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A cost effective low temperature approach for developing highly biocompatible quantum dots: The role of pH and Cd concentration on L-cysteine stabilized CdSe quantum dots

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ABSTRACT

Water dispersible CdSe quantum dots (QDs) were synthesized in aqueous solutions through a chemical precipitation technique followed by hydrothermal treatment employing L-cysteine as a stabilizer. The influence of precursor concentration and pH of the solution on the quality of CdSe QDs were studied and discussed. The as-synthesized CdSe QDs were characterized by powder X-ray diffraction (XRD) and high resolution transmission electron microscopy (HRTEM) to confirm their structure and surface morphology. The size of the synthesized QDs was found to increase with pH. The optical properties such as absorption and emission wavelengths have been examined using UV-Vis absorption spectroscopy (UV-Vis) and photoluminescence spectroscopy (PL). It is observed from the PL spectra that there is a continuous reduction in the photoluminescence intensity of the CdSe QDs, as the pH value increases. To confirm the capping of L-cysteine and to study the surface properties of the synthesized CdSe QDs Fourier Transform Infra-red (FT-IR) and Fourier Transform Raman (FT-RAMAN) analyses were performed and the results are reported.

Keywords: Quantum Dots; Bioimaging; Biolabelling; Photoluminescence; L-cysteine; Aqueous synthesis; Biocompatible.

INTRODUCTION

Quantum dots (QDs) are colloidal luminescent semiconductor nanocrystals synthesized from the elements belonging to the group II-VI or III-V of the periodic table. These semiconductor quantum dots (SQDs) possess unique optical, electrical and electronic properties that arise from the quantum confinement when the diameters are less than 10 nm [1]. Due to their size dependent properties such as enhanced photoluminescence, broad absorption and narrow emission spectra, excellent physical and chemical stability [2,3], CdSe an important II-VI SQDs with the direct band gap of 1.74 eV have gained tremendous attention not only in the field of optoelectronics [4], light emitting diodes [5], sensors [6] and solar cells [7,8] but also have immense potential for biological and biomedical research as bioimaging and biolabelling agents [9]. In recent days, the profound use of quantum dots in various bio-applications is because; the dimensions of these quantum dots are very much similar to the biomolecules, antibodies, DNA etc.

Over the past few years, researchers have focused on the controlled synthesis and fabrication of CdSe nanostructures. The two main synthetic procedures that were employed for the synthesis of quantum dots are; first, the organometallic approach using toxic trioctylphosphines (TOP) and trioctylphosphine oxides (TOPO) as the stabilizing agent [10] under high temperature, generally in the glove box. But the quantum dots synthesized through this approach are not compatible with the biological systems since they are highly toxic. The second one is the aqueous synthesis of quantum dots (i.e) directly synthesizing the nanocrystals using water as the solvent [11]. Till date, several synthetic methods such as wet chemical methods, sonochemical methods, templating methods, chemical vapor deposition method, reverse micelles technique etc. [12] have been developed for synthesizing

quantum dots in aqueous solutions. Aqueous synthesis of CdSe QDs are highly preferred because of their simple, highly reproducible, less cost and reduced toxicity synthetic procedures with good yield of quality nanocrystals.

Additionally, the surface of the QDs should be systematically controlled since because the high surface to volume ratio of the QDs reduces the photoluminescence efficiency resulted from the localized surface-trap states [12]. Therefore, proper surface modification of QDs is necessary to remove the local trap sites from the surface and to increase the quantum yield. Tingting Wang et al. have reported the synthesis of CdSe nanocrystals with controllable phase and morphology through a solvothermal process using cadmium nitrate as the precursor, in a mixed solvent system at a relatively higher temperature of 205 °C [13]. In a similar way, Xinlin Liu et al. successfully synthesized CdSe QDs in a hydrothermal process using cadmium chloride as the Cd precursor and the photocatalytic activities of the synthesized QDs were studied [14]. The main objective of our work is to synthesis good quality water soluble CdSe QDs that are biocompatible and the procedure involves a simple aqueous based chemical synthesis at low temperatures, avoiding the traditional highly toxic organometallic precursors. In this paper, we report on the aqueous synthesis of CdSe QDs with cadmium oxide, the least toxic Cd precursor and L-cysteine, a biocompatible polymer as the stabilizing agent. The effects of precursor concentration and pH value of the solution on the formation of structure and optical properties of the synthesized CdSe QDs are highlighted.

MATERIALS AND METHODS

2.1 Chemicals

Cadmium oxide (CdO, 98.9%) was purchased from Alfa Aesar, selenium powder from Loba Chemie, sodium borohydride (NaBH₄, 98%) from Avra and L-cysteine (C₃H₇NO₂S) and sodium hydroxide pellets (NaOH) were purchased from Merck. All the chemicals were used as received without any further purification. All the reactions were performed in standard glasswares using double distilled water and in the presence of argon gas atmosphere.

