2. LITERATURE REVIEW
Chapter 2

Literature Review

This chapter presents a review of earlier work done by different researchers on the use of multilayered/multijunction electrodes in PEC splitting of water. Some papers on carbon based metal oxides and on the effect of swift heavy ion (SHI) irradiation on metal oxide semiconductors have also been reviewed.

Agrawal et al (2003) described a wet chemical method to synthesize Ti-doped Fe$_2$O$_3$ (haemetite) powder using aqueous solution of Fe and Ti nitrates as precursor and glycerol as key reagent by sol-gel technique. On studying the physio-chemical properties of the Ti doped samples it was found that the electrical resistance of the samples decreased significantly with increasing Ti concentration from (2-4)% in iron oxides while no further drop in the resistance was observed with further increase in the Ti concentration beyond 4%. The minimum bias voltage for a 4% Ti doped samples under illumination decreased significantly with increase in pH from 11 to 13.

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) athermal annealing by irradiation of these films by swift heavy ions (SHIs) 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 the thermal annealing and thermal annealing on the structural and surface modifications of these thin films were 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 and athermal annealing. Results indicate that transient annealing by SHI irradiation induced highly textured c-axis oriented ZnO thin films.

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 photo-electrochemical cells (PECs). The property requirements for photo-electrodes, in terms of semiconducting and electrochemical properties and their impact on the PEC performance of have been outlined. Different types of PECs have been overviewed and the impact of the PEC structure and materials selection on the conversion efficiency of solar energy is considered. Trends in research in the development of high-efficiency PECs were discussed.

Carlsson and Holmstorm et al (1989) compared a Ga(As,P)/GaAs/Ga(As,P)/n⁺-GaAs with a conventional Ga(As,P)/n⁺-GaAs structure using a variety of photoelectrochemical techniques. The conventional sample had a terminating top layer with constant composition GaAs₀.₄₄₅P₀.₅₅, while, in a multijunction sample, a GaAs region was introduced between the graded region and the top layer, resulting in an interface with an abrupt heterojunction. This multijunction electrode showed several unusual PEC features, including a very low dark current over a wide potential region, both cathodic and anodic photo effects, and a pronounced decrease in photoactivity when going to shorter wavelengths.

Cesar et al (2006) deposited silicon doped nanocrystalline α-Fe₂O₃ thin films on F-doped SnO₂ glass substrates by ultrasonic spray pyrolysis (USP) and atmospheric pressure chemical vapor deposition (APCVD) at atmospheric pressure using iron(III)- acetylacetonate and iron pentacarbonyl with Tetraethoxysilane (TEOS) as silicon dopant. The photoanodes prepared by ultrasonic spray pyrolysis and chemical vapor deposition gave photocurrent density of 1.17 and 1.45 mA/cm², respectively at 1.23 V vs RHE. The film thickness of this TEOS Si-doped sample was 145 ± 20 nm and had a transmittance at 400 and 550 nm of 3.4% and 46% respectively. It was found that Si doping has influenced the morphology of the nanostructured α-Fe₂O₃ films by decreasing the feature size of the nanocrystallites to 200 ± 40 nm in length and 100 ± 15 nm in width.
Chandra et al (1990) prepared mixed oxide electrode of TiO$_2$-In$_2$O$_3$ by solid state sintering in the form of pellets and observed the enhanced photovoltage and photocurrent of 1.4 mA cm$^{-2}$ at 0.78 V. The Mott-Schottky plots in 1 M NaOH solution and temperature variation of electronic conductivity for TiO$_2$ as well as TiO$_2$-In$_2$O$_3$ suggested the decrease in band gap and slight shift in the flat-band potential of the mixed oxide electrode compared with TiO$_2$. The rate of hydrogen production was 1.8 ml h$^{-1}$. It was reported that the enhanced PEC activity is due to the formation of In$_2$O$_3$ photoactive islands thereby increasing the active surface area of the TiO$_2$-In$_2$O$_3$ mixed oxide electrode.

Duret and Grätzel (2005) deposited mesoscopic leaflet type structure of 200 nm α-Fe$_2$O$_3$ thin film on conducting fluorine doped tin oxide (FTO) glass substrate using ultrasonic spray pyrolysis (USP). Optical studies shown that two samples have one indirect (2.0 eV) and one direct (3.0 eV) electronic transition. The microscopic α-Fe$_2$O$_3$ layers produced by USP consisted mainly of 100 nm-sized platelets with a thickness of 5-10 nm. The dark current of the USP samples increased gradually at potentials greater than 1.2 V versus RHE to reach 0.15 mA/cm$^2$ at 1.6 V, whereas the dark current of the SP sample increased more steeply to reach 0.25 mA/cm$^2$ at 1.6 V. The photocurrent onset potential was at 550 and 1125 mV versus RHE for the USP and the SP samples, respectively indicating the need of higher applied potential to afford water oxidation for the SP samples than for the USP samples. The photocurrent of 1.07 mA/cm$^2$ and 14 μA/cm$^2$ at 1200 mV versus RHE was reported for the USP and the SP samples respectively.

Ferrari and Robertson (2000) have given the model and theoretical understanding of the Raman spectra in disordered and amorphous carbon. The nature of the $G$ and $D$ vibration modes in graphite is analyzed in terms of the resonant excitation of p states and the long-range polarizability of p bonding. Visible Raman data on disordered, amorphous, and diamond like carbon was classified in a three-stage model to show the factors that control the position, intensity, and widths of the $G$ and $D$ peaks.

Fujishima and Honda (1972) in their pioneering work were the first to report the photoelectrolysis of water using a single crystal of TiO$_2$ 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 because the pH differed in cathodic and anodic compartment.

**Gavrilenko et al (1990)** presented a model of electronic structure of graphite like carbon films, describing the semiconductor properties of the material. Spectra of the optical constants of microcrystalline carbon films in the region of wavelength, 400-800 nm were studied by the spectral ellipsometry and IR reflection methods. A number of distinctive features of the spectra associated with the both the appearance of the C-C and C-H type bands and direct energy gaps were found. Analysis of optical data using the proposed model makes possible a common interpretation of our results and literature data.

**Glisenti (2000)** reported the interaction between simple alcohols, methanol to 1-butanol with the Fe–Ti mixed oxides. The reactivity of the mixed system was studied both at atmospheric pressure and in vacuum conditions and compared with that of the pure oxides TiO₂ and Fe₂O₃. To understand the influence of the oxygen presence in the reaction mixture, the reactivity was investigated both in inert gas as well as in oxygen atmosphere. When compared with Fe₂O₃, the Fe–Ti–O mixed oxide seems to be less reactive with respect to the alcohols; the interaction between alcohol and surface is mainly molecular, as in the case of TiO₂. Moreover, the oxidizing power of the mixed oxide is lower than that of Fe₂O₃ only traces of carbonic compounds are evident.

