The summary of the literature comprising most significant and recently published reports on the preparation, characterization and application of semiconductor photoelectrodes in photoelectrochemical cells has been provided in this chapter. Several semiconductors and strategies/approaches adopted by different workers, have been elaborated, yet giving particular prominence on the use of CuO, SrTiO₃, ZnO and WO₃ thin films in PEC water splitting. Bilayered modification strategy has been attempted in recent years by researchers in order to fine-tune the properties of semiconductors for PEC splitting of water. The literature review presented below highlights such reports as well.

3.1 Photoelectrochemical Studies on Various Metal Oxide Semiconductors

Fujishima and Honda (1972) in their pioneering work were the first to report the photoelectrolysis of water using a single crystal of TiO₂ as the photoanode, at which O₂ evolved. Electrons released from anode travelled by a wire to Pt electrode, at which H₂ was evolved. The cell was chemically biased by varying the pH in cathodic and anodic compartment.

Wrighton et al (1976) studied irradiation of n-type semiconductor SrTiO₃ electrode in an electrochemical cell which resulted in the sustained conversion of H₂O into H₂ and O₂. In 9.5 M NaOH, oxidation occurred at the photoelectrode at potentials more positive than -1.3 V vs saturated calomel electrode (SCE), and H₂ evolution was observed at the Pt electrode which was not illuminated. Results showed for the first time that the electrolysis of H₂O could be driven photochemically without any external bias. The photoeffect obtained upon irradiation with light of shorter wavelength than 390 nm which corresponded closely to the known absorption edge for the valence band to conduction band transition in SrTiO₃. The photocurrent reached its maximum value near 330 nm and the response was nearly constant with increasing excitation energy. Quantum efficiency for electron flow was found to be 1.0 ± 0.20 upon irradiation with light of
shorter wavelength than 330 nm at applied potentials of ≥ 1.5 V. Current efficiency was excellent, producing $\text{H}_2$ and $\text{O}_2$ in the correct stoichiometric ratios. Photoelectrode stability was confirmed by experiments carried out in oxygen-18 labeled $\text{H}_2\text{O}$ and by the lack of weight loss in the SrTiO$_3$.

Kudo et al (1988) studied the effects of the calcination temperatures of SrTiO$_3$ powder on the photocatalytic activities. It was observed that the photocatalytic activity depends strongly on the calcination temperature of SrTiO$_3$. They examined the photodecomposition of water, the evolution of hydrogen from aqueous methanol solution and the evolution of oxygen from aqueous silver nitrate solution. The optimum calcination temperatures of SrTiO$_3$ for these reactions were different from each other.

Gratzel (2001) reported the conversion of sunlight to electrical energy using nanocrystalline materials in photoelectrochemical cells. Knowledge on the historical background, present status and development prospects for this new generation of photoelectrochemical cells using nanocrystalline structures has been presented in detail.

Khaselev et al (2001) investigated a monolithic, multijunction integrated PV/electrolysis configuration and demonstrated highly efficient solar to hydrogen conversion system. This configuration contained a tandem $n/p-n/p$ GaInP/GaAs junction in ohmic contact, through a thin metal layer, with a solution. For these studies, the area of the PV device and the electrolyzer was identical. The energy diagram of the configuration was evaluated and exemplified with $n/p$, $n/p$ GaInP/GaAs(Pt)/KOH electrolyte and triple-junction $p[i\{n\, \text{a-Si(Pt)}=\text{KOH}\}$ electrolyte photovoltaic-electrolysis cells. For a-Si system and GaAs/GaInP$_2$ system a solar-to-hydrogen conversion efficiency of 7.8 % and 16 % was demonstrated.

Lee et al (2001) studied Cu-doped ZnO (represented as ZnO:Cu) films prepared by RF magnetron co-sputtering of ZnO target with attached Cu chips. X-Ray diffraction
(XRD) spectra of deposited ZnO:Cu films was recorded and texture coefficient (TC) values for (002)-orientation were estimated. Optimal ranges of RF powers and substrate temperatures for obtaining high TC values were determined. Effects of Cu-doping conditions on TC values, electrical resistivity and relative Cu-compositions of deposited films were systematically investigated. X-Ray photoelectron spectroscopy (XPS) study suggested that the relative densities of metallic copper (Cu) atoms and CuO (Cu$^{2+}$) phases within deposited films may play an important role in determining their electrical resistivity. Highly resistive ZnO films with high TC values (80%) were achieved by Cu-doping. Surface acoustic wave (SAW) devices with ZnO:Cu (or ZnO) interdigital transducer were also fabricated to estimate the effective electromechanical coupling coefficient and insertion loss.

**Bak et al (2002)** in his review article on hydrogen generation from water using solar energy discussed the materials-related issues in the development of high-efficiency photoelectrochemical cells (PEC). The essential requirements for photoelectrodes, in terms of semiconducting and electrochemical properties and their impact on the PEC performance have been outlined. Different types of PEC systems have been overviewed and the impact of the PEC structure and materials selection on the conversion efficiency in presence of solar energy is considered. Research trends in the development of high-efficiency PEC devices were discussed.

**Balamurugan et al (2002)** deposited nanocrystalline copper oxide thin films by activated reactive evaporation and studied the effect of 120 MeV $^{107}$Ag$^{9+}$ ion irradiation on its structure, size and surface. They observed the transformation of CuO phase to Cu$_2$O during ion irradiation ($5 \times 10^{12}$ and $10^{13}$ ions cm$^{-2}$). The average crystallite size was also increased on irradiation from 4.9 nm to 6 nm as calculated by Scherrer’s equation. The bandgap was found to decrease from 2.48 to 2.39 eV, upon irradiation.

**Roy and Basu (2002)** investigated that zinc oxide was a versatile material for different commercial applications such as transparent electrodes, piezoelectric
devices, varistors, SAW devices etc. because of its high piezoelectric coupling, greater stability of its hexagonal phase and its pyroelectric property. Good quality of ZnO films were deposited on glass and quartz substrates by a novel CVD technique using zinc acetate as the starting solution. X-ray diffraction confirmed the crystallinity of the zinc oxide film and SEM study revealed uniform deposition of fine grains. Undoped ZnO films were used for detection of dimethylamine (DMA) and H$_2$ at different temperatures by recording the change in resistivity of the film in presence of the test gases.

**Zhou et al (2003)** reported the doping effects of Copper on the electrical conductivity of ZnO in simple binary system through the ac impedance spectroscopy. The Cu doping decreased the electrical conductivity of ZnO both in the grain and in the grain boundary by several orders of magnitude. Hydrogen was introduced into the Cu-doped ZnO specimens by the ion implantation technique. The electrical conductivity of the hydrogen-implanted layer increased by about 9 orders of magnitude. The mechanism for such type of hydrogen effect was also discussed.

**Chang et al (2004)** synthesized ZnO nanocrystals using a sol-gel method and their optical properties were investigated as a function of the ZnO nanoparticle size. It was observed that the photoluminescence spectrum showed two peaks: one was an ultraviolet (UV) exciton emission at around 363 nm and the other was a visible emission at around 500 nm that originated from deep-band traps. It was also analyzed that as the particle size was increased, the intensity of the visible emission decreased, while that of the UV emission increased. Both the UV and the visible emissions shifted to a lower energy with increasing particle size.

**Chaudhary et al (2004)** studied the effect of 170 MeV Au$^{13+}$ irradiation on photoelectrochemical (PEC) and structural properties of CuO thin films. The X-ray diffractograms of post-irradiated CuO thin films showed diffused nature towards higher theta value with the appearance of crystalline peaks, indicative of some randomization taking place at higher fluence, i.e. $10^{13}$ ions cm$^{-2}$. While, upon
irradiation, the size of particles/grains was decreased and the band gap energy was also shifted marginally. ERDA analysis indicated no change in stoichiometry of thin films even at higher fluence. The observed decrease in photoelectrochemical response, upon irradiation, was attributed to the creation of greater number of kink sites/dislocations, which may have acted as recombination centers for photogenerated charge carriers.

