

Synthesis and Characterization of Cysteine-Capped CdSe Nanoparticles Using an Alternative of Selenium

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Present work reports synthesis of L-cysteine capped CdSe nanoparticles at different temperatures *via* an aqueous medium, non-toxic and green colloidal route. Cadmium chloride ($\text{CdCl}_2 \cdot 5\text{H}_2\text{O}$) and sodium selenite (Na_2SeO_3) were used as cadmium and selenium sources respectively. The prepared nanoparticles are characterized by UV-visible absorption and photoluminescence spectroscopy, Fourier transform infrared, X-ray diffraction and transmission electron microscopy. The XRD patterns confirm a cubic phase structure of the prepared nanoparticles at 55, 75 and 95 °C, respectively. The TEM analysis, optical absorption and photoluminescence spectra shows epitaxial growth of CdSe nanoparticles as the temperature increases with average size diameter of 4.12 ± 0.32 , 5.02 ± 0.234 and 5.53 ± 0.321 nm for 55, 75 and 95 °C, respectively.

Keywords: Cadmium selenide, Nanocrystals, Semiconductors, Quantum dots, Chemical synthesis.

INTRODUCTION

Semiconductor quantum dots (QDs) are suitable for various uses in biological applications due to their broad absorption, bright luminescence, size tunable emission spectra and high photo-stability [1]. Semiconductor nanoparticles exhibit unique properties that are size-dependent which differ from their bulk counterparts [2]. Chemically synthesized nanoparticles have an advantage over physically prepared nanoparticles in that they are more easily tailored to have different shapes and sizes, characteristics that are challenging for conventional methods such as epitaxial growth or sputtering. The synthesis conditions and reagents can be used to control the sizes and morphologies of nanoparticles [3]. Quantum dots synthesized by organometallic route are hydrophobic in nature and cannot be used for biological applications. To use these quantum dots biologically they require ligand exchange or polymer encapsulation with hydrophilic ligands [4,5]. The direct use of amino acid containing multi-functional moieties could be a better approach because of its simplicity and eliminates the possibility of having competing hydrophobic groups on the surface of the nanoparticles.

Cadmium selenide nanoparticles are the most common types of II-IV semiconductor materials with a moderate energy band-gap of $E_g = 1.74$ eV [6]. A number of methods have been employed to synthesize CdSe which includes, hydrothermal [7], microwave [8,9], organometallic precursor [10-12] and green synthesis [13-15]. Water-soluble synthesis of semiconductor nanocrystals with thiols as capping agents has been developed as an alternative to original organometallic route, where precursors used are highly toxic, explosive and pyrophoric. Herein, we report on the synthesis and characterization of CdSe quantum dots through a facile, one pot and green route at low temperature using L-cysteine as a capping agent. The influence of reaction temperature on the absorption, fluorescence and morphology of the nanoparticles is studied.

EXPERIMENTAL

Cadmium chloride, sodium selenite, L-cysteine amino acid and sodium hydroxide were purchased from Sigma-Aldrich. All the chemicals were used as purchased without further purification.

Preparation of selenium source: Selenium source was prepared by dissolving 0.05 M of Na_2SeO_3 (0.5 g) with 2.0 M NaBH_4 (0.3783 g) in 50 mL distilled water which is taken in 100 mL beaker. The solution was stirred for 20 min until the brown solution forms that indicates the reduction of selenium.

Preparation of L-cysteine-capped Cu_2Se nanoparticles: Cysteine-capped CdSe nanoparticles were synthesized using one-pot synthetic approach directly in an aqueous medium. A solution of 0.1 M CdCl_2 (0.5g) in distilled 20 mL water was prepared at room temperature. A 30 mL of 0.2 M solution of L-cysteine was added into the CdCl_2 solution with a constant stirring until the mixture became turbid white. The pH of the solution was adjusted to from 5 to 11 by adding few drops of freshly prepared 1 M NaOH solution, which turned the solution transparent again. The desired quantity of the prepared Se source (here $\text{Cu}^{2+}:\text{Se}^{2-}$ is maintained 1:1) was added dropwise. The mixture has been refluxed for 1 h at 55, 75 and 95 °C. The formation of yellow to orange precipitate was observed which is an indication for the formation of CdSe nanoparticles. The particles were cleaned thrice with acetone. Water-soluble CdSe nanoparticles were collected for further characterization.

