

An investigation of Structural and Optical Properties of various Oxide-oxide and Sulfide-sulfide Core-Shell Nanocomposites to gauge potential applications in Photocatalysis and Photovoltaics

PREFACE

The study of semiconductor nanoparticles has emerged as an important area of research because of their novel optical and electrical properties. Again, coating a given ensemble of nanoparticles by another material yields core-shell nanostructures. Usually, the core material with a certain bandgap is capped by a material with a larger band gap where the conduction band energy of the capping material is higher than that of the core material and the valence band of the capping material is located at lower energy than that of the core material. The energetic situation is often called as TYPE 1 structure. The major outcome of this capping is that the exciton photogenerated in the core is prevented from spreading over the entire particle hereby allowing to recombine while spatially confined to the core. In most cases, this is accompanied by improved luminescence. Another core-shell structure namely TYPE 2 is found where both the conduction and valence band energies of the core are either at higher or lower energy than the shell. This results in spatial charge separation at the interface of the core and shell leading to abridged luminescence in the core-shell system.

Dye-sensitized solar cell (DSSC) has intensively attracted interest due to its potential and low-cost applications in future photovoltaic markets. However, these DSSC s based on TiO_2 possess lower energy conversion efficiency when compared with silicon solar cells. This is primarily due to charge recombination losses arising at the semiconductor/dye/electrolyte interface and low dye absorption towards the infrared regime. But, a core-shell structure is a suitable measure to minimize the charge recombination losses in DSSCs. These coating layers retards back transfer of electrons to the electrolyte and minimize charge recombination and also enhances the dye adsorption onto the porous electrode and, as a consequence, the dye loading, increasing the photocurrent [3,4]. It is well known that TiO_2 shows very little absorbance in visible

region. However its band gap may be tuned by coating with a shell layer. Such compounds exhibit improved absorbance in visible regime than the core TiO_2 .

Again, Photocatalysis is another promisingly applicable phenomenon which requires charge separation of electron and holes. This is favored by formation of core-shell nanostructures as charge separation occurs at the interface due to difference in band alignment of the two materials. Transition metal oxides are good photocatalytic materials due to large surface area. Now a days, typical composite nanostructures like core-shell nanostructure are fabricated inside nanorods with outside covered layers e.g. TiO_2/ZnO , ZnO/MgO and $\text{ZnO}/\text{Er}_2\text{O}_3$. Also there are reports on enhanced photocatalytic activity of core-shell TiO_2/MgO nanostructures where $\text{Mg}(\text{OH})_2$ gel was decomposed on TiO_2 particle surface resulting in highly nanoporous MgO coated TiO_2 particles.

TiO_2 and TiO_2 based photocatalysts and their applications are limited to UV regime only. Very few reports are obtained on visible light or day light photocatalysis. That is why, we attempted to obtain efficient day light photocatalytic activity for degradation of hazardous dye. To achieve this, we tuned the properties of some of the core-shell structures either by altering core parameters or by changing shell thickness so that we can know upto which limit the materials can exhibit excellent photoactivity. Also, we wanted to find a suitable alternative for TiO_2 based photocatalysts and prepared a novel core-shell structure $\text{Ag}_2\text{S}/\text{HgS}$ which has established itself as an efficient photocatalyst for degradation of Methylene Blue dye under daylight illumination. We have already mentioned the limitations of DSSC s associated with only one semiconductor. That is why, we chose TiO_2 which is already a well established photovoltaic material and then to coat it with three different oxide materials.

Our work in this thesis is mainly focused on TiO_2 nanoparticles and core-shell nanocomposites based on TiO_2 nanoparticles. To detect the influence of the insulating shell MgO on core TiO_2 , we even carried out extensive study upon the shell characteristics. The detailed study reported on the luminescence properties of MgO nanoparticles while we monitored different defect related emissions from the sample has been reported first by us to the best of our knowledge.

After seeing the modified applicability of TiO_2 by coating with other materials, we tried to see effect of TiO_2 coating layer on CdSe nanoparticles. We were successful in manufacturing an efficient photocatalyst in the form of CdSe- TiO_2 core-shell nanocomposite for degradation of methylene blue dye. We also made successful attempt to fabricate some simple photovoltaic devices by a simple laboratory method. In our thesis, we also reported a novel core-shell material Ag_2S - HgS and its potential application as a photocatalyst.

