Photoelectrochemical (PEC) water splitting represents an attractive route for the direct conversion of solar energy into hydrogen. In the quest for achieving the desired efficiency, balanced economics and prolonged durability of the photoelectrochemical (PEC) system for hydrogen generation, heterostructures consisting of two or more semiconductors are being looked upon as favourite material alternatives. Several metal oxide semiconductors are able to split water into hydrogen and oxygen upon illumination, but the efficiencies are still quite low. With the aim of improvement in the photoconversion efficiency of semiconductor electrode in PEC water splitting, i.e. bilayered semiconductor structures have been employed in the present work offering promising direction in the development of efficient photoelectrode for PEC splitting of water. Bilayered systems made from thin films of metal oxide semiconductors have broad range of functional properties and high potential in optical, electrical and electronic devices. Among various metal oxide semiconductors, cupric oxide (CuO), strontium titanate (SrTiO$_3$), zinc oxide (ZnO) and tungsten oxide (WO$_3$) have been chosen for this study as they are inexpensive, abundant, non-toxic, environmentally benign and possess well aligned band edges with each other and with redox potential of water.

In the present work, preparation (via Sol-gel technique), characterization and photoelectrochemical performances of various bilayered systems viz. CuO & SrTiO$_3$, CuO & ZnO, WO$_3$ & SrTiO$_3$ and ZnO & SrTiO$_3$ have been studied as a function of thickness. In addition, PEC performance of CuO/SrTiO$_3$ composite films was investigated at different sintering temperatures. The thesis also provides operating principles of the PEC device, the materials requirements and main bottlenecks. Various basic concepts are discussed along with some promising directions for future research in this important field of multidisciplinary research.

The thesis is divided into six chapters. Chapter-1 provides a brief understanding about inspiration for this research with an outline of the present work related to some bilayered systems in photoelectrochemical splitting of hydrogen. Following the introduction, Chapter-2 introduces basic theories associated with
photoelectrochemical concepts and bilayered systems as photoelectrodes in the photoelectrochemical cell. Chapter-3 examines the literature based on nanostructured bilayered semiconductors and provides a brief discussion on some recent research activities in the area of PEC water splitting. In Chapter-4, the experimental techniques used to fabricate and characterize the photoelectrodes are described. The results of the characterization and photoelectrochemical measurements are discussed in Chapter-5. Finally, Chapter-6 summarizes the main conclusions drawn from the present work and offers future directions.