Abstract

Colloidal composite semiconductor quantum dots (Q-dots) have attracted great attention due to their unique and intricate optical and electronic properties, which depends on specific material, size, shape and the composition. These characteristics arise from several phenomena viz. quantum confinement of charge carriers, surface effects and geometrical confinement of phonon etc. This turned semiconductor Q-dots into promising material for many applications such as, biological imaging, nanosensors, biomedical tags for fluoroimmunoassays, biographic optical memories, light emitting diodes, lasers, photonic band gap crystals and ultrafast photonic switches. However, the development of nanotechnology using these dots would demand an exact knowledge of the band structure and physicochemical properties of the semiconductor Q-dots, which in turn depends mainly on the band edge positions of these Q-dots.

Due to the lack of direct experimental measurements for the determination of these values, a common approach taken so far has been to assume band edge positions of the bulk material or of epitaxial super lattices. However, in case of colloidal Q-dots, the band edge values can differ considerably from that of the bulk. Optical spectroscopy has routinely been used for the estimation of band gap values, which provides the energies of allowed electronic transitions between the conduction band and valence band. However, it fails to predict the actual positions of these band edges, separately. On the contrary, these parameters are routinely determined from Scanning Tunneling Spectroscopy and Photo-electron Spectroscopy. However, the difficulties with these techniques is the involvement of serious instrumentation and tedious sample preparation protocols.

On the other hand, Cyclic Voltammetry (CV) has been successfully employed since several decades for the quantitative estimation of the HOMO and LUMO levels of electro-active molecular species. Like other redox molecules, semiconductor Q-dots also have discrete energy levels and is expected to undergo the electron transfer, mediated through the valence band edge and conduction band edge of the Q-dots. The anodic and cathodic peaks seen in the voltammograms could be attributed to the corresponding band edge positions viz. valence band edge and conduction band.
edge, respectively. The main advantage of CV is the mild experimental conditions at which the measurements have been performed, compared to the techniques viz. photoelectron and tunneling spectroscopy.

The goal of the present thesis work was to determine the band structure parameters of different semiconductor nanomaterials through size and stoichiometric and non-stoichiometric composition variation and to study the effect of charge injection on their electronic properties. For this purpose, the electrochemical (mainly cyclic voltammetry) and spectro-electrochemical measurements have been carried out on colloidal semiconductor quantum dots (Q-dots) and its nanocomposites.

On the basis of the data procured in this studies, the work has been organized and presented in the form of six chapters.

Chapter 1 will be devoted to the review of the research work related to the semiconductor nanomaterials. It includes a general introduction to the nanomaterials, its classification based on dimensionality followed by an elementary discussion about their exciting size and composition dependent physico-chemical properties. The main emphasis will be given toward the semiconductor Q-dots, especially, quantum confinement effect i.e. the effect of size reduction of the semiconductor materials to the size comparable to that of Bohr exciton diameter. The variation in electronic and optical properties of semiconductor Q-dots as a function of size as well as composition will also be discussed thoroughly. Different models and theories has been developed to study the electronic properties of semiconductor Q-dots. It includes, effective mass approximation, tight binding approach and the most versatile and recent one, semi-empirical pseudo-potential method (SEPM). A brief introduction will be given to these models and their applicability to study the electronic properties of semiconductor Q-dots. Further, the working principle of cyclic voltammetry and its potential application to determine the band structure parameters will be discussed in brief.

Chapter 2 will describe the cyclic voltammetric determination of quantum confinement and band structure parameters viz. conduction band edge, valence band
edge, and quasi-particle gap in p-type semiconductor (CdTe) Q-dots. These parameters are found to be strongly dependent on size of the CdTe Q-dots. The results obtained from voltammetry were compared with the spectroscopic measurements. A good correlation between the optical band gap values obtained from UV-vis absorption spectra and the quasi-particle gap determined from the cyclic voltammetry has been observed. It was observed that the conduction band states does not change appreciably with change in size while the valence band states shows continuous increase in energy with decrease in the size of the CdTe Q-dots. However, as reported by us for n-type CdSe Q-dots, the reverse trend has been observed for the variation in band state positions. Thus, based on this results and our earlier reported work on CdSe Q-dots, it can be claimed that cyclic voltammetry can be used as a tool to distinguish between n-type and p-type semiconductor. To the best of our knowledge, for the first time, cyclic voltammetry has been used to study the quantum confinement in p-type semiconductor Q-dots.