In **Chapter 1**, we have discussed about changes in properties of a material when the size is reduced from bulk to nano. We also discussed about the basic mechanisms of photocatalysis and photovoltaics. A brief literature review is also covered in the chapter on the importance of core-shell particles and how they are promising candidate for photocatalysis and photovoltaic applications. The chapter is ended with a note on motivation of our research work.

In **Chapter 2**, we have reported a novel core-shell Ag_2S - HgS nanoparticles and went through detailed investigation on the structural as well as optical properties of the nanostructure. We found that upon increasing shell thickness, a transition from TYPE 1 to TYPE 2 core-shell is observed in the nanostructure which is a very interesting phenomenon. Also we performed photocatalytic activity study for degradation of Methylene Blue dye and the core-shell nanostructure was able to establish itself as potential candidate for photodegradation under sunlight.

In **Chapter 3**, we have covered pristine TiO_2 along with core-shell TiO_2 - MgO nanostructures. We reported in details the structural and optical changes those occurred in the core-shell structure upon annealing the core at different temperatures. We found that the lifetime of charge carrier is enhanced in the core-shell structure indicating prominent charge separation in the sample. We also discussed in abundance about the temperature dependent luminescent properties of shell MgO nanoparticles by monitoring F , F_2^{2+} and F^+ defect related emissions. The photocatalytic behavior of core-shell TiO_2 - MgO nanostructures was investigated under daylight for degradation of Methylene Blue dye

under daylight and it is found that the sample is a far better photocatalyst than its core counterpart.

In **Chapter 4**, we focused on various structural and optical properties of core-shell TiO_2 - SnO_2 nanostructures with three different shell concentrations. Unlike typical core-shells where the optical properties are generally more or less same with the core, here we observed optical properties resembling more of the shell rather than the core. At highest shell thickness, it was behaving entirely like the shell SnO_2 . The XPS spectra confirmed the presence of oxygen vacancies in the core-shell structure. While executing the photocatalytic degradation experiment for the same dye as in earlier chapters, we found that the core-shell sample with utmost shell thickness did not exhibit any photoactivity due to the saturation thickness of the shell for which the charge carriers were unable to tunnel through and reach the surface of the sample to take part in photodegradation.

In **Chapter 5**, we discussed two core-shell structures both TYPE 1 in bulk band alignment namely TiO_2 - ZrO_2 and CdSe-TiO_2 . For the 1st core-shell structure a quasi TYPE 2 band alignment is obtained in the nanoscale due to generation of various defect related states between the conduction band and valence band of the shell which favors ambient charge separation in the system. An anomaly occurred in this sample as the crystallite size of the core-shell was found to be less than the core and also a red shift in Raman spectrum was observed. For CdSe/TiO_2 core-shell like nanocomposite also, it has been found that the core-shell structure is very useful in degrading methylene blue under daylight.

In **Chapter 6**, we reported on fabrication of films from the already synthesized nanopowders. We prepared TiO_2 , TiO_2 - MgO , TiO_2 - SnO_2 and TiO_2 - ZrO_2 films on ITO coated glass from the existing samples. We found the structural properties similar to that of the nanoparticles which has been investigated with XRD. We also executed electrical characterizations both under dark and visible light illumination and found promising results for TiO_2 , TiO_2 - MgO and TiO_2 - SnO_2 films. So, we attempted to fabricate some simple photovoltaic devices by taking the films as photoanodes and Pt coated conducting glass slides as photoanode. An iodine based liquid electrolyte was used where a piece of thin parafilm was used as spacer between anode and cathode. Reasonable fill factors were

attained in the devices for illumination under daylight and the core-shell films performed better than core TiO₂ film.

In **Chapter 7**, a summary of all the works carried out has been provided along with their future prospects.

Detailed analysis of various core-shell nanostructures has shown that CdSe-TiO₂ exhibits highest photodegradation efficiency of 97%. Further, from the perspective of photovoltaics, highest fill factor was achieved for TiO₂-MgO core-shell film (0.58).