Miller et al (2004) developed a multijunction photoelectrode using Fe$_2$O$_3$/electrolyte photoelectrochemical as top junction with two underlying amorphous silicon/germanium (a-Si:Ge) solid-state junctions fabricated onto stainless-steel foil coated with a thin film of nickel-molybdenum hydrogen catalyst on the back surface for hydrogen production. These monolithically stacked solid-state structure, absorb strongly in the 500-700 nm and 600-900 nm ranges providing the supplementary voltage bias needed to sustain the hydrogen (HER) and oxygen evolution reactions (OER), respectively, occurring simultaneously at the catalyzed back surface and the Fe$_2$O$_3$ front surface, respectively. From the initial test results for dark and AM1.5 illuminated performance, 0.6-0.65 V bias savings in the light were observed, consistent with the incorporated single-junction solid-state device.

Park et al (2004) investigated the structural and optical properties of ZnO thin films grown by RF magnetron sputtering system on Si substrates and the as-prepared films were characterized by photoluminescence, X-ray diffraction, scanning electron microscopy and transmission electron microscopy. In optimized growth conditions, ZnO films showed strong UV emission of the ZnO band-edge, weak deep-level emission and an additional peak near 425 nm. Also, the shift of the blue-region peak (410-425 nm) might be related to the grain size. Thermal treatment led to the improvement of ZnO film quality, showing strong UV emission and the elimination of blue emission.
Wang (2004) reported that zinc oxide is a unique material that exhibits semiconducting and piezoelectric dual properties. Using a solid-vapour phase thermal sublimation technique, nanocombs, nanorings, nanohelixes/nanosprings, nanobelts, nanowires and nanocages of ZnO have been synthesized under specific growth conditions. These unique nanostructures unambiguously demonstrate that ZnO probably has the richest family of nanostructures among all materials, both in structures and in properties. The nanostructures could have novel applications in optoelectronics, sensors, transducers and biomedical sciences. This article reviews the various nanostructures of ZnO grown by the solid-vapour phase technique and their corresponding growth mechanisms. The application of ZnO nanobelts as nanosensors, nanocantilevers, field effect transistors and nano-resonators has been demonstrated.

Miller et al (2005) prepared a multijunction hybrid photoelectrode for hydrogen production incorporating metal-oxide photoelectrochemical top junction deposited onto an underlying solid state junction generating additional voltage bias for efficient water splitting. Iron oxide (Fe$_2$O$_3$) films and tungsten-trioxide (WO$_3$) films prepared by eight and nine reactive runs of sputtering at 10m Torr pressure to minimal thickness of 10 kA˚ and 20 kA˚ reported a photocurrent of 0.1 mA/cm$^2$ in 1N KOH and 1N H$_3$PO$_4$ solution. A small increase in the photocurrent with initially Mo doped sputter deposited tungsten-trioxide films was also reported. Photocurrent of 0.45 mA/cm$^2$ in 1N H$_3$PO$_4$ and stable operation at 0.7 % STH (solar to hydrogen), for over 10 h in acid media under 1 sun condition was reported for hybrid prototype photoelectrode with an active area of 2.5 cm$^2$.

Chauhan et al (2006) investigated the structural, morphological, optical and photoelectrochemical properties of sol-gel synthesized CuO thin films sintered at different temperatures (400-650°C). The study suggested that thin films of CuO sintered at lower temperatures (400°C) were better for photoconversion than thick films or the films sintered at much higher temperatures. Maximum value of photocurrent was observed for films sintered at 400°C which was nearly five-fold
higher compared to the observed value with films sintered at 650°C. SEM study suggested that rise in sintering temperature leads to more fragmentation in the grain agglomerates, which may be due to an increase in the number of recombination centres which efficiently trap photogenerated electron-hole pairs.

**Srinivasan et al (2006)** prepared zinc oxide thin films on different substrates by the sol-gel method using 2-methoxyethanol solution of zinc acetate dihydrate stabilized by monoethanolamine. The photoluminescence spectra of the films show the band-edge and sub-band transitions. They observed that the intensity of the band edge emission peak increases, while the intensity of the deep level emission peak decreases in the films coated on sapphire substrate. Transmittance spectra showed that the films were transparent beyond 400 nm. The structural property of the films has been evaluated using X-ray diffraction. They also observed that the X-ray peak intensity of the film (002) grown on sapphire substrate was higher than the films grown on glass and quartz substrates. The AFM images showed improvement in the surface of the annealed films as compared to the as-grown ZnO films coated on sapphire substrates.

**Ashrafi et al (2007)** presented a review on zincblende (ZnO) and stability of metastable ZnO phases. Common II-VI compound semiconducting materials were found to be stable thermodynamically with zincblende phase, while the II-O materials such as zinc oxide (ZnO) and beryllium oxide were stable with wurtzite phase, and cadmium oxide (CdO) and magnesium oxide (MgO) were found to be stable in rocksalt phase. Thermodynamically the zincblende ZnO was reported to be in a metastable phase which was free from the giant internal electric fields in the (001) directions and has an easy cleavage facet in the (110) directions for laser cavity fabrication that combined with evidence for the higher optical gain. The zincblende materials were found to have lower ionicity that leads to the lower carrier scattering and higher doping efficiencies. Even with these outstanding features in the zincblende materials, the growth of zincblende ZnO and its
fundamental properties were found to be still limited. Recent progress in growth and fundamental properties of zincblende ZnO material has been reviewed.

**Yang et al (2007)** prepared nanostructured tungsten trioxide (WO\(_3\)) thin films by sol-gel route from aqueous peroxopolytungstic acid (PTA) precursor solutions. It was demonstrated that films with different morphologies can be synthesized by simply adjusting the pH of PTA precursor solution using different mineral acids such as HCl and HClO\(_4\) and this control of film texture represents a way of optimizing photocurrent yield. The best WO\(_3\) films generated anodic photocurrents of 3.8 mA/cm\(^2\) for oxidation of methanol under AM 1.5 simulated solar illumination.

**Agrawal et al (2008)** deposited ZnO thin films using atom beam sputtering and their modifications have been shown by two processes: (a) thermal annealing of ZnO thin films in oxygen and (b) thermal annealing by irradiation of these films by swift heavy ions (SHI) in a high vacuum chamber. The as-deposited films showed the nanocrystalline nature with a preferred orientation along the c-axis of the hexagonal structure as revealed by X-ray diffraction (XRD) and Raman spectra. The influence of thermal annealing on the structural and surface modifications of these thin films was investigated. XRD and Raman spectroscopy confirmed the improvement in the crystallinity of ZnO thin film by both thermal annealing and SHI irradiation. It was concluded that the modification of nanocrystalline ZnO thin film could be possible by both thermal annealing and SHI irradiation. Results indicated that transient annealing by SHI irradiation induced highly textured c-axis oriented ZnO thin films.

**Paulauskas et al (2008)** investigated single crystals of various \(n\)-type semiconducting oxides in order to better understand the relationship between their photoelectrochemical behavior and their optical properties. The single crystals used in this study were all \(n\)-type and consisted of: KTaO\(_3\), BaTiO\(_3\), SrTiO\(_3\) and ZnO. Current density vs applied potential measurements indicated that all the crystals exhibited diodic properties when in contact with a highly basic electrolyte (8.5 M
NaOH at room temperature). Results indicated that the spectral quantum yield of the crystals is related to the penetration depth of the incident light, which means that electron-hole pairs formed far from the semiconductor-liquid junction are less likely to be collected than those formed near the surface (i.e. inside the depletion regions). Additionally the quantum yield was found to decrease with time.

**Caglar et al (2009)** investigated the electrical conductivity, structural and optical properties of ZnO nanostructured semiconductor thin film prepared by sol-gel spin coating method. The X-ray diffraction result indicated that the ZnO film has the polycrystalline nature with average grain size of 28 nm. The optical transmittance spectrum indicated the average transmittance higher than 90 % in the visible region. The optical band gap and optical constants (refractive index, extinction coefficient, real and imaginary parts of the dielectric constant) of the films were determined. The dependence of electrical conductivity of the film on temperature was measured to identify the dominant conductivity mechanism. The electrical conductivity and optical results revealed that the ZnO film was $n$-type nanostructured semiconductor with a direct band gap of about 3.30 eV at room temperature.