2.2 Synthesis of CdSe quantum dots

Aqueous synthesis of CdSe quantum dots stabilized by L-cysteine is described in detail: In a three necked flask equipped with septum and a gas adapter, 20 ml NaHSe solution was prepared by mixing sodium borohydride and selenium powder in certain mmol in distilled water under constant stirring, until the solution turned colourless. The reaction was performed in the presence of argon gas atmosphere. The Cd solution was prepared by mixing CdO and L-cysteine in 60 ml distilled water, with rapid stirring. The pH of the solution was adjusted to 9 with dropwise addition of 1 M NaOH. After one hour stirring, the addition of Cd solution into NaHSe in the presence of argon gas atmosphere resulted in a clear orange coloured solution indicating the formation of CdSe quantum dots. This solution was then transferred into a Teflon-lined autoclave and kept in an electrical oven at 160 °C. The precipitate was collected by centrifugation and then vacuum dried to harvest nanopowder.

The formation of CdSe QDs can be explained from the reduction reactions given below:



The reactions were performed to synthesize CdSe QDs with two different concentrations of CdO (i.e) 1 mmol and 2mmol. The samples were labeled as Cd-1 and Cd-2. The mmol ratio of Cd:Se:L-cyst was kept as 1:0.5:4 for the synthesis of Cd-1 and as 2:0.5:4 for the synthesis of Cd-2.

Similar reactions were performed for the synthesis of CdSe QDs in the mmol ratio of 2:0.5:4 with varied pH values from 9 to 12. The samples were labeled as Cd-9, Cd-10, Cd-11 and Cd-12. A change in the colour of the solution was observed when the pH value increased from 9 to 12. The colour changed from orange to reddish orange, then to dark reddish and finally reddish brown.

2.3 Characterization

The structural properties of the synthesized samples were studied using powder X-ray diffraction on a Rich Seifer with monochromatic nickel filtered CuK_α radiation ($\lambda = 1.5461 \text{ \AA}$) in the 2 θ range of 10° to 70°. The size and shape of the synthesized nanocrystals were estimated using the JEOL JEM 2100 High Resolution Transmission Electron Microscopy (HR-TEM) with an accelerating voltage of 200 kV coupled with EDS. UV-Vis spectroscopy analysis was carried out to study the optical properties using a Perkin - Elmer (Lambda EZ-210) spectrophotometer in the wavelength range of 200 nm to 900 nm. The photoluminescence spectra of the samples were recorded with a JobinYvonFluorolog-3-11 spectrofluorimeter with Xenon lamp 450W as source at room temperature using 400 nm as the excitation wavelength. The FTIR spectra of the samples were obtained by the conventional KBr pellet technique, in a Perkin Elmer spectrometer operating in the range of 4000 to 400 cm⁻¹.

The Raman spectra were recorded at room temperature using the Bruker RFS 27: stand alone FT-Raman Spectrometer with Nd: YAG 1064 nm as the laser source.

RESULTS AND DISCUSSION

3.1 X-ray diffraction study

L-cysteine capped CdSe QDs exhibiting both cubic zinc blende and hexagonal wurtzite structure were synthesized through the aqueous synthesis reactions between Cd^{2+} and Se^{2-} , with a small variation in the mmol concentration of the Cd precursors. Figure 1 depicts the powder X-ray diffraction pattern of CdSe quantum dots synthesized with two different mmol concentrations of Cd precursor. The positions of the diffraction peaks at 25.45° , 42.33° and 49.89° can be assigned to the (111), (220) and (311) phase of the cubic zinc blende structure (JCPDS Card 19-0191) [15], whereas the diffraction peaks at 25.64° , 35.46° , 42.41° , 46.02° and 50.02° can be indexed to the wurtzite phase (JCPDS Card 65-3436) with (002), (102), (110), (103) and (201) reflections. The X-ray diffraction pattern signifies the importance of precursor concentration from the structural transformation observed in the synthesized samples. Further, the possibility to synthesize both zinc blende and wurtzite structured CdSe QDs simply by changing the concentration of precursors is confirmed. From the above results, the sample exhibiting wurtzite structure synthesized from aqueous solutions at pH 9 was further preceded for studying the influence of pH.

