Chapter 4

SUMMARY AND CONCLUSIONS

The research work presented in this thesis leads us to draw the following conclusions. Simple microwave irradiated (SMI) solvothermal synthesis is a cost effective and less time consuming technique for preparing metal oxide semiconductor nanocrystals. Ru (II) is the most efficient dye due to its numerous advantageous features, such as good absorption, long excited-state lifetime, and highly efficient metal-to-ligand charge transfer. Ru bipyridyl complexes are excellent photosensitizers due to the stability of the complexes excited states and the long-term chemical stability of oxidized Ru (III). The standard dye used in traditional DSSCs is tris (2,2’-bipyridyl-4,4’-carboxylate) ruthenium (II) (N₃ dye). The major challenge in the fabrication and commercialization of DSSCs is the low conversion efficiency and stability of the cell. The degradation of the cell based on dye sensitization, undesirable electrolyte properties and poor contact with the electrodes are the main causes of the poor performance of DSSCs. To enhance the performance of the DSSCs, several research directions are suggested: (i) improving the dye stability by finding the optimum parameters to slow the dye degradation; (ii) improving the dye structure to absorb more light at longer wavelengths; (ii) improving the morphology of semiconductors to attaining the best electronic conduction to reduce the dark current; (iv) using dye and electrolyte additives to enhance the cell performance; and (v) improving the mechanical contact between the two electrode. Thus, the choice of materials is very important in the fabrication and deployment of DSSCs because the conversion efficiency and stability of the cell do not depend on a single factor alone.

In order to overcome this above problems, high yield Ti₁₋ₓSnₓO₂ (where x = 0.0, 0.25, 0.50, 0.75 and 1.0) and 5 mole % Ru doped Ti₁₋ₓSnₓO₂ (Ti₁₋ₓSnₓO₂:Ru)
nanoparticles with a desirable size distribution were successfully prepared with a crystallite size between 13 to 18 minutes. Ethylene glycol (EG) was used as the solvent for the preparation of the pure and doped samples. Ethylene Glycol was used for two purposes, i) it is used for the reaction medium and ii) it is used as a stabilizer to prevent the grain growth, thus the agglomeration of the particles were restricted for all the as-synthesized nanoparticles. The resultant precipitate was collected, centrifuged and washed several times with double distilled water and acetone before drying in a heating oven at 60 °C for 10 hr.

The phase and purity of the as-synthesized Ti\(_{(1-x)}\)Sn\(_x\)O\(_2\) and 5 mole% Ru doped Ti\(_{(1-x)}\)Sn\(_x\)O\(_2\) (Ti\(_{(1-x)}\)Sn\(_x\)O\(_2\):Ru) nanoparticles were determined by powder XRD spectra. From the XRD data it was confirmed that the significant observations was that as x increases from x = 0.25–0.75, the intensity of prominent peaks (1 1 0) of SnO\(_2\) increases while that prominent peak (2 0 0) of TiO\(_2\) decreases. When x = 0.0, the diffraction peaks were assigned to the tetragonal phase of anatase structured titanium dioxide (JCPDS file No. 89-4921) and x = 1.0, the peaks were assigned to the tetragonal phase of rutile structured tin dioxide (JCPDS file No. 41-1445). The qualitative XRD peak analysis revealed that only Ti\(_{(1-x)}\)Sn\(_x\)O\(_2\) (x = 0.25, 0.50 and 0.75) nanocrystals got formed and no phases of other oxides, impurities or separate nucleation of Ti/Sn/O has occurred. More interestingly, when Ru is added into the pure Ti\(_{(1-x)}\)Sn\(_x\)O\(_2\) no diffraction peaks correspond to RuO have been observed in the PXRD pattern. However the broadening of the peak was slightly increased as well as the peak intensity was also decreased. Thus the crystallite size and volume of the unit cell were slightly changed. This revealed that the Ru was incorporated with the host Ti\(_{(1-x)}\)Sn\(_x\)O\(_2\) matrix.

The lattice parameter of the TiO\(_2\) (x = 0.0) and SnO\(_2\) (x = 1.0) nanoparticles closely matched with the standard values known for the respective bulk systems. In all the other cases of Sn incorporated samples (x=0.25, 0.50 and 0.75), the lattice parameter values decrease in ‘c’ direction whereas increases in ‘a’ direction without affecting the tetragonal...
structure. This effect, witnessed as a shift in the peak position along higher 2θ side as well as the host atoms (Ti) were substituted by intervening Sn atoms with respect to variation of composition from x = 0.00 to 1.00. Irrespective with the variation of lattice parameter in ‘a’ or ‘c’ direction the overall unit cell volume decreased with the increasing concentration of Sn in the host Ti_{(1-x)}Sn_{x}O_{2} matrices. The decrease of unit cell volume might be due to smaller ionic radii of Sn. The ionic radii of Ti is 1.00 Å whereas Sn is 0.83 Å. The PXRD spectra have also been used to study the crystallinity of the samples. The lattice parameters of Ru doped Ti_{(1-x)} Sn_{x}O_{2} nanoparticles were slightly changed to that of pure Ti_{(1-x)}Sn_{x}O_{2} nanoparticles. The calculated lattice parameters of pure and doped Ti_{(1-x)}Sn_{x}O_{2} nanoparticles. Synthesized nanoparticles were of good crystalline nature it showed that the characteristic peaks were higher in intensity.