**Gupta et al (2009)** prepared nanostructured zinc oxide thin films (ZnO) on conducting glass support ($\text{SnO}_2$: F overlayer) via sol-gel method using the precursor colloidal solution of zinc acetate-2-hydrate in ethanol and 2-methoxy ethanol. Films were obtained by spin coating at 1500 rpm under room conditions (28-35°C) and were subsequently sintered in air at three different temperatures (400, 500 and 600°C). The evolution of oxide coatings under thermal treatment was studied by glancing incidence X-ray diffraction and scanning electron microscopy. Average particle size, resistivity and bandgap energy were also determined. Photoelectrochemical properties of thin films and their suitability for splitting of water were investigated. Study suggested that thin films of ZnO sintered at 600°C were better for photoconversion than the films sintered at 400 or 500°C which was
attributed to the better optical absorption and decreased electrical resistivity of the samples.

Holladay et al (2009) discussed that currently, hydrogen was primarily used in the chemical industry, but in the near future it will become a significant fuel. There were many processes for hydrogen production. In this paper, technologies related to hydrogen production from both fossil and renewable biomass resources including reforming (steam, partial oxidation, auto thermal, plasma, and aqueous phase) and pyrolysis have been reviewed. In addition, electrolysis and other methods for generating hydrogen from water, hydrogen storage related approaches, and hydrogen purification methods such as desulfurization and water-gas-shift have been discussed.

Li et al (2009) investigated the photoelectrochemical performance of MTiO$_3$ (M = Ca, Sr, and Ba) titanate cells by measuring the photocurrent-voltage characteristics and electrochemical impedance spectroscopy (EIS) under simulated sunlight AM 1.5 illumination conditions (100 mW cm$^{-2}$). The dye-sensitized MTiO$_3$ (M=Ca, Sr and Ba) showed much higher open-circuit voltage ($V_{oc}$) and short-circuit current density ($J_{sc}$) than those of corresponding materials without dye-sensitization. The $V_{oc}$ and $J_{sc}$ of the dye-sensitized cells increased in the order with CaTiO$_3$ > BaTiO$_3$ > SrTiO$_3$. Especially, the microtubule CaTiO$_3$ DSSC exhibits relatively a good photoelectrochemical performance, with the open-circuit voltage of 0.7 V and the current density of 0.26 mA cm$^{-2}$.

Bar et al (2010) investigated the electronic surface structure of Mo-incorporated WO$_3$ (WO$_3$:Mo) using direct and inverse photoemission and compared to that of pure (Mo-free) WO$_3$. The films were found to be n-type with an electronic surface band gap of 3.27 eV. The conduction band minimum (valence band maximum) was 0.64 eV above (2.63 eV below) the Fermi level and at most 0.38 eV above the H$^+$/H$_2$ reduction potential (at least 1.66 eV below the H$_2$O/O$_2$ oxidation potential). The findings suggested the formation of built-in potential at WO$_3$:Mo/WO$_3$ junction.
which may lead to improved photoelectrochemical performance of $\text{WO}_3$:Mo/$\text{WO}_3$ bilayer structures compared to respective single layered photoanodes.

**Hod et al (2010)** presented a new approach for inhibiting back electron transfer in a catechol-sensitized type-II dye-sensitized solar cells (DSSC) using a thin layer barrier coating of SrTiO$_3$ between the semiconductor and the sensitizer. An improvement of 18 % in the short-circuit current and up to 70 % in charge collection efficiency was achieved by applying an energy barrier layer coating of SrTiO$_3$ on CSSCs (catechol-sensitized type-II DSSCs), compared with the non-coated solar cells. The coating operates as an inhibitor for the back-electron transfer process, which opens up new possibilities for the improvement of type-II DSSCs.

**Li et al (2010)** investigated the photoelectrochemical activity of nanocrystalline $\text{WO}_3$ films synthesized on FTO glass substrates by the polymeric precursor method. By utilizing X-ray diffraction, scanning electron microscopy and UV-visible absorption spectroscopic techniques, the effect of substrates and temperature on the crystal structure and crystalline formation of $\text{WO}_3$ was investigated. Results indicated that the films coated on FTO glass substrate annealed at 400-550°C for 3h were distorted cubic $\text{WO}_3$. $\text{WO}_3$/FTO film calcined at 450°C produced a significant photoanodic current (2.70 mA/cm$^2$) at 1.4 V (vs. RHE) under the illumination of a 500 W Xenon lamp. It was concluded that nanocrystalline $\text{WO}_3$ films exhibited excellent adherence and mechanical stability, were highly photoactive and had a stable performance, making them promising materials for use in photoelectronic device applications.

**Li and Zhang (2010)** provided brief overview of some recent research activities in the area of hydrogen generation from PEC water splitting based on nanostructured semiconductor materials, with particular emphasis on metal oxides. Both scientific and technical issues have been critically analyzed and reviewed.
Lopes et al (2010) studied photoelectrochemical and electrical properties of undoped-Fe$_2$O$_3$ using two and three - electrode configurations in PEC water splitting for solar hydrogen production. In both situations, the impedance analysis showed that the charge transfer resistance significantly reduced under irradiation. The two electrode configuration allowed the study of the overall charge transfer phenomena occurring at the semiconductor, within the electrolyte and at the counter electrode side of the cell whereas the three - electrode configuration gave more detailed information concerning the double charged layer at the semiconductor/electrolyte interface.

Chiang et al (2011) reported copper oxide nanoparticles fabricated by flame spray pyrolysis and spin-coating methods and served them as photocathodes for photoelectrochemical splitting of water. The valence band edge and conduction band levels were calculated to lie at -5.00 eV and -3.56 eV with respect to the vacuum respectively. The net photocurrent density was measured to be 1.20 mA/cm$^2$ at applied voltage of -0.55 V vs Ag/AgCl in 1 M KOH electrolyte with 1 sun (AM1.5G) illumination which corresponds to the total conversion efficiency ($\epsilon_{\text{eff, total}}$) and photon-to-hydrogen generation efficiency ($\eta_c$) as 1.48% and 0.91%, respectively. As sintering temperature was increased to 600°C, crystalline diameter increased from 28 nm (before sintering) to 110 nm and the bandgaps decreased from 1.68 eV to 1.44 eV. Thus, the bandgap of the CuO thin film was found to be 1.44-1.64 eV based on sintering temperature and duration.

Solanki et al (2011) studied the effect of 120 MeV Ag$^{9+}$ ion irradiation on photoelectrochemical properties of SrTiO$_3$ thin films deposited on ITO coated glass by sol-gel spin-coating technique. Irradiation of SrTiO$_3$ thin films was found to be effective in improving its photoelectrochemical properties. A noticeable decrease in the average grain diameter from 36 to 26 nm, reduction in bandgap from 3.55 to 3.43 eV and increase in surface roughness after irradiation contributed in enhancing photoelectrochemical activity of SrTiO$_3$ thin films. Thin films irradiated at fluence $3 \times 10^{12}$ ions cm$^2$, when used in PEC cell exhibited enhanced photocurrent of 0.16 mA/cm$^2$. 

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mA cm² at zero bias conditions, which was four times higher than that of the unirradiated sample.

**Choudhary et al (2012)** reviewed the studies reported in the literature based on heterojunction/bilayered systems, which has been considered as effective tool towards extending the spectrum towards the visible range and for effective separation of charge carriers leading to development of efficient solar hydrogen production system. This communication describes the basic principles involved and summarizes most of the work done in this domain. Band gap, electronic band edge alignment of the materials with each other and with the redox potential of water, lattice mismatch of the materials and optimization of thickness of each layer at the junction in the PEC devices considered to be crucial for attaining enhanced photoresponse and efficiency.

### 3.2 Review of Recent Reports on Bilayered Systems

This section provides a brief discussion on some recent research activities in the area of PEC water splitting based on nanostructured bilayered semiconductor materials. Summary of various bilayered systems so far studied in photoelectrochemical splitting of water has been presented material wise.