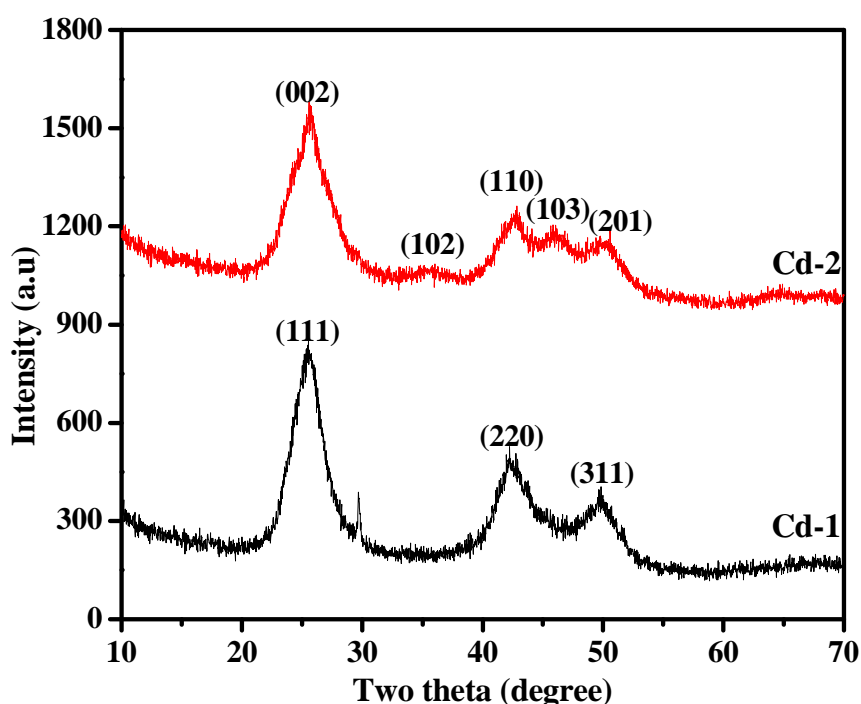


Figure 1: Powder X-ray diffraction patterns of Cd-1 and Cd-2 CdSe quantum dots

Figure 2 compares the X-ray diffraction pattern of CdSe QDs synthesized with different pH values. The diffraction peaks clearly evidenced the formation of wurtzite peaks as the value of pH increases from 9 to 12. From the obtained diffraction patterns, it is interesting to note the evolution of wurtzite peaks (100) and (101) with higher intensities as the pH value increases. The diffraction peaks for all the samples revealed the good crystallinity and high purity, without any peaks for impurity. The peak broadening indicated the fine nanocrystalline nature and the reduced size for the synthesized samples [2,16]. In addition, it is worthwhile to highlight that the pH of the solution plays an effective role in the structural formation of CdSe QDs.

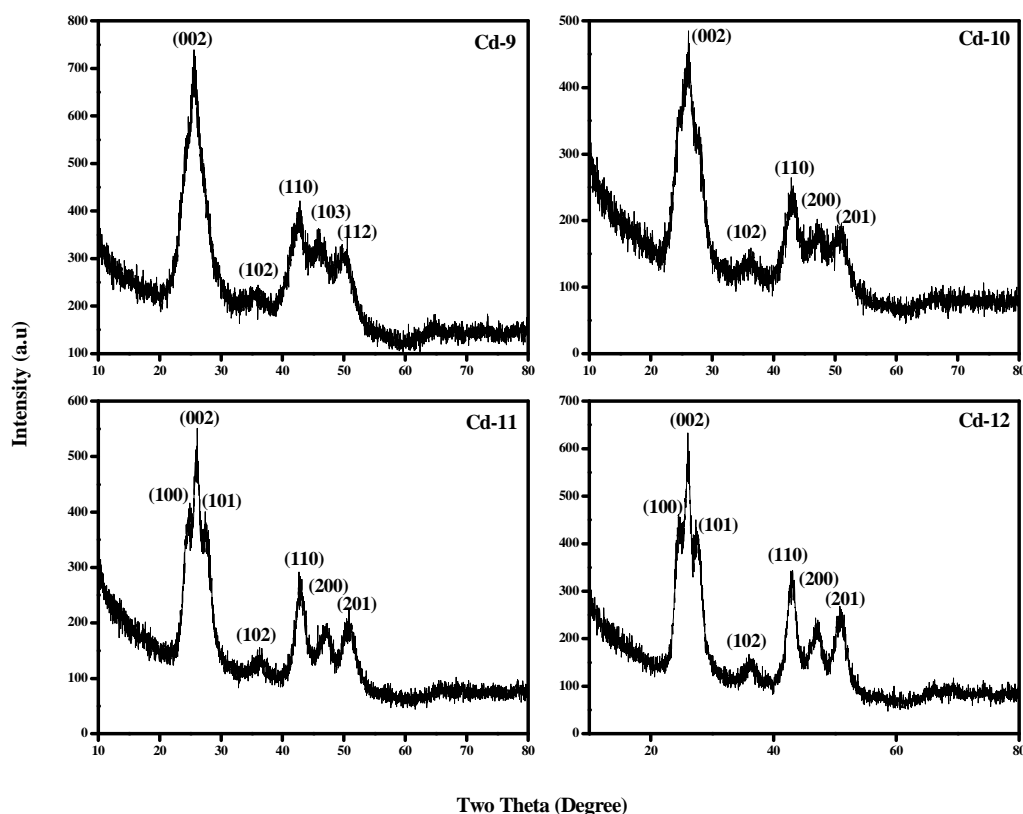


Figure 2: Powder X-ray diffraction patterns of Cd-9, Cd-10, Cd-11 and Cd-12 CdSe quantum dots

