Up-Scalable Synthesis of Size-Controlled White-Green Emitting Behavior of Core/Shell (CdSe/ZnS) Quantum Dots for LED Applications

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Research on CdSe/ZnS core–shell quantum dots (QDs) was synthesized by a chemical route using bio-conjugated organic amino acid (L-Cysteine). The structural, morphological, and optical properties of the nanocrystal powder samples were analyzed using various characterization techniques. The diameter of the resulting QDs was about 3 nm with uniform size distribution. The optical properties QDs exhibited an absorption and emission peak at 515 and 525 nm respectively, at room temperature. The QDs through emission in the spectral range at 516–535 nm is special for their application in green LEDs and white-light generation. The high optical properties performance of the QDs nanocomposites gained indicates that the materials are promising for (LED) applications.

Keywords: CdSe/ZnS, Core–Shell Quantum Dots, Luminescence, Optical Properties, Green and White-Light LEDs.

1. INTRODUCTION

In recent years, the unique arrangement of the optical and the electronic properties of core–shell quantum dots (QDs) have been demoralized for optoelectronic devices. Core–shell quantum dots (QDs) have involved considerable attention as potential applicants in several applications including LED displays, photoluminescent, chemiluminescent and the biological labels.1–3 The core–shell quantum dots (QDs) with emission in the spectral range at 500–550 nm are used for application in LEDs for recent study.4 The numerous semiconductor QDs of II–VI group metal chalcogenides, such as, ZnS, CdSe and CdTe have been studied by the researchers because of their quantum confinement effects which include size dependent photoemission properties. The photoluminescence (PL) spectra of these QDs can be turned over a wide range of the electromagnetic spectrum with control in size and composition. Last studies are being carried out on the effect of size on their physico-chemical properties. Since, of their small size and large number of cations, for co-ordination sites, nanocrystallites can enhance the rate of chemical reactions (QDs) and are increasingly gaining popularity as reactive nanocrystallites.

As their size decreases to their Bohr radius (usually around a few nanometers), all the electronic properties changes. The QDs require many advantages associated toward organic dyes, such as, PL intensity bands
with narrow bandwidth and the high photo-stability against photo lightening studies. The properties of QDs have possible application fashionable biomedical labels and the light harvesting devices. Many synthesis routes have been developed throughout the last past decades including organometallic precursor route, non-organometallic precursor route, microwave irradiation route, solvothermal route and sonochemical route. The QDs nanoparticles involving metals, semiconductors or oxide nanocrystals in the core, with shells composed for different materials have been investigated broadly studies. The preparation method of Murray et al. reported that the decomposition for dimethyl cadmium had been adopted to synthesize nanocrystals of the type of CdSe@ZnS, CdSe@ZnSe and CdSe@CdS. Recently, core shell growth was attained by the injecting the precursor’s materials into a dispersal containing the core nanocrystals. The injection is carried out at a slightly lower temperature to force shell growth, evading independent nucleation. Therefore, a combination of diethylzinc and the bis(trimethylisilyl)sulfide injected into a hot solution containing the core CdSe nanocrystals to enclose them with a ZnS layer. Cumberland et al. have synthesized inorganic CdSe/ZnS core/shell quantum dots with 5.4 nm of average size using a single-source precursor with hexadecylamine (HDA) as a capping ligand. Xin et al. have successfully synthesized CdSe/ZnS QDs of 2.6 nm size with two amino acid namely, histidine and the N-acetyl-cysteine as an organic capping agent. TOPO and Iridium (Ir) complex modified CdSe/ZnS QDs were synthesized by Hsieh et al. In their results the average diameter of TOPO and Ir (Iridium) capped CdSe/ZnS QDs were found to be 6.8 and 7 nm respectively. Zhao et al. have labeled a process for transferring octadecylamine (ODA) stabilized CdSe/ZnS core–shell semiconductor nanocrystals (ODA-QDs) from chloroform into water through a ligand exchange process with a dendron conductor nanocrystals (ODA) stabilized CdSe/ZnS QDs were modified with 6-ferrocenyl-1-hexanethiol (FcHT) or 11-ferrocenyl-undecanethiol (FcUT) via ligand exchange process by Dorokhin et al. and the average diameter of the QDs estimated to be 5.2 nm from TEM studies. Altogether these methods include the hot co-ordination solvent method using tri-n-octylphosphine oxide (TOPO) and trioctylphosphine (TOP) which is identified as a prominent method to synthesize semiconductor QDs. However, these methods require higher temperature and toxic materials. The objective of present research work is to study the emerging an environmental plasenger method to synthesis CdSe/ZnS QDs for the first time unlike previous researchers. The as-prepared QDs were characterized by structural (XRD), morphological (SEM/EDX, TEM) and optical properties (UV and PL) studies.

