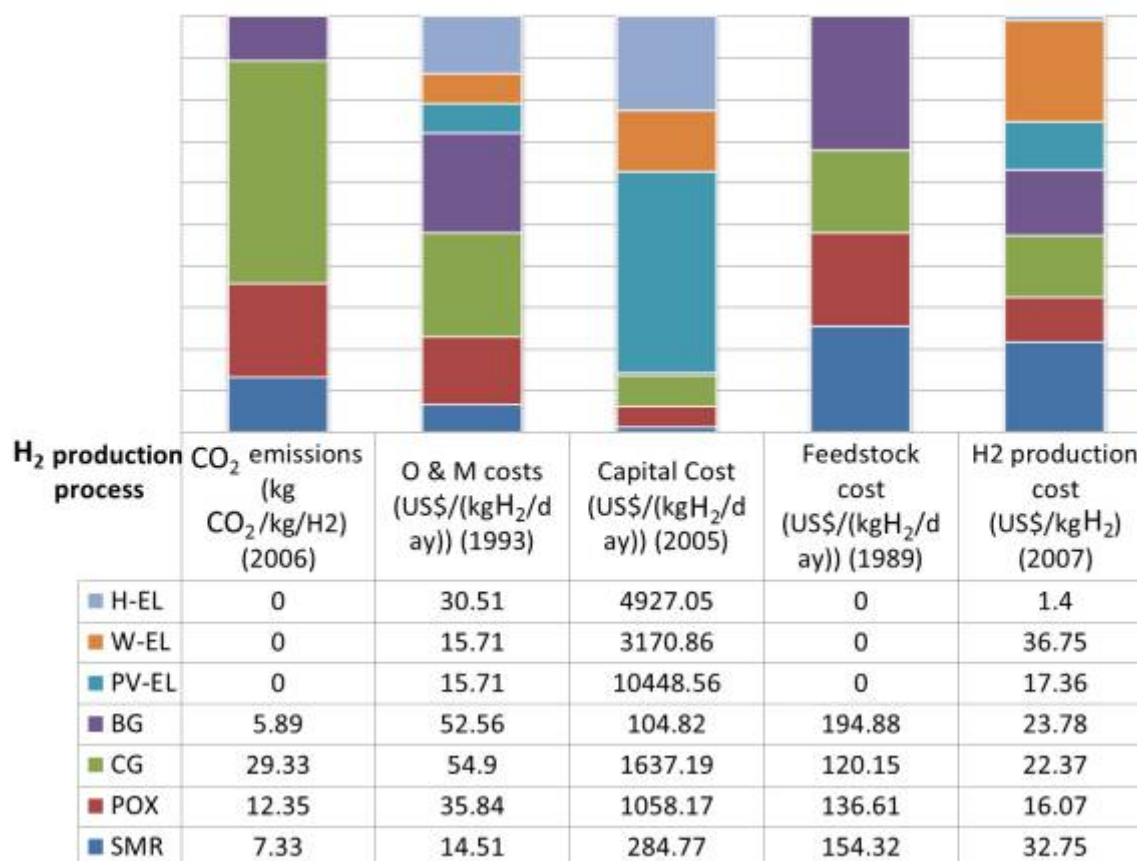
electrolysis [125]. While the use of nuclear energy for hydrogen production is attractive from a carbon-limiting perspective, it raises other serious environmental and health concerns related to the mining and processing of uranium, the potential for accidents, and the management and disposal of radioactive wastes [134].

1.9.3.7 Biological processes

Due to increased attention to sustainable development and waste minimization, research in bio-hydrogen has substantially increased over the last several years. The main bioprocess technologies used for bio-hydrogen production include: photolytic hydrogen production from water by green algae or cyanobacteria (also known as direct photolysis), dark-fermentative hydrogen production during the acidogenic phase of anaerobic digestion of organic material, photo-fermentative processes, two stage dark/fermentative, and hydrogen production by water-gas shift [94,139-150].

