ABSTRACT

Semiconducting materials are promising materials in different field of nanoscience and technology. Tin Sulfide (SnS) is a significant and functional material in the semiconductor engineering. Considering the importance and various applications of SnS nanocrystals the work is mainly planned to grow SnS nanocrystals in a simple and cost effective way. The research works cover the growth, characterization and applications of SnS nanocrystals. The grown nanomaterials are applied in ethanol Gas Sensor, Si based Heterojunction Solar Cells and natural Dye Sensitized Solar Cells. The grown nanomaterials are also used to investigate the molecular interaction with protein.

The SnS nanoparticles are grown with the variation of growth conditions as well as growth process to apply the materials in device fabrication. The effects of various growth conditions such as growth time, growth temperature, doped as well as bio synthesis on the growth of SnS nanocrystals have been investigated. The grown samples have been characterized structurally through X- ray diffraction (XRD), transmission electron microscopy (TEM), field emission scanning electron microscopy (FESEM), atomic force microscopy (AFM) and selected area diffraction (SEAD). The elemental compositions of the grown samples were analyzed through EDAX analysis. The optical properties of the grown materials have been investigated through UV-VIS absorption spectroscopy and photoluminescence (PL) spectroscopy. The optical band gap of samples has been calculated from optical absorption spectra.

We have successfully synthesized SnS nanoparticles in a simple cost effective chemical reduction method by varying growth time i.e 3 hours to 14 hours. The grown samples have been ultra-sonicated in ethanol. The dispersed sample has been characterized structurally and optically. The crystallite size increases with increase of growth time. The band gap is maximum for 3h grown sample and decreases for samples grown for longer time. Photoluminescence spectra show possible defect states. Energy dispersive X-ray analysis shows that stoichiometry is well maintained for sample grown for 7h.

SnS nanoparticles have been synthesized by simple wet chemical precipitation method using triethylamine (TEA) at room temperature. The grown samples were characterized by X-ray diffraction, Transmission electron microscopy (TEM), Field emission Scanning electron Microscopy (FESEM), Optical absorption spectra and PL. XRD image shows that the particles are orthorhombic structure. The TEM image shows that particles are chain-like shape and crystal size is about 20 nm. FESEM result also support the TEM result. AFM image shows that the surface roughness of the as prepared SnS nanocrystals is about 1.76 eV. PL spectra of SnS shows an emission peak at 698.79 nm which is due to band to band transition.

SnS nanocrystals were also synthesized by simple wet chemical precipitation method with the variation of growth temperature. The growth temperature was varied from 14^{0} C to 70^{0} C. XRD results shows that the crystals are orthorhombic in phase. TEM images indicate that the grain sizes are almost spherical within the range 5 nm to 10 nm. A decrease in band gap is observed as particle size increase with increase of growth temperature. The temperature variation of p-type SnS nanocrystals indicates electrical conductivities were ranging from 0.020 to 0.037 Ohm⁻¹cm⁻¹ and carrier concentrations were varying from 7.05 × 10^{13} cm⁻³ to 1.54×10^{14} cm⁻³.

SnS and SnS-Ag nanocomposite were synthesized by cost effective solvothermal technique. The as synthesized materials have been studied by structurally and optically through various tools and techniques. Structural characterization was investigated through by X-ray diffraction (XRD), Transmission Electron Microscopy (TEM) and Field Emission Scanning Electron Microscopy (FESEM). Elemental compositions were confirmed by

Electron Diffraction X-ray Analysis (EDAX). The Optical properties were characterized by UV-VIS absorption spectra, Photoluminescence spectra (PL) and Time Correlated Single Photon Counting (TCSPC). XRD results suggest that the samples are in orthorhombic structure in phase. The particle size has been estimated from TEM study. The calculated the band gap values were 2.04 eV and 1.80 eV of SnS and SnS-Ag nanocomposite respectively. A decrease in the band gap energy of SnS-Ag nanocomposite was observed compared to SnS.