Physical measurements: The optical properties of the materials were determined by placing the water dispersion of the nanoparticles into quartz cuvettes (1 cm path length) using distilled water as a solvent. The PG Instruments Ltd T80+ UV-visible spectrometer were used to carry out the absorption measurements. Emission spectra of the particles were recorded on a JASCO spectrofluorometer FP-8600 spectrometer with a xenon lamp at room temperature. Infrared spectra of the nanoparticles were recorded on PerkinElmer spectrum 400 FT-IR spectrometer ranging from 500 to 4000 cm^{-1} . The samples were placed onto the universal ATR sample holder and pressed on top by gauge force arm. X-ray diffraction (XRD) patterns of powdered samples were carried out on Bruker D8 advance using a Co (1.78898 nm) radiation source operating at 40 kV, for 2θ values over 20-80°. The morphology of nanoparticles was determined by Technai G2 TEM spirit operated at 200 kV. Transmission electron microscopy samples were prepared by drop-casting the nanocrystal dispersion in distilled water onto the carbon-coated copper grids and allowed to dry at room temperature.

RESULTS AND DISCUSSION

UV-visible absorption spectra of synthesized cadmium selenide nanoparticles are shown in Fig. 1(I). A large blue-shift absorption from their bulk materials was observed for synthesized cadmium selenide nanoparticles. This was also confirmed by the band gap estimation from the energy curves shown in Fig. 1(II) were located at 2.08, 1.98, and 1.96 eV, respectively. The absorption spectra revealed the band edges are located at approximately 596, 626, and 633 nm for the temperatures of 55, 75, and 95 °C, respectively. The band-edges suggest that the particle size increases with an increase in reaction temperature. It was suggested that at higher temperatures, the smaller particles diminished while the larger ones grew due to the Oswald ripening.

The emission spectra of synthesized CdSe nanoparticles are shown in Fig. 1(III). The maximum emission were found to be at 562, 576, and 593 nm for the temperatures of 55, 75, and 95 °C respectively. All the samples show a well-defined emission band with monodispersity particle distributions. However, as the reaction temperature has increased a red-shift has been also observed in the photoluminescence emission peak. This red-shift indicated growth of the nanoparticles as the temperature increases.

The FT-IR spectra were taken to study the interaction of the capping molecules with the surface of the nanocrystals. The spectra of free L-cysteine and L-cysteine-capped CdSe nanoparticles synthesized at 95 °C are shown in Fig. 2. Pure L-cysteine shows characteristic peaks appearing at 2966 cm^{-1} (O-H *cm*⁻¹), 2853 cm^{-1} (C-H *str.*), 1690 cm^{-1} (C=O group) and 1523 cm^{-1} (N-H *str.* amino group). These bands between the regions of 3100-2750 cm^{-1} from the carboxyl groups disappear when L-cysteine is bonded to the nanocrystals surface. This implies that the nanocrystals interact with L-cysteine through the COO^- moiety on the carboxylic group. Upon interaction with the nanocrystal, the cadmium selenide draws the electron density towards itself resulting in the weakening of the other bonds and thus their disappearance in the spectra.

The XRD patterns of synthesized CdSe nanoparticles are shown in Fig. 3. The diffraction peaks indicate the nanocrystalline nature. These peaks at angles (2θ) of 29.52°, 49.92°, and 58.96°, which were indexed to (111), (220), and (311) reflection planes of the cubic structure of CdSe (JCPDS File

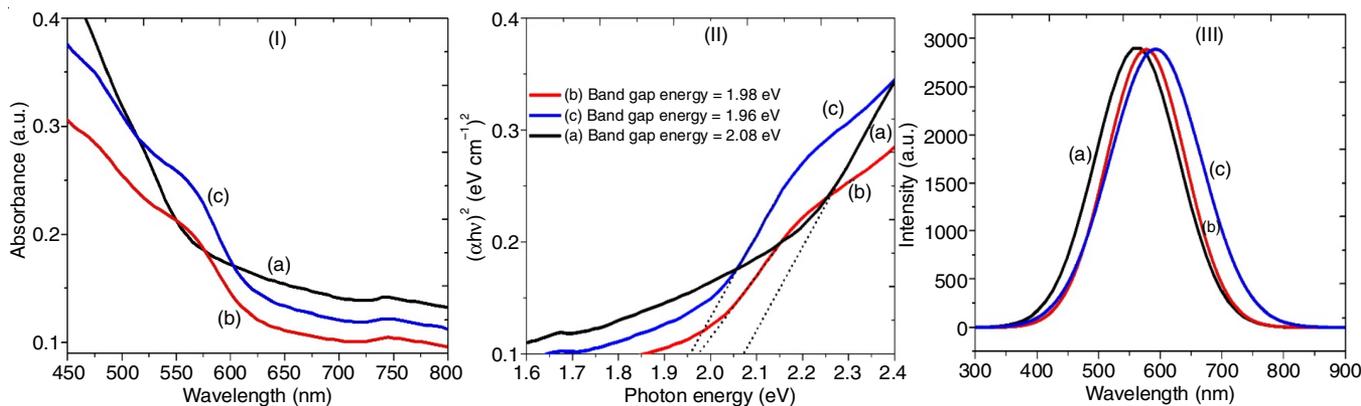


Fig. 1. Absorption spectra (I), its corresponding tauc plot (II) and emission (III) spectra of L-cysteine-capped CdSe quantum dots synthesized at (a) 55, (b) 75 and (c) 95 °C

