Synthesis, Properties and Potential Applications of Semiconductor Quantum Particles

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Studies of quantum dots (Q dots) or nanometer sized compound semiconductors with diameters in the range of 1-20 nm have generated a great deal of interest due to fundamental and technological applications. A number of devices have already been fabricated employing quantum dots. This paper presents the recent advances in the synthesis of compound semiconductor quantum dots and their potential use in electronic devices. Our work on self-organization of Q-dots using a wet chemical route has also been presented. Optical properties of these Q-dots using absorption spectroscopy technique have been discussed in the light of the existing theoretical models.

Key Words: Quantum dots, luminescence

INTRODUCTION

Semiconductor quantum dots have aroused great scientific and technological attention due to their possible application as luminescent devices[1], quantum dot lasers[2], biological labels[3], photo detectors[4], light emitting diodes[1], chemical sensors[5] etc. Semiconductor quantum dots refer to those semiconducting materials whose dimension lie in the nanometer range. Their electronic state lies between the molecular and bulk materials. The transition from bulk to molecular like behavior in these materials occurs when their dimension is decreased below the corresponding Bohr exciton radius. Nanocrystalline materials posses distinct behavior from bulk because of two reasons:

(1) Large surface to volume ratio associated with smaller size which results in change in chemical and physical properties.
(2) Confinement of electrons within a small dimension leads to changes in electronic and physical properties of the material.

Several theoretical models have been proposed to account for the electronic structure and optical properties of the quantum dots.

The effective mass approximation is based on the assumption of parabolic relation between the electron energy E and the wave vector k. Brus[6,7] using effective mass approximation (EMA) and taking into account Coulombic

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interaction between electron and hole, calculated the energy eigen states. In the strong confinement regime ($R/a_B \ll 1$), the ground state energy can be expressed as:

$$E = E_g + \frac{\hbar^2}{2\mu}\left(\frac{\pi}{R}\right)^2 - 1.8\frac{e^2}{\varepsilon R} \tag{1}$$

Where, E_g is the bulk bandgap (E_g=1.7 eV for CdSe), μ is the reduced mass of electron & hole and R is the particle size.

The EMA has been used to calculate the HOMO-LUMO gap for various semiconducting nanocrystals. For larger sizes of the nanocrystallites the infinite potential EMA gives a good description of the size dependence of HOMO-LUMO gap variation with size. However, it grossly overestimates the change in the band gap for smaller nanocrystals. One possible cause of breakdown of EMA may be the assumption of parabolic energy bands of the form $\hbar^2 k^2/2m_e$ which is accurate only for small values of k. Other factors, including the unrealistic boundary constraint, inappropriate treatment of the screened coulomb interaction, the oversimplified description of the crystal potential as a spherical well of infinite depth should also affect the predicted size dependence.

To overcome the shortcomings of parabolic band approximations the hyperbolic band model (HBA) has been proposed. The main improvement of the hyperbolic band model over Brus model is the inclusion of the effect of electron and hole band non-parabolicity. In this model, the hole and electron bands are hyperbolic, but approach the parabolic behavior at the Γ point of the Brillouin zone. The Coulomb corrections to the overall band gap shift are presumed to be small and are neglected within this model. On the basis of these assumptions, the following analytical formula has been derived by Wang[8] for the size dependent energy E(R):

$$E_g(R) = \left[E_{gBulk}^2 + \frac{2\hbar^2 E_g \pi^2}{m_0 R^2} \frac{1}{2}\left(\frac{1}{m_e^*} + \frac{1}{m_h^*}\right) \right]^{1/2} \ \text{----} \ (2)$$

Another scheme to study the electronic structure of various metals, semiconductors and nano clusters is the tight-binding (TB) method or Linear combination of atomic orbital (LCAO) approach which was first described by Slater and Koster[9]. Compared to the plane wave method, it is computationally less expensive. Therefore, it can be easily used to study complex systems such as complex alloys, doped compounds etc. Empirical Pseudopotential Method was suggested to investigate the electronic and optical properties of bulk semiconductor materials by Cohen *et al*[10].

The optical absorption spectrum of a nanocrystalline semiconductor provides a direct method for evaluation of quantum size effects. The excitonic peak is expected to appear in the absorption spectra as a shoulder right before the absorption edge. Below the Bohr exciton radius, the absorption spectra for semiconductor quantum dots exhibit fine structure due to the presence of discrete energy levels.