Nitrogenase and hydrogenase play very important role in biological hydrogen production. Sucrose, when used as a substrate, can yield up to 28% of energy in the form of hydrogen. Biological hydrogen production offers advantage over other processes such as electrochemical and thermo chemical routes in terms of low energy requirements and lower initial investment cost but suffers comparatively low conversion efficiencies. Biological experimentation should continue in order to drive up the hydrogen production rate and efficiencies.

Table 1.5 Aggregated Data for Criteria-alternative Options [151]



A study carried out by Pilavachiet. al compares seven hydrogen production methods namely steam methane reforming (SMR), partial oxidation of hydrocarbons (POX), coal gasification (CG), biomass gasification (BG), the photovoltaic-electrolysis system (PV-EL), the wind turbine–electrolysis system (W-EL), the hydropower-electrolysis system (H-EL). The comparison has been made based on five criteria’s viz. CO₂ emissions, operation and maintenance (O&M) costs, capital cost, feedstock cost and hydrogen production cost using the Analytical Hierarchy Process (AHP) [151]. In the majority of cases, the processes that combine renewable energy sources with electrolysis (PV-EL, W-EL and H-EL) are considered to be better than the conventional processes (SMR, POX, CG and BG) and are higher in ranking. On the contrary, the conventional hydrogen production processes (SMR, POX, CG and BG) rank last in most of the cases. More specifically, in most of the cases the first in ranking hydrogen production process is considered to be the hydropower-electrolysis system (H-EL) and the worst is coal gasification (CG) [151] as shown above in the Table1.5.

Presently, natural gas reforming, coal gasification and water electrolysis are proven technologies for hydrogen production that are employed on an industrial scale throughout the world. Steam reforming of natural gas is the most widely used process in the chemical and petro-chemical industries and currently is the cheapest method for hydrogen production; and has the lowest CO₂ emissions of all fossil production routes. Electrolysis is preferred if high-purity hydrogen is required but it is more expensive. With an assumed increase in natural gas prices, coal gasification becomes the most economical option from around 2030 onwards. Biomass gasification, though at an early stage currently is expected to become the cheapest renewable hydrogen supply option in the coming decades, although biomass has restricted potential and competes with other bio fuels as well as heat and power generation. Biomass gasification can be applied in small decentralised plants during the early phase of infrastructure rollout and in centralised plants in later periods. Steam reformers and electrolyzers can also be scaled down and implemented on-site at fuelling stations (although still more expensive), while coal gasification or nuclear energy are suitable for large-scale, central production only and therefore restricted to later phases with high hydrogen demand [118].

Full benefits of hydrogen as a clean, versatile, and efficient fuel may be realized only if hydrogen is produced from renewable energy sources (solar, wind, biomass) via variety of pathways and methods, but only a few of them are commercially viable currently and these sources may provide local sources for hydrogen production but certainly will not be able to match the volumes of hydrogen required globally as the new energy source [95,152]. Renewable pathways for producing hydrogen avoid generating global warming pollutants in the first place and, depending on the viability of carbon capture and storage may therefore prove more attractive in the long run. At present, however, these options are generally more expensive. Yet even with CO₂ recovery and sequestration costs included, hydrogen production from fossil fuels is estimated to be much less costly than electrolytic hydrogen in large-scale markets [153]. A recent US Energy Information Association report suggests that solar is most likely the only source of energy capable of producing enough hydrogen required by a hydrogen economy [109].

Table 1.6 Comparison of reformation processes for production of hydrogen [94]

Technology	Advantages	Disadvantages
Steam Reforming	Most extensive industrial experience Oxygen not required Lowest process temperature Best H ₂ /CO ratio for H ₂ production	Highest air emissions
Auto-thermal Reforming	Lower process temperature than POX Low methane slip	Limited commercial experience Requires air or oxygen
Partial Oxidation	Decreased desulfurization requirement No catalyst required Low methane slip	Low H ₂ /CO ratio Very high processing temperatures Soot formation/handling adds process complexity

Currently the cost of hydrogen is more than twice as much as that of diesel and petrol on per unit's energy basis and substantial progress is needed to make environmentally sustainable hydrogen production pathways cost-competitive vis-a-vis petroleum fuels, even assuming that hydrogen powered vehicles will be significantly more efficient than their conventional gasoline-powered counterparts [107,134].

