Synthesis and Characterization of Semiconductor Nanocrystals: Photoluminescence and Size Tunability

Neelam Hazoor Zaidi

Abstract- Semiconductor nanoparticles are presently of great interest for their practical applications such as zero-dimensional quantum confined materials and for their applications in optoelectronics and photonics. The optical properties get modified dramatically due to the confinement of charge carriers within the nanoparticles. Similar to the effects of charge carriers on optical properties, confinement of optical and acoustic phonons leads to interesting changes in the phonon spectra. In the present work, we have synthesized nanoparticles of CdSe using thermal decomposition technique. Transmission electron Microscopy (TEM), Absorption spectroscopy and fluorescence spectroscopy have been used for characterization. Under room temperature condition highly luminescent particles emit in visible region, can be synthesized. Broadening of this photoluminescence spectra is due to the defects such as vacancies, which are probably located close to the surface in case of nanoparticles.

Keywords: Nanoparticles, optical properties, photoluminescence,

I. INTRODUCTION

I.1 Semiconductor Nanocrystals and their properties

Semiconductor nanocrystals are the subject of a thriving area of physical and synthetic inorganic chemistry, motivated by both fundamental science and the long term technological potential of these materials. Semiconductor nanoparticles are tiny light emitting particle on the nanoscale (1-100nm). Researchers have studied these particles intensely and have developed them for broad application in solar energy conversion, optoelectronic device, cellular imaging and ultra sensitive detection. Nanocrystals bridge the gap between small molecules and large crystals, displaying discrete electronic transitions reminiscent of isolated atom and molecules, as well as enabling the exploitation of the useful properties of crystalline materials. Bulk semiconductors are characterized by composition-dependent band gap energy (Eg), the minimum energy required to excite an electron from valence band to the vacant conduction band (fig.1). With the absorption of a photon of energy greater than Eg, the excitation of an electron leaves an orbital hole in the valance band. The negatively charged electron and positively charged hole may be mobilized in the presence of an electric field to yield a current. Relaxation of the exited electron back to the valance band annihilates the exciton and may be accompanied by the emission of a photon, a process known as radiative recombination. [1]

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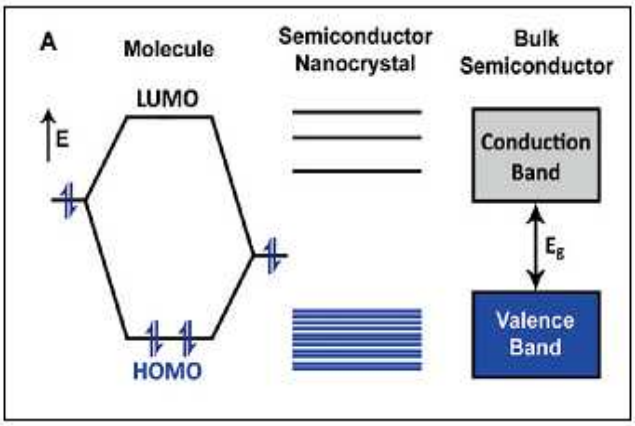

Figure I.1 Electronic energy states of a semiconductor in the transition from discrete molecules to the nanosized crystal and bulk crystals. Blue shading denotes ground state electron occupation

Semiconductor nanocrystals are commercially marketed for application as luminescent bio-labels and have been demonstrated in regenerative solar cells, optical gain devices and electroluminescent devices [2, 3]. Semiconductor nanocrystals are novel materials with interesting optical, electrical and magnetic properties.

I.2 Quantum Dots or Semiconductor Nanocrystals

Quantum dots can be considered as zero dimensional objects. Confinement is exerted in all three dimensions. For this the density of states is discontinuous. [4]

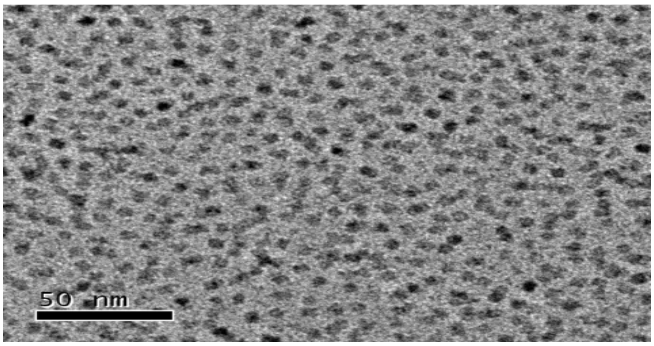

Figure I.2 Spherical semiconductor nanocrystals. (TEM micrograph of CdSe quantum dots)

