Synthesis characterisation series of newly fabricated type II CdSe CdSe/CdTe nanocrystals and their optical properties

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Abstract Nanocrystalline semiconductors exhibit different properties due to two basic factors. They possess high surface to volume ratio and the actual size of particle can determine the electronic and physical properties of the material. The small size results in an observable quantum confinement effect, defined by the increasing bandgap accompanied by the quantization of the energy levels to discrete values. In present work we have synthesized the series of cadmium selenide/cadmium telluride (CdSe/CdTe) core/shell and CdSe/CdTe/CdS core/shell/shell to investigate the biexciton energy through transient absorption measurements. These structures are type II nanocrystals are with a hole in the shell and the electron confined to the core. We specifically investigate the effect of nanoparticle shape on the electronic structure and ultrafast electronic dynamics in the band-edge exciton states of CdSe quantum dots, nanorods, and nanoplatelets. Particle size was chosen to enable straightforward comparisons of the effects of particle shape on the spectra and dynamics without retuning the laser source. In our results the Uv-vis showed only a mild redshift in the first excitonic an elongated tail with increasing shell thickness. High resolution Transmission Electron Microscopy (HRTEM) shows the slight agglomeration of the nanocrystals but still the size distribution was calculate able. Spherical small crystals ranging from 5.9 nm to 10 nm are observed. CdTe/CdSe structures were quasi spherical with a rough diameter 6 nm with some little agglomerated structure. . The spherical nanocrystals could be peanut shaped oriented along the c axis or the spherical only, which could explain the two peak emission. p-XRD results indicate the predominant wurtzite structure throughout.

1. Introduction

In last 20 years the quantum dots (QDs) which are also known as the crystals at the nano-scale are major focus of the research in the material science [1],[2],[3]. The luminescence properties of the nano-crystals semiconductor have given the edge over the traditional glowing dyes due to size tuneable emission [4], wide range of the photoexcitation properties [5],[6]. When these properties combine together these produce very good properties which significantly enhance the properties such as photoemission, high fluorescence and considerable battle to photo bleaching [7].

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The Quantum Dots have the potential to confine the imagination when the laser light is being thrown, however it depends on the size of nanocrystals because the smaller size NCs can glow more than the bigger size one. The role of NCs becomes more important because of its unique internal heterostructure, these properties make them use in the wide variety of the fields among them are telecommunication, LED, optoelectronics [9] and impressive application in bio labelling [10]. Peculiar properties of semiconductor particles when these are enough smaller than 10 nm in diameter size , these behave someway or other just like the single atom, in spite of being made up of thousands of atoms. These type of the semiconductors are highly applicable in computer chips and lasers, these can be define as the quantum dots [10],[11]. The semiconductor particles ranging from 1-10 nm are refereed as quantum dots and from 10-100 nm are termed as nanomaterials. Any material above to 1000 nm is termed as bulk materials, these does not have properties like the nanomaterials.

The nanocrystals have been changed to water soluble to make them useful for many biological, biochemical and industrial applications. Further the nanoparticles have made its way in the application as photovoltaic cell to increase its efficiency of converting occurrence beam energy into electrical energy. The other major fact which makes the semiconductor NPs useful in the light emitting diodes (LED) is in fact its band gap, which make these materials to transform electrical generated power into light with 30% efficiency [12]. In addition to above described properties there are huge applications in electronic devices like computers to cellular phones [21].

Interestingly, the semiconductor nanomaterial properties are entirely different than their bulk materials. In the bulk materials the electrons have range of the energies which are foud in different energy levels [22],[23]. This is all due to their packing pattern that almost infinite lattice of molecule can be formed leading them to hold the countless number of energy levels. Such type of the energy levels formulates the valance and conduction bands, these are split by the forbidden electron energy known as an energy or band gap.

2. Experimental/Synthesis

2.1 Synthesis of CdSe NCs:

Cadmium Selenide (CdSe) quantum dots (QDs) were grown at relatively high temperature using colloidal synthesis method [13]. CdSe was syntheized using Cadmium Oxide in the mixture of Oleylamaine and Octadecylamine (ODE) and Selenium powder in the elemental form. The summary of the synthesis is given below in detail.

