MODIFICATION OF OPTICAL AND STRUCTURAL PROPERTIES OF COLLOIDAL SEMICONDUCTOR NANOSTRUCTURES VIA SURFACE TREATMENT AND HETERO-STRUCTURING

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by

UDIT SONI

Department of Chemistry

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to the

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Dedicated to
My Parents

CERTIFICATE

This is to certify that the thesis entitled, "**MODIFICATION OF OPTICAL AND STRUCTURAL PROPERTIES OF COLLOIDAL SEMICONDUCTOR NANOSTRUCTURES VIA SURFACE TREATMENT AND HETERO-STRUCTURING**" being submitted by **Mr. UDIT SONI** 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 him. **Mr. UDIT SONI** has worked under my guidance and supervision. He has fulfilled the requirements for the submission of this thesis, which to my knowledge has reached the requisite standard.

Date

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ABSTRACT

Semiconductor nanocrystals or quantum dots have attracted much attention in recent decades due to their promising applications in Light emitting diodes (LEDs), photovoltaics and in the field of biotechnology as fluorescent labels for detection of biomarkers and as biological sensors. Quantum dots are a class of semiconductors, which are composed of periodic groups of II-VI, III-V, or IV-VI materials (like CdSe, CdS,CdTe, ZnS and InP) with size below 10nm showing size dependent optical, electronic and chemical properties. Modification of nanocrystal surfaces and deposition of other semiconductor materials too modifies the optical and structural properties; the main focus of work in the present thesis. The present thesis is mainly focused on designing of hetero-nanocrystals (core-shell, core-intermediate-shell and noble metal tipped nanostructures) and tailoring their optical and electronic properties by surface engineering. The detailed plan of work is as follows:

Chapter I of the thesis is devoted towards the extensive literature survey on past and present research work of semiconductor nanocrystals. It summarizes the general review on various methods for the synthesis of nanomaterials and different techniques for the surface modification of nanomaterials. This chapter introduces the reader about the rationale and objectives of the present research work.

In **Chapter II**, methods used for the syntheses of nanocrystals and their further modifications are described in this chapter. The preparation of the injection solutions of Cd, Zn S, Se, Te and Au, used in the synthesis of core, core/shell and hybrid nanocrystals are discussed. Brief accounts of the absorption spectroscopy, steady

state/time resolve fluorescence spectroscopy, X-ray diffraction, transmission electron microscopy and other techniques used to characterize the newly synthesized materials are provided.

In **Chapter III**, the role of surface atoms on the emission from core/shell nanocrystals have been emphasized and was shown to depend on whether the surface is anion rich or cation rich. A cation-rich surface enhances the emission intensity, while an anion-rich surface leads to weakening of the fluorescence signal. The increase in the fluorescence intensity is due to the fact that cation has stronger binding with the ligands, which implies better surface passivation. This fluorescence behavior of nanocrystals is strongly correlated to the surface dangling bonds which create trap states in between conduction and valance band of nanocrystals and provide an unwanted non-radiative pathway for the excitons to relax.

The unique fluorescence properties of colloidal semiconductor nanoparticles with anion rich surface have potential as local nanosensors; CdSe nanoparticles with anion rich surfaces placed in metal ion solution demonstrate significant changes in fluorescence intensity and this phenomenon can potentially be used for optical probing of metal ions at room temperature.

In **Chapter IV**, the structural properties of nanocrystals have been shown to greatly influence their optical and electronic properties. A well-controlled phase transition should give a deep insight into the mechanism of the growth of crystals and could as well be useful for sensing applications involving phase changes. In this chapter, we report how the surface of nanocrystals influences the evolution of a particular type of crystal structure and the transition in the case of CdSe, CdS and CdTe. Our findings throw new light on the possible mechanism for the formation of zinc blende and wurtzite CdSe nanocrystals. The phases of cadmium chalcogenide nanocrystals can successfully be controlled only by varying the ions on the surface of nanocrystals.

In **Chapter V**, we have synthesized dual emitting C/I/S (core/intermediate/shell) semiconductor nanocrystals consisting of a CdSe core and a ZnSe outer shell separated by a CdS layer. The origin of the resulting two emissions from these C/I/S structures was investigated and it was found that they are from two different channels: one from the CdSe/CdS core which is a Type-I system and the other from CdS/ZnSe shell which is a Type-II system. In C/I/S system, the CdS layer between CdSe and ZnSe is not only working as barrier but it is also participating in the formation of Type-II system with outer ZnSe shell within the heterostructures.

In **Chapter VI**, we have synthesized gold decorated CdSe nanocrystals of different size by using simple room temperature solution phase colloidal methods. Optical properties and charge transfer dynamics of semiconductor nanocrystal of CdSe carrying gold domains at their surface were studied by various techniques such as absorption and steady state/time resolve fluorescence spectroscopy. The fluorescence of such hybrid-nanostructure was found to be quenched dramatically compared to that of both CdSe nanocrystals. Fluorescence study indicates that an extra rapid non-radiative channel is opened up due to the charge transfer (electron) from the CdSe to the directly attached Au domain, leading to efficient electron–hole separation in this system. Detailed study of the effect of size of CdSe on the charge separation dynamics is also carried out.

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