

Excimer like Photoluminescence Spectra of CdSe/ZnS Quantum Dots

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Abstract—The spectral properties of CdSe/ZnS core-shell quantum dots (QDs) have been studied under different organic solvents, concentrations and temperatures. Our results showed that the absorption spectra of CdSe/ZnS in benzene have only one peak around 280 nm under wide range of concentrations, and the shape of the absorption remained unchanged. On the other hand, the photoluminescence (PL) spectra of CdSe/ZnS in benzene showed two peaks one around 375nm and the other around 550nm. The effects of concentration and the temperature on CdSe/ZnS in benzene, under same conditions, were studied. The photoluminescence at 550nm became increasingly stronger for higher concentration and lower temperature. These are analogues to the excimeric behavior of organic molecules. To the best of our knowledge, this is the first report with convincing evidences for the excimer – like behavior of CdSe/ZnS core/shell QDs.

Index Terms—photoluminescence spectra, quantum dots, excimer, solvent influence

I. INTRODUCTION

The semiconductors nanocrystals, or so called quantum dots (QDs) are nanoparticles with a typical size of 2-20 nanometers (nm) consisting of few hundreds to few thousand atoms in each particle. Quantum dots are new nanomaterials which have properties that are intermediate between those of bulk materials and those of isolated or discrete molecules [1].

Quantum dots can be made from a wide variety of material; the most common QDs are the binary semiconductor materials containing the II-VI elements, e.g, cadmium sulfide (CdS), cadmium selenide (CdSe), cadmium telluride (CdTe), zinc selenide (ZnSe), lead sulfide (PbS), and mercury sulfide (HgS) etc. These semiconductor QDs, in the bulk, usually have band gap energy less than 4 eV. In all these nanocrystal QDs the atoms are aligned periodically with certain crystal lattice structure, such as the cubic zinc blende or hexagonal

wurtzite structure of the CdS and ZnS QDs [2]. Because of these reasons, the nanocrystal quantum dots display unique electronic and optical properties including size-tunable light emission, simultaneous excitation of multiple fluorescence, high quantum yield and long-term photo-stability. They have attracted a lot of both theoretical and experimental research interest for more than two decades [3]-[7]. These properties can be drastically changed, while maintaining the material morphology, by simply varying the number of atoms in each quantum dot. In such nanoparticles, the size of the quantum dot can be used to tune the emission spectral range over a major part of visible spectrum due to quantization effect: e.g., in the case of CdSe, the spectral range can be tuned from deep red ~1.7 eV to green ~2.4 eV by reducing the dot diameter from 20 to 2nm [8]-[10]. It has been also shown that the core shell quantum dots overcoated with higher band gap inorganic materials exhibits high PL quantum yield compared to the uncoated QDs, perhaps due to the elimination of surface non radiative recombination defects [11].

The photo luminescence spectra of CdSe/ZnS were found to be red shifted from the absorption maximum. This was observed more strongly in very small size quantum dots; such a shift towards red in emission of CdSe/ZnS quantum dots has been attributed to the recombination of weakly overlapping surface-localized carriers. This effect, has also been explained as a recombination of the optically forbidden ground state exciton split from the first optically active state by quantum dots shape, electron-hole exchange interaction and intrinsic asymmetry of lattice [12].

Shu-Man Liu et al studied CdSe semiconductor nano clusters over-coated with CdS shell in aqueous solution. Based on their experimental results and theoretical calculation, a model of excimer formation within nano clusters was proposed to explain the large Stokes' shift [13].

In our work presented here, the spectral properties of CdSe/ZnS in different concentrations and temperatures were described in a particular solvent environment (e.g. Benzene). The results showed that semiconductor CdSe/ZnS quantum dots could exhibit excimer like behavior in such environment. Similar experiments done in three more different types of the solvent environments showed that such excimer like formation was strongly prevented in polar solvents. To the best of our knowledge, this is the first report with convincing evidences for the excimer like behavior of CdSe/ZnS QDs