Pure SnS, Fe doped SnS and Mn doped SnS nanocrystals were prepared by simple chemical precipitation method. The structural and optical properties of the as prepared nanoparicles were studied. XRD results indicate the orthorhombic crystal phase of the as prepared samples. TEM results show that the crystal size increase with increase of doping and the grain size is greater for Mn doped SnS nanoparticles. A decrease in the band gap of Mn doped SnS was observed compared to pure as well as Fe doped SnS.

SnS nanoparticles have been used to fabricate different types of devices in a cost effective way. The as grown time varying SnS NPs are deposited on glass for the fabrication of gas sensor. The sensing measurements were done at operating temperature ranging between 250 °C and 300 °C for SnS based sensor. Here we have chosen three operating temperature i.e. 250 °C, 275 °C and 300 °C. The sensitivity in dry air conditions becomes maximum for 7 hours SnS sample at 300 °C. The percentage of sensitivity of 7 hours samples at 300°C was 61%. The gas sensing properties has been studied in dry air as well as humid conditions. The stability of the sensors has been also studied over 4 weeks and this indicates good stability.

The SnS/Si as well as SnS:Ag/Si heterojunction solar cell has been fabricated. Open circuit voltage (V_{oc}), short circuit current (J_{sc}), fill factor (FF) as well as power conversion efficiency (η) were also calculated. The efficiency of SnS-Ag/Si heterojunction is greater

than the SnS/Si heteojunction. The increase in conversion efficiency is due to the scattering effect from silver (Ag) nanoparticles.

The as grown Fe doped and Mn doped SnS nanocrystals have been applied for fabrication of dye sensitized solar cell. Anthocyanin is a type of natural dye which was found in the various leaves of plants, flowers and fruits. These natural dyes are used as photo sensitizer in the fabricated dye sensitized solar cell. Acalypha Wilkesiana leaf extract was used as natural dye which can increase the power conversion efficiency of the fabricated solar cells. The performances of the fabricated dye sensitized solar cell were studied through the current (I)-voltage (V) study. The open circuit voltage (V_{oc}), Short circuit current (Jsc), Fill factor (FF) as well as power conversion efficiency (η) were also studied.

SnS nanoparticles were also synthesized by the extract of Gymnema Sylvestre leaves in aqueous medium through green synthesis. The leaves extract of Gymnema Sylvestre plant have been employed as an efficient capping agent for the synthesis of SnS NPs. Low cost natural dye sensitized solar cells (DSSCs) based on chemically grown as well as green synthesized SnS NPs were fabricated. Acalypha Wilkesiana leaf extract was used as the natural dyes as a photosensitizer. The fabricated dye sensitized solar cell has been characterized through J-V study. Comparative studies of the efficiencies of the fabricated solar cell have been investigated. The fill factor, open circuit voltage and short circuit current density of the fabricated dye sensitized solar cell were also estimated.

Finally, the bimolecular interaction of bovine serum albumin (BSA) with SnS materials has been studied through different tools and techniques. The BSA-SnS NPs interaction, complexation formation and conformational changes of protein (BSA) with the SnS nanoparticles were investigated by microscopic as well as spectroscopic measurements. The quenching of fluorescence spectra under the association of SnS nanoparticles was used to study the molecular interaction of bovine serum albumin (BSA) with SnS nanocrystals. The

interaction and the formation of SnS@BSA bioconjugate also investigated using optical spectroscopy measurements. A spontaneous binding process happened in between BSA and SnS nanocrystals which were confirmed by UV–VIS and fluorescence spectra. A little red shift in the optical absorption spectra of protein (BSA) was detected due to binding of protein (BSA) with SnS NPs. The SnS nanoparticles quench the fluorescence spectra of bovine serum albumin. The Stern–Volmer quenching constant, Hill coefficient (n), nature of binding as well as binding constant (K_b) of the BSA – SnS NPs conjugates were also calculated.

The objective of my thesis is to synthesize good quality SnS nanocrystals by cost effective methods. We have synthesized different sizes of the nanocrystals by changing the growth conditions as well as growth technique. The nanostructured SnS have been applied in fabrication of devices as ethanol gas sensor, heterojunction solar cell with Si, dye sensitized solar cell using natural dye. Also the molecular interaction of SnS nanocrystals with bovine serum albumin (BSA) is studied. The thesis consists of eight chapters.