1.9.4 Hydrogen as energy carrier

Hydrogen has in recent years has been attracting a lot of attention as a preferred energy carrier especially for transportation applications due to a number of reasons: (a) it is believed to be a clean fuel, which emits almost nothing other than water at the point of use; (b) it can be produced using any energy sources, with renewable energy being most attractive; and (c) it works with fuel cells and together, they may serve to contribute towards sustainable energy supply [97,154].

Hydrogen is a colourless, odourless and non-toxic gas [155,156]. Hydrogen has the highest specific energy content of all conventional fuels and is the most abundant element in the universe

[96,111]. Hydrogen has a high energy yield of 120 MJ/kg, which is about 2.75 times greater than hydrocarbon fuels but density of liquid hydrogen is much less than gasoline [153]. In fact, hydrogen is the lightest gas on the earth and it is about 14 times less dense as compared to dry air. These properties give hydrogen both advantages and disadvantages. The advantage is that hydrogen stores approximately 2.6 times more energy per unit mass than gasoline, meaning that hydrogen has higher heating or calorific value than gasoline. The disadvantage is that it needs an approximately 4 times more volume than gasoline to store the same energy due to its lower volumetric energy density. Hydrogen can be used as a fuel directly in an IC engine as it is not different from other fuels used in the IC the engines [157]. In fact, the blending of hydrogen and ethanol has been used as an alternative to renewable fuel in a carbureted spark ignition engine [158,159].

Mustafa Balat reported the physical and chemical properties of hydrogen in comparison to gasoline and methane (Table 1.7). It indicates that hydrogen has a wide range of flammability in comparison with other fuels. Hydrogen engines, therefore, can be operated more effectively on excessively lean mixtures than gasoline engines. 4% hydrogen by volume along with air produces a combustible mixture. Hydrogen has very low ignition energy (0.02 MJ). Compared to other fuels, it has a higher ignition temperature. The hydrogen flame speed is nearly an order of magnitude higher (faster) than that of gasoline. Hydrogen has very high diffusivity. This ability to disperse in air is considerably greater than gasoline and is advantageous for two main reasons: (1) it facilitates the formation of a uniform mixture of fuel and air, and (2) if a hydrogen leak develops, the hydrogen disperses rapidly. Thus, unsafe conditions can either be avoided or minimized. The very low density of hydrogen results in two problems when used in an internal combustion engine: (a) a very large volume is necessary to store enough hydrogen to give a vehicle an adequate driving range, and (b) the energy density of a hydrogen–air mixture, and hence the power output, is reduced [96].

Table 1.7: Physical and Chemical properties of Three Fuel Options (Hydrogen, Methane, and Gasoline) [96]

Property	Hydrogen	Methane	Gasoline
Molecular weight (g/mol)	2.016	16.04	~110
Mass density (kg/Nm ³) at P =1 atm = 0.101 MPa, T = 0C	0.09	0.72	720-780 (liquid)
Mass density of liquid H ₂ at 20 K (kg/Nm ³)	70.9	-	-
Boiling point (K)	20.2	111.6	310-478
Higher heating value (MJ/kg) (assumes water is produced)	142.0	55.5	47.3
Lower heating value (MJ/kg) (assumes steam is produced)	120.0	50.0	44.0
Flammability limits (% volume)	4.0-75.0	5.3-15.0	1.0-7.6
Detonability limits (% volume)	18.3-59.0	6.3-13.5	1.1-3.3
Diffusion velocity in air (m/s)	2.0	0.51	0.17
Ignition energy (mJ) – At stoichiometric mixture – At lower flammability limit	0.02 10	0.29 20	0.24 n/a
Flame velocity in air (cm/s)	265-325	37-45	37-43
Toxicity	Non toxic	Non toxic	Toxic above 50 ppm

