CHALCOPYRITE AND HYBRID SEMICONDUCTORS SYNTHESIZED BY NON-VACUUM BASED METHODS

by

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Dedicated to
My Parents

CERTIFICATE

This is to certify that the thesis entitled **"Chalcopyrite and Hybrid Semiconductors Synthesized by Non-vacuum Based Methods"** being submitted by **Aneeta Kharkwal** to the Indian Institute of Technology, Delhi for the award of the degree of Doctor of Philosophy in Chemistry, is a record of bonafide research work carried out by her. Aneeta Kharkwal has worked under our guidance and supervision. She has fulfilled the requirements for the submission of this thesis, which to our knowledge has reached the requisite standard.

The results contained in this dissertation have not been submitted, in part or in full, to any other university or institute for award of any degree or diploma.

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ABSTRACT

The vacuum deposition techniques for thin film solar cells suffer from a large capital cost and low material utilization. As an alternative, solution-based deposition techniques are widely considered to be a route to low-cost and high-throughput electronic device fabrication. Although numerous methods for the preparation of nano materials ink have been established, there is still a need of suitable methods to overcome the problems of size distribution, agglomeration, extraction from precursors i.e. yield of these materials to utilize them for device fabrication. Therefore the present thesis is focused on the synthesis and charecterization of semiconductors and their hybrids, that can be used as a nanoparticle ink for non-vacuum deposition of thin film for solar cells.

This thesis first deal with the synthesis of semiconductor ZnO and its hybrid with CdSe quantum dots, and described the effect of linkers with varied carbon chain lengths on the photosensitization mechanism of ZnO nanocrystals with CdSe QDs. The CdSe QDs were attached to ZnO NPs with and without the aid of bifunctional linker mercaptopropionic acid (MPA) and thiogycollic acid (TGA). Emission intensity profiles of ZnO-CdSe composites (with and without linker) show that the emission yield of CdSe system decreases with the increase in concentration of ZnO particularly in the presence of ligands, which is indicative of a better coordination of quencher ZnO and CdSe and effective charge transfer from CdSe to ZnO as well. The charge transfer in CdSe-ZnO nanocomposites is more in the presence of linker because the thiol group of the linker replaces the TOPO capping of CdSe. Removal of TOP/TOPO capping agent leads to sufficient interaction between CdSe-ZnO and consequently higher PL quenching is observed. This allows electron transfer to occur, leading to the formation of separate electron-hole pairs that subsequently recombine nonradiatively. MPA-linker owing to its

longer carbon chain facilitates efficient charge transfer from CdSe to ZnO as compared to the corresponding TGA-linker.

Here ZnO is an inexpensive and non-toxic material but the eficient usage of ZnO by itself in solar energy conversion devices is prevented by its wide band gap and the optical activity of ZnO can be increased by adsorbing CdSe molecules on the semiconductor surface. But CdSe contains toxic elements like Cd, therefore to reduce their use this thesis has been also focused on the synthesis of less toxic chalcopyrite semiconductor meterials like $CuInS_2$ and $CuInSe_2$ and their hybrid materials.

In present thesis highly luminescent $CuInS_2$ (CIS) nanoparticles generated by thermal decomposition of copper indium ethylxanthate which has been reported for the first time. This method has been found to be a simple, versatile and low temperature one for the controlled production of good-quality, band gap tunable and highly luminescent CIS nanoparticles in a single-pot. These CIS nanoparticles can absorb or emit photons of a wider electromagnetic spectrum, from the visible into the near-IR range. Further a suitable low temperature method has been developed to prepare core shell CIS-CdS and CIS-ZnS structures which show enhanced fluorescence as well as photostability as compared to the CIS core. From the various experimental studies, it can be concluded that the low temperature deposition (80 °C) used in the present case, has successfully prevented the further growth of CIS NPs by Ostwald ripening or alloying due to cationic diffusion into the inner core. The heterogeneous nucleation over CIS core results in CdS or ZnS shell growth onto CIS core and hence a red shift in absorption is accompanied with a marginal variation in PL peak position.

For organic-inorganic hybrid, a new approach for the in situ synthesis of CIS nanoparticles using copper indium ethylxanthate (CIX) in a conducting polymer P3HT with different ratio of P3HT and $CuInS_2$ have been reported. The results shows that the

presence of polymer influences the nanoparticle size in the solution and during the synthesis the polymer act as a capping agent preventing extensive particle growth. This finding supports the concept that polymer chains act sterically to stabilize nanoparticle growth in solution. Also, the higher reduction in PL intensity with increase in CIX precursor concentration implies that with increase in particle size of CIS, results in efficient charge transfer from polymer to CIS nanoparticles. It appears that higher PL quenching obtained is dependent on both higher CIS concentration and increased in CIS particle size as well. To confirm this, the charge transfer studies of P3HT-CIS nanocomposites by ex-situ synthesis of CIS were performed. From the PL quenching spectra of in-situ and ex-situ nanocomposites, we have also observed that the charge transfer is more efficient in in-situ composites as compared to ex-situ ones due to higher phase segregation in ex-situ polymer-CIS composite. The efficient charge transfer in in-situ as compared to ex-situ method may be exploited to generate as potential active layer for organic-inorganic hybrid photovoltaic devices.

This thesis also summarizes the applicability of the solvothermal method in the preparation of CIS by parametric variation such as effect of reaction time, different solvent and sulfur sources have been demonstrated. It has been observed that the solvent plays an important role in the phase determination of CIS, as synthesis in ethanol results in the chalcopyrite phase (CH), while, in ethylenediamine, wurtzite phase (WZ) of the CIS nanoparticles is formed. These finding indicates that the variable degrees of coordinating interactions of solvent with the cations are critical for the crystal phases determination of the resulting NPs. The phase selection of WZ-CIS or CH-CIS is greatly determined by the nucleation stage, while the following crystal growth stage as apparently marginal influence on it. It was also observed that, in solvothermal process, sulfur source mainly influences the growth of NPs rather than phase determination. Also

to facilitate efficient charge/energy transfer across organic-inorganic interface for application in photovoltaics, role of P3HT polymer matrices and CIS (WZ-CIS or CH-CIS) has been identified.

The present thesis also focused on synthesis of $CuInSe_2$, $CuInGaSe_2$ and related materials by colloidal synthesis method using TOP/TOPO as a surfactant. In the synthesis of CIS/Se & CIGS/Se nanoparticles expensive and scarce element like indium is used, which affects large-scale production of cells. To achieve the goal of cost-effective photovoltaic technology, it is necessary to explore new materials like $Cu_2ZnSnSe_4$ and other quaternaries of these chalcopyrite-like semiconductors. The elements zinc and tin in these compound semiconductors are relatively cheap and more abundant compared to indium and gallium used in CIGS/Se thin film solar cells. So after the successful synthesis of CISe & CIGSe nanoparticles the possibility of replacement of indium and gallium in CIGSe with zinc & tin and synthesis of CZTSe nanoparticleshas been explored by the same method employed for the synthesis of CIS/CIGS nanoparticles. The CIGSe and CZTSe nanoparticles were characterized by electrical measurements. It exhibits current in mA and shows photoresponse for CIGSe/CZTSe capped with TOPO-related ligands.

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