Quantum dots are a class of semiconductors, which are composed of periodic groups of II-VI, III-V, or IV-VI materials (like ZnO, CdSe, CdS, PbSe, InP) with size ranging from 1.5 to 20 nanometers (10-50 atoms) in diameter. At this small size the movement of electrons is restricted in all directions due to which quantum confinement effect is observed [4]. This quantum confinement effect leads to atom like quantized energy levels in quantum dots. Hence, quantum dots are also called

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as artificial atoms. The usefulness of quantum dots comes from the fact that their peak emission frequency can be tuned by varying their size and composition [5-9], while the bulk semiconductors have fixed energy transitions.

I.3 Quantum Confinement effect and Size dependent control of Band gap in Quantum dots

In bulk semiconductor material, energy levels are very close and can be described as continuous. There exists a region of forbidden electron energies called the band gap, which is characteristic of a semiconductor. Electrons occupying energy levels below the band gap are described as being in the valence band (VB) and those above are in the conduction band (CB). The majority of electrons are in VB. For the electrons to excite to conduction band it has to acquire energy enough to cross the band gap. The excitation of an electron from the valence band to the conduction band leaves behind a hole in the VB. This excited electron-hole pair is called an exiction. The excited electron when falls back across the band gap to valence energy levels emits electromagnetic radiation with wavelength corresponding to band gap energy. The movement of the electron is from the edge of one band to another. Since the band gap is fixed in bulk material due to continuous energy levels and large number of atoms, the transition results in fixed emission frequencies. This is what we call as bulk band gap energy. Excitons have an average physical separation between the electron and hole, referred to as the Exciton Bohr Radius (a_B) which is different for each material. In bulk, the dimensions of the semiconductor crystal are much larger than (a_B). When the size of a semiconductor crystal becomes small enough that it approaches the size of material's Exciton Bohr Radius electron energy levels become discrete [8-9], a situation called "Quantum Confinement". Under these conditions the semiconductor material ceases to resemble bulk, and instead can be called a quantum dot. Due to discrete energy levels quantum dots don't have fixed energy transitions.

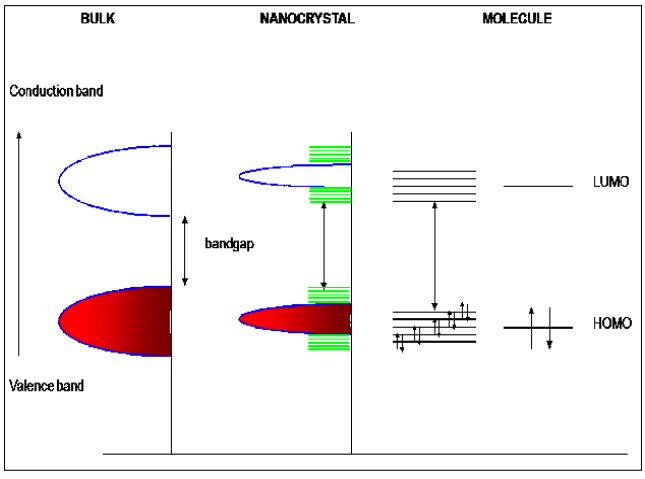

Figure I.3 Band structure of nanocrystal compared with that of bulk semiconductor

Since the energy levels are discrete, the addition or subtraction of just a few atoms has the effect of altering the boundaries of the bandgap. One can apply the "particle in a box" model to energies of quantum dots. According to "particle in a box" model, the energy difference between two levels is inversely proportional to the dimensions of the box. Hence, the band gap in quantum dot will always be energetically larger; therefore, we refer to radiation from to quantum dots to be blue shifted. Because the emission frequency of a quantum dot is dependent on the band gap, it is therefore possible to control the output wavelength of a dot with extreme precision by varying the size of Quantum dot. For example, the band gap of CdSe can be varied from 1.9eV to 2.7eV by changing the size of the particle from 5.5 nm to 2.3 nm. Quantitatively, the size dependence of optical and electronic properties of nanocrystals are explained by effective mass approximations (EMA) based on the effective masses of electron (m_e^*) and hole (m_h^*). For nanocrystals in strong confinement regime (where the radius, R of nanocrystal is much smaller than a_B) the following expression for the band gap has been proposed by Brus [5].

$$E(R) = Eg + \frac{\hbar^2}{2}\left(\frac{1}{m_e^*} + \frac{1}{m_h^*}\right)\frac{\pi^2}{R^2} - 1.786\frac{e^2}{\epsilon R}$$

Where E_g is the bulk band gap. The second term is the kinetic energy term. The third term arises due to the Columbic attraction between the electron and the hole.