#### 3.2.1 CdS based Bilayered Systems

CdS photoelectrodes coated with titania nanosheets were studied by **Yamada et al in 2005** towards protection of surface from photocorrosion and to enhance the catalytic activity for water oxidation. Titania coated CdS electrodes containing Cu(II), Ni(II), and In(III) ions exhibited suppressed dissolution but no photocurrent was recorded in Na₂SO₄ solution at the applied potential of 0.20 V (vs Ag/AgCl), probably because these metal ions act as the recombination center for photoinduced electron-hole pairs in CdS. The corrosion of CdS/titania electrodes prepared with Zn(II) and Cd(II) ions, was blocked apparently due to the stabilization of surface S⁻ radicals by the formation of metal complexes. Under dark condition, metal ions were
blocked for anodic corrosion, while the surface of CdS/titania electrodes corroded under irradiation similarly as in bare CdS indicating that Zn(II) and Cd(II) ions between titania sheets are not stable for the oxidation with the holes of CdS. For bare CdS, photocurrent increased initially because of the dissolution of CdS surface. When the surface was coated with one layer of titania nanosheets (TiO$_x$) with cationic polymer PEI (polyethyleneimine), the dissolution was delayed but the photocurrent was decreased and also significant decrease in photocurrent was observed upon doubly coating the TiO$_x$. These observations confirmed that the photocurrent for CdS/PEI/TiO$_x$/PEI/TiO$_x$ originates from the corrosion of CdS through an opening in the deposited nanosheets.

Yin et al in 2007, proposed a unique fabrication route of core/sheath heterostructure CdS/TiO$_2$ nanotube arrays by ac electrodeposition method. It was found that core/sheath CdS/TiO$_2$ nanotube arrays electrode could potentially improve the efficiency of charge separation by increasing contact areas of CdS with electrolyte and CdS with TiO$_2$ compared with sandwich electrodes. They reported that magnitude of the photocurrent density is related to the CdS deposition time, i.e. the CdS thickness. Thus, CdS nanotube arrays with thick walls have more band bending than a thin walled similar array and the rate of surface recombination decreases with the large band bending of the thicker walls, thereby increasing the photocurrent. Additionally, as the tube length of TiO$_2$ nanotube columnar structure was increased, more photons were absorbed and consequently the photocurrent increased. Though the tube length was increased, the bulk and surface recombination rate of photoexcited electron-hole pairs were much less than the charge transfer rate at the interface. This may be due to the core/sheath heterostructure CdS/TiO$_2$ architecture that resulted into a more effective surface area available to the electrolyte that enabled transport of holes to oxidizable species in the electrolyte.

In 2008, Chi et al developed CdS-sensitized nanocrystalline TiO$_2$ photoanode for water decomposition offering photoconversion efficiency of 3.67 % under visible
light illumination. The higher efficiency obtained in the CdS/TiO$_2$ system implies that applied potential helps in the effective separation of photoexcited electron-hole pairs which therefore, increases the energy conversion efficiency of the photoelectrode. Thicker TiO$_2$ film resulted in a higher value of photocurrent (5.5 mA cm$^{-2}$) which has been ascribed to the larger surface area available for incorporation of CdS and also the incorporation of CdS extends the optical absorption of TiO$_2$ electrode to visible light, enhancing the visible-light-induced photocurrent. In CdS/TiO$_2$ photoelectrode, the photoexcited electrons in the CdS can be easily injected into the conduction band of TiO$_2$, as the conduction band of CdS aligned higher than that of TiO$_2$. The injected electrons were accumulated on conduction band of TiO$_2$ and transferred to counter electrode where water was reduced to hydrogen. In order to prevent the photocorrosion by reducing the holes of CdS, S$^{2-}$ and SO$_3^{2-}$ were used as sacrificial reagents.

### 3.2.2 CdSe based Bilayered Systems

Photoelectrochemical behaviour of sequentially deposited SnO$_2$ and CdSe on an optically transparent electrode (OTE) has been reported by **Nasr et al in 1997**. The favourable energetic positioning of the band edges of SnO$_2$ and CdSe leads to improved performance of OTE/SnO$_2$/CdSe over OTE/CdSe in terms of enhanced efficiency and stability. In OTE/SnO$_2$/CdSe electrode, upon illumination electron-hole pairs were generated in visible light responsive CdSe. The photogenerated electrons in CdSe readily migrated to the lower-lying conduction band of SnO$_2$ and migrated through the film to the back contact OTE and contribute to the photocurrent, while the holes were scavenged by the electrolyte. Consequently, the photogenerated electrons escape from recombination with photogenerated holes in CdSe and are collected in higher concentration at the back contact OTE producing enhanced photocurrent.

**Aloney et al in 2009** reported 10 mA/cm$^2$, current density under illumination of 1950 lux light intensity by using CdSe/ZnSe/1M NaOH-Na$_2$S-S/C (graphite) based PEC cells. The PEC cell performance has been reported to improve with increased
deposition time however dissolution of film was also observed in case of deposition time duration greater than 60/60 minutes, which is attributed to the increase in rate of dissolution than the rate of deposition after attaining the maximum thickness. The performance of these cells also improved by increasing the deposition current density ($J_D$) during preparation of photoelectrodes, but at $J_D > 10$ mA/cm$^2$ the films did not adhere properly to the substrate and got dissolved in the electrolyte.

The annealing effect on the photoelectrochemical performance of CdS/CdSe-sensitized TiO$_2$ photoelectrode has been discussed by Chi et al in 2010. They concluded that higher annealing temperature (400°C) may activate oxidation and decomposition of the sensitizers which may be harmful to the photoelectrodes but optimal annealing (~300°C) can increase the crystallinity of the CdS and CdSe and also enhance the charge transport characteristic of the photoelectrode, leading to better performance of the TiO$_2$/CdS and TiO$_2$/CdSe electrodes, though with little effect on inhibition of photocorrosion.

### 3.2.3 CdS and CdSe based Bilayered Systems

The stability of the PEC performance of the semiconductor electrode (CdSe/CdS) in redox electrolyte was accounted by Martirosyan et al in 2001. It was found that the presence of Cd in the redox electrolyte (NaOH:S:Na$_2$S) protects the substrate (CdSe/CdS) against the attack of the electrolyte, which may eventually cause short-circuiting in the PEC process. Mahapatra et al in 2010 electrodeposited mixed CdS-CdSe on nickel substrate and used thymol blue as a sensitizer to the redox electrolyte and reported 5% conversion efficiency of CdS-CdSe electrode in PEC cell against 4.42% without the addition of dye. The improved performance of PEC cell comprises of CdS-CdSe semiconductor electrode attributed to reduction in band gap, higher value of flat band potential and smaller electron affinity of the semiconductor electrodes. Addition of small amount of suitable dye to the redox electrolyte could enhance the efficiency, mainly due to increase in the density of charge carriers but the enhancement in efficiency values obtained after the addition of dye was not so
significant, which may be due to the existence of surface states, acting as recombination centres for electron-hole pairs.

In 2010, Lee et al introduced a cascade structure of TiO$_2$/CdS/CdSe in which band edges of the three materials aligned in stepwise manner which was beneficial in the transport of excited charge carriers across the composite electrode. Current response of electrodes at externally applied positive bias increased in the order: TiO$_2$/CdSe $\approx$ TiO$_2$/CdSe/CdS $<$ TiO$_2$/CdS $<$ TiO$_2$/CdS/CdSe, indicating that TiO$_2$/CdS/CdSe electrode has a band edge structure with superior ability for charge transfer. The stepwise band-edge structure built in the TiO$_2$/CdS/CdSe electrode and also the electric field in space-charge region, was favourable to the electron injection and hole recovery of the system, responsible for the high photocurrent in the TiO$_2$/CdS/CdSe electrode. While, for the inverse (TiO$_2$/CdSe/CdS) structure, the band edges of intermediate CdSe were higher than those of CdS, resulting in energy barriers for injected excited electrons from the outer CdS layer and transferring hole from the inner CdSe layer. Thus, significant recombination of electron and hole was expected leading to low photocurrent. A similar work on CdS and CdSe nanoclusters co-sensitized TiO$_2$ NTWs (nanotubes with nanowires) arrayed films prepared by SILAR (successive ionic layer adsorption and reaction) deposition method has also been reported by Cheng et al in 2012. The stepwise band-edge structure in the TiO$_2$/CdS/CdSe/ZnS heterojunction electrode is suggested to create efficient charge transfer channel and towards triggering a high resistance to transport excited electrons back to the electrolyte. The enhanced photoelectrochemical response of heterojunction may also be attributed to the morphology of TiO$_2$ NTWs, formation of fine heterojunction between CdS and TiO$_2$ and broader spectral response of CdSe than CdS in the solar region.