Another important property of hydrogen is its versatile nature. Hydrogen, can be converted to other forms of energy in five different ways; i.e., in addition to flame combustion, it can be converted directly to steam, converted to heat through catalytic combustion, act as a heat source and/or heat sink through chemical reactions, and converted directly to electricity through electrochemical processes whereas the other fuels can be transformed into other forms of energy only through combustion. In other words, hydrogen is a versatile fuel [160].

1.9.4.1 Environmental and health aspects of using hydrogen as a transportation fuel

Transport sector is a major contributor of the global fossil fuel combustion-related CO₂ emissions. Total fossil fuel-related CO₂ emissions increased to 28.8 Gt in 2007 from 20.9Gt in 1990 and transport sector accounted for 4.58 (1990) and 6.63 (2007) Gt, representing an increase of approximately 45% [161]. According to the World Energy Outlook 2009, global energy-related CO₂ emissions could increase to over 40Gt by 2030 and transport emissions would make up over 9Gt of it [162]. These emitted pollutants have a serious negative impact on the health and environment. The health impacts include various respiratory health problems, eye irritation, allergies, myocardial ischemia and angina [163]. The various environmental impacts include global warming, air pollution, smog, acid rain etc.

Technologies for fossil fuel extraction, transportation, processing and particularly their end use (combustion), have harmful impacts on the environment, which cause direct and indirect negative effects on the economy [115]. The CO₂ emission per unit of fossil fuel energy (in GJ) depends on fossil fuel type, and is around 85.5 kg CO₂ for coal, 69.4 kg CO₂ for petroleum and 52 kg CO₂ for natural gas. It is expected that emissions of CO₂ will reach 8.2–10.0 gigatonnes in around 2020. Global climate change due to CO₂ emissions is possibly the most important environmental problem that human beings face [98]. Hydrogen powered vehicles are zero emission devices at the point of use, with consequential local air quality benefits. Hydrogen powered fuel cells could contribute to reducing or eliminating emissions of CO₂ and other greenhouse gases from road transportation vehicles [111,118]. Hence, hydrogen powered energy systems appear to be an attractive alternative to current fossil fuel-based energy systems in the future [111].

1.9.4.2 Hazard and Safety considerations of using hydrogen as a fuel

The fuels having low density and high diffusion coefficient are considered to be safer. Higher specific heat causes a fuel to be safer, since it slows down the temperature increases for a given heat input. Wider ignition limits, lower ignition energies, and lower ignition temperatures make the fuels less safe, as they increase the limits in which a fire could commence. Higher flame temperature,

higher explosion energy, and higher flame emissivity make a fuel less safe, since its fire would be more damaging [115]. The characteristics related to fire hazard of fuels is summarised in table 1.8.

Table 1.8: Characteristics related to Fire Hazard of Fuels [164]

Property	Gasoline	Methane	Hydrogen
Density ^a (kg/m ³)	4.40	0.65	0.084
Diffusion coefficient in air ^a (cm ² /s)	0.05	0.16	0.610
Specific heat at constant pressure ^a (J/g K)	1.20	2.22	14.89
Ignition limits in air (vol%)	1.0-7.6	5.3-15.0	4.0-75.0
Ignition energy in air (mJ)	0.24	0.29	0.02
Ignition Temperature (°C)	228-471	540	585
Flame Temperature in air (°C)	2197	1875	2045
Explosion energy ^b (g TNT/kJ)	0.25	0.19	0.17
Flame emissivity (%)	34-43	25-33	17-25
^a At normal temperature and pressure.			
^b Theoretical maximum; actual 10% of theoretical.			