I.4 Synthesis of semiconductor nanocrystals

Nanocrystals can be synthesized from a variety of materials and in several different media. Quantum dot can be synthesized by chemical and physical method. Thermal decomposition of the precursor leads to nucleation and growth. Over the year various approaches have been used to prepare colloidal semiconductor nanocrystals. Colloidal quantum dots can be prepared by thermal hydrolysis and condensation.

I.5 Characterization of nanocrystals

Nanocrystals can be characterized by absorption and photoluminescence spectroscopic method.

1.5.1 Absorption spectra

Absorption of a photon by nanocrystals occurs if its energy exceeds the band gap. Due to quantum confinement, decreasing the particle size results in hypsochromic (blue-) shift of the absorption onset[10]. A relatively sharp absorption feature near the absorption onset corresponds to the exciton peak i.e. the lowest exited state exhibiting large oscillator strength. While its position depends on the band gap and consequently, on the particle size, its form and width is strongly influenced by the distribution in size. [1]

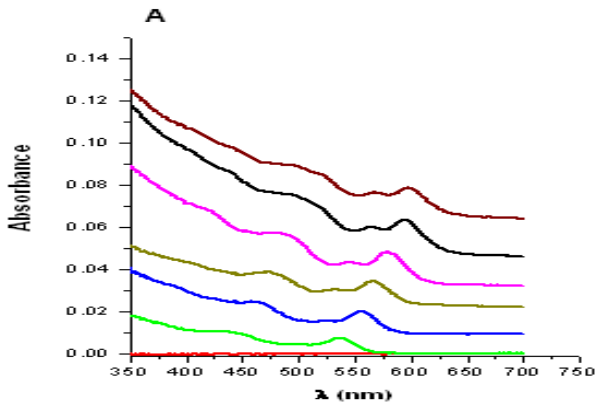

Figure I.4 Absorption spectra of CdSe semiconductor nanocrystals showing size tunability

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I.6 Photoluminescence

Photoluminescence is the process in which the substance absorbs the photon and reradiates the photons. The emitted photon have an energy corresponding to the band gap of nanocrystals and for this reason the emission colour can be tuned by changing the particle size. Efficient room temperature band edge emission are only observed for nanocrystals with proper surface passivation and perfect crystal structure, because otherwise charge carrier are very likely to be trapped in surface states, defect states enhancing the non-radiative recombination.

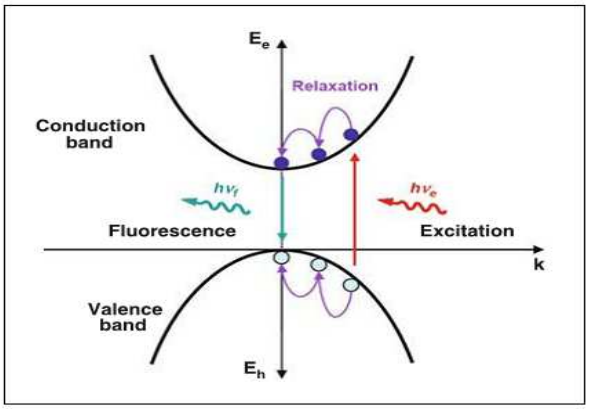

Figure I.5 Fluorescence in bulk semiconductor

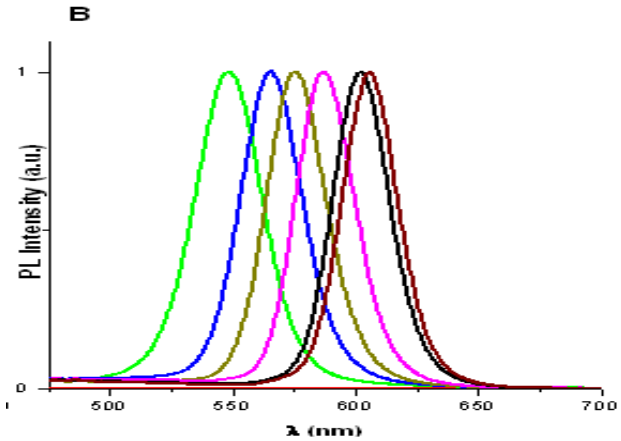

Figure I.6 Fluorescence spectra of CdSe semiconductor nanocrystals showing quantum confinement and size tunability. [1]

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