The crystallite size of the as-synthesized nanoparticles was calculated from PXRD data. It was clearly confirmed that the major diffraction peaks were broadening in nature. Also, it is observed that the intensity of the major diffraction peaks varied (decrease/increase) with respect to the incorporation of Sn into the host Ti_{(1-x)}Sn_{x}O_{2} lattices, which means that the crystallite size has been modified. The major diffraction peaks were broadening in nature. Also, it was observed that the intensity of the major diffraction peaks varied (decrease/increase) with respect to the incorporation of Sn into the host Ti_{(1-x)}Sn_{x}O_{2} lattices, which means that the crystallite size has been modified. The crystallite size of the pure TiO_{2} was showed approximately 4 nm. As the dopants was introduced the crystallite was increased.

The strain values revealed that, Ru doped alloyed Ti_{(1-x)}Sn_{x}O_{2} (x = 0.25, 0.50 and 0.75) nanoparticles showed compressive strain whereas for x = 0.0 and 1.0 it showed tensile strain. Irrespective with the composition of Sn and dopant (Ru) in Ti_{(1-x)}Sn_{x}O_{2}, the obtained values of compressive or tensile strain were very low, which proved that the strain has negligible effect in XRD broadening for the as-synthesized pure and doped
nanoparticles. However the obtained strain values were relatively smaller than the respective undoped Ti\textsubscript{(1-x)}Sn\textsubscript{x}O\textsubscript{2} nanoparticles. This small tensile strain and compressive strain at nanoscale generally arose due to the change in shape, size and morphology of the particles.

Morphological studies showed that the presence of fine particles in spherical shape which were nearly ordered, but slightly differ in grain size. The FESEM images showed that the particles can be resolved to be slightly agglomerated and of size in the range 11–23 nm, however the boundaries between single crystallites were clearly observable. These nanoparticles were relatively uniform in size and better dispersed. The Ru doped Ti\textsubscript{(1-x)}Sn\textsubscript{x}O\textsubscript{2} nanoparticles with different concentration of Sn content showed about similar morphology, indicating that the Ru doping does not cause marked changes of the morphology. From the FESEM micrographs, it revealed that the particle size increased with the increasing Sn content in the Ti\textsubscript{(1-x)}Sn\textsubscript{x}O\textsubscript{2} whereas decreased with the incorporation of Ru in the Ti\textsubscript{(1-x)}Sn\textsubscript{x}O\textsubscript{2} lattices.

TEM analysis revealed that the Sn incorporated as well as Ru doped particles were spherical in shape with a narrow size distribution. The size of the particles is in the range of 10-15 nm and 17-22 nm for x = 0.00/0.50 and 1.00, respectively, with the average particle size. It was confirmed from the compositional studies that the atomic percentage of Ti, Sn, Ru and O were nearly same as the initial atomic percentage taken in the solid solutions. The atomic percentage of Ti decreased with the increasing Sn content in the host lattice as well as the incorporation of Ru as dopant in the host Ti\textsubscript{(1-x)}Sn\textsubscript{x}O\textsubscript{2} matrices. This showed that Ti ions have successfully replaced by Sn and Ru counterparts.

The PL spectra of prepared samples were obtained as a result of the competition among electron-hole separations, electron-phonon scattering and electron-hole recombination. The spectra showed that besides the sharp peaks due to phonon modes
(Raman) near 2.2 to 2.5 eV. Both the samples showed two broad PL emission peaks in the visible region. TiO$_2$ has a direct band gap was subjected to dipole-forbidden transition. PL spectra of anatase TiO$_2$ materials were attributed to three kinds of physical origins: self-trapped excitons, oxygen vacancies and surface states (defects). Most of the surface states were oxygen vacancies or the Ti$^{4+}$ ions adjacent to oxygen vacancies. PL measurement of pure Ru doped TiO$_2$ nanoparticles showed clear emission bands. The blue-green emission of 485 nm ($\sim$2.547 eV) in TiO$_2$ : Ru. Strong peak observed in red shift for doped substances. It might be due to incorporation of dopant ions which introduced a shallow energy level near valence band. The violet emission observed around 419 nm was associated to oxygen vacancies. This could be attributed to the charge transfer from Ti$^{3+}$ to oxygen anion in a [TiO$_6$]$^{8-}$ complex associated with oxygen vacancies at the surface, indicating the band was originating from the intrinsic state rather than the Ru doped SnO$_2$ showed a strong UV emission at 360nm, corresponding to the band gap of SnO$_2$ (3.56ev) which partially overlapped with Raman scattering of water. The latter peak appeared at a constant frequency difference from excitation. It showed that the photoluminescence emission spectra of Ru doped SnO$_2$ exhibit emission at 437nm. The emission maximum of 437 nm was lower than the band gap of the SnO$_2$ bulk, this peak can be attributed to the contribution of oxygen vacancies dopant segregation, and lattice disorders inside the lattice of SnO$_2$ surface state.

UV analysis revealed that the undoped TiO$_2$ sample showed absorption at around 383 nm (3.35eV) (i.e., in the UV range) which occurred due to the charge transfer from the valence band (mainly formed by 2p orbitals of the oxide anions) to the conduction band (mainly formed by 3d $t_{2g}$ orbitals of the Ti$^{4+}$ cations). The Ru-doped TiO$_2$ different samples having absorption bands in the wavelength range approximately 270-380 nm (visible region) and band gap energy range 3.44-3.77eV have been observed. It might be due to the crystal field splitting of and charge transfer from Ru$^{2+}$ to Ti$^{4+}$.