Hydrogen is four times as diffusive as natural gas, and 12 times as diffusive as gasoline as it is very light and its density is 6.9% that of air. Therefore the risk of fire or explosion is very less as a hydrogen leak rapidly dissipates as it rises from its source. Due to its non-toxicity, a hydrogen leak would not cause environmental damage. In a confined space, hydrogen could lead to fire or explosion if mixed with air. Any fire started would burn out quickly as the hydrogen is dissipated. It is difficult to make a hydrogen-air mix explode- a transient spark can set it off -but it will burn rather than explode, in open air [165]. Some studies have suggested that hydrogen vehicles would have lower risks than petrol vehicles in confined spaces as petrol leaks would create a larger cloud of flammable gas. Hydrogen blazes with little radiation of heat, so nothing would burn unless it was immediately next to the flame [165]. Another safety advantage is that it's clear flame cannot sear

skin at a distance because of the little thermal radiation emitted by the flame due its lack of soot content. Hydrogen can burn in lower concentrations and this can cause safety concerns [98,101].

T.Nejat et al. compared three fuels for safety aspects as given in Table 1.9. For each of the toxic elements and fire hazard characteristics, it ranks the fuels from 1 to 3, 1 being the safest and 3 the least safe. It was reported that hydrogen was the safest fuel with a safety factor of 1.00. Next to hydrogen was methane with a safety factor of 0.80 and gasoline was reported to be the least safe fuel among the three with a safety factor of 0.53 [115].

Table 1.9: Safety Ranking of Fuels [164]

Characteristic	Fuel ranking		
	Gasoline	Methane	Hydrogen
Toxicity of fuel	3	2	1
Toxicity of combustion (CO, SO _x , NO _x , HC, PM)	3	2	1
Density	3	2	1
Diffusion Coefficient	3	2	1
Specific Heat	3	2	1
Ignition Limit	1	2	3
Ignition energy	2	1	3
Ignition temperature	3	2	1
Flame temperature	3	1	2
Explosion energy	3	2	1
Flame emissivity	3	2	1
Total	30	20	16
Safety factor	0.53	0.80	1.00
1, safest; 2, less safe; 3, least safe			

1.10 Importance of water splitting for photocatalytic application for organic pollutant degradation

The main environmental problems associated with water body pollution are typically those caused by the discharge of untreated effluents released by various industries (textile, paints, dye and

intermediates, printing, petroleum, food processing, pharmaceutical). Wastewater from textile dye industry is itself a large contributor to this and contains a huge amount of complex components, wide spectrum of organic pollutants with high concentration of Biochemical Oxygen Demand (BOD)/ Chemical Oxygen Demand (COD) and other toxic elements. Such reactive dyes are a serious harm to environment and thus needs to be degraded before being discharged to water bodies. One of several potential techniques for this is photo catalysis and metal-oxide based photo catalysts are rapidly gaining popularity in this direction. Metal oxides such as ZnO and BiVO₄ have been explored extensively for their photo catalytic activity in their pure form as well as with several modifications such as doping (with unique and interesting metals as well), composites, heterostructures, polymer assisted and carbon modified in order to further enhance the photo catalytic efficiency in UV/visible region of solar spectrum and natural sunlight. Suitable band gap and band edge positions are required conditions for efficient water breakup and high photon absorption. Photo catalytic activity depends on many factors such as synthesis method, morphology, size, illumination type and choice of dye among others. Therefore, this property has been deeply studied on metal-oxides on various aspects of degradation of dye and organic pollutants to combat the issue of water pollution which is a major global problem now.