2. EXPERIMENTAL PROCEDURE

2.1. Synthesis

All the chemical reagents used in the experiments such as, zinc nitrate (Zn(NO₃)₂·H₂O, Merck, India) cadmium nitrate (Cd(NO₃)₂·H₂O, Merck 98%), sodium selenite (Na₂SeO₃, Merck 98%) thioacetamide (C₂H₅NS) were of analytical grade and were used as received without further purification. L-Cysteine was used as the organic capping agents in the present experiment. In a typical synthesis procedure of ZnS, 2.97 g of (Zn(NO₃)₂·H₂O) and 2.5 g of thioacetamide were taken in the 1:3 molar ratio; each reagent was separately dissolved in 10 ml Millipore water and then mixed thoroughly. The synthesis procedure of CdSe is already described by our group. The as prepared ZnS and CdSe are mixed thoroughly with 25 ml L-Cysteine. After stirring for 2 hrs, the mixture was transferred into a Teflon lined stainless autoclave of 200 ml capacity (with 75% filling). The autoclave was sealed tightly and heat treated at 200 °C in an electrical oven for about 6 hrs and then allowed to cool down to room temperature naturally. Finally, a deep dark red powder was collected, after centrifugation and it was repeatedly washed with water and ethanol to remove unwanted species present in the product. Finally, the sample was dried at 120 °C for 3 hrs.

2.2. Characterization Techniques

Powder XRD measurement was performed on Rich Seifer X-ray diffraction system, with monochromatic Nickel filtered CuKα (1.5406 Å) radiation. Energy dispersive X-ray (EDX) analyses were recorded for compositional analysis of the materials. X-ray detector located inside a scanning electron microscopy (SEM). The electron beam was accelerated at 20 kV. High resolution transmission electron microscopy measurements were carried out using JEOL 3010 operated at 25 kV. Specimens were prepared by depositing a drop of nanoparticles in hexane solution onto a formvar-coated copper grid and letting it dry in air. UV-Vis absorption spectrum and photoluminescence (PL) spectrum were recorded by using Varian Cary 5E spectrometer and Jobin Yvon Flurolong-3-11 spectrometer respectively. In the PL study, a 450 W Xenon lamp was used as the excitation source and a photomultiplier tube as the detector.

3. RESULTS AND DISCUSSION

3.1. Powder X-ray Diffraction Analysis

Structural characterization (crystallinity and phase analysis) of synthesized products were conducted by the Powder XRD patterns of monodispersive CdSe/ZnS QDs are
shown in Figure 1. The development of the powder X-ray diffraction patterns during the growth of the shells around spherical ZnS nanoparticles shows that the hexagonal (wurtzite) phase of CdSe. The higher intensity and the smaller width (002) of the reflection peaks as shown in Figure 1, show that the right panel of CdSe/ZnS QDs is identical with the c-axis of the wurtzite structure. XRD analysis observed peaks can be indexed to the wurtzite structure, with a lattice constant slightly beaten from that of bulk CdSe due to CdSe/ZnS coating, which were well consistent with the characterized peaks of wurtzite hexagonal CdSe/ZnS core–shell (JCPDS card Nos: 77-2307, 89-7385). The peak (002) is narrow; it is lower in intensity than that for bare CdSe QDs. The decrease in intensity of the (002) peak and the shift of all peaks to higher angle are consistent with previous reports.16 Additional, the XRD peaks are broadened due to their small size distribution. All the peaks are well-defined representative the high crystalline nature of the specimen. This designates intensification in crystallinity due to the size enlargement of the nanoparticles. The average crystallite size was obtained from the XRD peaks using the Scherrer equation:12