15 mL of oleylamine was degassed under vacuum for 20 minutes at 100 ℃. Under the N_2, 0.45 mL of 0.45 Se stock solutions was then added degassed for 20 minutes under vacuum. Under N_2 the temperature was increased to 300 ℃, 3 mL of Cd Oleate solution (0.3 m) loaded in syringe was then injected quickly into the reaction flask. The temperature was then set at 280 ℃ for 25 minutes. Cleaned using 1:1 butanol : methano (degassed anhydrous). Re-dispersed in small amount of hexane (degassed anhydrous).

The CdSe nanoparticles have different diameter ranging from 4 to 12 nm depend on the injected amount of selenium into the solution, obviously this will affect the order to vary the emission wavelengths. A varying range of photoluminescence from 500 to 610 nm can be achieved by varying the TOPSe used and the reaction time as these were two major factors which affects the size of the resultant nanoparticles [14].

2.2 Synthesis of core/shell and core/shell/shell Naocrystals

The synthesis of core /shell CdSe/CdTe and core/shell/shell CdSe/CdTe/CdS were also synthesized and their optical properties investigated using Uv – vis and photoluminescence techniques. The aim of these investigations was to determine the biexciton energy through transient absorption measurements. In this synthesis the CdSe was used a core and the CdTe was grown using both the cadmium and tellurium precursors which were added separately. The summary of synthesis is given below [15].

2.3. Synthesis of Cadmium Stock solution

Cd stock solution- CdO 0.8 g added to already degassed 20 ml of Oleic acid and 20 ml ODE heated to 240 ℃ under N_2 to from a clear solution. Tellurium stock solution – Te powder 0.125 g dissolved in already degassed 2.9 ml of TBP (tributyl phosphine) and 9.5 ml of ODE.

The Te stock solution was injected hot to a Cd solution at 300 ℃ in less than a 2 second. As soon as the Te-solution added to Cd-solution, the colure turned dark brown. It was then cooled to 250 ℃ for growth of nanoparticles for 20 minutes. Then cooled to 60 ℃ and added 10 ml of dry methanol, re-dispersed in toluene – methanol cycles to remove any un-reacted solvents. It was finally dispersed in toluene for further use. The CdTe was also shelled from 1 ml thickness to 5 ml thickness to investigate the stability and optical properties of these materials [16].

3. Result and Discussion

3.1 Optical Properties

The Uv – vis and photoluminescence spectra are given in figure (1-3). Figure 1 show the absorption data of CdSe core and CdSe/CdTe core shell with increasing shell thickness. Figure 2 explain the elongated tail with increasing shell thickness and weakening of the first excitonic absorption features.

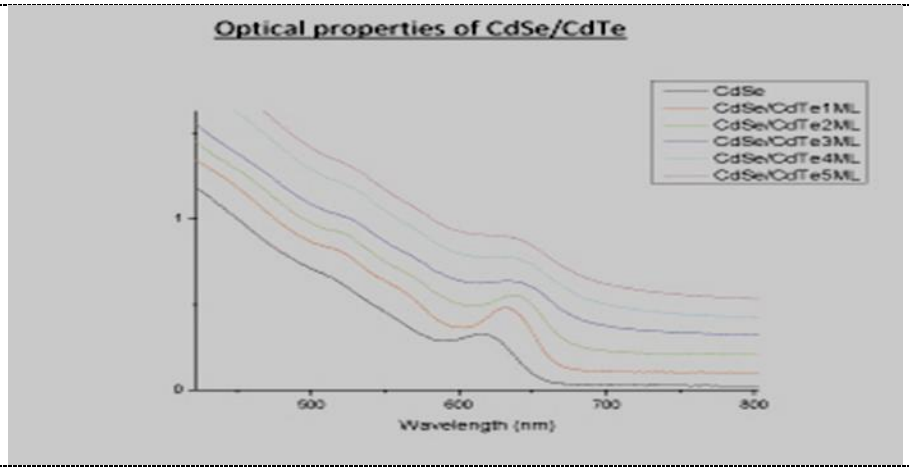


Figure 1. Absorption data of CdSe core and CdSe/CdTe core shell with increasing thickness.