1.10.1 Problem Statement

Poor management of organic waste leading to water pollution and associated environmental challenges are twin issues of utmost importance that requires our prime concern and attention. With 20 percent of all fresh water pollution being caused during textile treatment and dyeing, global textile and clothing industry still remains the major contributor to water pollution in 21st century [166]. The industries use millions of gallons of water every day and generate a large amount of pollutants and liquid effluents which are not treated to be removed before disposing off to water bodies. This release of organic waste causes a significant and unimaginable harm to the environment and human beings. Toxic content must be reduced or eliminated before it is consumed for drinking or other daily activities by a large number of people. Thus, it is utterly necessary to

take urgent actions or provide for solutions before the contamination of the water becomes an alarming and irreversible threat to the environment. Various effluents from textile mills contains high values of COD, BOD [167] and solid suspensions which leads to depletion of dissolved oxygen causing an adverse effect on the aquatic photosynthesis process causing imbalance in the ecological system [167,168]. The BOD and COD ratio measurement offers a good indication of the organic pollution load of water. Ratio between 1:2 and 1:3 is generally acceptable and implies easy degradability of the wastes [168].

With more than 3600 different types of textiles dyes, azo dyes almost constitutes 60-70% of all organic dyes produced globally, dyeing section alone contributes to 15%-20% of the total waste water flow and around 72 toxic chemicals found in water solely comes from textile dyeing [168-170]. Increased pollutants, with rising global consumption of fresh water doubling every 20 years, the population that is allergic to chemicals will reach 60 percent by the year 2020 [170].

Therefore, in view of the above problems, there is an urgent need to find out solutions to resolve such issues which are economic, efficient and cleaner at the same time. More than 85% of unwanted matter can be removed by various effluent treatment methods [171]. Among several water-treatment techniques, best possible alternative is photo catalysis which is fast gaining popularity and help in fighting the emission of pollutants by various industries. Photo catalysis can cause fast and complete degradation of organic compounds efficiently. They can treat the effluents for reduction in COD, BOD and other dissolved salts levels in wastewater. It is an upcoming green technology which is residue-free providing a large scope for research and improvement. For this purpose, a large number of photo catalysts, such as TiO_2 , ZnO , WO_3 , MgO , Fe_2O_3 , BiVO_4 , Bi_2O_3 [172-179] have already been explored so far to name a few.

Amongst these, ZnO and bismuth has caught attention to a great extent. They are versatile and are emerging as a leading candidate in this direction. They are environmentally benign element and a large class of photo catalysts exists especially for bismuth based materials which makes them

stand apart and unique with rest of photo catalysts. Bismuth is a stable element owing to higher atomic mass and is relatively less toxic and thus finds its use in a growing number of applications such as pharmaceuticals, pigments in the cosmetic industry, phosphor, magnetic materials, gas sensors and catalysts [180-184]. Freshly produced bare bismuth appears silvery white in colour but on oxidation shows a pink touch to its surface. Versatile and flexible use of bismuth salts in synthesis and its multifaceted applications has clearly been highlighted by constantly increasing number of publications in this field. Despite being a post-transition metal, it acts as a semiconductor when deposited as sufficiently thin layers [185]. Therefore nanoscale bismuth is applied to catalysis and when modified suitably gives enhanced photo catalytic results and improves the efficiency of the system. Favourable characteristics of bismuth salts such as advantages of a unique crystal structure, excellent optical and electronic properties, low toxicity and ease of synthesis, associated with low cost, make them attractive and practical catalyst [186,187]. Moreover, its loosely bound structure, indirect band transitions and intrinsic internal electric field assists the photo generated electron-hole pair's separation and their charge transfer. Besides many such advantages, bismuth tends to suffer from certain issues like unfavourable band edge positions, fast recombination of photo generated charge carriers and photo stability.

As a result of increasing concern about green and clean photo catalysts, zinc and bismuth based catalysts have become our main focus. The aim of this study is to provide a deep insight and knowledge of metal oxides as photo catalysts. They are capable of forming variety of exciting materials in terms of complex compounds, multiple oxides, composites, heterostructures etc that are useful for photocatalysis application. With so many varied possibilities of this material, we try to give a detailed view of above mentioned oxide semiconductors. The study has been systematically summarized in terms of their fundamental and scientific aspects of synthesis process, morphology, energy band, surface area and their mechanisms of degradation which might be helpful to researchers entering this area and many academic groups around the world that are working in this direction.