3.2 HRTEM analysis

The surface morphology and the particle size of the synthesized CdSe QDs were analyzed from HRTEM studies. Figure 3 shows the typical HRTEM micrographs for the synthesized samples with different pH. The HRTEM images of the synthesized CdSe confirm the formation of spherical shaped quantum dots for all the samples investigated in this study. The clear display of lattice fringes in the micrographs reveals the good crystalline nature of the samples. The QDs synthesized with pH 9 (i.e Cd-9) were found to be well dispersed, spherical and monodisperse without any agglomeration. The QDs samples Cd-10, Cd-11 and Cd-12 were highly agglomerated with large sized quantum dots than Cd-9.

The average particle diameter of the QDs is found in the range between 1.1-3 nm for Cd-9, 4.2-5.4 nm for Cd-10, 5-6 nm for Cd-10 and around 8-11 nm for Cd-12. The inset of the figure shows the selective area diffraction (SAED) pattern for the synthesized CdSe quantum dots. From the selective area diffraction (SAED) pattern obtained for all the samples, the formation of wurtzite structure can be confirmed. The diffraction rings corresponding to the reflections of wurtzite structure are clearly indicated in the SAED pattern. The chemical composition of the as-synthesized CdSe QDs was investigated from EDX analysis. The EDX spectra of the samples showed only the peaks for Cd, Se and Cu. The Cu peak arises from the copper grid. No other peaks were observed, thus indicating the high purity of the samples.

3.3 UV-Vis Absorption Spectroscopy

In order to study the optical properties of the as-synthesized CdSe QDs with varied pH values UV-Vis absorption and photoluminescence studies were carried out. The UV-Visible absorption spectrum of CdSe quantum dots synthesized with different pH values are shown in Figure 4. The absorption spectra consisted of an absorption shoulder at 513 nm for Cd-9, 531 nm for Cd-10, 532 nm for Cd-11 and 520 nm for Cd-12 which is blue shifted from the corresponding bulk CdSe absorption value signifying the quantum confinement of the CdSe quantum dots. It is also depicted from the absorption spectra that the excitonic peaks are red shifted towards higher wavelength indicating the increase in size of the as-synthesized CdSe quantum dots as the pH of the solution increases [17]. From the UV-Vis absorption spectra, the increased band gap energies for Cd-9, Cd-10, Cd-11 and Cd-12 are calculated as 2.42 eV, 2.34 eV, 2.33eV and 2.38 eV, in contrast with bulk band gap of CdSe (1.74 eV). This shifting

is attributed to the strong quantum confinement effect observed in the synthesized samples of CdSe. The particle size estimated from the maximum excitonic peaks for Cd-9, Cd-10, Cd-11 and Cd-12 were 2.7nm, 3 nm, 3nm and 2.8 nm.

