Photoelectrolysis of water, *i.e.*, photodecomposition of water into hydrogen and oxygen as a result of light absorption in semiconductor electrode, is seen as the most promising method of hydrogen production. The efficiency of water photolysis is prominently reported to be dependent on material properties (especially structural, optical, electrical and electronic) of the semiconductor used as photoelectrode. The bilayered heterojunction architecture apparently plays a crucial role in the performance of the semiconductor in PEC devices. In order to improve the efficiency of PEC water splitting to produce hydrogen, some factors such as band gap, electronic band edge alignment of the materials with each other and with the redox potential of water and optimization of thickness of each material at the junction are found to be crucial. Choice of proper electrolyte, film thickness, annealing temperature of the films etc. could also improve the process. Attention should therefore be focused on the optimization of the above said various experimental parameters in order to improve the performance of PEC cell. Bilayered semiconductor structures, thus, appear to be a promising direction in the development of efficient photoelectrode for PEC splitting of water.

Single layered/pristine thin films of semiconductors did not exhibit promising performance in PEC activity due to various factors such as high bandgap, poor surface charge transfer, high resistivity etc. It was also observed that bilayering of two semiconductors of varying bandgap was promising towards achieving significant photoelectrochemical activity.

Present study, thus, deals with the investigation of photoelectrochemical performance and water splitting efficiency of nanostructured bilayered thin films comprising of CuO, SrTiO₃, ZnO and WO₃. The work has been focused on fabrication of various bilayered combinations by sol-gel spin-coating technique with variation in thickness and sequence of layering, characterization (XRD, UV-Vis, SEM, EDAX, AFM) and was analyzed with respect to photoelectrochemical splitting of water. The sol-gel method, used in preparation of thin films studied, has advantages over other fabrication processes because of its simplicity, low cost, easy control over the
deposition parameters and relative simplicity to scale up. The effect of varying thickness of CuO in CuO/SrTiO$_3$, SrTiO$_3$/CuO, CuO/ZnO, ZnO/CuO and WO$_3$ in WO$_3$/SrTiO$_3$ on the phase formation, absorption energy, resistivity, open-circuit potential, flatband potential, photocurrent density and photoconversion efficiency have also been studied in detail (Chapter 5). Effect of sintering temperature on photoelectrochemical performances of various thicknesses of CuO/SrTiO$_3$ composites has been discussed. It has been observed that the combinatorial approach of using the above mentioned metal oxide photoelectrodes in PEC water splitting offers favorable effect on absorption energy, band energy positions with respect to redox levels of electrolyte, flat band potential ($V_{FB}$), open circuit potential ($V_{oc}$) and photocurrent density ($J_p$).

**Following conclusions emerge from the present study:**

- XRD analysis reveals dominant formation of cubic phase of SrTiO$_3$, hexagonal phase of ZnO, orthorhombic phase of WO$_3$ and monoclinic phase of CuO. All bilayered systems exhibited the peaks corresponding to both the semiconductors involved in their preparation.

- Mixed oxide formation was also observed in bilayered systems, viz. $[(Sr_{0.2}Cu_{0.8})Ti_{1.065}O_3]$ in CuO/SrTiO$_3$ and SrTiO$_3$/CuO; SrWO$_4$ in WO$_3$/SrTiO$_3$ and SrTiO$_3$/WO$_3$; and $[Zn(ZnTi)O_4]$ & $[Sr_2Zn_4Ti_{15}O_{36}]$ in ZnO/SrTiO$_3$ and SrTiO$_3$/ZnO. No mixed oxide phase formation was observed in CuO/ZnO and ZnO/CuO bilayered systems.

- Bandgap analysis using UV-visible studies exhibited improved absorption in the visible region in all bilayered thin films of various combinations studied in the present work.

- Cross sectional-SEM and EDAX analysis reveals both quantitative and qualitative information about both semiconducting layers present in the studied bilayered system.

Resistivity of all bilayered thin films decreased from their pristine counterparts due to increase in conductivity *i.e.* facile charge separation on account of proper band edge positioning at the semiconductor/semiconductor and semiconductor/electrolyte interface.


Maximum PEC response was observed for CuO/ZnO bilayered system *i.e.* 1.48 mA/cm$^2$ under UV-visible illumination and 2.64 mA/cm$^2$ under visible light illumination at -0.9 V/SCE. These photoelectrodes also offered the best applied bias photon-to-current efficiency (ABPE) values (*i.e.* 1.95 % at -0.9 V/SCE) calculated from their I-V curves.