\[
L = \frac{0.89\lambda}{\beta \cos \theta}
\]

Where \(L\) is the average crystallite size (Å), \(\lambda\) is the wavelength of the incident X-ray beam (1.54 Å), \(\beta\) is the full width at half maximum (FWHM) (rad), and \(\theta\) is the Bragg angle. The average crystallite size was 3.024 respectively.

3.2. SEM and EDX Analysis
Surface morphology landscapes of as-prepared CdSe/ZnS core–shell quantum dots were analyzed with SEM and their micrographs are shown in Figures 2(a)–(c). It is clearly obvious from the images that the clusters of primary ZnS nanoparticles are adsorbed over the surface of CdSe crystallites of nearly smooth and spherical surface. Additional interesting observation is that the present methodology favoritisms operative regulator over the particles size and shape as shown in Figures 2(a)–(b). The chemical purity and the stoichiometry of the CdSe/ZnS samples were tested by EDX. Figure 2(c) indicates energy representative spectrum of the L-Cysteine covered CdSe/ZnS QDs. The EDX spectrum reveals the elemental constitutions of CdSe/ZnS QDs. The observed peaks and their position were very well match with the reported work.17 Despite, capping agent with other organic surfactant, the as-prepared CdSe/ZnS QDs does not show the presence of any kind of organic impurity in its present here. The organic residuals can be systematically removed by several cycles of washing/centrifugation/separation at a certain rotation speed. From the spectrum, the trace of Cu signals is noticed which are attributed to the copper grid.
used for SEM imaging. The powder XRD pattern and EDX analysis confirmed the structure, purity and composition of the obtained product. X-ray diffraction analysis confirmed the crystallization of hexagonal CdSe/ZnS phase.

### 3.3. TEM Analysis

The TEM images and the particle size and shape of the particles of CdSe/ZnS core–shell QDs were investigated by TEM. Figures 3(a)–(d) shows the TEM images for hydrothermally full-grown CdSe/ZnS core–shell QDs. It is interesting to note that the presence of highly monodispersed and absolute spherical QDs. Additional, a close examination of Figures 3(a)–(c) suggests that the less agglomeration of QDs. As seen in the TEM image, honeycomb of QDs size is ranging from 2–4 nm. Essentially, that the mean particle size determined by the TEM is very close to the average crystal size calculated by the Debye–Scherrer formula from the XRD pattern. This is in good agreement with the results of XRD analysis. Supplementary, we surveyed approximately 150 QDs and their histograms in Figure 4, shows the average diameter is about 3 nm and the particles have a narrow size distribution. To be sure that as prepared nanocrystals has distinct core–shell structure, separated and purified nanocrystals before and after growing of the product. To achieve good reproducibility in the synthesis of core–shell QDs, paid special attentions to optimize each preparation stage. The growth of ZnS shell on CdSe core is accompanied by significant broadening of particles size distribution. We found that the parameter (L-cysteine), which is affecting the size distribution of colloidal nanoparticles play a vital role. L-cysteine is not only functions as a stabilizer in true system but also offers S atoms from its gradual decomposition in the later stage of the synthesis. L-cysteine (1.21 g) would be inducing the formation of core/shell structure in the synthesis as shown in Figure 5. The highly water soluble and

![Figure 3](image-url)

**Figure 3.** Bright field mode TEM image of CdSe/ZnS QDs.

![Figure 4](image-url)