### 3.2.4 Copper Oxide based Bilayered Systems

Wijesundera et al in 2010 electrodeposited single-phasic Cu$_2$O on Ti/CuO electrodes in an aqueous solution containing 0.1 M sodium acetate and 0.01 M cupric acetate in the potential range of −250 to −550 mV/SCE. Well-covered
photoactive n-type Cu$_2$O thin films were electrodeposited on the Ti/p-CuO electrode at -550 mV/SCE in similar electrolytic conditions in which Cu$_2$O was deposited on the Ti substrate. It was concluded that the thicknesses of the CuO and Cu$_2$O semiconducting layers and annealing of the CuO/Cu$_2$O heterojunction plays a major role in enhancing the photoresponse in the PEC water splitting. Zhang et al in 2012 introduced a proficient two-step electrochemical strategy for the fabrication of highly efficient and stable copper oxide composite photocathode materials. The photocurrent density of copper oxide composite was found to improve more than 2 times than that for bare Cu$_2$O electrode and the stability was also significantly enhanced from 30.1 % to 74.4 %. It was concluded that the CuO (top layer) in the Cu$_2$O/CuO composite facilitates reduction of Cu$_2$O photocorrosion and act as recombination inhibitor for the photogenerated electrons and holes from Cu$_2$O, which leads to enhanced stability and PEC performance of Cu$_2$O/CuO composite. The appropriate band energy structure of Cu$_2$O/CuO composite permits the transfer of photogenerated electrons from Cu$_2$O to the conduction band of CuO where the recombination of the electrons and holes considerably get reduced due to the involvement of phonon during transition in CuO. Moreover, Cu$_2$O/CuO composite showed absorption of large portion of solar spectrum which is facilitated by narrow band gap of CuO, leading to a remarkable enhancement in PEC performance of Cu$_2$O/CuO composite.

3.2.5 TiO$_2$ based Bilayered Systems

A good amount of work has also been reported using TiO$_2$ as one of the materials in bilayered photoelectrodes in PEC water splitting. Liu et al (1993) reported improved charge separation in the coupled TiO$_2$/CdSe system offering advantageous effect in improving the photocurrent stability of semiconductor photoelectrode. The open-circuit voltage of these films was found to be independent of film thickness and remained constant around -650 mV exhibiting that the photoelectrochemical effect was initiated by the excitation of CdSe, and there was no direct contribution from the TiO$_2$ film in initiating the photoelectrochemical effect. The mechanism of charge separation in thin CdSe films is reported to be governed by the different
rates of electron and hole transfer at the semiconductor/electrolyte interface. The major issue in attaining photocurrent stability was increased recombination of charge carriers. By coupling CdSe thin film with TiO$_2$ film, it was possible to inject photogenerated electrons into the conduction band of TiO$_2$ which may have retarded the charge recombination within the CdSe film.

Attempts have been made to address the corrosion limitation of Cu$_2$O by electrodeposition of Cu$_2$O/TiO$_2$ heterojunction configuration by Siripala et al in 2003. They explained that the light absorbed by the Cu$_2$O layer produces charge carriers where the excited electrons were driven to the TiO$_2$/electrolyte interface through conduction band of TiO$_2$ while holes were driven to the counter electrode by back contact. Thus, the charge separation basically occurred at the Cu$_2$O/TiO$_2$ interface. Similarly, sensitization of TiO$_2$ with copper oxide was introduced by Vigil et al in 2005 using microwave-activated chemical bath deposition (MW-CBD) technique. Electrons were injected from copper oxide to TiO$_2$ in Cu$_2$O–porous TiO$_2$ heterostructure upon illumination, requiring no external bias for photocurrent generation in PEC, as confirmed by photocurrent spectra and its time behaviour. Hou et al in 2009 investigated the photoelectrochemical activity of Cu$_2$O/TiO$_2$ nanotube heterojunction arrays, synthesized by photoreduction of Cu$_2$O nanoparticles on TiO$_2$ nanotube arrays. On the basis of electrochemical impedance spectroscopy and photocurrent measurements, it was apparent that the interaction between $p$-type Cu$_2$O and $n$-type TiO$_2$ in Cu$_2$O/TiO$_2$ nanotube heterojunction array promotes the enhancement in charge separation efficiency and extended response of TiO$_2$ into visible region.

In 2007, Yin et al prepared ZnFe$_2$O$_4$/TiO$_2$ coupled semiconductor system by dip-coating technique and observed a remarkable red-shift of the fundamental absorption edge with the increase in ZnFe$_2$O$_4$ thickness in the ZnFe$_2$O$_4$/TiO$_2$ multilayered films. It was found that the photocurrent was mainly influenced by the thickness of ZnFe$_2$O$_4$. It was concluded that the difference in band-gap positions of ZnFe$_2$O$_4$ and TiO$_2$ may lead to improved efficiency and enhanced concentration of
photogenerated carriers in ZnFe$_2$O$_4$/TiO$_2$ coupled semiconductor system, and thus greatly (five fold) enhance the photocurrent of ZnFe$_2$O$_4$/TiO$_2$ as compared to TiO$_2$ films. **Seabold et al in 2008** fabricated CdTe/TiO$_2$ bilayered photoelectrode by electrochemically filling tubes and tube-to-tube voids of TiO$_2$ nanotube arrays with CdTe. It was found that thinner and smooth CdTe coating on the TiO$_2$ tubes facilitates efficient electron transfer at the CdTe/TiO$_2$ junction and hole transfer at the CdTe/electrolyte junction, minimizing electron-hole recombination in the CdTe layer. Furthermore, the photocurrent generated by the CdTe layer alone was unstable, but CdTe/TiO$_2$ electrode generated stable photocurrent, indicating that the efficient removal of photons, generation of electrons and holes from the CdTe layer were also beneficial for kinetically suppressing photocorrosion in the CdTe layer. CdTe/FTO exhibited $p$-type behavior and generated cathodic photocurrent, while CdTe/TiO$_2$ electrodes generated anodic photocurrent, indicating that formation of TiO$_2$/CdTe/electrolyte junction and the injection of photogenerated electrons from CdTe to TiO$_2$ were more favoured than that from CdTe to the electrolyte.

**Kale et al in 2009** fabricated multi-layered photoelectrodes ITO/TiO$_2$/In$_2$S$_3$/CdSe and analyzed the role of every descending bandgap energy layer on the performance of PEC cell. It has been reported that photons having less energy than the band gap of TiO$_2$, upon irradiating $n$-TiO$_2$/n-In$_2$S$_3$/n-CdSe interfaces, generate electron-hole pairs which may be separated by the presence of electric field in the depletion region of TiO$_2$/In$_2$S$_3$/CdSe. The presence of TiO$_2$ thin film in multi-layered electrode blocks electron- hole recombination due to its more negative conduction band level with respect to NHE. It was also observed that the electrodes with three successive descending bandgap energies exhibited a good absorbance as photons of all energies could be absorbed, resulting in better photoconversion efficiency performance than the bilayers (ITO/TiO$_2$/In$_2$S$_3$ and ITO/In$_2$S$_3$/CdSe).

**Dang et al (2010)** reported significantly improved photoelectrochemical performance of TiO$_2$/CdS composite film electrode as compared to ITO/TiO$_2$ film, which opened the gateway for TiO$_2$ microporous structures sensitized by CdS thin
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films to be used for fabricating high efficiency devices. When TiO$_2$/CdS composite photoelectrode were irradiated by visible light, electrons generated in CdS were quickly transferred into the conduction band of the TiO$_2$ and the holes accumulated in the valence band of the CdS, thereby reducing probability of electron decay and successful charge separation was achieved. **Hensel et al in 2010** investigated the synergistic effect of CdSe quantum dots (QDs) sensitization and elemental (nitrogen) doping on enhanced photoelectrochemical performance of TiO$_2$ nanostructured (nanoparticles and nanowires) photoanodes. Significant enhancement in charge transport and PEC performance in case of composites was observed than that for N-doped TiO$_2$ or CdSe QD sensitized TiO$_2$. It was explained that conduction band edge alignment of CdSe QDs and TiO$_2$ nanoparticles permit efficient electron transfer from CdSe to TiO$_2$ which leads to increased photocurrent.