**Gnatyuk et al (2005)** prepared optically transparent, crack-free Mesoporous TiO₂ and ZrO₂ doped TiO₂ thin film by sol-gel technique using the non-ionic amphiphilic triblock copolymer Pluronic P123 as the template. The calculated film thickness of the films prepared by one coating were in the range of 70-80nm while the corresponding refractive index were in the range of 1.9-2.1. It was reported that catalytic activity of the mesoporous TiO₂ and TiO₂/ (5-30%) ZrO₂ films in the ethanol Photo-oxidation increased with increasing specific surface area and surface acidity of the sample.

**Gratzel (2011)** in this article reported the conversion of sunlight to electrical 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 have been presented.

**Hotchandani and Kamat (1992)** elucidated the picosecond laser flash photolysis and PEC studies on the charge-transfer processes in CdS-ZnO coupled semiconductor systems. Charge injection from excited CdS into ZnO occurs within the laser pulse duration of 18 ps. The feasibility of employing a colloidal CdS-ZnO system in a photoelectrochemical cell was demonstrated by modifying the surface of an optically transparent electrode with ZnO and CdS colloids. An incident photon-to-photocurrent conversion efficiency of 15% was reported for TE/ZnO/CdS at 420 nm.

**Huang et al (2012)** prepared a variety of carbon-modified titania powders using a commercial available titania powder. The catalyst modified with cyclohexanol exhibited the best activities of 62%, 62%, 59%, and 54% for the total NOx removal under UV, blue, green, and red light irradiation, respectively. Analysis of UV-visible spectrum indicated that carbon modification promoted visible light absorption and red shift in band gap. XPS spectroscopic analysis identified the existence of carbonate species (C=O), which increased with the increasing carbon number of precursor molecule. Photoluminescence spectra demonstrated that the carbonate species suppressed the recombination rate of electron-hole pair. As a result, a mechanism of visible-light-active photocatalyst was proposed according to the formation of carbonate species on carbon-modified TiO2.

**Hwang et al (2009)** investigated the Si/TiO2 nanowire heterostructures to determine their potential for the photo-oxidation of water. It was observed that highly dense Si/TiO2 core/shell nanowire arrays enhanced the photocurrent by 2.5 times compared to planar Si/TiO2 structure due to their low reflectance and high surface area. It was showed that n-Si/n-TiO2 nanowire arrays exhibited a larger photocurrent and open circuit voltage than p-Si/n-TiO2 nanowires due to a barrier at the heterojunction. Increase in the photocurrent was attributed to the use of n-Si/n-TiO2 heterojunctions because n/n junctions enhance the charge separation and minimize recombination.
Ingler and Khan (2004) synthesized Mg-doped iron (III) oxide thin film electrodes exhibiting p-type behavior by spraying solutions of different concentrations (0.09-0.12 M) of iron (III) chloride hexahydrate (FeCl₃·6H₂O) with various mass percentage (10-12%) of magnesium nitrate hexahydrate (Mg(NO₃)₂·6H₂O) on indium doped tin oxide-coated glass (ITO) substrate using spray pyrolytic method. The highest photocurrent density of 0.22 mA/cm² at 0.2 V/SCE was reported for Mg-doped p-Fe₂O₃ samples prepared at the optimal substrate temperature of 390 °C. A peak photoconversion efficiency of 0.33% and total conversion efficiency of 0.97% was found to be at total spray of 130 s for a spray period of 10 s. X-Ray diffraction (XRD) studies revealed the mixed structures of α and γ-Fe₂O₃ with presence of MgO for the Mg-doped p-Fe₂O₃ thin films. The higher photocurrent density of Mg doped Fe₂O₃ was attributed to the presence of mixed oxides (α and γ Iron oxide with MgO) in spray pyrolytically synthesized samples.

Ingler and Khan (2005) synthesized stable Cu-doped iron (III) oxide thin film electrodes exhibiting p-type behavior using spray pyrolytic deposition (SPD) method by spraying solutions of different concentrations (0.9–0.12 M) made by mixing iron (III) chloride hexahydrate (FeCl₃·6H₂O) and various concentrations of Cu²⁺ (0.011–0.0132 M) in the form of copper nitrate hexahydrate (Cu(NO₃)₂·6H₂O) in absolute ethanol on conducting tin oxide-coated glass substrates for photoelectrochemical water splitting. The highest photocurrent density of 0.94 mA/cm² was observed under an illumination intensity of 40 mW/cm² for Cu-doped samples prepared using an optimal 0.01155M Cu²⁺ at an optimal substrate temperature of 395 °C with a total spray time of 100s at 0.0V vs. SCE. These Cu-doped p-Fe₂O₃ thin films were found to generate an optimum photoconversion efficiency of 1.3%. X-ray diffraction (XRD) data revealed that these films have mixed structures (α-Fe₂O₃ and CuFe₂O₄). The Cu dopant level in p-Fe₂O₃ was found to be 0.20% from X-ray photoelectron spectroscopic (XPS) data.

Ingler et al (2004) synthesized nanocrystalline zinc doped p-Fe₂O₃ films by spraying solution of iron(III) chloride hexahydrate, FeCl₃·6H₂O with varying doping concentration of (0.0077 to 0.011M) zinc nitrate hexahydrate, Zn(NO₃)₂·6H₂O in 100% ethanol on Indium doped conducting tin coated glass substrate (ITO) for its use in photoelectrochemical water splitting. The highest
A photocurrent density of 1.1mA/cm² was reported for the 0.11M FeCl₃.6H₂O and 0.0088M Zn(NO₃)₂.6H₂O solution in 0.5M H₂SO₄ electrolyte solution. The zinc-doped p-Fe₂O₃ showed a maximum quantum efficiency of 21.1% at 325 nm and the threshold was observed at 590 nm corresponding to a band gap of 2.1 eV. Mott-Schottky data showed a flatband potential of 0.0 V (vs SCE) at an ac frequency of 2500 Hz and acceptor density of 4.4 x 10¹⁸ cm⁻³. X-ray photoelectron spectroscopy (XPS) and X-ray diffraction (XRD) measurements indicated that spray pyrolytically synthesized p-Fe₂O₃ has mixed structures of α-iron-(III) oxide and zinc(II)iron(III) oxide (ZnFe₂O₄). The presence of which has shown improved magnetic and conductive properties.