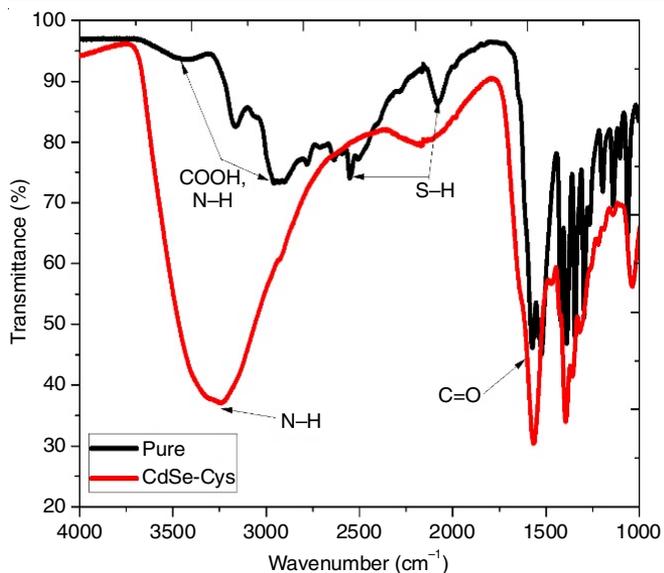


Fig. 2. FTIR spectra of (a) free L-cysteine, (b) L-cysteine-capped CdSe nanoparticles synthesized at 95 °C

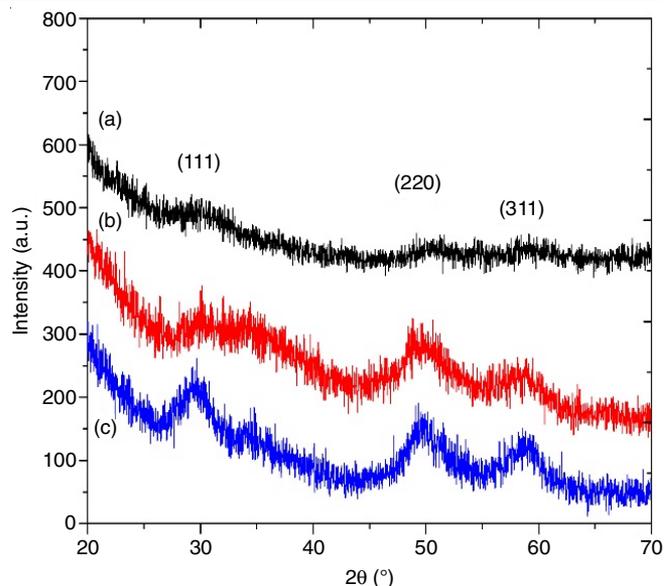


Fig. 3. XRD patterns of L-cysteine-capped CdSe nanoparticles prepared at (a) 55, (b) 75 and (c) 95 °C

No: 03-065-3415), respectively. However, it was compared with the standard diffraction pattern and no peaks of impurities were detected indicating the high purity of the products. In these samples (111) plane is very clear and abundant which indicated preferential growth of crystallites in this particular direction which implies that the growth of CdSe particles can be controlled by the temperature. There is generally an increase in crystallinity in the nanoparticles as the temperature is increased as evident from more pronounced peaks at higher temperature compared to amorphous peaks appearing at 55 °C.