The photoelectrochemical performance of TiO$_2$ nanotube arrays sensitized by low band-gap materials, *viz.* CdS and CdSe has also been investigated by **Shin et al in 2010**. Remarkable increase in photocurrent from about 0.2 mA cm$^{-2}$ (for 400 nm TiO$_2$ nanotubes) to about 5.0 mA cm$^{-2}$ (for the CdS or CdSe modified nanotube arrays) with 8.5 % conversion efficiency has been reported. The photocurrent response of the CdS or CdSe modified TiO$_2$ nanotube arrays has been reported to be 25 times higher than that of unmodified TiO$_2$ nanotube arrays. CdSe decorated TiO$_2$ nanotube arrays on the other hand with relatively short nanotubes (3 µm tube length) showed significant photocurrent value (10 mA cm$^{-2}$), which confirmed that the charge-transfer processes between the well connected aggregated CdS or CdSe nanoparticles facilitates fast transfer of the photogenerated electrons from one CdS or CdSe to another and ultimately to the conduction band of TiO$_2$, leading to reduced electron-hole recombination. In the same year **Zhang et al** accounted the photoelectrochemical performance of vertically aligned TiO$_2$-SrTiO$_3$ heterostructure array having controlled growth of SrTiO$_3$ particles over TiO$_2$ nanotube arrays and found that only well-dispersed SrTiO$_3$ nanocrystallites on TiO$_2$ nanotube arrays, enhanced the overall PEC performance. They reported that TiO$_2$/SrTiO$_3$ composite heterostructure obtained with 1 h or less hydrothermal treatment exhibited the best
PEC performance with nearly 100% increase in external quantum efficiency at 360 nm as compared to the untreated TiO$_2$ nanotube electrode, which is attributed to enhanced crystallinity of SrTiO$_3$, higher stability and a large negative flatband potential, indicative of large accumulation of electrons in the coupled heterostructure and decreased recombination of charge carriers.

WO$_3$/TiO$_2$ nanotube array electrode have also been fabricated via wet impregnation method by Wang et al in 2011, which exhibited higher separation efficiency of photogenerated electron-hole pair and yielded higher steady-state photocurrent for oxidizing glucose as compared with the pure TiO$_2$ nanotube array electrode. PEC studies were performed with electrolytes containing different concentrations of glucose. The photoelectrochemical oxidation of glucose with TiO$_2$ and WO$_3$/TiO$_2$ nanotube array electrodes was investigated at constant potential bias (0.8 V) offering higher current in high concentration range of glucose (< 2 mM) for WO$_3$/TiO$_2$ nanotube array electrode as compared with TiO$_2$ nanotube array electrode. This suggests that the photoelectrocatalytic reaction of glucose on the surface of WO$_3$/TiO$_2$ nanotube array electrode is faster than that on the surface of TiO$_2$ nanotube array electrode. Upon UV light illumination of WO$_3$/TiO$_2$ nanotube array electrode, the photogenerated electrons got transferred from the conduction band of TiO$_2$ to that of WO$_3$ as analyzed by EIS measurement and the holes were effectively scavenged by water or glucose, resulting in effective charge carrier separation and improved photoelectrochemical oxidation performance for glucose in WO$_3$/TiO$_2$ nanotube array electrode than that of TiO$_2$ nanotube array electrode. Yang et al in 2011 fabricated TiO$_2$ annotate by loading CuO and WO$_3$ on TiO$_2$ by wet impregnation method. At 1 V, the photocurrent and hydrogen generation rate of Cu-WO$_3$ loaded annotate was found to be higher than that of unloaded and pure WO$_3$ loaded annotate and the photocurrent increases with the WO$_3$ concentration. It was concluded that the improvement in efficiency of photoelectrocatalytic properties carried out by co-loading of Cu-WO$_3$ on TiO$_2$ annotate.
Park et al in 2011 fabricated multi-layered BiO$_x$–TiO$_2$ electrodes with high doping of Bi (25 mol%) and observed that along with high dopant amount they retained photoelectrocatalytic and electrocatalytic activities. When exposed to light, the BiO$_x$–TiO$_2$ electrodes generated higher current than IrO$_2$ and SnO$_2$ electrodes due to the synergistic behavior of BiO$_x$–TiO$_2$ electrocatalysts. These electrodes were studied for degradation of phenol and hydrogen production under direct UV irradiation. The anodic photocurrent for BiO$_x$–TiO$_2$ electrode increased by ~ 50% under illumination on addition of phenol to the electrolyte, which was attributed to the charge carriers produced upon irradiation of BiO$_x$–TiO$_2$ anode and inhibition of recombination of charge carriers by the electron donor i.e. phenol. Dai et al in 2011 investigated photoelectrocatalytic activity for degradation of methyl orange (MO) solutions upon visible-light irradiation by BiOI/TiO$_2$ NTs (p–n junction). They reported high photocurrent density in BiOI/TiO$_2$ NTs as compared to the respective pure BiOI and TiO$_2$ counterparts which was attributed to the p–n junction, which can reduce the recombination of photogenerated electrons and holes by the internal electrostatic field in the junction region and an external electrostatic field which enhance the transfer and separation of photogenerated electrons and holes in BiOI/TiO$_2$ NTs. Thus, the combined effect of the internal and external electric fields is reported to result the highest photocurrent density in such p–n heterojunction. The enhanced PEC activity of BiOI/TiO$_2$ NTs was attributed to the synergistic effect of strong visible-light absorption, p–n junction structure and the applied external electrostatic field.

Lin et al in 2009 studied combination of highly conductive TiSi$_2$ nanonets (NNs) with photoactive TiO$_2$ coating. Upon illumination, charge carriers were generated, out of which electrons were collected in the TiSi$_2$ core and readily transported away whereas holes were transferred to the electrolyte for further chemical reaction. In TiO$_2$/TiSi$_2$ heterostructures, the TiO$_2$/electrolyte junction area and the charge transport was increased by passing through more conductive TiSi$_2$. A similar piece of work based on composite photocatalyst comprised of titania (TiO$_2$) nanotubes (NTs) coupled with titanium disilicide (TiSi$_2$) nanoparticles has also been reported.
by Banerjee et al in 2011. A novel architecture, TiSi$_2$ nanorods inside TiSi$_2$ nanotubes, was prepared. A combination of better solar light absorption (TiSi$_2$) and high charge transport properties (one-dimensional TiO$_2$ NTs) has been reported for the excellent photoactivity of this hybrid material. Upon UV-Vis irradiation, electrons of both semiconductors (TiSi$_2$ and TiO$_2$) were excited and injected from TiSi$_2$ to TiO$_2$. Simultaneously, more photoelectrons were generated from TiO$_2$ NTs by harvesting UV photons. Therefore, a high concentration of electrons was obtained in the conduction band of TiO$_2$ compared to TiO$_2$ alone. In addition to thermodynamically favourable energy bands, geometric architecture of the composite was also reported to be an important factor which controls the lifetime of charge carriers. One-dimensional TiO$_2$ NTs collect the photoelectrons from TiSi$_2$ and pass them to the back contact. The holes (from both TiSi$_2$ and TiO$_2$) generated in the process transferred to the solid-liquid interface to generate protons from the solution.

Efforts have also been made by Sharma et al in 2010 to prepare Fe-TiO$_2$/Zn-Fe$_2$O$_3$, in which thickness of Fe-TiO$_2$ film deposited on ITO was varied while thickness of overlying Zn-Fe$_2$O$_3$ film was kept constant and the system was studied as photoelectrode in PEC cell for generation of hydrogen through water splitting. A 10 fold enhancement in photocurrent density at 0.95 V/SCE was observed for Fe-TiO$_2$/Zn-Fe$_2$O$_3$ photoelectrodes than that of Zn-Fe$_2$O$_3$, which is attributed to efficient separation of photogenerated charge carriers at the interface, reduction in resistance and improved light absorption ability.