The blue shift of inter band electronic transition is given by (Brus[11])

$$\Delta E(R) = E(R) - E_g \qquad \text{---- (3)}$$

The size dependent blue shifts are clearly demonstrated in our experimental study shown in fig 1 for CdSe quantum dots. The absorption edge exhibited a blue shift from 720 nm (for bulk CdSe) to 436 nm as the size was reduced to 1.9 nm. The experimentally observed blue shifts for CdSe have also been compared with the theoretical calculations using EMA, TBA and HBA in fig 2.
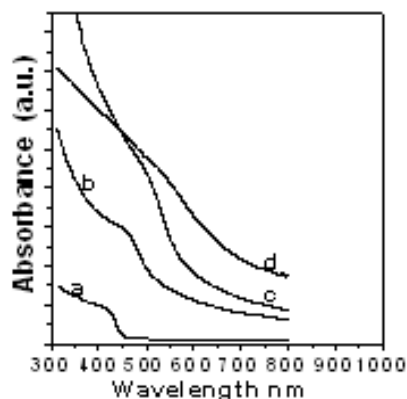
Figure 1. Optical absorptionspectra of CdSe quantum dots with mean diameters: (a) 1.9nm (b) 2.8 nm (c) 3 nm (d) 13 nm. The corresponding absorption edges are 436, 480, 536 and 610 nm respectively.
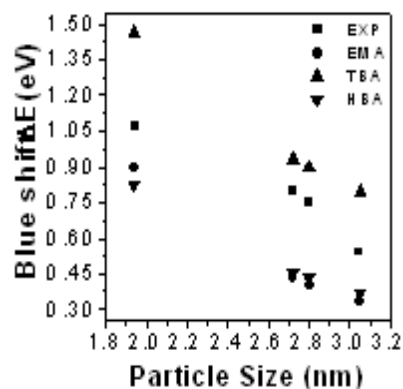
Figure 2. A comparison of experimentally observed blue shifts ΔE with those calculated using EMA, TBA and HBA models.

It is obvious from figure 2 that the experimentally observed blue shifts did not agree with any of the three models for the entire range of particle size. The EMA and Hyperbolic band approximation underestimated the blue shifts while the tight binding approximation overestimated the values. Our experimental results thus highlight the inadequacy of these three models. A major cause of the inadequacy may be the complete neglect of the effect of the cappant layer used to stabilize the quantum dots[12].

Synthesis of Compound Semiconductor Nanomaterials

A number of approaches have been adapted to synthesize the nanomaterials. These can be broadly classified into the following three categories viz: 1.Vapor Phase Synthesis 2. Wet Chemical Synthesis 3. Mechanical Attrition. The various techniques in the above categories, used for nanomaterial synthesis have been summarized in table 1. We will briefly discuss the chemical synthesis route in this paper.

TABLE 1:
VARIOUS FABRICATION TECHNIQUES FOR NANOSTRUCTURE MATERIALS.

Vapor Phase Synthesis	Wet Chemical Synthesis	Mechanical Synthesis
*Epitaxial Deposition		
- MBE	*Colloidal Solution	*Nano Scale Milling
- MOCVD	- Micelles	- Lithography
- MOMBE		- Ball Milling
*Thermal Evaporation Technique	*Chemical Solution Deposition	- Etching
- Direct Thermal Evaporation	- Polymers	
- Electron Beam Evaporation	- Zeolites	
*Sputtering Technique	- Langmuir Blodgett films	
- Rf Sputtering		
- Magnetron Sputtering	*Electro Chemical Deposition	
- Glow Discharge Sputtering	- Electrophoresis	
- Ion Beam Sputtering	- Chemical Bath Deposition	
- Reactive Sputtering	- Auto Catalytic Synthesis	
*Laser Ablation		
*Pulse Laser Deposition		

Chemical Synthesis

(a) Arrested Precipitation

In this approach controlled chemical reaction between appropriate precursors in an aqueous or non-aqueous medium is exploited. Precipitation of the nano particles may occur via homo or heterogeneous nucleation as the ionic product exceeds the solubility product. Once the nuclei are formed, growth may proceed by diffusion. The reaction parameters such as reactant activity, temperature, pH and the presence of catalyst can be controlled to obtain a desired growth rate and particle size. A large number of compound semiconductors structure CdSe, ZnS, ZnSe, CdS, CdTe, ZnTe, GaAs have been synthesized via arrested precipitation route[13-20].