Ismail et al (2005) prepared binary and ternary mixed oxide of Y/Fe/Ti with homogeneous distribution of yttrium and iron oxides into TiO₂ by sol–gel method using metal alkoxide precursors in presence of acid–base catalysts. The structural features of Y₂O₃/Fe₂O₃/TiO₂ mixed oxide fired at 550°C were investigated by XRD, FT-IR, SEM, AFM, XPS and surface area measurements. XRD data did not show any presence of Fe₂O₃ particles in the mixed oxide system which confirm that Fe³⁺ enters the TiO₂ lattice substitutionally. FT-IR showed that the absorption of both Y₂O₃ and Fe₂O₃-doped TiO₂ was similar to pure TiO₂. This indirectly indicated the dissolution of Y₂O₃ and Fe₂O₃ into the TiO₂ lattices. A preliminary investigation of photocatalytic activity of mixed oxide on EDTA photo-oxidation showed that Y/Fe/Ti was more photoactive than pure TiO₂.

Kale et al (2008) designed working photoelectrode, ITO/TiO₂/In₂S₃/CdSe in addition to separate ITO/TiO₂/In₂S₃, ITO/In₂S₃/CdSe photoelectrodes for the comparison in their PEC performance. The role of every layer of descending band gap energy on the performance of photoelectrochemical cells was also demonstrated. It was observed that absorption edge of TiO₂ shifts towards longer wavelength side with addition of In₂S₃ and CdSe films, respectively. The conversion efficiency for the TiO₂/In₂S₃/CdSe multi-band gap system is 0.13% and fill factor is 36%. Efficiency of In₂S₃/CdSe without TiO₂ was 0.10% with fill factor of 19% and photo-conversion efficiency for TiO₂/In₂S₃ electrode was only 0.07%.
Kale et al (2009) used complete wet chemistry to grow amorphous electrodes of multiple band gap energies in the form of layered structures. Electrode composed three successive descending band gap energies highlighted good absorbance in the span of visible range and therefore, better photoconversion efficiency performance than the bilayers. Using wet chemistry, electrode of multiple band gap energy starting from wide titanium dioxide (TiO$_2$) to narrow range cadmium selenide (CdSe) was synthesized. Complete utilization of solar spectrum by initializing the film of wide band gap energy (absorbs high energy photons) permitting to narrow band gap films (absorbs low energy photons), was explored in the manuscript. The role of every layer of descending band gap energy on the performance of photoelectrochemical cells was demonstrated. The three layered electrode exhibited a good absorbance followed by photoresponse as compared to the bilayers.

Kanga et al (2003) obtained nanometer particles of two Fe$_x$O/TiO$_2$'s with high photocatalytic activities through hydrothermal treatment and impregnation method. XRD results did not show the peaks assigned to the Fe components for example (Fe$_2$O$_3$, Fe$_3$O$_4$, FeO$_3$, and Fe metal) on the external surface of the anatase structure in the Fe$_x$O/TiO$_2$ attained through hydrothermal treatment but showed good incorporation of Fe into the TiO$_2$ anatase structure with particle size below 50 nm after synthesis at 200 °C for 4 h in isopropyl alcohol without any treatment. The FeO$_3$ component on the external surface of the TiO$_2$ anatase structure was identified in the Fe-loaded TiO$_2$ prepared through the impregnation method. FT-IR spectroscopy and DSC analysis confirmed the Fe$_x$O/TiO$_2$ particle attained through the hydrothermal treatment had higher hydrophilic property than the other catalysts. It has been reported that Fe$_x$O/TiO$_2$ synthesized through hydrothermal treatment showed slightly higher conversion of CHCl$_3$ than Fe-loaded TiO$_2$ particle prepared through the impregnation method.

Kay et al (2006) deposited thin film of silicon doped Fe$_2$O$_3$ on conducting SnO$_2$-coated glass at 415°C using Fe(CO)$_5$ and TEOS (tetraethoxysilane) by APCVD (atmospheric chemical vapor deposition method) method. Single crystalline iron oxide electrode reported a best photocurrent of 2.2mA/cm$^2$ at 1.23 V$_{RHE}$ and IPCE (incident photon to current conversion efficiency) of 42% at
370 nm in 1.5 global AM sunlight of 1000 W/m² under illumination in 1 M NaOH. HRSEM data revealed a highly developed dendritic nanostructure of 500 nm thickness with a feature size of only 10-20 nm at the surface. A small gain in the efficiency was reported with the deposition of a thin insulating SiO₂ layer between the substrate and the film and with deposition of monolayer of catalytic cobalt on the iron oxide film. A mechanistic model involving stepwise accumulation of four holes by two vicinal iron or cobalt surface sites was also discussed to explain the photooxidation of water.

Khaselev et al (2001) investigated on a monolithic, multijunction integrated PV/electrolysis configuration and demonstrated a 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 a-Si(Pt)=KOH} electrolyte photovoltaic-electrolysis cells. For a-Si system and GaAs/GaInP₂ system a solar-to-hydrogen conversion efficiency of 7.8% and 16% was demonstrated.

Khedr et al (2007) investigated the solid–solid interactions between nanosized pure and NiO substituted ferric and titanium (IV) oxides using XRD technique and microstructure studies, also magnetic properties were studied using vibrating samples magnetometer (VSM). The substituted amounts of Ni²⁺ taken for investigation was x = 0, 0.2, 0.4, 0.6, 0.8 and 1 mole. A mixture of equimolar proportions of finely powdered Fe₂O₃ and TiO₂ was mixed with NiO, ball milled, compressed at 250 kg/cm² and fired at 1200°C for 4 h. The addition of NiO with x = 0, 0.2, 0.4, 0.6, 0.8 and 1 mole led to the formation of new phases of nanosized NiTiO₃ and NiFe₂O₄, while by the increase of Ni²⁺ up to 0.6, the extent of NiTiO₃ increased then decreased to zero at x = 0.8, on the other hand the extent of NiFe₂O₄ increases and Fe₂TiO₅ decreased by increasing amount of Ni²⁺ substitution. All these nanosized samples exhibited a catalytic activity towards H₂O₂ decomposition and the values of rate constant showed an increase with increasing amount of Ni²⁺ substitution, the most acidic active sites were exhibited by
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specimens substituted with x = 0, concluding that H₂O₂ decomposition was not favored on acidic active sites.

**Kuang et al (2009)** prepared the anodic TiO₂ nanotube (NT) arrays modified by Fe₂O₃ with high sensibility in the visible spectrum using sequential chemical bath deposition (S-CBD). The titania NTs modified by Fe₂O₃ showed higher photopotential and photocurrent values than those of unmodified titania NTs. The enhanced photoelectrochemical behaviors was attributed to the modified Fe₂O₃ which increased the probability of charge–carrier separation and extends the range of the TiO₂ photoresponse from ultraviolet (UV) to visible region due to the low band gap of 2.2 eV of Fe₂O₃.