II. EXPERIMENTAL

CdSe/ZnS quantum dots were prepared following the previously reported procedures: TBP (tributylphosphine), TOPO (trioctylphosphine oxide), HDA (hexadecylamine) or ODPA (octadecylphosphonic acid) capped CdSe nanocrystals were synthesized using standard published methods [14]. We deposited about five monolayers of ZnS around the CdSe cores by using the recently developed successive ion layer adhesion and reaction (SILAR) technique [15]. To optimize the ZnS shell growth around the CdSe core by SILAR using ZnO and S as precursors, a stock solution of 0.1 M concentration was prepared for ZnO, oleic acid and ODE (1-octadecene) that were used for Zn coating and elemental sulphur and ODE for S coating. The purified CdSe QDs were added to a reaction flask consisting of HDA and ODE where Zn and S stock solutions were added under argon flow to grow the ZnS shell. To optimize the shell growth, the reaction temperature was controlled between 200 °C to 240 °C.

The absorption and photoluminescence (PL) spectra of CdSe/ZnS core-shell quantum dots in various organic solutions were studied under wide range of concentrations and temperatures. The spectra for the fresh solutions were measured in a small quartz cuvette with the dimensions 1 × 1 × 4 cm with an optical path length of 1 cm.

UV-Vis absorption spectra were taken using a Perkin Elmer spectrophotometer (Lambda 950) and the photoluminescence (PL) was measured on a Perkin Elmer LS55 spectrofluorometer.

III. RESULTS

The purified quantum dots nano crystal were dispersed in different solvents in different concentrations and U-V absorption and photo luminescence emission and excitation spectra were taken and presented below to give insight into the excimeric state behavior of this nanocrystal.

Fig.1 shows the absorption spectra of CdSe/ZnS quantum dots of different concentrations ranging from 9.0mg to 300mg of CdSe/ZnS in 5ml of benzene. It shows that there is a well defined absorption band at 280nm and optical density increased with increasing concentration. It is important to notice that there was only one absorption band at 280nm for all the above the concentrations. Note that the absorbance was not to the scale.

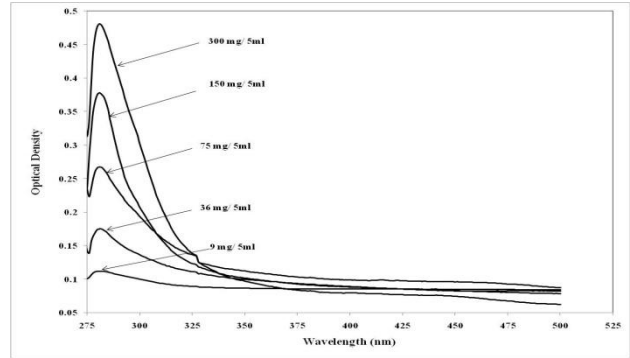


Figure 1. Absorption spectra of CdSe/ZnS quantum dots for different concentrations from 9.0mg to 300mg in 5ml of benzene.

Comparing the spectra of fig. 1 with photoluminescence emission spectra (PLES) depicted in fig.2, it could be seen that the PLES, as excited at 280nm have a primary peak at 375nm and small shoulder at 550nm.

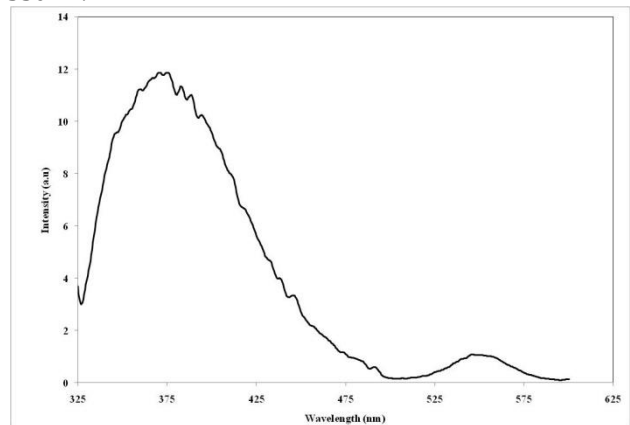


Figure 2. Photoluminescence emission spectra of CdSe/ZnS quantum dots for the concentration of 9.0mg in 5ml.

The PLES of CdSe/ZnS in benzene at low concentration (18 mg in 5ml) were obtained under two different wavelengths of excitation (280nm and 330nm). In both cases one could get the same spectral profile (with the primary band at 375nm and secondary at 550nm) but with different intensity as shown in fig.3. This is indicative of purity of sample.