1.10.2 Consumption of water in textile industry

After agriculture sector, finishing and textile dyeing industry is no.1 chemically intensive industry to create a huge pollution problem. Industries manufacture more than 3600 individual textile dyes today. Various processes of textile manufacture including printing and dyeing uses more than 8000 chemicals. A few of them are listed in Table 1.10. Needless to mention, these reactants are very fatal causing damage to health of a human, directly or indirectly. Textile processes such as printing and dyeing requires large quantities of water. On an average, about 1.6 million litres of water is utilized daily for a production of 8000 kilogram of fabric per day by a medium textile mill. 8% of this is consumed in printing and 16% in printing. Depending on the type of dye used the consumption of specific water for dyeing changes from 30-50 litres per kilogram of cloth. Of total waste water flow, nearly 15%-20% is contributed by dyeing section. To produce enough fabric to cover one sofa, it takes about 500 gallons of water. As per estimation by the World Bank 17-20% of water pollution from industries comes from textile dyeing and finishing treatment given to fabric. Some 72 toxic chemicals have been identified in water solely from textile dyeing, 30 of which cannot be removed [188]. This represents an appalling environmental problem for the textile and clothing manufacturers.

Table 1.10 The varieties of commonly used fiber [189]

The variety of fiber	The commonly used dyes
Cellulose fiber	Direct dyes, Reactive dyes, Vat dyes, Sulfide dyes, Azo dyes
Wool	Acid dyes
Polyester	Azo dyes, Disperse dyes
Polyacrylonitrile fiber-wool	Cationic dyes, Acid dyes
Silk	Direct dyes, Acid dyes
Polyacrylonitrile fiber	Cationic dyes, Acid dyes
Vinylon	Direct dyes, Vat dyes, Sulfur dyes, Acid dyes,
Polyester-cotton	Disperse / Vat dyes, Disperse / Insoluble dye

1.10.3 Hazards of water pollution

Millions of gallons of the discharge consisting organic chemicals from dyeing, hazardous virulent waste, full of colour and finishing salts are regularly out flowed by mills. Effluent becomes highly toxic due to the presence of naphthol, sulphur, nitrates, vat dyes, soaps, acetic acid, chromium compounds and heavy metals like arsenic, copper, cadmium, lead, nickel, mercury, cobalt and certain auxiliary chemicals. The often discharge of high pH and temperature mill effluent is also extremely damaging.

The presence of colloidal matter along with oily scum and colours increases the turbidity renders water with a foul smell and bad appearance which prevents the piercing of solar light important for the process of photosynthesis [170]. This causes interference at air water interface with the oxygen transfer mechanism. The most serious effect of textile waste is depletion of dissolved oxygen in water as it is indispensable for aquatic life. This hampers the process of water self purification.

Textile effluent is a cause of significant amount of environmental degradation and human illnesses. Globally, approximately 40% of colorants used contain organically bound chlorine known as carcinogen. Chlorine based disinfectants are commonly used in water, textile industry organic waste such as dye which chemically react with these chlorine based disinfectants and produces chemical vapours which causes skin allergy and causes harm to the lungs to children.

Table 1.11 Specific pollutants from textile and dyeing processing operations [190]

Process	Compounds
Desizing	Sizes, enzymes, starch, waxes, ammonia.
Scouring	Disinfectants and insecticides residues, NaOH, surfactants, soaps, fats, waxes, pectin, oils, sizes, anti-static agents, spent solvents, enzymes.
Bleaching	H ₂ O ₂ , AOX, sodium silicate or organic stabilizer, high pH.
Mercerizing	High pH, NaOH
Dyeing	Colour, metals, salts, surfactants, organic processing assistants, sulphide, acidity/alkalinity, formaldehyde.

Printing	Urea, solvents, colour, metals.
Finishing	Resins, waxes, chlorinated compounds, acetate, stearate, spent solvents, softeners.