**Kumar et al (2011)** studied nanostructured undoped and zirconium doped hematite thin films synthesized using electrodeposition method for their implementation as photoanode in photoelectrochemical (PEC) cell for hydrogen generation. XRD, Raman, XPS, SEM and UV-visible spectroscopy techniques were used to characterize the thin films. Highest photocurrent density of 2.1 mA/cm² at 0.6 V/SCE was observed for 2.0 at.% Zr⁴⁺ doped α-Fe₂O₃ sample with solar to hydrogen conversion efficiency of 1.43%. Flatband potential (-0.74 V/SCE) and donor density (2.6×10²¹ cm⁻³) were found to be maximum for the same sample. These results suggest substantial potential of hematite thin films with controlled doping of zirconium in PEC water splitting applications.

**Kumari et al (2006)** reported PEC response of Zn doped Fe₂O₃ thin films prepared by spray pyrolysis method. Photocurrent density was found to depend upon the doping concentration of Zn. Maximum photocurrent density of ~0.64 mA cm⁻² at an applied potential of 0.7 V/SCE was observed for 5.0 at% doping concentration. All the samples of doped/undoped α-Fe₂O₃ were characterized for phase formation, particle size, nature of charge carrier, bandgap, resistivity and carrier density. The flatband potential of ~0.78V/SCE and depletion layer width of 28.7 Å were calculated from the Mott–Schottky plot for 5.0 at% doping concentration.

**Kumar et al (2012)** reported the PEC response of 100 MeV Si⁵⁺ ion irradiated hematite thin film, synthesized by electrodeposition method. The grain size, surface morphology, optical absorption edge, capacitance measurements and
photoelectrochemical response of these films were studied and analyzed before and after exposure to irradiation. Irradiated samples exhibited significantly better photoelectrochemical response than the unirradiated \( \alpha-Fe_2O_3 \) sample. Photocurrent density was observed to increase at lower ion fluence and the film irradiated at a fluence of \( 5 \times 10^{12} \) ions/cm\(^2\) exhibited maximum photocurrent density. Crystallinity of the films and particle size were also observed to increase after irradiation up to this fluence. The irradiation caused a decrease in the resistivity, increase in donor density and increase in flatband potential for the sample irradiated at this fluence which may be responsible for its better photoelectrochemical properties.

Kumari et al (2010) reported the PEC response of nanoporous hematite \( (\alpha-Fe_2O_3) \) thin films doped with \( Ti^{4+} \) deposited by spray-pyrolysis. X-ray diffraction, field emission scanning electron microscopy, UV–visible absorption and photoelectrochemical studies were performed on the undoped and \( Ti^{4+} \) doped hematite thin films. Morphology of \( \alpha-Fe_2O_3 \) thin films was observed to be nanoporous, with increased porosity (pore size \( \sim \)12 to 20 nm) on increasing doping concentration. A significant decrease in the bandgap energy from 1.95 to 1.27 eV was found due to doping. \( \alpha-Fe_2O_3 \) film doped with 0.02 M \( Ti^{4+} \) ions exhibited best solar to hydrogen conversion efficiency (photoconversion efficiency) of 1.38% at 0.5 V/SCE.

Li and Zhang (2010) in this review article provided brief overview of some recent research activities in the area of hydrogen generation from PEC water splitting based on nanostructured semiconductor materials, with a particular emphasis on metal oxides. Both scientific and technical issues have been critically analyzed and reviewed.

Lin et al (2008) evaluated degradation performance of 4-chlorophenol (4-CP) using \( TiO_2/WO_3 \) and \( TiO_2/SnO_2 \) systems and characterized using BET surface area analyzer, UV–vis spectroscopy, SEM, XRD and electron spectroscopy for chemical analysis (ESCA). It was found that band edge wavelength increased to 475 nm and \( Eg \) decreased to 2.61 eV in \( TiO_2/WO_3 \) system as compared to the single \( TiO_2 \). 4-CP degradation efficiency increased as compared to single \( TiO_2 \) or \( WO_3 \). The
TiO$_2$/WO$_3$ degradation of 4-CP at 369 nm was inhibited. The degradation efficiency of TiO$_2$/SnO$_2$ also suffered at 369 nm, and only slightly increased at 435 nm as compared to single TiO$_2$ or SnO$_2$ system.

Lin et al (1989) reported a one-step method to split water into hydrogen and oxygen by using a triple stack amorphous silicon solar cell with an n-i-p-n-i-p-n-i-p structure. The photoconversion efficiency of 5% was reported under simulated 1 AM, 100mW/cm$^2$ solar radiation using this arrangement. A single unit electrolyzer system with multistacks of amorphous silicon p-i-n cells was used to evolve hydrogen fuel. The hydrogen gas was produced at the platinum/ n-a-Si and oxygen at the ruthenium oxide side of the cell under the simulated AM 1 solar radiation, respectively.

Lindgren et al (2003) prepared nanocrystalline porous nitrogen doped TiO$_2$ thin films by DC magnetron sputtering; films were deposited in plasma of argon, oxygen and nitrogen with varying nitrogen contents. All nitrogen doped films showed visible light absorption in the wavelength range from 400 to 535 nm. The nitrogen doped TiO$_2$ generated an incident photon to current efficiency response in good agreement with the optical spectra. For the best nitrogen doped TiO$_2$ electrode, the photo induced current due to the visible light and at moderate bias was increased around 200 times compared to the behavior of pure TiO$_2$ electrodes.

Liu and Kamat (1993) investigated the photoelectrochemical effects at CdSe thin film electrodes (thickness 30- 200 Å) synthesized by electrochemical and chemical deposition methods, monitoring open- circuit voltage and short-circuit current at varying film thickness and incident light intensities. By coupling CdSe thin film with a TiO$_2$ particulate film, it was possible to inject photogenerated electrons into the conduction band of TiO$_2$ and thus retard the charge recombination within the CdSe film and hence, improving the photocurrent stability of thin semiconductor films.

Liu et al (2004) fabricated Mercurochrome-sensitized composite TiO$_2$/SnO$_2$ and ZnO/SnO$_2$ photoelectrochemical cells (DSC) from the mixture of the SnO$_2$ particles and the semiconductor colloid (TiO$_2$, ZnO) and studied the influence of the mixed ratios on the performance of the composite semiconductor photoelectrochemical
cells. By comparing the composite TiO$_2$/SnO$_2$ and ZnO/SnO$_2$ cells with the corresponding TiO$_2$ and ZnO cells, a great improvement in the incident photon to current conversion efficiency of the composite cells was reported. Reported value of the efficiencies for these cells of TiO$_2$, TiO$_2$/SnO$_2$, ZnO/SnO$_2$ and ZnO were 5.00%, 4.73%, 4.64% and 3.96% respectively, which were comparable to those of the TiO$_2$ cell. It was concluded that the composites of TiO$_2$/SnO$_2$ and ZnO/SnO$_2$ improved the separation of the photogenerated electrons and the holes in the mercurochrome-sensitized semiconductor photoelectrochemical cells. Hence, the composite of the semiconductors with different band gap proved itself to be an efficient method to improve the separation of the photogenerated electrons and the holes in the dye-sensitized solar cell.