**Figure 4.** Size distribution chart of CdSe/ZnS quantum dots.
biocompatible L-cysteine capped CdSe/ZnS QDs having narrow size distribution were synthesized without using any additional stabilizer. We have chosen L-cysteine amino acid to cap CdSe and ZnS nanoparticles as it passivates the surface states more effectively than other thiols. Moreover, L-cysteine provides biologically active end groups for possible targeting specific cell sites. Adjustable PL most with respect to particle size can lead to the development of suitable fluorescent biological probes. Therefore, the efforts have been taken to establish the feasibility to prepare narrow size CdSe/ZnS QDs. L-cysteine plays three essential roles: acts as a source for sulphide ions, growth moderator and stabilizer in the present study.

3.4. Optical Absorption Study

Figure 6 shows UV-Vis absorption spectrum of L-cysteine capped sample at room temperature. The sample shows excitonic peak at 515 nm. For bulk CdSe, direct band gap was found to be 1.74 eV. An absorption peak for CdSe is therefore expected at 716 nm. Yet, there is a strong blue-shift in the absorption spectrum (515 nm) indicating that the particles must be smaller than the Bohr radius \(a_B\) of exciton, which is 5.4 nm as reported for CdSe. The as-prepared CdSe/ZnS QDs size is around \(R = 3\) nm in the present work. Thus, the decreased \((R \ll a_B)\) regime indicate that the strong-quantum confinement effect.

3.5. Photoluminescence Study

To improvement more thoughtful of the optical properties of these CdSe/ZnS NPs, we have also carried out their photoluminescence spectra assessment. In common, PL of CdSe/ZnS QDs shows strong emission bands in UV (at 390 nm) region, blue (at 450 nm) and green (at 540 nm) emission bands in the visible region. The intensive PL emission spectrum indicated that it has potential application in light emitting devices and LED’s. Commonly, the PL intensity of bare water-soluble CdSe NPs was weak, but after coating with shells, nanoparticles would have relatively favorable optical properties because of reducing non-radioactive recombinitation by confining the wave function of electron–hole pairs to the interior of NPS, so up to now CdS, ZnS and ZnSe with a larger band gap have been used as an inorganic shell material to coat CdSe NPs. In comparison to the organometallic routes, the aqueous approaches have many advantages, such as simple, green, highly reproducible.

From the Figure 7, a sharp absorption features \((\lambda_{\text{abs}} \sim 515\text{ nm})\) suggest monodispersity of CdSe/ZnS nanoparticles and the narrow PL emission in Figure 1 \((\lambda_{\text{emi}} \sim 525\text{ nm})\) indicates near band edge emission. The fact that the PL emission maximum lies close to its absorption-onset indicates that the PL emission arises because of the direct recombination between LUMO and

Figure 6. UV-vis absorption spectrum of CdSe/ZnS QDs.

Figure 7. Photoluminescence spectrum of CdSe/ZnS QDs.
HOMO charge carriers.\textsuperscript{21} QDs with emission in the spectral range from 516 to 538 nm are of special interest for the preparation of QDs based green and white LEDs. So, we suggest that CdSe/ZnS core shell QDs prepared in the present study is promising candidates\textsuperscript{17} for light harvesting applications. The emission properties of semiconductor nanoparticles can be characterized by the fundamental emission parameters like, the emission color and color purity. The full width at half maximum (FWHM) of the emission peak is the measure of the color purity. Less value of FWHM indicates more pure emission. Figure 1, shows the FWHM of the emission peak. Recently, it was found that the FWHM values of narrow PL peak values are around 23 and 41 nm as reported.\textsuperscript{22}