This trend is clear in both figure (1 & 2) the effect of thickness of CdTe shelling from 1 ml to 5ml, the weakening of excitonic peak which predominant in first case.

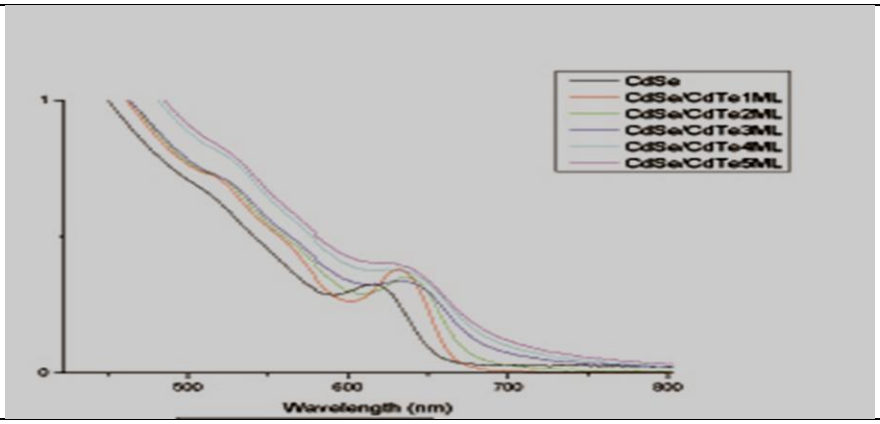


Figure 2. Absorption data of CdSe core and CdSe/CdTe core shell highlighting the elongated tail with increasing shell thickness and the weakening of first excitonic feature.

Figure (3) show the photoluminescence of CdSe core and CdSe/CdTe core shell nanoparticles with increasing shell thickness. It was observed during these photoluminescence studies that when there was low concentration of selenium used there was very low or no emission found. This shows that selenium has important role in luminescence properties of the reported materials [18].

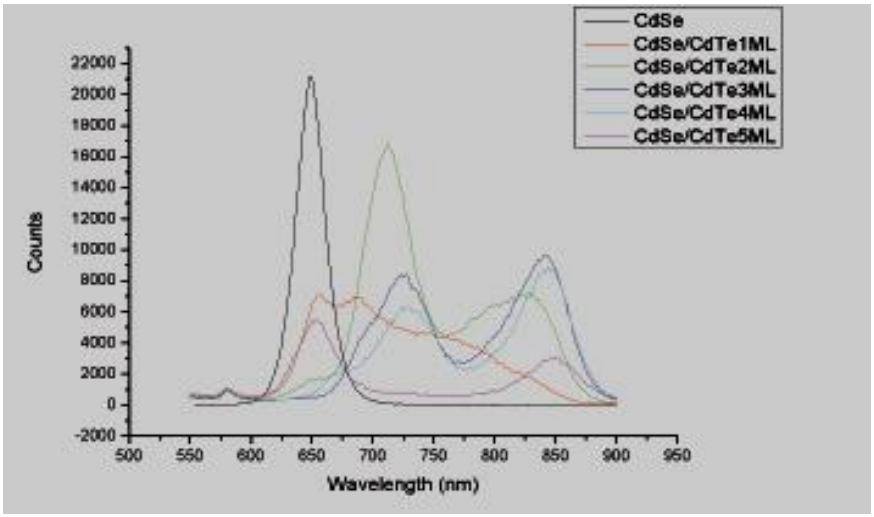


Figure 3. The photoluminescence of CdSe core and CdSe/CdTe core shell.