Luo et al (2007) prepared n-type semiconductor thin films of WO$_3$, Fe$_2$O$_3$ and the composite structure of WO$_3$/Fe$_2$O$_3$ on FTO by sol-gel method and their structures and optical properties were characterized by XRD, SEM and UV–Vis spectrometry. The results showed that PCD of WO$_3$/Fe$_2$O$_3$ heterojunction is $6\mu$Acm$^{-2}$, greater than that of the Fe$_2$O$_3$ film ($2.5\mu$Acm$^{-2}$), suggesting that IPCE of Fe$_2$O$_3$ (<1%) covered with WO$_3$ is significantly improved (2.5-3.2%), particularly at 398 nm even though no photocurrent is generated in WO$_3$ film. Therefore, the interface between WO$_3$ and Fe$_2$O$_3$ played an important role in improving the conversion efficiency.

Miller et al (2003) designed triple-junction amorphous silicon (a-Si) solar cells demonstrating photovoltaic (PV) efficiencies up to 12.7% and open-circuit voltages up to 2.3 V by depositing it onto stainless-steel foil substrates for photoelectrochemical (PEC) tests. In order to achieve high efficiency in multijunction amorphous silicon devices, careful current matching in each of the junctions was done by adjustment of the absorption spectra through bandgap tailoring. Thus, the top n-i-p junction on a-Si triple-junction cell was designed to absorb most strongly in the 350–500 nm range. This photoelectrode was fabricated on SS with the back surface catalyzed for the hydrogen evolution reaction, and the front surface deposited with a-Si:nip nip/ITO/SC structure. Possible candidate for
SC materials include dye-sensitized titanium dioxide (TiO₂), tungsten trioxide (WO₃), and iron oxide (Fe₂O₃).

Miller et al (2004) developed a multijunction photoelectrode using an Fe₂O₃/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 Fe₂O₃ front surface, respectively. From the initial test results for dark and AM1.5 illuminated performance, a 0.6–0.65 V bias savings in the light were observed, consistent with the incorporated single-junction solid-state device.

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 films and tungsten-trioxide films prepared by eight and nine reactive runs of sputtering at 10m Torr pressure to minimal thickness of 10kÅ⁰ and 20kÅ⁰ reported a photocurrent of 0.1mA/cm² and in the range of mA/cm² respectively in 1N KOH and 1N H₃PO₄ solution. A small increase in the photocurrent with initially Mo doped sputter deposited tungsten-trioxide films was also reported. The photocurrent of 0.45mA/cm² in 1N H₃PO₄ and stable operation at 0.7% STH (solar to hydrogen) for over 10h in acid media under 1 sun condition was reported for hybrid prototype photoelectrode with an active area of 2.5cm².

Mishra et al (2003) studied the photoelectrochemical response of nanostructured-TiO₂ photoelectrode for five different electrode areas (0.21, 0.50, 0.72, 1.47 and 1.85 cm²) prepared by hydrolysis of titanium tetraisopropoxide Ti[OCH(CH₃)₂]₄ followed by the deposition with spin on technique. The effect of electrode area on the output power in a chemical fuel (i.e., H₂) producing PEC cell was studied and
optimum electrical output and hydrogen production rate was obtained for electrode having an area $\sim 0.5\text{cm}^2$.

**Miyake and Kozuka (2005)** prepared Fe$_2$O$_3$-Nb$_2$O$_5$ coated films of various Nb/(Fe + Nb) mole ratios on nesa silica glass substrates from Fe(NO$_3$)$_3$.9H$_2$O - NbCl$_5$ - CH$_3$(CH$_2$)$_2$CH$_2$OH - CH$_3$COOH solutions by the sol-gel method. The photoanodic properties were studied in a three-electrode cell arrangement with an aqueous buffer solution of pH 7, an aqueous solution of 0.2M Na$_2$B$_4$O$_7$, 0.14 M H$_2$SO$_4$, and 0.3 M Na$_2$SO$_4$, as the supporting electrolyte. A change in the crystalline phases was observed from $\alpha$-Fe$_2$O$_3$ to $\alpha$-Fe$_2$O$_3$ + FeNbO$_4$ when the Nb/(Fe + Nb) mole ratio increased from 0 to 0.25 and an increase in the photoanodic current under white light and monochromatized light illumination was reported for both visible and ultraviolet regions. When the Nb/(Fe + Nb) ratio increased over 0.25, the crystalline phases changed to FeNbO$_4$, FeNbO$_4$ + Nb$_2$O$_5$, or Nb$_2$O$_5$, and the photoanodic current decreased. For the sample consisting of $\alpha$-Fe$_2$O$_3$ and FeNbO$_4$ (Nb/(Fe + Nb) = 0.25) photoresponse extending to 600 nm and an IPCE of 18% at a wavelength of 325 nm was found.

**Mohapatra et al (2007)** synthesized hematite ($\alpha$-Fe$_2$O$_3$) nanostructures on a titania (TiO$_2$) nanotubular template made by pulsed electrodeposition technique. The TiO$_2$ nanotubes were prepared by the sonoelectrochemical anodization method and were filled with iron (Fe) by pulsed electrodeposition. The Fe/TiO$_2$ composite was then annealed in an O$_2$ atmosphere to convert it to Fe$_2$O$_3$/TiO$_2$ nanorod–nanotube arrays. The length of the Fe$_2$O$_3$ inside the TiO$_2$ nanotubes was be tuned from 50 to 550 nm by changing the deposition time. The present approach was good to design variable one-dimensional metal oxide heterostructures.

**Mor et al (2007)** showed high-efficiency visible spectrum water photoelectrolysis using self-aligned, vertically oriented Ti-Fe-O nanotube array films. Ti-Fe metal films of variable composition, iron content ranging from 69% to 3.5%, co-sputtered onto FTO-coated glass were anodized in an ethylene glycol + NH$_4$F electrolyte. The resulting amorphous samples were annealed in oxygen at 500 °C, resulting in nanotubes composed of a mixed Ti-Fe-O oxide. Some of the iron goes into the titanium lattice substituting titanium ions, and the rest either forms gama-Fe$_2$O$_3$.
crystallites or remains in the amorphous state. Depending upon the Fe content, the band gap of the resulting films ranged from about 380 to 570 nm. The Ti-Fe oxide nanotube array films were utilized in solar spectrum water photoelectrolysis, demonstrating 2 mA/cm² under AM 1.5 illuminations with a sustained, time-energy normalized hydrogen evolution rate by water splitting of 7.1 mL/W.hr in a 1 M KOH solution with a platinum counter electrode under an applied bias of 0.7 V.