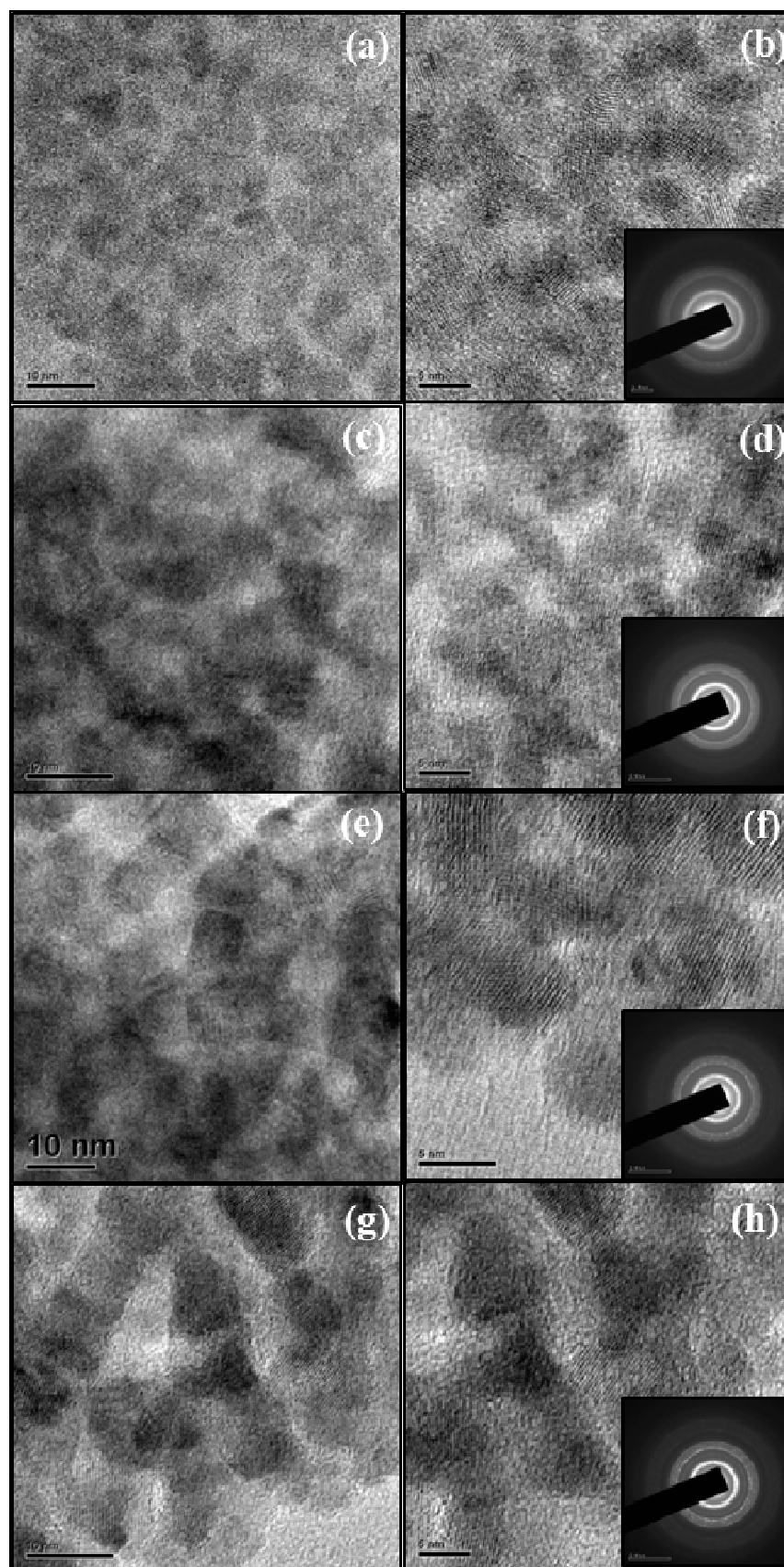


Figure 3: HRTEM images and SAED pattern of (a) (b) Cd-9, (c) (d) Cd-10, (e) (f) Cd-11 (g) (h) Cd-12 CdSe quantum dots

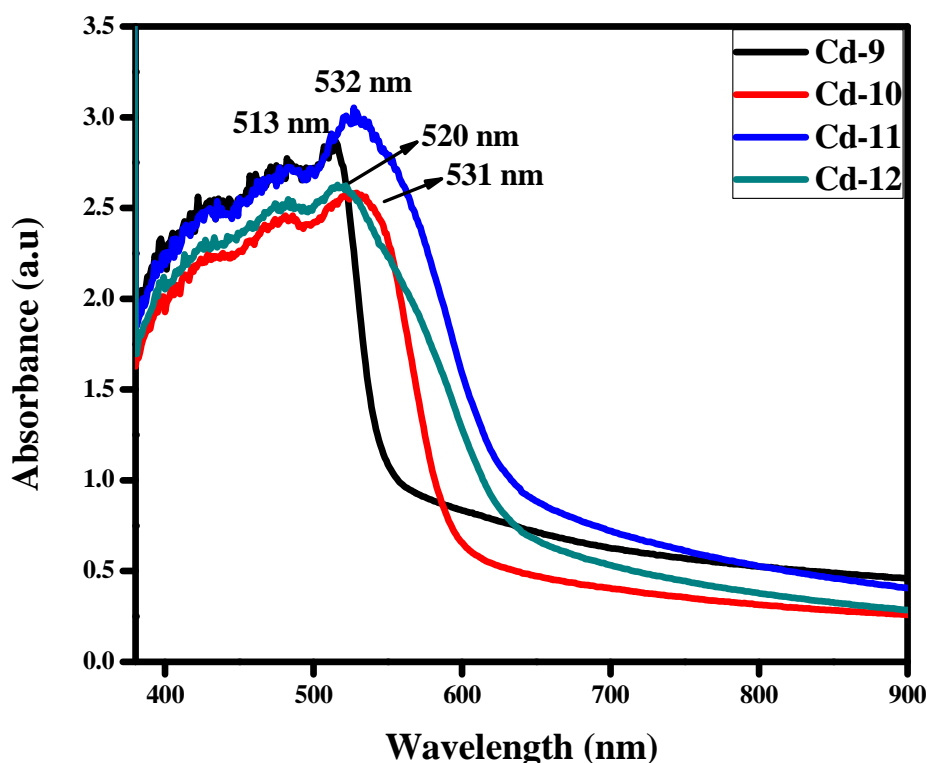


Figure 4: UV-Vis absorbance spectra of Cd-9, Cd-10, Cd-11, Cd-12 CdSe quantum dots