Sharma et al in 2012 comprises another system of bilayered Fe-TiO$_2$/Zn-Fe$_2$O$_3$ photoelectrode, PEC response was optimized with respect to thickness of the overlying layer of Zn-Fe$_2$O$_3$. Bilayered Fe-TiO$_2$/Zn-Fe$_2$O$_3$ photoelectrode was observed to possess enhanced efficiency for separation of charge carriers and could generate nine folds better photocurrent density than pure Fe-TiO$_2$. It was concluded that thickness of the Zn-Fe$_2$O$_3$ was found to be crucial in deciding photoelectrochemical properties of Fe-TiO$_2$. Improved absorption, mixed oxide
formation and higher value of flatband potential in bilayered films were found to be responsible for better performance of modified photoelectrode.

3.2.6 ZnO based Bilayered Systems

Hotchandani et al in 1992 developed coupled semiconductor films for PEC water splitting and elucidated the charge-transfer processes in CdS-ZnO coupled semiconductor systems. Coupling the ZnO film with CdS particles lengthen its photoresponse in the visible region. The long lifetime of charge carriers in CdS-ZnO system as analysed by picosecond laser flash photolysis experiments confirmed the role of coupled semiconductor systems in retarding the recombination of trapped charge carriers. Better charge separation in the coupled semiconductor system lead to an enhancement in the efficiency of interfacial charge transfer to the adsorbed substrate. Upon optical excitation of CdS, the photogenerated electrons were readily transferred to ZnO while the holes accumulated at the CdS particle. At the interface, thin junction of Zn$_x$Cd$_{1-x}$S was formed which was reported to be responsible in improving the process of charge separation by providing the necessary energy gradient for the flow of electrons towards ZnO film.

Important observation of p-i-n heterojunction and calculation based understanding of lattice mismatch between the two materials at the heterojunction was made by Zhang et al in 2004. They found that Cu$_2$O/ZnO/ITO heterojunction exhibits a distinct property with smaller turn-on voltage, due to the tunnel recombination process that was based on the existence of the interface defect states in Cu$_2$O and ZnO. This heterojunction structure offered an easy way for electron injection from n-type ITO to the p-type Cu$_2$O and blocked the back hole injection from the p-to-n side under the forward applied voltage. In addition, the semi-insulated ZnO layer makes smoother energy band edge between Cu$_2$O and ITO, which resulted in decrease in interfacial conduction and valence band discontinuities and an easy transition between bulk energy bands of Cu$_2$O and ITO.
**Wang et al (2010)** reported CdS and CdSe quantum dot co-sensitized with ZnO nanowire arrayed photoanode for PEC water splitting offering photocurrent density of ~12 mA/cm² at 0.4 V vs Ag/AgCl. This structure was analogous to tandem cell structure, in which ZnO nanowire arrays were deposited on ITO substrate followed by sensitization of CdS and CdSe quantum dots on each side. The photocurrent and IPCE were increased than that of quantum dot sensitized structures as a result of the proper band edge alignment of CdS and CdSe in electrolyte. Furthermore, the double-sided design exhibited better efficiency for charge collection than that of single-sided co-sensitized layered structures, which was attributed to direct contact between quantum dot and nanowire. It was concluded that the electron transfer in the CdSe-CdS-ZnO was less efficient compared to electron transfer in CdS-ZnO-ZnO-CdSe, which is attributed to the proper alignment of Fermi levels of CdS, CdSe and ZnO. Moreover, the conduction band edges of CdS and CdSe were close enough allowing electrons to delocalize between the conduction bands. Although the electrons created in CdSe can be transferred to ZnO through the CdS layer, the presence of intermediate layer in CdSe-CdS-ZnO may increase the chance of electron-hole recombination and limits its electron collection efficiency.

**Dang et al in 2010** attempted ZnO/CdS bilayered film as a working electrode in PEC cell and found better PEC performance of bilayered film than ITO/ZnO film. They also observed inverse relation between the amount of V_{oc} (465mV) and J_{sc} (412 μA) with the thickness of CdS (70-180 nm), explained by Anderson’s model. In ZnO/CdS nanocomposite, CdS acted as a visible sensitizer while ZnO, being a wide band semiconductor, apparently responsible for charge separation, thereby suppressed the recombination process. Thus, ZnO/CdS nanocomposite thin films can absorb significant portion of visible light and smoothly transfer the photoexcited electrons into the ZnO conduction band. The lifetime of electrons increased upon diffusion in the conduction band of ZnO, an area with non-availability of free holes under visible light excitation.
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The effect of annealing temperature on the optical properties and band-gap energy of ZnO/NiO multilayer thin films fabricated by CBD method has been studied by Ajuba et al in 2010. They found that the bandgap energy decreases with increase in annealing temperature which may be either due to evaporation of water molecules off the films and/or reorganization of the films.

3.2.7 TiO$_2$ and ZnO based Bilayered Systems

Liu et al in 2004 fabricated mercurochrome-sensitized composite TiO$_2$/SnO$_2$ and ZnO/SnO$_2$ PEC cells and examined the influence of mixed ratios of TiO$_2$/SnO$_2$ and ZnO/SnO$_2$ on the performance of the composite semiconductor in the PEC cells. The energy barrier between different semiconductors contributed in the improvement of the $J_{sc}$ by suppressing recombination of photo-induced electrons and holes in the oxidized dye resulting in the improvement of the IPCE of the composite TiO$_2$/SnO$_2$ and ZnO/SnO$_2$ cells as compared to corresponding TiO$_2$ and ZnO composite cells.

Paracchino et al in 2011 reported a modified approach with multiple layer ALD (atomic layer deposition) protection strategy utilization to offer improved corrosion protection for the photoelectrodes used in PEC cell. Photocurrent 7.6 mA/cm$^2$ at potential of 0V for FTO/ Cu$_2$O/Al doped ZnO/TiO$_2$/Pt nanoparticles and 100 % Faradaic efficiency was reported. Aluminium doping in this case was considered to stabilize ZnO layer in the photoelectrode. The electrodes showed good photocurrents even after 1 h of testing but the photocurrent decreased with time without structural failure of the protecting layers or significant chemical degradation of Cu$_2$O, which was probably due to electron accumulation in the TiO$_2$ layer (by Ti$^{3+}$ traps), whose Fermi level was not optimally positioned for water splitting. It was observed that the photoelectrons generated in Cu$_2$O flowed without hindrance into Al:ZnO and to TiO$_2$, but as the Fermi level of TiO$_2$ in the dark was found to be very close to the water reduction potential, electrons readily moved into the electrolyte and accumulated in the protective layer as long-lived Ti$^{3+}$ states.
3.2.8 \textit{Fe}_2\textit{O}_3, \textit{WO}_3 and \textit{SrTiO}_3 based Bilayered Systems

Higher photocurrent and higher IPCE in case of \textit{SrTiO}_3/\alpha-\textit{Fe}_2\textit{O}_3 heterojunction was found than that of the single \textit{SrTiO}_3 or \alpha-\textit{Fe}_2\textit{O}_3 film as reported by \textbf{Wang et al in 2007} which may be due to the electric field formed by the junction at the interface and the special band structures of \textit{SrTiO}_3 that favour the transfer of holes from \alpha-\textit{Fe}_2\textit{O}_3 to \textit{SrTiO}_3, and the improved charge separation at the \textit{SrTiO}_3/\alpha-\textit{Fe}_2\textit{O}_3 interface. Thus, it was concluded that the additional \textit{SrTiO}_3 layer facilitates increased separation of charge carriers along with the rapid transfer of holes to the electrolyte.