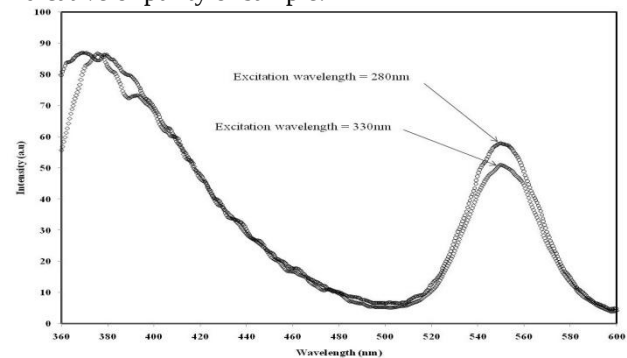


Figure 3. Photoluminescence emission spectra of CdSe/ZnS quantum dots for the concentration of 18 mg in 5ml for two different wavelengths of excitation (280nm and 330nm).

Fig.4 shows the PLES as excited at 280nm for different concentration (9.0mg to 300mg of CdSe/ZnS in

5ml of benzene). It clearly shows that the weak secondary band at 550nm became stronger and stronger; and for the concentration around 300mg of CdSe/ZnS in 5ml of benzene the peak around 550nm became the primary band and the one at 375nm became the secondary band.

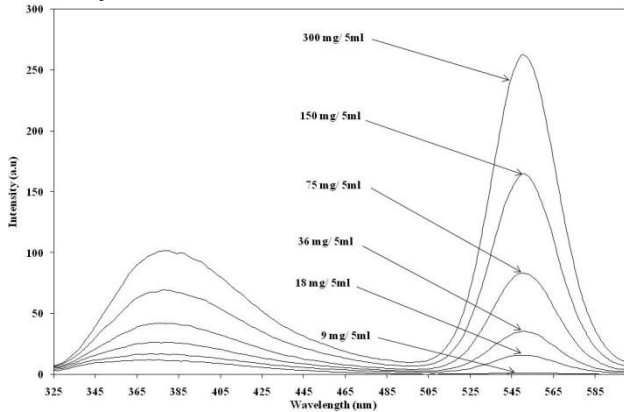


Figure 4. Photoluminescence emission spectra of CdSe/ZnS quantum dots for concentrations from 9.0mg to 300mg in 5ml of benzene.

The fig.4 also displays that the intensity of the band of 550nm increased by increasing the concentration. For the same set of concentrations; there was only one band at 280nm as shown in Fig.1. This is strongly indicative of excimer-like behavior of CdSe/ZnS quantum dots.

In order to confirm this, the spectral profiles of 300 mg of CdSe/ZnS in 5ml of benzene were taken under different temperatures. Fig.5 shows the PLES as excited at 280nm for three different temperatures. It's clear that as the temperature was increased above room temperature, (from 298K to 323K) the band at 550nm became weaker than at 380nm. i.e.,

$$\frac{I_{550}}{I_{375}}(323K) < \frac{I_{550}}{I_{375}}(298K)$$

The reverse took place with 550nm becoming stronger and stronger than 375nm band when temperature was lowered. i.e.,

$$\frac{I_{550}}{I_{375}}(283K) > \frac{I_{550}}{I_{375}}(298K)$$

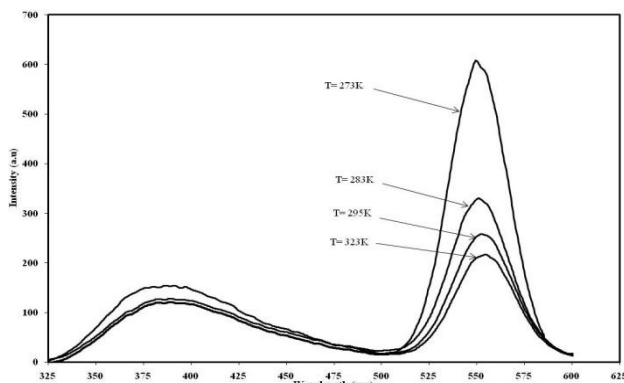


Figure 5. Photoluminescence emission spectra of CdSe/ZnS quantum dots for concentrations of 300mg in 5ml of benzene under different temperatures.