3.4 Photoluminescence spectroscopy

The room temperature photoluminescence spectra of CdSe QDs recorded with 400 nm excitation wavelength for the samples are shown in Figure 5. The PL emission spectrum depicts the strong excitation peaks for the synthesized CdSe QDs with peaks centered at 601 nm for Cd-9, 605 nm for Cd-10, 643 nm for Cd-11 and at 663 nm for Cd-12.

The PL emission spectrum clearly demonstrates the apparent red shift of the emission peaks as the pH increases, indicating the increase in the diameter of the synthesized QDs. In addition, it is observed that the increase in the solution pH from 9 to 12 leads to a dramatic decrease in the luminescence intensity of the emission spectra and the intensity found to be the highest for the sample Cd-9. The higher PL intensity for the CdSe sample (Cd-9) is because of the higher recombination of electrons and holes in the photochemical process. The sharp, strong and narrow PL emission peaks for Cd-9 reveal the monodispersion of the synthesized sample. For the samples Cd-10, Cd-11 and Cd-12, the emission spectra have been broadened displaying the variation in the size of the quantum dots. The full width half maximum (FWHM) for the emission spectrum of Cd-9 is quite narrow, whereas the width increases with increased pH values [18]. The pH of the precursor solution was found to have a significant influence on the optical properties of the as-synthesized CdSe nanoparticles. Furthermore, it can be finalized that lower pH value of the solutions would enhance the luminescence intensity for the QDs.

The results observed in the absorption and emission spectra for the synthesized samples are in agreement with size determination from the HRTEM micrographs.

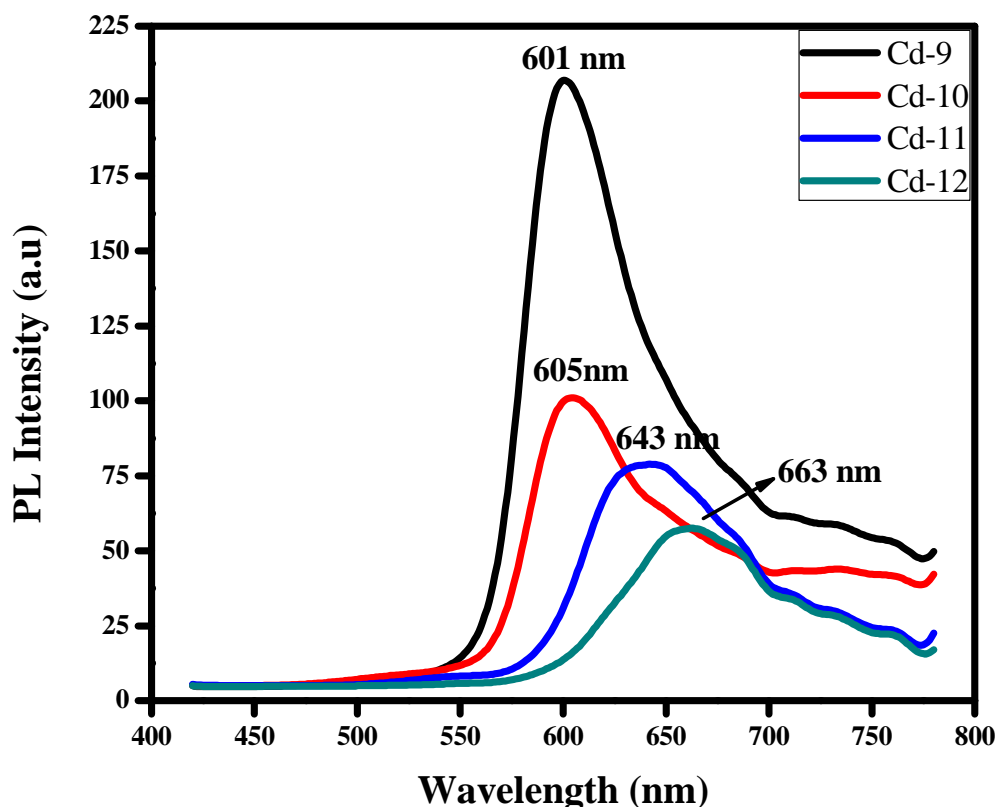


Figure 5: Photoluminescence spectra of Cd-9, Cd-10, Cd-11, Cd-12 CdSe quantum dots