In UV studies it was further confirmed that in case of CdSE core, CdSe/CdTe core shell with the increasing thickness of CdTe shelling and increasing concentration of selenium the redshift has been observed which show the tendency of these particles to grow larger. By increasing the concentration of selenium, but keeping the concentration time constant, the red shift observed was greater than 70 nm highlighting that this has a larger effect on the size of the nanoparticles when compared with the length of the reaction. Fluorescent intermittency is also known as blinking in emission is common but at the same time it is not process confined to quantum dots [17]. Fluorescent intermittency is observed in dye molecules, fluorescent proteins, single polymer segments, porous silicon and high harvesting complex [17].

3.2 HRTEM and XRD Studies

High resolution Transmission Electron Microscopy (HR-TEM) images are shown figure (4-5). Figure 4 show the low and high images showing CdSe nanocrystals with an average diameter of 5.9 nm. The reaction time is still an important factor in the determination of particle size by TEM.

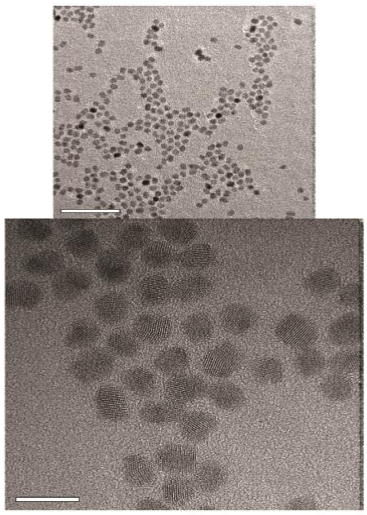


Figure 4. Low and high Resolution Images showing CdSe nanocrystals with an average diameter 0f 5.9 nm.

To ensure that the reaction finished after the desired time, the flask was cooled using a water bath or compressed air. As expected with a short reaction time the particle synthesized was small and luminescent to words the blue region of the visible spectrum [19]. It can be seen in the high resolution image of CdSe the crystals are spherical and peanut size and all the noncoastal are separated from each other.

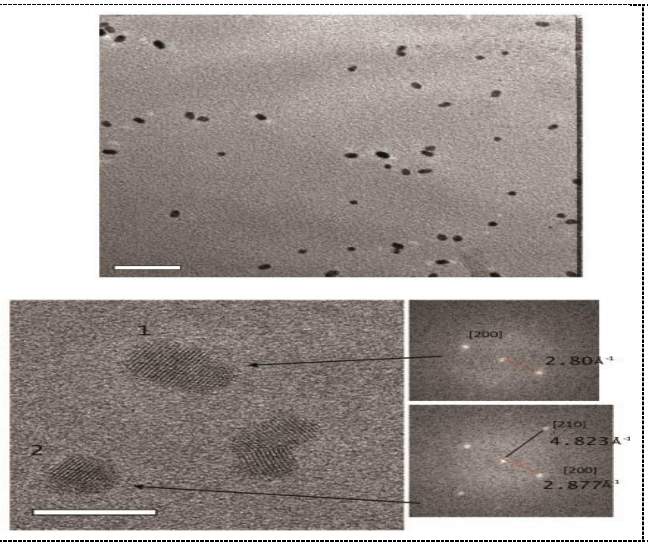


Figure 5. Low and High Resolution images of CdSe/CdTe having peanut and spherical nanocrysts 1.

Shows a probable wurtzite structure showing the [100] lattice 2 shows a probable wurtzite structure There is little chance of agglomeration of these particles. The lattice fringes are very clear which correspond to XRD pattern in figure 6. TEM image of the CdSe/CdTe core shell 5ml thickness are shown in figure 5. These images confirm the spherical and peanut shaped nanocrystals for the core shell nanocrystals. The crystal lattice marked as 1 show probable wurtzite structure showing the [100] and lattice 2 also showing the same type of wurtzite structure. FFT of the high resolution images indicated a wurtzite structure for both the spherical and peanut shaped nanocrystals.