Such excimer like properties was found dependent on the solvent environment also. Fig.6 shows the dual emission band of steady state photoluminescence (PLES) for different set of solvents, all for the same concentration (300mg of CdSe/ZnS). It can be seen that in fig.6a the emission at 550nm (due to excimer like formation of quantum dots) was strongly favored by the non-polar solvents (like benzene) than by polar solvents like dimethyl fumarate (DMF) as shown in fig.6c. In some of intermediate polar solvents like ethyl acetate and n-butyl acetate, the intensity band of the two bands at 550nm and 375nm became almost comparable as shown in Fig.6b.

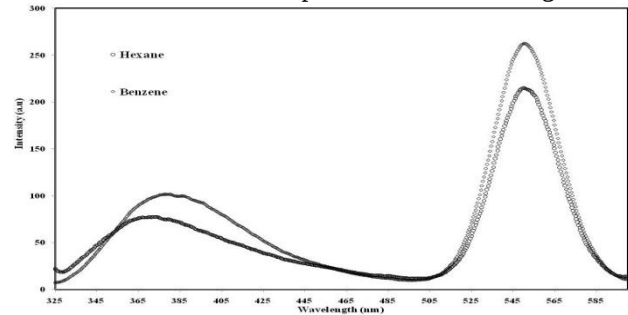


Figure 6. a: Photoluminescence emission spectra of CdSe/ZnS quantum dots for the concentrations of 300mg in 5ml in non-polar solvents

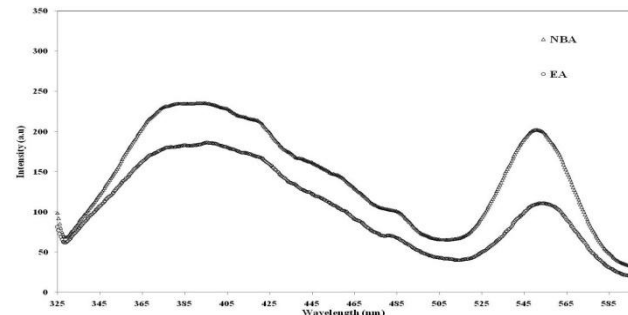


Figure 6. b: Photoluminescence emission spectra of CdSe/ZnS quantum dots for the concentrations of 300mg in 5ml in intermediate polar solvents

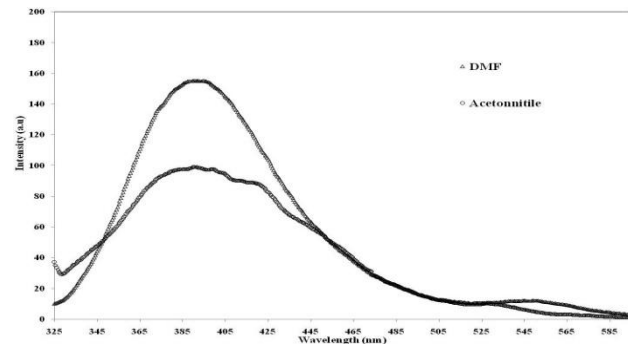


Figure 6. c: Photoluminescence emission spectra of CdSe/ZnS quantum dots for the concentrations of 300mg in 5ml in high polar solvents.

Fig.7 is a representation of I_{550}/I_{375} , the relative photoluminescence (PL) emission intensity at 550nm and 375nm bands, as a function of polarity (dielectric constant) of solvents. The linear fit is a strong indication that polar solvent deter excimer formation.

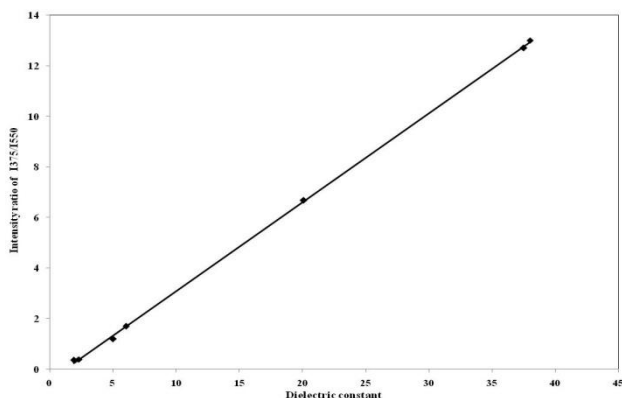


Figure 7. The relative intensities of photoluminescence emission at 550nm and 375nm bands (I550/I375), as a function of polarity (dielectric constant) for different solvents.