3.5 FT-IR analysis

In order to determine the chemical composition and to confirm the capping of L-cysteine in the synthesized CdSe QDs the FTIR analysis was performed. From the FTIR spectra it is observed that, for the synthesized CdSe QDs (Cd-9, Cd-10, Cd-11 and Cd-12) almost all the peaks are common with slightly shifting behavior towards larger and shorter wavenumbers with increased pH of the solutions. The strong and broad bands around 3430 cm^{-1} , 3405 cm^{-1} , 3448 cm^{-1} , 3422 cm^{-1} for samples with increased pH values can be attributed to the hydroxyl bond (-OH stretching), which confirms that the water molecules remain intact on the surface and its width arises as the formation of inter and intramolecular hydrogen bond as reported by Oluwafemi et al. 2010. The small bands at 1117 cm^{-1} , 1000 cm^{-1} , 1008 cm^{-1} and 1119 cm^{-1} correspond to the C–O stretching vibrations. The small peaks at 629 cm^{-1} , 638 cm^{-1} , 646 cm^{-1} and 657 cm^{-1} are due to stretching vibrations of Cd–Se bonds. The IR band in the region between 600 cm^{-1} and 700 cm^{-1} justifies the presence of thiol sites on the surface of quantum dots due to the capping of L-cysteine [19]. Additionally, the bands at 1605 cm^{-1} , 1579 cm^{-1} , 1587 cm^{-1} , 1597 cm^{-1} due to the -NH_2 bending vibrations and the bands at 1388 cm^{-1} , 1379 cm^{-1} , 1387 cm^{-1} , 1417 cm^{-1} resulted from C=O vibrations further confirmed the presence of L-cysteine and the formation of CdSe quantum dots with increased pH.

3.6 FT-Raman analysis

FT-Raman analysis was performed to study the sample qualities such as microcrystallinity, homogeneity and surface conditions for the as-synthesized CdSe quantum dots with increased pH values. Figure 7 depicts the Raman spectra of L-cysteine capped CdSe quantum dots (Cd-9, Cd-10, Cd-11 and Cd-12). From the Raman spectrum, it is observed that the CdSe QDs exhibit three prominent peaks with bands at 71 cm^{-1} (1LO), 142 cm^{-1} (2LO) and 237 cm^{-1} (3LO) for Cd-9, 75 cm^{-1} (1LO), 167 cm^{-1} (2LO) and 253 cm^{-1} (3LO) for Cd-10, 81 cm^{-1} (1LO), 157 cm^{-1} (2LO) and 254 cm^{-1} (3LO) for Cd-11 and 77 cm^{-1} (1LO), 200 cm^{-1} (2LO) and 253 cm^{-1} (3LO) for Cd-12 which can be attributed to the longitudinal optical (1LO) and its first (2LO) and second overtone (3LO) phonon modes of the CdSe QDs. For the samples, Cd-10, Cd-11 and Cd-12, all the three vibrational modes are shifted towards higher frequencies [20] compared to Cd-9, which provides an additional evidence to confirm the increase in size of the synthesized quantum dots with increased pH solutions.