The TEM images of all synthesized cadmium selenide nanoparticles and the corresponding size distribution are shown in Fig. 4. The TEM generally revealed that particles were spherical in shape. The average particle diameter of particles synthesized at 55, 75 and 95 °C were 4.12 ± 0.321 nm, 5.02 ± 0.234 nm and 5.53 ± 0.321 nm, respectively. The synthesized nanoparticles confirming the optical properties yield from UV-Vis absorption and photoluminescence emission spectra as well the XRD data are in an agreement with the TEM analysis. Furthermore, the size distribution was homogeneous of the

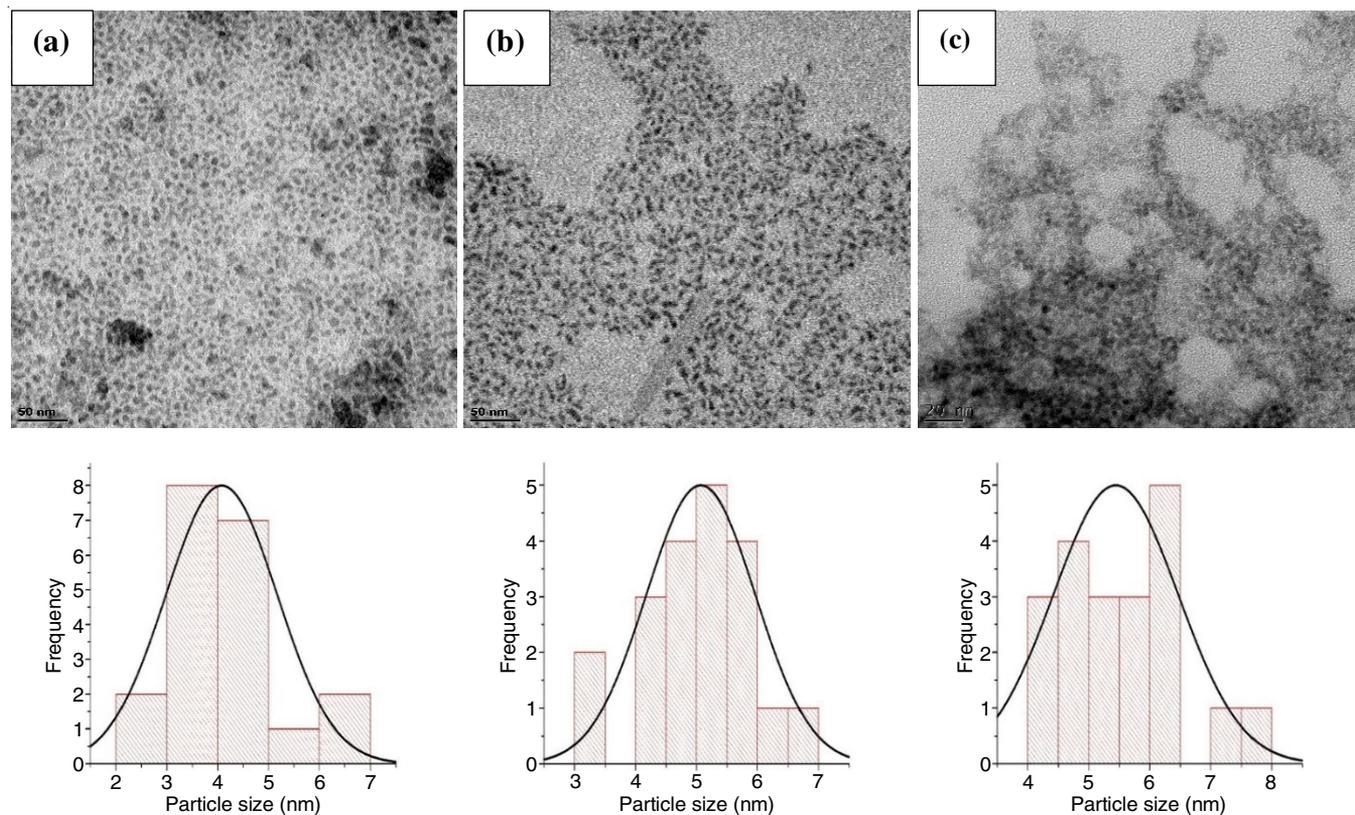


Fig. 4. TEM images and size distribution curve of L-cysteine-capped CdSe nanoparticles prepared at (a) 55, (b) 75 and (c) 95 °C

synthesized nanoparticles as proved by the emission spectra. It is also noted that the increase in temperature results in an increase in the average particle size of cadmium selenide quantum dots. This confirms that temperature controls the size and distribution of cadmium selenide nanoparticles.

Conclusion

In summary, synthesis of CdSe nanocrystals have been synthesized through an aqueous medium colloidal route *via* the direct use of hydrophilic ligand was successful. The L-cysteine showed moderately good capping ability for the nanoparticles. The X-ray diffraction measurement confirms the structure of single cubic of CdSe nanoparticles. The TEM studies of cadmium selenide nanoparticle show that particle size increases with the increase in reaction temperature. The optical absorption properties is found that band gaps show some dependency from the reaction temperature used in the synthesis of nanoparticles.

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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