The present sample showed least value of FWHM (typically <20 nm), which is even comparable to emission observed by single dot spectroscopy, indicating better homogeneity in the emission properties of the CdSe/ZnS QDs. Small stokes shift and narrow PL FWHM indicate that the as synthesized CdSe/ZnS QDs are with regular surface and a narrow size distribution.\textsuperscript{23} The shape of the intensive PL peak emission is dominated by band gap luminescence and no deep trap emission was deducted. In the present work, PL spectrum of CdSe/ZnS QDs sample at 350 nm was used as an excitation wavelength. While, the emission peak did not shift when excited at other wavelengths, which suggested that the emission was due to a real electronic transition of QDs. The fluorescence spectrum of L-cysteine coated nanoparticles is shown in Figure 7. The absorption edges are found to be blue shifted with respect to their bulk counterpart indicating the quantum confinement effect in the QDs.\textsuperscript{24} There are some key parameters that determine the applicability of luminescent nanocrystals in the LED devices. They are (i) High luminescence quantum efficiency (ii) Stability of luminescent properties under real operation conditions and (iii) Solubility of nanocrystals in desired solvent. All these problems deal with the proper passivation of dangling bonds present on the nanocrystal surface. Attaching the organic ligands to the nanocrystal surface can provide solubility to nanocrystals and in certain cases, can allow high PL quantum efficiency.\textsuperscript{25} However, the organic ligands are label and in dynamic equilibrium with the surrounding medium. As a result, the luminescence efficiency is strongly dependent on nanocrystal’s surroundings. The fabrication of highly luminescent alloy nanocrystals with the radii around the corresponding Bohr radius bears the potential to significantly improve the performance of QDs base optoelectronic devices, which are mainly limited to by the inhomogeneous broadening in the optical properties due to the size inhomogeneity.\textsuperscript{4}

The high quality of our green LED and white light generation QDs is attributed to two possible reasons:\textsuperscript{24–27} First, as an alternative to the refluxing route, the high temperature adopted by the hydrothermal route allows the reaction to proceed and conclude in a closed condition within 70 min.\textsuperscript{28–33} In the present study, the hydrothermal route greatly speeds up the reaction and improves the spectral properties of the resulting QDs, because of higher reaction temperature.\textsuperscript{34} This is extraordinarily beneficial for reducing surface defects of QDs and for enhancing the quality of QDs.\textsuperscript{35–37} Therefore, in the absorption spectrum, the absorption edge at 515 nm and in the emission spectrum, emission at 525 nm is a clear indication of visible light response of the particles and thus showing the promise for various fluorescence applications.\textsuperscript{38} On the other hand, decreasing the molar ratio of ligand-to-Zn will promote the formation of thio-Zn complex for getting high quality CdSe/ZnS QDs. On the other hand, thioacetamide and L-Cysteine must be ensured sufficient to deliver constancy and the surface passivation of growing QDs during the synthesis process.\textsuperscript{39} Though, that the QDs of the resulting decreased affectedly with the further increase of the ligand-to-Zn molar ratio. Since, that the excessive increase of the ligand-to-Zn molar ratio deteriorates the PL intensity.\textsuperscript{40–41} The present examination delivers a valuable artificial direction for manufacturing water-soluble and the fluorescent CdSe/ZnS QDs, which can be applied in biology, optical coding, or optoelectronic devices.

4. CONCLUSIONS

Summarizing, we have developed a novel type synthesis of luminescent semiconductor nanocrystals consisting of CdSe core and ZnS as outer shell. The size of CdSe/ZnS QDs was successfully controlled by environmental friendly solvent. The powder XRD pattern and EDX analysis confirmed the structure, purity and composition of the obtained product. X-ray diffraction analysis confirmed the crystallization of hexagonal CdSe/ZnS QDs. The absorption and emission edge is a clear indication of visible light response of the particles and thus showing the promise for various light harvesting and fluorescence applications. QDs with emission in the spectral range of 516–535 nm are special for their application in green LEDs and white-light generation. The material has potentially lower toxicity and better protection of surrounding medium from the toxic element present in the emitting CdSe core by non-toxic ZnS shell which will enhance the luminescence behavior.

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References and Notes


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