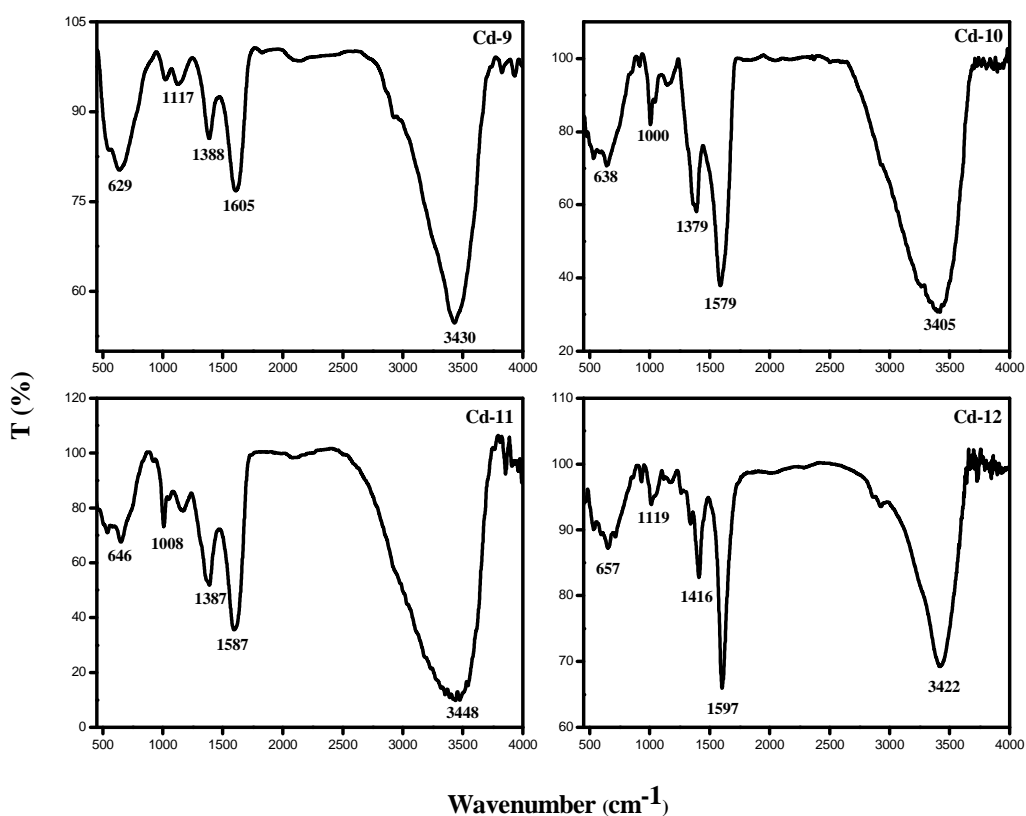


Figure 6: FTIR Spectra of Cd-9, Cd-10, Cd-11, Cd-12 CdSe quantum dots

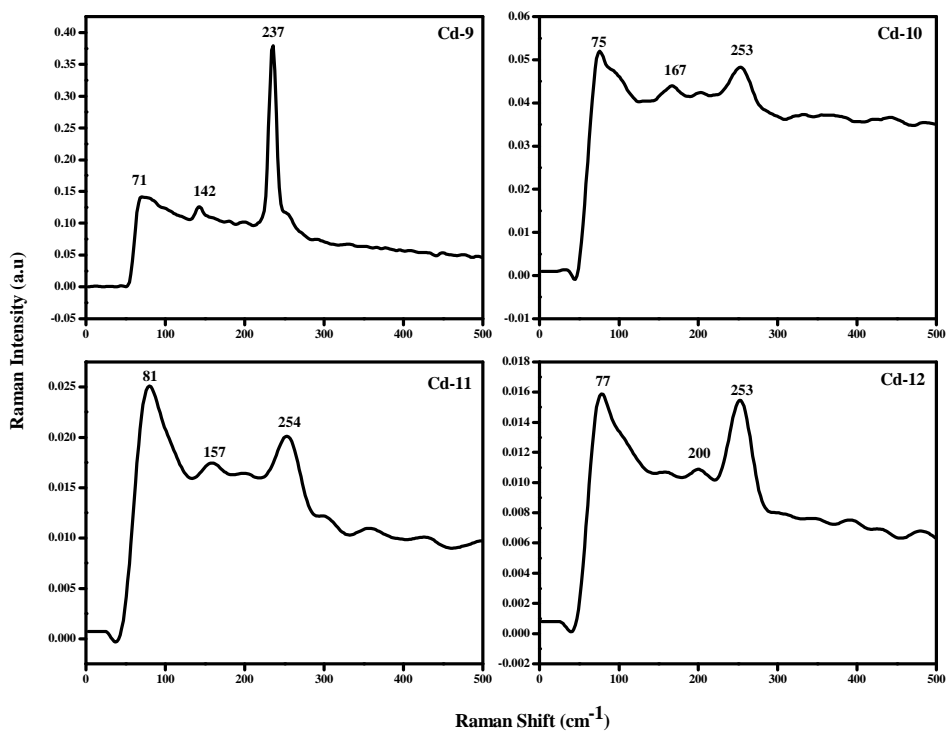


Figure 7: FT-RAMAN Spectra of Cd-9, Cd-10, Cd-11, Cd-12 CdSe quantum dots

CONCLUSION

In summary, we have successfully synthesized water dispersible CdSe quantum dots with different Cd precursor concentration and pH solutions and the role of pH on the properties of quantum dots have been studied. It is well understood from the above results, that the pH of the solution and Cd precursor concentration played a vital role in the growth of CdSe quantum dots with zinc blende and wurtzite structures. The optical measurements clearly depicted the increase in size of the quantum dots from the red shift of the absorption peaks as the pH value increases. Moreover, the luminescence peaks with high intensity was only observed for the quantum dots synthesized with pH 9 and the emission intensity started to decline with a shift towards higher wavelength for the quantum dots with increased pH. The HRTEM measurements evidenced that the quantum dots synthesized with pH 9 were of high quality with well dispersed and monodispersed particles of size ranging between 1-3 nm. Thus it can be concluded that, these synthesized quantum dots can be further preceded for biological applications by capping CdSe with an inorganic shell of greater stability.

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