Mora et al (2007) studied the Morphological, optical and photocatalytic properties of TiO₂, Fe₂O₃ and TiO₂-Fe₂O₃ samples deposited on glass substrate by the sol-gel/immersion method. UV visible absorption spectra showed the absorption edge for TiO₂, Fe₂O₃ and TiO₂-Fe₂O₃ samples in the 350-300 nm, 600-450 nm and 450-350 nm range respectively. Photocatalytic activities of the samples were studied by the photodecomposition of methylene blue (MB) under visible light illumination. It was reported that photocatalytic activity of the samples increased with increase in number of coatings. The Fe₂O₃ was reported as more photoactive than the TiO₂ catalyst and the explanation of the reaction mechanism using Fenton reaction was made in which the Fe³⁺ and the FeOH²⁺ played an important role.

Osaka et al (1985) studied iron oxide/n-Si heterojunction electrode as a photoanode in photoelectrochemical cell. The influence of the top layer modification of the electrode with Pd or RuO₂ was also investigated. The efficiencies of PEC cell were found to be 1.34% and 1.60% for a Pd-and a RuO₂-modified electrode, respectively in 0.2 M KOH solution containing 0.2 M K₄[Fe(CN)₆] and 0.01 M K₃[Fe(CN)₆] at a xenon lamp intensity of 55 mW cm⁻². It was found that the use of iron oxide made the photoanode highly stable, as compared to an electrode such as RuO₂/n-Si. The addition of Pd or RuO₂ on the heterojunction electrode surface enhanced the optical-to-electrical conversion efficiency.

Pal et al (1999) prepared binary mixed oxide of Fe/Ti (1:1 composition) with homogeneous distribution of iron into the TiO₂ by sol-gel impregnation using metal alkoxide precursors. The characterization results indicated the formation of rutile and pseudobrookite phase (Fe₂TiO₅) at higher firing temperatures (700 and 900°C) and mixture of anatase and rutile phase at low sintering temperature (500°C).
to the presence of increasing amount of inactive \((\text{Fe}_2\text{TiO}_3)\) pseudobrookite phase, Photocatalytic activity of Fe/Ti oxide reduced to large extent at high sintering temperature of the sample. The sample sintered at 500°C showed highest activity for the degradation of aqueous solution of O-Cresol.

**Papp et al (1994)** prepared \(\text{WO}_3/\text{TiO}_2\) mixed powders and \(\text{MoO}_3/\text{TiO}_2\) mixed oxide powders prepared by an impregnation technique. The reproducibility of the sample was reported as the 0.001mm/g. XRD data revealed the presence of 70% anatase and 30% rutile phase with average particle size of 17 nm and 25 nm for these two phases respectively. It was observed that addition of \(\text{WO}_3\) or \(\text{MoO}_3\) to \(\text{TiO}_2\) greatly enhanced its photocatalytic properties. The maximum photocatalytic activity and surface acidity was reported for 3 and 2.5% mol % concentration of the \(\text{WO}_3\) and \(\text{MoO}_3\) samples. Beyond these concentrations, the surface acidity remains almost constant and a decrease in the photoactivity was observed.

**Prakasam et al (2006)** presented for the first time the fabrication of the self-organized nanoporous iron (III) oxide (hematite) via potentiostatic anodization of iron foil. Depending upon the anodization conditions and electrolytic composition i.e the potential and bath chemistry, the pore diameters range from 50 to 250 nm and 300-600 nm in length with a pore depth of approximately 500 nm. The initial effects of electrolytic composition, anodization bath temperature and applied potential on the dimensions of the as-synthesized nanoporous structure were examined. Crystallization and structural retention of the synthesized structure was achieved upon annealing the initial amorphous sample in a nitrogen atmosphere at 400°C. The crystallized nanoporous film, having a 2.2 eV bandgap, reported a net photocurrent density of 0.51 mA cm\(^{-2}\) in 0.5 M H\(_2\)O\(_2\) +1M NaOH at 0.6 V versus Ag/AgCl under simulated AM 1.5 global sunlight.

**Sartoretti et al (2003)** reported deposition of thin film \(\text{Fe}_2\text{O}_3\) photoanodes onto conducting glass substrates by the spray pyrolysis of ferric chloride and ferric acetylacetonate precursors, with view to their application in a tandem PEC cell for the light-induced splitting of water. The effects of the employed precursor compounds, dopants Ti(IV) and Al(III)) and preparation conditions upon photoelectrochemical characteristics of the films were discussed. Electrodes of with 5% titanium and up to 1% aluminium doping were found to afford higher
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photocurrents in 0.1M NaOH, recorded at 0.45V vs. NHE with IPCE of 3.7% than undoped electrodes.

Sartoretti et al (2005) fabricated thin-film Fe₂O₃ photoanodes on conducting glass substrate (FTO) by spray pyrolysis using ferric chloride and ferric acetyl acetonate solutions for photoelectrolysis of water. It was reported that addition of dopants increased the photocurrent by increasing the photoconductivity. SEM analysis shown the average particle size of 450 nm and 380 nm for (5% Ti) and (5% Ti and 5% Al) doped samples. The largest photocurrent of 4.38mA/cm² at 0.45V vs. NHE was reported for a nine layers of iron oxide sample in 0.1M NaOH solution. The photoelectrode doped with (4% Zn²⁺ along with 5% Ti) showed a clear shift by 0.22V of the onset potential and a steeper increase in the photocurrent with applied voltage.

Satsangi et al (2006) presented the PEC study on spray pyrolytically synthesized Zn-doped α-Fe₂O₃ thin films prepared by spraying 0.15 M precursor solution prepared by dissolving Fe(NO3)3.9H2O with various doping concentrations (0.5, 1.0, 1.5, 5.0 and 10.0 at%) of Zn(NO3)2.6H2O in double-distilled water deposited onto conducting FTO substrate. The current-voltage characteristics at the junction indicated the n-type behavior of Zn doped samples in 13pH NaOH. Photocurrent density was found to depend upon the doping concentration of Zn. Maximum photocurrent density of ~ 0.64 mAcm⁻² at an applied potential of 0.7 V/SCE was observed for 5.0 at% doping concentration of Zn. The flatband potential of −0.78V/SCE and depletion layer width of 28.7 Å were calculated from the Mott–Schottky plot for 5.0 at% doping concentration.

Satsangi et al (2008) summarized and compared the photoelectrochemical response of nanostructured thin films/pellets of Fe₂O₃ prepared and modified by various dopants and techniques. It was reported that thin films prepared by spray pyrolysis having particle size of 20–30 nm exhibited better photoresponse as compared to the films prepared by sol–gel methods; further improvement on doping with Zn was also found. The photoelectrochemical response of various nanostructured hematite films/pellets indicated that 5.0 at% Zn doped hematite film prepared by spray pyrolysis offered the best photocurrent of 422.6 μA/cm² at 0.6V/SCE in comparison to films prepared by other methods and dopants. These films were further modified
by depositing Zn dots on the surface of $\alpha$-Fe$_2$O$_3$ films using thermal evaporation method and irradiating it with 170 MeV Au$^{13+}$ ions. A significant increase in photoresponse of these modified films was observed when used as electrode in PEC cell. The enhanced photoresponse of the thin films was attributed to the surface modifications. The investigation highlighted the advantage of Zn-dotted islands on the surface of hematite electrode as compared to Zn doping. The photocurrent density was observed to increase by a factor of 20 with Zn-dotted Fe$_2$O$_3$, in comparison to undoped samples.