The solvent environment not only changes the properties of aggregation, but the quantum efficiency of photoluminescence [16]. This is shown in Table I. Where, it can be clearly seen that quantum efficiencies increase in *non polar* solvents like, benzene.

TABLE I. QUANTUM YIELD OF (CdSe/ZnS) QUANTUM DOT IN DIFFERENT SOLVENTS AT CONCENTRATION 300MG IN 5ML.

Solvent	Quantum Yield
Hexane	0.39
Benzene	0.54
n-Butyl acetate	0.39
Ethyl acetate	0.43
Acetonitrile	0.32
Dimethyl fumarate	0.35
Ethanol	0.27
Methanol	0.23

Another important property of solvents influence upon the spectral properties is Stokes' shift, which is a measure of changes in the dipole moment of the species when it goes to the excited state from the ground state.

Fig.8 gives the variation of Stokes' shift as a function of dipole factor of the solvent as defined by Mataga et al [17]. It can be seen that this quantum dot undergoes significant changes in the electron delocalization and becomes more polar in the excited state than in the ground state.

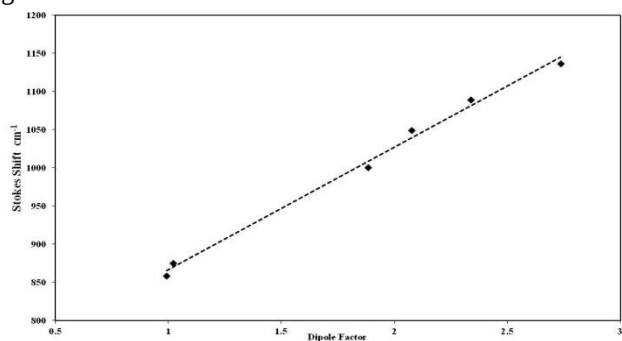


Figure 8. Stokes' Shift Vs Dipole factor

IV. DISCUSSION

Quantum dots are novel, synthetic nanocrystals with fascinating properties, yet to be fully understood. Though the basic materials are CdSe and ZnS which are inorganic semiconductor materials, the electron cloud associated with these materials exhibit behaviors compared to the π electron cloud of organic dyes. Because of these, quantum dots have strong absorption and broad emission characteristics, unthinkable in bulk CdSe or ZnS. The photon absorption and emission in quantum dots are due to excitons, which are completely different from π electron cloud of organic molecules, say coumarin. The purpose of this paper is to gain insight into the spectral behavior of these novel materials in view of strong similarities to organic molecule.

These are nanocrystals, with the size of 2-3nm, do not easily go into solution, in the same way a coumarin dye does in alcohol. Yet these quantum dots have exhibited excimer like behavior, often common in perylene or MEH-PPV [18].

An excimer means one quantum dots must be in the excited state and other in the ground state. Such transient species must have shorter life time of the order of few hundred nanoseconds. Also since the quantum dots is highly polar (as shown by large Stokes' shift of 100nm, in comparison to coumarin dye of 60nm), each particle strongly polarizes the environment solvent and gets entrapped in the cage of polar solvents. This could be the reason for low concentration of the excimer (with FES at 550nm) in polar environment like DMF or acetonitrile. But the non polar solvents like benzene or hexane could not trap such a particle and permits the aggregation with another ground state particle.

One could visualize that a highly excited polar nanoparticle could induce polarization with the ground state, unexcited particle and make a transient, associated state. This could be the reason for high concentration of excimer (with band at 550nm) in higher proportion than monomer (375nm band) in hexane like solvent. All these results presented here strongly support the extraordinary level of electronic cloud delocalization and high degree of polarity, shown by the excitons of quantum dots, much similar to the π electron cloud of coumarin [19].

V. CONCLUSION

In this communication, we have been able to show that the quantum dot nanocrystals of CdSe/ZnS in organic solvents exhibits excimer like spectral behavior, with excimer formation strongly favored in non-polar solvents. All these because of the excitons of these nanoparticles undergo gross changes in the electronic configuration. These nanocrystals behave very much like organic dye molecule.

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