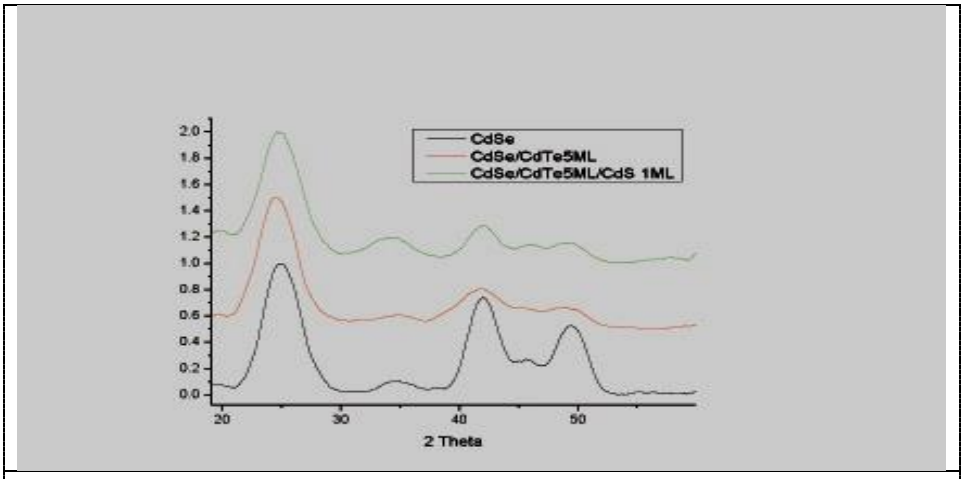


Figure 6. XRD data of CdSe CdSe/CdTe CdSe/CdTe/CdS. All showing the wurtzite crystal structure.

The spherical nanocrystals could be peanut shaped nanocrystals oriented along the c axis or the presence of spherical only, which could explain the two peak emission. The structural pattern was determine using powder X-Ray diffraction (p-XRD) shown in figure 6. CdSe nanocrystal exist in two different crystalline lattice structures can be either wurtzite (w, hexagonal) or cubic [20-21]. The XRd data of CdSe , CdSe/CdTe 5ml/ CdS 1ml all show the wurtzite crystal throughout. The CdS shelling was carried out to protect the CdTe from oxidation.

4. Conclusion

Absorption and photoluminescence measurements showed a redshift of the exctonic peak and PL emission. The PL emission red shifted from a core PL of 595 nm to 650 nm for the shelled structure. The HRTEM images of CdTe showed the nanocrystals to be peanut shaped with a wurzite lattice. The wurzite peanut shaped structures are predominant in p-XRD results. Absorption and Photoluminescence measurements showed a slight blue shift from a core emission of 650 to 642 nm. The blue shift is typically indicative of alloying. Therefore it could be concluded that this structure could be producing quasi type –II structure whilst also having strain alloying effects to actually increase the conduction band-gap of the core.

High Resolution Transmission Electron Microscopy (HRTEM) was conducted on previously dried solutions and showed little agglomerations of nanocrystals howver it was not difficult made getting a size distribution. There were predominantly small spherical crystals 5.9 nm for the CdTe core but quite a few large nanocrystals possibly agglomerated nanocrystals in excess of 10 nm.

The CdTe/CdSe structures were quasi spherical with a rough diameter 6 nm with some little agglomerated structure. The spherical nanocrystals could be peanut shaped oriented along the c axis or the spherical only, which could explain the two peak emission. p-XRD results indicate the predominant wurtzite structure throughout.

5. Summary

Photoluminescence properties, size and shape of the nanocrystals play an important role in deciding nanomaterial for different applications and uses. Core/shell, core/shell/shell nanocrystals of CdSe, CdTe and CdS synthesized, characterized by Uv – Spectroscopy, Photoluminesnce Spectroscopy (PL), Transmission Electron Microscopy (TEM) and X-Diffraction (XRD) techniques. Result shows with increasing thickness of CdTe shell, the redshift is observed in Uv –studies which is indicative of tendency of these particles to grow larger. Most of the nanaocrystals synthesized are ranging in between 5.9 nm to 10 nm having peanut shaped wurzite structures.

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