Shaban and Khan (2011) reported photoresponse of visible light active carbon modified titanium oxide (CM-n-TiO$_2$), hydrogen modified titanium oxide (HM-n-TiO$_2$), carbon modified iron oxide (CM-n-Fe$_2$O$_3$), carbon modified tungsten oxide (CM-p-WO$_3$) towards water splitting reaction. Carbon and hydrogen in titanium oxide were found to be responsible for red shift from UV region to visible region which in turn enhanced the photoconversion efficiency by an order of magnitude for water splitting reaction. Photocurrent densities and photoconversion efficiencies of regular n-TiO$_2$ and CM-n-TiO$_2$ towards water splitting reaction under monochromatic light illumination from a xenon lamp and sunlight were compared and found in reasonable agreement.

Sharma et al (2010) modified nanostructured thin film of Zn-Fe$_2$O$_3$ with underlying layer of Fe-TiO$_2$ and studied as photoelectrode in photoelectrochemical (PEC) cell for generation of hydrogen through water splitting. The Zn-Fe$_2$O$_3$ thin film photoelectrodes were designed for best performance by tailoring thickness of the Fe-TiO$_2$ film. A maximum photocurrent density of 748 mA/cm$^2$ at 0.95 V/SCE and solar to hydrogen conversion efficiency of 0.47% was observed for 0.89 µm thick modified photoelectrode in 1 M NaOH as electrolyte and under 1.5 AM solar simulator. To analyze the PEC results the films were characterized for various physical and semiconducting properties using XRD, SEM, EDX and UV-Visible spectrophotometer. Zn-Fe$_2$O$_3$ thin films modified with Fe-TiO$_2$ exhibited improved visible light absorption. A noticeable change in surface morphology of the modified Zn-Fe$_2$O$_3$ film was observed as compared to the pristine Zn-Fe$_2$O$_3$ film.
Flatband potential values calculated from Mott-Schottky curves also supported the PEC response.

Sharma et al (2012) developed a visible-light sensitive bilayered photoanode of Fe–TiO$_2$/Zn–Fe$_2$O$_3$ by spray pyrolytically depositing Zn–Fe$_2$O$_3$ layers onto predeposited Fe–TiO$_2$ thin film on ITO substrate. Fe–TiO$_2$/Zn–Fe$_2$O$_3$ photoelectrodes were characterized by XRD, Raman, AFM, UV-vis absorption spectroscopy. Photoelectrochemical properties of bilayered Fe–TiO$_2$/Zn–Fe$_2$O$_3$ photoelectrode were studied by Mott–Schottky curves and I–V characteristics. Bilayered Fe–TiO$_2$/Zn–Fe$_2$O$_3$ photoelectrode was observed to possess much higher separation efficiency of photogenerated charge carriers and could generate nine times better photocurrent density than pure Fe TiO$_2$. Solar to hydrogen conversion efficiency exhibited by this electrode was 0.77%.

Shiyanovskaya and Hepel (1999) analyzed the photogeneration capability of the bicomponent WO$_3$/TiO$_2$ films prepared by the thermal vacuum evaporation method. XRD revealed the presence of anatase phase with a small quantity of rutile phase, which was beneficial toward high photocurrent generation in comparison to the rutile phase. The electron injection into the bulk of WO$_3$ matrix layer decreased the probability of surface recombination and thus providing a high open area of the matrix layer accommodating the considerable number of TiO$_2$ particles even when employing a very thin layer of TiO$_2$ particles even (ca. 50nm).

Singh et al (2009) irradiated hematite (α-Fe$_2$O$_3$) thin films deposited on a conducting glass substrate with 120MeV Ag$^{9+}$ ions. Their structural evolution was determined by x-ray diffraction and Raman spectroscopy. The irradiation of the samples of α-Fe$_2$O$_3$ was found to be effective in improving its photoelectrochemical response. The film irradiated at a fluence of 1×10$^{13}$ ions cm$^{-2}$ showed a significantly higher photocurrent density than the unirradiated α-Fe$_2$O$_3$. This effect was correlated with the transition from the α-Fe$_2$O$_3$ to the Fe$_3$O$_4$ phase and the reduction in grain size that were observed on irradiation with Ag$^{9+}$ ions. The measured flatband potential and donor density of the sample were also maximum at a fluence of 1×10$^{13}$ ions cm$^{-2}$.
Singh et al (2008) synthesized nanocrystalline nitrogen doped TiO$_2$ by hydrolysis of titanium tetra isopropoxide using an ammonia solution by wet chemical method. Maximum photocurrent density of 2.06 mA/cm$^2$, was obtained for TiO$_2$ prepared with 15% NH$_3$, at an applied potential of 0.15 V/SCE. TiO$_2$ with 2.42eV bandgap exhibited the best photocurrent density in the PEC cell. The XRD results showed the presence of pure anatase phase, the crystallinity of which was found to increase upon increasing the concentration of ammonia solution. The bandgap energy of TiO$_2$ changed from 2.81 to 2.10 eV on increasing the concentration of ammonia from 15 to 25%, showing ammonia was used for bandgap tailoring of TiO$_2$. Thus, it was observed that reduction in the bandgap only up to a certain extent of TiO$_2$ doping leads to an efficient PEC system.

Sivula et al (2011) wrote a review article on use of hematite in PEC splitting of water for hydrogen generation. This review is based on the new insights into the basic material properties, the attractive aspects, and the challenges in using hematite for photoelectrochemical (PEC) water splitting are first examined. Next, recent progress enhancing the photocurrent by precise morphology control and reducing the overpotential with surface treatments are critically detailed and compared. The latest efforts using advanced characterization techniques, particularly electrochemical impedance spectroscopy, have also been presented. These methods help to define the obstacles that remain to be surmounted in order to fully exploit the potential of this promising material for solar energy conversion.

Solanki et al (2011) studied the effect of 120 MeV Ag$^{9+}$ ion irradiation on photoelectrochemical properties of SrTiO$_3$ thin films deposited on Indium doped tin oxide (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 3×10$^{12}$ ionscm$^{-2}$, when used in PEC cell exhibited enhanced photocurrent of 0.16 mA cm$^{-2}$ at zero bias conditions, which was four times higher than that of the unirradiated sample.
Song et al (2001) observed that on covering the surface of TiO₂ nanoparticles with highly acidic semiconductors, such as MoO₃ and WO₃, the stability of colloidal suspensions in aqueous solution can be greatly improved. It was attributed to the fact that on modifying the surface with MoO₃ or WO₃ the TiO₂ nanoparticles become much more hydrophilic and can be more stably suspended in aqueous solution. The photocatalytic activity of WO₃/TiO₂ film was 2.8-3 times that of pure TiO₂ film in decomposition of gas-phase 2-propanol, while MoO₃/TiO₂ film was less effective.