**Chapter 3** deals with the voltammetric investigations on the CdS$_x$Se$_{1-x}$ alloy Q-dots pertaining to study the effect of alloying the Q-dots on its electronic band structure. The composition dependent electrochemical properties of CdS$_x$Se$_{1-x}$ alloy quantum dots (Q-dots) ($x = 0.0, 0.2, 0.4, 0.6, 0.8,$ and $1.0$) were studied. For the first time, use of Voltammetry for the estimation of composition dependent band gap, band edge positions and band gap bowing in CdS$_x$Se$_{1-x}$ Q-dots is demonstrated. Band gap bowing was found to be more prominent for electrochemical band gap than in optical band gap, and is attributed to the surface sensitivity of the former. Voltammetric data shows that the electrochemical band gap (Eg) values are sensitive to the S mole fraction. For $x = 0.0$, Eg is equal to that of CdSe, it increases with increase in $x$ and reaches a value corresponding to that of CdS at $x = 1.0$. The optical band gap as determined from UV-Vis spectroscopic studies shows good agreement with that of the electrochemical band gap.

**Chapter 4** explain the effect of electrochemical charge injection on the photoluminescence (PL) of TOPO capped CdSe Q-dot monolayers. The photoluminescence of TOPO capped CdSe quantum dots (Q-CdSe) monolayer deposited on indium tin oxide (ITO) substrate and incorporated into an electrochemical cell has been
studied. The electron and hole injection was carried out by applying negative and positive potentials, respectively to the monolayer of Q-CdSe in dimethyl formamide (DMF) electrolyte with tetrabutyl ammonium hexafluorophosphate (TBAPF$_6$) as a supporting electrolyte and in the Ar atmosphere. It has been observed that when positive potential is applied to the monolayer, PL is irreversibly quenched. The PL peak intensity decreases with applied potential upto 2.0 V vs Pt quasi-reference electrode (QRE) and remains almost at the same level even after reversing the potential from 2.0 V to 0.0 V. While, when negative potential is applied, the quenching is observed; however, it is reversible. The PL peak intensity decreases with increasing potential from 0.0 V to -2.0 V and then it increases on reversing the potential from -2.0 V to 0.0 V. The results could prove helpful in explaining the phenomena of photoluminescence intermittancy or blinking in semiconductor quantum dots.

Chapter 5 describe a simple strategy for the synthesis of water soluble, luminescent, citrate-capped CdSe quantum dots (Q-CdSe) and their applications to selective detection of silver ions. The steady state photoluminescence (PL) spectra show single, narrow emission band at ca. 554 nm without any contribution from the trap states. The effect of various ions including physiologically important metal ions (viz. K$^+$, Ca$^{2+}$, Fe$^{3+}$, Zn$^{2+}$, Mg$^{2+}$, Mn$^{2+}$, Cu$^{2+}$, Ag$^+$, Pb$^{2+}$ and Cd$^{2+}$), on the PL intensity of citrate-capped Q-CdSe has been studied. Among these, selective luminescence quenching with Ag$^+$ ion was found to be predominant. Under the optimum conditions, the response was linear between 1.7 to 18 $\mu$M. The quenching constant $K_{SV}$ was found to be ca. $3.4 \times 10^5$ M$^{-1}$. The mechanism of photoluminescence quenching of Q-CdSe by metal ions (Ag$^+$) is also discussed. Based on these studies, the potential use of Q-CdSe as a luminescent probe for the selective detection of silver ion has been proposed.

Chapter 6 Here, we have presented a brief summary and concluding remarks from the entire work discussed in the thesis. Also, a brief remarks have been made on the future aspects of the present investigations. Specially, the determination of band structure parameters for different semiconductor Q-dots systems to study the effect of doping magnetic impurities, coupling of Q-dots and “multi exciton generation”.

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