1.10.4 Classifications of textile wastes

1.10.4.1 Hard-to-treat wastes

Hard-to-treat wastes include organic materials which are non-biodegradable such as certain solvents and surfactants. Primarily, these also include metals, colors, toxic organic compounds, phenol, phosphate etc. They produce aquatic toxicity as they resist biological effluent treatment process.

1.10.4.2 Hazardous or toxic wastes

They are generally classified as sub group of hard-to-treat waste. They include materials such as chlorinated solvents, metals, volatile organic materials and non-biodegradable surfactants. Source of these wastes also include non-textile processes like boiler chemicals, machine cleaning etc.

1.10.4.3 Dispersible wastes

These include wastes from print pastes, batch dumps of unused process chemicals, wastes from back coating operations etc.

1.10.4.4 High volume wastes

Common high volume wastes include wash water from printing, dyeing operations, preparatory, and the exhausted dye baths. These can be reduced by equipment modification and recycle process.

Table 1.12 Standards for effluents from textile industry [191]

Parameter	Concentration not to exceed, milligram per litre (mg/l), except pH
pH	5.5 – 9.0
Total suspended solids	100
Bio-chemical oxygen demand (BOD)	30
Chemical oxygen demand (COD)	250

Total residual chlorine	1
Oil and grease	10
Total chromium as Cr	2
Sulphide as S	2
Phenolic compounds as C ₆ H ₅ OH	1

1.11 Objectives of the present study

The central objective of the present thesis work is to prepare metal oxide semiconductors, ZnO, BiVO₄ and ZnO/BiVO₄ nanocomposites through chemical route (hydrothermal) technique, and study their visible light induced photoelectrochemical and photocatalytic reactions for water splitting and organic pollutant degradation applications. With an aim to increase the photoresponse of the samples, effect of parameters like synthesis temperature, duration, effect of mechanical milling and annealing process on nanocomposite/photocatalysts have been studied.

Broad objectives of the present work can be mentioned as

1. The preparation of pristine and nanocomposite samples of ZnO and BiVO₄ by hydrothermal method.
2. The optimisation of various samples by varying synthesis conditions including synthesis temperature, annealing temperature and milling process.
3. Characterization of semiconductor samples, including XRD, TEM, SEM, XPS, UV-vis, DRS, steady state and dynamic PL.
4. PEC studies on pristine and various nanocomposite thin film samples as photo anodes in conjunction with platinum as counter electrode and Ag/AgCl as reference electrode.
5. Photo catalytic studies on pristine and various nanocomposite samples using two model organic contaminants, MB and RhB.
6. Determination of band edge potentials using Mulliken's Electronegativity theory proposing

action of mechanism.

7. Efficiency calculations of various pristine and nanocomposite samples in PEC and photo catalytic water splitting process.
8. To study photo stability and test repeatability of pure and composite photo catalysts.

1.12 Organization of the Thesis

The thesis has been organised into following chapters:

Chapter 1: This chapter gives a description of choice of materials for photo-electrochemical cell and photocatalysis technology for hydrogen generation and pollutant degradation respectively, challenges involved in it and strategies to resolve them. Further this chapter gives a brief overview about the urgent need for renewable energy for applications in the field of hydrogen generation and waste water treatment by organic pollutants degradation.

Chapter 2: This chapter gives the experimental methods for synthesis and discusses the effects of various parameters on the quality of materials. Various techniques employed for characterization of semiconductor materials have been discussed.

Chapter 3: This chapter presents the results and discussion for photo-electrochemical and photo catalysis systems. Results have been analysed and discussed.

Chapter 4: This chapter describes the investigation of photo catalytic properties of pristine and composite samples using model organic pollutants.

Chapter 5: This chapter describes the investigation of photo electrochemical properties of pristine and composite samples using three electrode system.

Chapter 6: Finally, chapter 6 summaries the dissertation and proposes future directions relevant to the present work.