Su et al (2011) reported photoelectrochemical water splitting using a novel heterojunction WO₃/BiVO₄ photoanode. The heterojunction films are prepared by solvothermal deposition of a WO₃ nanorod-array film onto fluorine-doped tin oxide (FTO) coated glass, with subsequent deposition of a low bandgap, 2.4 eV, visible light responding BiVO₄ layer by spincoating. The heterojunction structure offered enhanced photoconversion efficiency and increased photocorrosion stability. Compared to planar WO₃/BiVO₄ heterojunction films, the nanorod-array films showed significantly improved photoelectrochemical properties due to the high surface area and improved separation of the photogenerated charge at the WO₃/BiVO₄ interface.

Tan et al (2009) studied the synthesis of FeTi intermetallics from mixed oxide precursors using the method of electro-deoxidation. Fe₂O₃ and TiO₂ mixed in molar proportions of 1:2 were sintered at temperatures ranging from 900 °C to 1300°C. The sintered pellet of mixed oxides, connected as cathode, was then electrolyzed in a molten CaCl₂ at 900 °C using a graphite anode at a potential of 3.2 V. The electrolysis yielded the target composition FeTi in substantial amounts only when the sintering temperature was close to or above 1100 °C. The process of deoxidation was followed with the use of interrupted experiments. This was shown that the two-phase structure of Fe₂TiO₅ and TiO₂ in the oxide pellet reacts with the molten salt even before the electrolysis forming CaTiO₃, transforming the rest into a mixture of ilmenite (FeTiO₃) and a spinel phase (Fe₂TiO₄).

Tomaszewski et al (2007) studied the effect of sodium content of the glass support on the crystallinity of sputtered TiO₂ films and also photocatalytic breakdown of
ethanol has been done. It was found that the activity of the as-deposited (amorphous) films does not depend on the type of support used. The chemical composition of the glass support does influence the activity of annealed films. It was found that on using soda-lime glass support, sodium diffuses into the film upon annealing, suppressing anatase crystallization and decreasing its photocatalytic activity. To decrease the influence of sodium, soda-lime glass coated with an e-beam evaporated SiO$_2$ barrier layer was used with good result. A reduced sodium concentration in the film leads to well crystallized anatase after annealing.

Wang et al (2007) prepared semiconductor films of SrTiO$_3$, $\alpha$-Fe$_2$O$_3$ and their heterojunction SrTiO$_3$/\$\alpha$-Fe$_2$O$_3$ FTO by spin-coating method and their structures and properties were characterized by XRD, SEM and photoelectrochemical measurements. It was observed that the photocurrent and the IPCE or external quantum efficiencies of the SrTiO$_3$/\$\alpha$-Fe$_2$O$_3$ heterojunction were higher than that of the single SrTiO$_3$ or $\alpha$-Fe$_2$O$_3$ film, particularly under visible light irradiation.

Yang et al (2000) prepared TiO$_2$ photocatalysts loaded with noble metal or transition-metal oxide and studied the influences of preparing procedures on the photocatalytic activity toward degradation of formaldehyde. The experiments showed that Pt/Fe$_2$O$_3$/TiO$_2$ exhibited an applicable photoactivity with the photochemical conversion efficiency of 74\% in the degradation of formaldehyde. The photocatalytic oxidation of HCHO was carried out with two steps: firstly, HCHO was oxidized into HCOOH, and then converted into final product of CO$_2$.

Yin et al (2007) prepared ZnFe$_2$O$_4$/TiO$_2$ double-layered films on indium-tin oxide (ITO) substrate by a dip-coating method, and the optical absorption and photocurrent of the as-prepared films were measured. It was found that in the double-layered films, the onset of fundamental absorption edge shifted to a longer wavelength, and even shifted to a longer wavelength than that of ZnFe$_2$O$_4$-only film as the ZnFe$_2$O$_4$ layer thickness increases. Application of the coupled photoanodes double-layered films composed of ZnFe$_2$O$_4$ and TiO$_2$ was found to increase the photocurrent. It was found that the photocurrent density of ZnFe$_2$O$_4$/TiO$_2$ double-layered films first increased and then decreased with increasing the ZnFe$_2$O$_4$ layer.
thickness. A five-fold increase in the photocurrent density was obtained compared with TiO₂ only films under optimum condition.

Zhang and Lei (2007) prepared Fe₂O₃–TiO₂/ACF (activated carbon fiber) photocatalyst by metal organic chemical vapor deposition to solve simultaneously two major difficulties in the TiO₂ liquid-solid photocatalytic system: effective immobilization of the TiO₂ particles and improvement of the catalytic activity under visible light. XRD results revealed that Fe₂O₃–TiO₂ coating mainly composed of anatase TiO₂, α-Fe₂O₃ phases and little Fe₂Ti₃O₉. It was also reported that the porous structure of ACF was preserved well after loading with Fe₂O₃–TiO₂ coating. UV-VIS diffuse reflectance spectra showed a slight shift to longer wavelength and an enhancement of the absorption in the visible region for Fe₂O₃–TiO₂ coating compared to pure TiO₂ samples. The Fe₂O₃–TiO₂ samples exhibited good photocatalytic activities for the degradation of the methyl orange under visible light irradiation. The stable performance revealed that the Fe₂O₃–TiO₂ coating were strongly adhered to the ACF surface, and thus as prepared catalyst could be reused showing potential application to waste water treatment.

Zhang et al (2007) prepared TiO₂/Cu₂O composite films by electrochemical method and coated through spraying method. They investigated the effects of composite films with different ratio of TiO₂ and Cu₂O on photodegradation of methylene blue dye under visible light. It was found that photocatalytic activity of TiO₂/Cu₂O composite film in the presence of FeSO₄ and EDTA was much higher than for only TiO₂ and Cu₂O film. No degradation of methylene blue was observed in the absence of FeSO₄ and EDTA.

Zhang et al (1998) prepared heterostructured TiO₂/Fe₂O₃ composite film by spin-coating. The results of surface photovoltaic spectroscopy (SPS) and electric-field-induced surface photovoltaic spectroscopy (EFSPS) showed that the composite film had the extended photovoltaic response which can be modified by the external electric field. An energy band model was proposed to explain the achievements of efficient charge separation. When this composite film was irradiated with visible light, the characteristic photovoltaic response band of Fe₂O₃ was detected.