Other bilayered systems *viz.* wide/mid bandgap semiconductors (WO$_3$/SrTiO$_3$) as well as wide/wide bandgap semiconductors (ZnO/SrTiO$_3$) exhibited smaller improvement in photocurrent density than that of pristine thin film samples. Intermediate value of photocurrent density has been observed for ZnO/CuO (1.67 mA/cm$^2$), CuO/SrTiO$_3$ (1.85 mA/cm$^2$) and SrTiO$_3$/CuO (1.59 mA/cm$^2$) bilayered thin films at -/+ 0.9 V/SCE under visible light illumination. Significantly enhanced photocurrent in above samples can be attributed to
better optical absorption and facile charge transfer at the interface, suggesting that these bilayered thin films can be used as efficient photoelectrode for photosplitting of water.

- The results obtained have been explained using energy band diagram of each bilayered system designed on the basis of calculated band edge positions respective to NHE and SCE scale. Flatband potential values obtained by Mott-Schottky plots were employed to examine conductivity of all bilayered thin film samples. It was observed that only CuO/ZnO and CuO/SrTiO$_3$ exhibited $p$-type conductivity while all the other bilayered systems exhibited $n$-type conductivity.

- Bilayered systems (viz. CuO/SrTiO$_3$ and CuO/ZnO) in which $p$-type semiconductor (i.e. CuO) deposited over ITO substrate and overlayered by $n$-type semiconductor (i.e. either SrTiO$_3$ or ZnO) showed cathodic photocurrent ($p$-type conductivity). On the other hand, bilayered systems in which $n$-type semiconductor is overlayered by $p$-type semiconductor (as seen in SrTiO$_3$/CuO and ZnO/CuO bilayered systems), exhibited anodic photocurrent ($n$-type conductivity). The nature of conductivity i.e. $p$- or $n$-type nature exhibited by the bilayered system depends upon the conduction and valence band edge positions of the semiconductors at the interface and direction of flow of charge carriers across the junction.

- In CuO/SrTiO$_3$ composites, intensity of all the XRD peaks increased with the sintering temperature indicating better crystallization at higher temperature. It was observed that resistivity and surface roughness of composites were affected by the variations in sintering temperature. Surface roughness was found to increase with the sintering temperature and grain agglomeration was observed in the films sintered at higher temperature (600°C) as evident from AFM and SEM images.
All CuO/SrTiO$_3$ composites of varying thicknesses sintered at 400˚, 500˚ and 600˚C temperatures exhibited $p$-type conductivity and showed cathodic photocurrents. Maximum PEC response was observed for CuO/SrTiO$_3$ composites sintered at 500˚C i.e. 1.13 mA/cm$^2$ at -0.9 V/SCE under visible light illumination. The results reveal that combinatorial approach of a low bandgap material (CuO) and a wide bandgap material (SrTiO$_3$) with an optimum thickness (690 nm) and sintered at optimal temperature (500˚C) significantly enhances photoelectrochemical response in the visible region.

It may be, therefore, concluded on the basis of results presented and discussed that significant photocurrent with enhanced efficiency was obtained by combination of nanostructured wide band gap metal oxide with low band gap metal oxide. It may also be concluded that the prescribed modification technique, i.e. bilayered systems in PEC water splitting turns out to be a promising approach which allows absorption of large part of the solar spectrum, leads to improved charge separation across the junction and reduction in recombination losses. Further studies are expected to improve the experimentally achieved photocurrent values and a detailed understanding of the interfaces in the bilayered structure and behaviour of photons and excited electrons in the PEC system is also required.

The experimental work presented in this thesis is an attempt which has led to some useful inferences that may be seen as one humble contribution to the ongoing extensive research in PEC area, all over the world, where researchers are working to explore different possible variations in the experimental parameters to optimize the process. Based on the conclusions of this study more work can be planned on the use of bilayered systems in PEC water splitting process. To develop high performing photoelectrochemical system some other characterizations techniques viz. Electrochemical impedance spectroscopy (EIS), Time-resolved spectroscopy, Surface-restricted grating method, Potential modulation-induced microwave reflectance method, Photoluminescence spectroscopy etc. are expected to help in
understanding the actual distribution and diffusion length of charge carriers at semiconductor/semiconductor and semiconductor/electrolyte interface.

The bilayered systems employed during the study, especially wide/small bandgap semiconductor based systems have the potential to be further developed as cost-effective photoelectrochemical devices but much more work is necessary before commercial viability of the process is ascertained. Although some effort have been made in the present study for the optimization of parameters viz. thickness and sintering temperature in the bilayered systems, yet many hurdles have to be surmounted before the desired goal of generation of technologically and economically sustainable hydrogen from water splitting using solar energy is realized.