A major problem associated with the precipitation technique is stabilization and prevention of particle agglomeration. The different approaches to attain size control and stabilization can be grouped into two categories viz. **(i) Electrostatic ii) Steric**

In the electrostatic stabilization the repulsive forces between the neighboring electric double layers surrounding two adjacent nanoparticles is used to prevent agglomeration. However, this method is effective in dilute aqueous or polar organic media. A change in electrolyte concentration can destroy the double layer resulting in particle agglomeration.

A more popular approach is to use steric forces. Certain surfactant molecules with electron donor head group can be selectively adsorbed on the nanoparticle surface with their backbones pointing outward into the solution. The lyophillic chains of the surfactant backbones interact with the solvent molecules. In case the particles tend to approach each other, the motion of backbones gets restricted

producing an entropic effect. Steric stabilization can be used in aqueous as well as nonaqueous medium even in presence of impurities. High concentrations of nanoparticles can be stabilized using steric influences. This approach has been used by us to self organize semiconductor quantum dots on a variety of substrates.

Fig 3a gives a schematic representation of the effect of adsorption leading to self organization. Fig 3b shows a high resolution atomic force microscope image of a typical film with highly organized CdSe quantum dots. Typical size of the individual quantum dot was 1.9 nm as shown. Our ability to obtain a highly organized growth of CdSe quantum dots is indeed novel in term of the simplicity of approach by exploiting the steric influences of the adsorbed surfactant molecules during assembly.
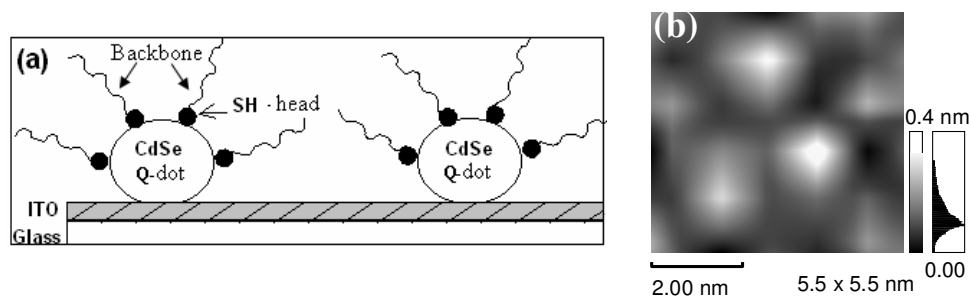
Figure 3 (a) Schematic representation of surfactant adsorption and mutual repulsive interactions giving rise to self-assembled CdSe quantum dots and (b) high resolution two dimensional 5.5 x 5.5 nm^2 AFM image of Q-CdSe sample (a) grown on ITO substrate using mercaptoethanol.

(b) Electrodeposition

Electro deposition of nano materials has been successfully used to grow multilayers, nano wires and quantum dots of metallic ceramics, semiconductors and polymeric substances. It is a relatively inexpensive technique with high throughput. It is also capable of generating complex patterns on conducting substrates. Multilayers of metals have been electrodeposited using pulse-plating[21]. Electrodeposition of conducting polymer semiconductor nanocomposite has also been reported by diksha *et al*[12]. Nanowires[22] have also been electrodeposited using porous membranes. CdTe quantum dots were also grown[23] using under potential deposition of monolayers of Cd and Te alternatively on a substrate.

Conclusions

A redeeming feature of chemical route is the ability to grow self-organised nanostructures. The possibility of using a surfactant with variable backbone length but the same functional head group can be exploited to control separation between the neighboring quantun dots. The resulting modulation of dielectric

constant can be used to develop photonic band gap materials. In principle, chemical self assembly can also be used to grow a three dimension network of quantum dots by choosing a surfactant with two functional head groups. A better understanding of the interaction between the surfactant molecules & the Q-dot will however be necessary before full technological potential of the chemical self-assembly can be exploited.

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