A similar report on \textit{WO}_3/\textit{Fe}_2\textit{O}_3 bilayered semiconductor in PEC water splitting has also appeared by \textbf{Luo et al in 2007}, which reported higher photocurrent density and higher IPCE values of \textit{WO}_3/\textit{Fe}_2\textit{O}_3 heterojunction than that for \textit{Fe}_2\textit{O}_3 and \textit{WO}_3 alone. In \textit{WO}_3/\textit{Fe}_2\textit{O}_3 electrodes, the conduction band of \textit{WO}_3 is higher than that of \textit{Fe}_2\textit{O}_3, which makes the transfer of photo-generated electrons easier and decreases the combination between the electrons and the holes. Thus, the \textit{WO}_3/\textit{Fe}_2\textit{O}_3 interface improved the photocurrent and IPCE of the composite structure. In 2009, \textbf{Sivula et al} introduced host/guest (\textit{WO}_3/\textit{Fe}_2\textit{O}_3) architecture in which hematite has been reported to act as the guest absorber and a scaffold host material (\textit{WO}_3) was chosen on the basis of lower lying conduction band than that of hematite to allow efficient electron transport across the host/guest interface and larger band gap than hematite so that the scaffold host material did not compete with the light absorption. Increased photocurrent in PEC was observed, which was due to photon absorption by \textit{WO}_3 followed by hole transfer to the \textit{Fe}_2\textit{O}_3. Further, the quantum efficiency was improved by using the host/guest approach with thinner layer of iron oxide and scaffold layer with increased roughness and porosity, which allowed 20\% increase in the photocurrent for hematite. Accordingly, increased quantum efficiency especially from wavelengths near the hematite absorption edge where photons have long penetration depths was also observed, as the greater fraction of photons may be absorbed near the hematite/electrolyte interface.
Kuang et al in 2009, investigated improved photoelectrochemical behaviour of Fe$_2$O$_3$-modified TiO$_2$ nanotube (NT) arrays which is attributed to the increased probability of charge carrier separation that extends the range of TiO$_2$ photoresponse from ultraviolet (UV) to visible region due to the low band gap (2.2 eV) of Fe$_2$O$_3$. Under UV–Vis illumination, electrons were excited from the valence band (VB) to the conduction band (CB) of anatase. In the absence of Fe$_2$O$_3$, most of the charge carriers quickly recombine but when Fe$_2$O$_3$ nanoparticles were attached to the surface of the TiO$_2$ NTs, the relative position of the Fe$_2$O$_3$ CB edge permitted the transfer of electrons from the TiO$_2$ surface allowing charge separation, stabilization and hindered recombination. With the increasing amount of Fe$_2$O$_3$ deposited on the TiO$_2$ NT, the probability of the photo-generated e$^-$$\cdot$h$^+$ recombination increases as all the photoelectrons on the nanoparticle cannot be scavenged immediately by the applied bias. Fe$_2$O$_3$ then becomes the recombination centre of e$^-$$\cdot$h$^+$ induced by light, resulting in decrease of photoactivity with higher Fe content.

An important finding showing the possible explanation for improved photoelectrochemical performance of WO$_3$:Mo/WO$_3$ bilayered system compared to single layer i.e. WO$_3$ or WO$_3$:Mo photoelectrode was reported by Gaillard et al in the year 2010. Electron transport property of pure WO$_3$ was reported to be limited by crystallographic shear defect planes in the lattice. It was observed that Mo incorporation in WO$_3$ resulted in reduction of PEC activity than that for pure WO$_3$ which may be due to formation of defects by Mo incorporation, where photogenerated charge carriers were trapped. 20 % enhancement in photocurrent density was observed for WO$_3$:Mo/WO$_3$ bilayered system and 100% improvement in photocurrent density of WO$_3$:Mo based system was investigated than that for pure WO$_3$ at 1.6 V vs SCE. The remarkable improvement in PEC performance of WO$_3$:Mo/WO$_3$ bilayered photoelectrode is attributed to modification in chemical and electronic surface properties of WO$_3$ by overlying WO$_3$:Mo thin film while maintaining its morphological and bulk properties and positive influence of high crystallinity of WO$_3$ on coherent growth of overlying WO$_3$:Mo thin film (for
improved efficiency). Favourable energetic positions, efficient charge collection and built-in electric field at WO₃/WO₃:Mo junction has also been beneficial for the movement of holes from WO₃ towards electrode surface and electrons towards back-side electrode.

Significantly enhanced photoresponse of Fe₂O₃/ZnFe₂O₄ compared to the bare Fe₂O₃ electrode was investigated by McDonald et al in 2011. ZnFe₂O₄ has band edges shifted to 200 mV in the negative direction from that of Fe₂O₃ which allowed the improved separation of charge carriers at the Fe₂O₃/ZnFe₂O₄ interface. Further improvement in photocurrent was observed through the Al³⁺ treatment of the composite electrodes, which may form thin solid solution coating layers (i.e. ZnFe₂-xAlₓO₄ or Fe₂-xAlₓO₃) and reduce surface states that may serve as the electron-hole recombination centers. Fe₂O₃ core with ZnFe₂O₄ shell structure may allow the photon generated holes in the Fe₂O₃ core to be transferred to the ZnFe₂O₄ layer and then consumed at the ZnFe₂O₄/electrolyte junction. This can effectively increase photon to photocurrent conversion ratio of Fe₂O₃ that has an extremely short diffusion length of hole. The photon generated electrons in the ZnFe₂O₄ layer may be transferred to the Fe₂O₃ core and move to the back contact.

Su et al in 2011 reported WO₃/BiVO₄ nanorod-array heterojunction photoanode prepared by solvothermal deposition method for PEC water splitting with photocurrent density 1.6 mA/cm² at 1.0 V/SCE, which is higher than that for the planar sample (0.8 mA/cm² at 1.0 V). The WO₃/BiVO₄ heterojunction offered improved photoconversion efficiency and photocorrosion stability. The nanorod-array films showed significantly improved photoelectrochemical properties than that of planar WO₃/BiVO₄ heterojunction films, probably due to the high surface area and improved separation of the electron-hole pairs at WO₃/BiVO₄ interface. More precisely, WO₃/BiVO₄ nanorod-array heterojunction was formed vertical to the substrate, along which light is absorbed. Thus, more carriers were generated close to the heterojunction where they were efficiently separated. In addition, the large surface area is offered by nanorod array structures which provide a direct
path for the movement of electrons toward the substrate and a short path for holes to reach the aqueous electrolyte for water oxidation.

### 3.2.9 Silicon based Bilayered Systems

In order to achieve efficient water splitting, composite semiconductor electrode $n$-Si/$p$-CuI/ITO/$n$-$i$-$p$ a-Si/$n$-$p$ GaP/ITO/RuO$_2$ has been fabricated by Yamane et al (2009). PEC cell comprised of $n$-Si/$p$-CuI/ITO/$n$-$i$-$p$ a-Si/$n$-$p$ GaP/ITO/RuO$_2$ photoelectrode, generated 1.88 mA cm$^{-2}$ photocurrent density under simulated solar illumination with 2.3 % efficiency. The electrode showed a stable photoanodic current due to oxygen evolution with a large negative photo shift ($V_p$) of about 2.2 V from the corresponding anodic current at the RuO$_2$ electrode. They found that the efficiency can be increased by using GaP with a well-regulated $p$-$n$ junction and the addition of $n$-$i$-$p$ a-Si to $n$-$p$ GaP/ITO/RuO$_2$ resulted into a shift in the onset potential of the anodic photocurrent towards more negative value (0.9 V).

Yu et al in 2009 investigated the photoelectrochemical performance of $n$-$n$ and $p$-$n$ SiNW (nanowire) heterojunction with TiO$_2$ fabricated by chemical etching of Si wafer. When SiNW/TiO$_2$ heterojunction system was illuminated with solar light, the short wavelength (UV light) and long wavelength (visible light) portions were absorbed by TiO$_2$ and SiNW respectively. TiO$_2$ serves as window layer in the heterojunction array and allow visible light to permeate through it and absorbed by SiNW. The window effect of heterojunction photoelectrode leads to absorption of both visible and UV portion of the solar spectrum, resulting into enhanced photoelectrochemical performance of the heterojunction system. It was observed that the existence of window effect only in $n$-$n$ junction may lead to superior photoconversion ability of $n$-SiNW/TiO$_2$ rather than $p$-SiNW/TiO$_2$ heterojunction system.