Preface

Economically viable renewable energy sources are vital for the development of a globally sustainable society. The importance of renewable energy sources has been increased for both energy supply and ecological conservation reasons. Solar energy has the largest potential to satisfy the future global need for renewable energy sources. Solar light can be distinguished as direct and diffuse light. Diffuse light arises by scattering of the sunlight in the atmosphere. Materials with rough surfaces such as sensitized solar cells (SSC) perform relatively better compared with other solar cell technologies under diffuse light conditions. SSC technology offers the potential to design solar cells with a large flexibility in shape, color, and transparency. A challenging but attainable goal for the present SSC technology is to achieve efficiency above 15%. The use of mesoporous metal oxide semiconductor electrodes with a high internal surface area in SSC is essential to enhance the light harvesting capacity of the cell and hence its efficiency.

Nanotechnology opens a door to handling the materials effectively and creating various nanostructures for use in SSCs. The metal oxide films such as ZnO or SnO₂, when comprised of nanoparticles, nanowires, nanorods, branched nanowires/nanorods or oxide aggregates provide large surface area to photoelectrode film for dye adsorption with effective light harvesting and good charge transport or collection.

Versatility, relative ease of preparation of nanostructured-mesoporous metal oxide films, convenience of scale-up and economy are the advantages of the wet chemical approach to advanced materials synthesis. SILAR and CBD are the most suitable methods for creating nanostructured-mesoporous metal oxide films.

In the present work, a significant effort has been devoted to the investigation of nanostructured-mesoporous ZnO and SnO₂ metal oxide films as a suitable semiconductor photoelectrode for Dye/Quantum sensitized solar cells. The main objectives of the present study are to synthesize ZnO and SnO₂ films by single and double step chemical methods using SILAR and CBD techniques, tuning the properties by annealing and doping, and sensitization of the films using organic
dyes and quantum dots of inorganic compounds. Structural, morphological, optical and electrical characterization and porosity studies of the pristine and photo-characteristics of the dye/quantum dot sensitized films are carried out for SSC applications. This study includes ZnO films with thirty different morphologies and seven SnO₂ films with crystallite size 4-8 nm, synthesized using different zinc and tin precursors and various complexing agents.

The thesis, which focuses on the aspect of synthesis and characterization of ZnO and SnO₂ film electrodes and their sensitization using dye/quantum dots, comprises of nine chapters. 178 figures, 60 tables and a bibliography of 683 references support the discussions. Conclusion section is given at the end of each of the main discussions in a chapter.

The thesis starts in Chapter 1 with a brief introduction to nanotechnology, renewable energy sources, photovoltaic devices and properties of the nanostructured films. Properties and fabrication methods of nanostructured metal oxides ZnO and SnO₂ are explored. Structure, operational principles and characteristics of Dye/quantum dot sensitized solar cells are presented in this chapter. ZnO and SnO₂ film photoelectrodes used in SSC are discussed and reviewed.

Chapter 2 explores the methods of synthesis and characterization tools used in the present study. The general deposition methods especially about the features of wet chemical methods, successive ionic layer adsorption and reaction (SILAR) and chemical bath deposition (CBD) used in the present study, experimental arrangements and the respective processes are explained in detail with schematic diagrams. Film characterization tools such as X-ray diffraction (XRD) and scanning electron microscopy (SEM) for the structural and morphological characterization, energy dispersive X-ray (EDAX) technique for compositional analysis, gravimetric method and cross-sectional SEM analysis for thickness, UV-Vis-NIR absorption-transmission-reflectance spectra for optical studies, current-voltage characteristics for electrical studies, optical and imbibition methods for porosity studies are elaborated in this chapter. Necessary theory and formulas to determine the parameters are explained at the end of each technique.
The successful outcome of an experimental work and related processes is the foundation of an application. Wet chemical synthesis of reproducible ZnO films on unseeded glass substrates is not an easy task. Chapter 3 deals with the synthesis of nanostructured ZnO film photoelectrodes on unseeded glass substrates by SILAR technique. Mesoporous ZnO films with nanoflower, nanorod and nanoflake morphology grown with various zinc precursors and different complexing agents are elucidated in this chapter. Zinc sulfate, zinc nitrate, zinc acetate and zinc chloride are the zinc precursors employed in the deposition. Complex agents like ammonia, lithium hydroxide, monoethanolamine, triethanolamine, sodium hydroxide and hexamine are utilized. The effect of annealing in air on various properties of the films investigated is briefed.

The subsequent Chapter 4 deals with the synthesis of ZnO film photoelectrodes with morphologies of nanoflowers, nanorods, nanoflakes, microspheres and microdisc on unseeded glass substrates by CBD method. Ammonia, monoethanolamine, diethanolamine, triethanolamine, hydrazine hydrate, ethylenediamine, hexamine and trisodium citrate are used alone and together as complex agents, while zinc sulfate and zinc nitrate are being used as the zinc precursors to prepare the various nanostructured films discussed in this chapter. Results and discussion in Chapter 3 and 4 explores that nanostructured films with excellent crystallinity possess high specific surface area, moderate porosity, good optical and electrical properties.

Transparent, conductive and nanostructured films are a kind of outstanding functional materials in the field of SSCs. Chapter 5 brings forth the importance of doping the ZnO films to enhance structural, optical and electrical properties. Aluminium, magnesium and selenium doped ZnO films with nanoflower and nanorod morphologies, synthesized using SILAR and CBD techniques are illustrated. Enhancements of properties such as better conductivity, transmittance and size improvements have been achieved by doping.

The properties of ZnO strongly depend on its morphology and microstructure and it is essential to prepare high-quality textured films for its application in SSCs. The synthesis of ZnO films with nanorod morphology by two-
step chemical processes are illustrated in Chapter 6. SILAR and CBD methods employed for preparing seeded substrates and the ZnO film synthesis on the seeded substrates by the same methods are discussed. Use of seeded substrates in the film synthesis mainly enhanced the crystallinity, modified the morphology/surface coverage and electrical conductivity of the ZnO films.

Wet chemical synthesis of SnO\textsubscript{2} films at low temperature (<373K) is seldom reported and it is a challenging task to prepare quality films with high crystallinity. Chapter 7 explores the synthesis of nanostructured SnO\textsubscript{2} films at room temperature and at temperatures less than 373K using the environmentally benign wet chemical method SILAR using low cost stannic chloride and stannic sulfate as tin precursors. Various SnO\textsubscript{2} films prepared with the complex agents triethanolamine, glacial acetic acid, ethanol solution, monoethanolamine and, with combination of triethanolamine and ammonium chloride at room temperature and at 353K are discussed. Brief discussions of the effect of annealing on the properties of the films are presented. SnO\textsubscript{2} films are invariably porous and they yield large specific surface area together with high roughness. Films exhibit good optical and electrical properties.

Chapter 8 opens the door to dye/quantum dot sensitization of the ZnO and SnO\textsubscript{2} films and exposes the potential of the films to be used as photoelectrodes in DSSCs and QDSSCs. Various photoelectrodes of ZnO and SnO\textsubscript{2} constructed by organic dye sensitization using rose bengal and also by deposition of inorganic semiconductor CdS and PbS QDs by SILAR method are explored in this chapter. The photo-characteristics of the ZnO and SnO\textsubscript{2} photoelectrodes are thoroughly analyzed and the dye adsorption capability and the enhancement of light harvesting capacity are illustrated in this chapter.

Chapter 9 presents the summary of the study and scope for future work.