

## Environmental Friendly Novel Synthesis Route for CdS Quantum Dots

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In the present work, we have made an attempt to prepare the CdS QDs using novel simple chemical route under room temperature such as uncapped and polymer capped CdS QDs. Further their structural and optical properties were investigated through XRD, TEM, FTIR, UV-VIS and PL techniques. From the XRD analysis, a cubic-hexagonal crystal structure was observed. From the HRTEM analysis, a well grown spherical shaped surface morphology was observed with their sizes 3-5 nm. From the FTIR analysis, the interaction between L-cysteine and CdS QD were confirmed. From the UV analysis, an enhanced absorption nature was observed due to the quantum confinement effect. From the PL analysis, a blue-shifted emission behavior was observed due to the small-sized particles. Hence, the prepared CdS QDs are suitable for opto-electronic as well as bio-imaging applications. Hence, their observed interesting results are discussed in detail.

**Keywords:** CdS, Fluorescent quantum dots, Environmental friendly route.

### 1. Introduction:

The semiconductor nanocrystals or quantum dots (QDs) have been much attention due to their size-dependent photophysical and photochemical behaviors. The photophysical and photochemical behaviors of QDs are naturally associated with their size, surface states and defects because of quantum confinement effect in nanometer scale. These are much useful for various applications [1-4]. CdS is one of the well known wide bandgap and light sensitive semiconducting material. The bandgap energy is increased when it is in the form of QD is called as blue-shift while interesting optical behaviors were occurred due to quantum confinement effect [5-6]. Actually, the CdS QDs has shown blue-green photoluminescence which was due to deep level sulfur vacancy states resulted from the deviation in the stoichiometry. A strong excitonic emission was obtained when the absence of sulphur vacancy states is resulted as reported elsewhere. Further it can give various color emissions depending upon metal surfactants and dopants [7-9]. In this regard, several methods have been used for the synthesis of CdS QDs, however, most of them are environment hazards (not environmental friendly). Therefore to solve these problems, in the present work, we have made an attempt to prepare the CdS QDs using novel simple chemical route under room temperature such as uncapped and polymer capped CdS QDs. This synthesis route shows an environmental friendly nature as well as

efficient production. Further, their structural and optical properties were studied in details.

### 2. Materials and Methods

#### 2.1. Chemicals and reagents

Cadmium chloride ( $\text{CdCl}_2$ , 98%, Sigma), sodium sulfide ( $\text{Na}_2\text{S}$ , Fulka), polymer (L-Cysteine) and double distilled water (DD water) have been used to prepare the quantum dots. All these used chemicals were purchased from standard chemicals company and also used without any further purification.

#### 2.2. Synthesis of quantum dots

For the synthesis of uncapped CdS QDs, 0.01 M of cadmium chloride ( $\text{CdCl}_2$ ) solution was prepared by dissolving it in double distilled water (DD water) and keeping the as prepared solution under ultrasonic agitation, at room temperature. In this solution an equimolar concentration of freshly prepared sodium sulfide ( $\text{Na}_2\text{S}$ ) was added drop wise to obtain CdS QDs. The as obtained product is a colloidal suspension, and which was washed several times in DD water to remove any excess  $\text{Na}_2\text{S}$ . After washing several times, the dispersed particles were centrifuged at 10,000 rpm and then dried under a rotary vacuum condition for few days [10]. The dried crystal product was fine grained and to get a reddish-yellow powder.

For the synthesis of polymer capped CdS QDs, the above mentioned same procedure were followed, but the difference was polymer solution were added before the addition of  $\text{Na}_2\text{S}$  solution. For this, the stabilizing agent 0.01 M of L-Cysteine (L-Cys) was introduced to cover the QDs surface. Here L-Cys can attach onto the surface of CdS QDs with respect to sulfide ions at the surface of QDs, leading to the formation of L-Cys capped CdS QDs.

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**2.3. Characterization:**

The crystal nature was confirmed using XRD technique, PANalytical diffractometer (model: X' Pert PRO). The surface morphology images were recorded using (model: JEOL-300) HRTEM. A double-beam UV-Visible-NIR spectrophotometer (model: SHIMADZU 3600) was used for optical absorption studies. FTIR spectra were also recorded from these samples to know the functional groups using FTIR spectrometer (model: Bruker Tensor-27). Room temperature excitation and emission spectra were recorded from a Horiba Jobin Yvon spectrofluorometer(model: FLUOROMAX-4).

**3. Results & Discussion:**

**3.1. Structural analysis:**

**3.1.1. XRD:**

Figure 1 shows the X-ray diffraction patterns of (a) uncapped CdS and (b) polymer capped CdS QDs. The obtained diffraction peaks are matched with the standard cubic and hexagonal CdS crystal systems (JCPDS card no.: 10-0454 and 41-1049). The observation is believed to be the chance of superposition of cubic-hexagonal crystal nature and the similar result was observed in previous reports [11-13].

The crystalline size or average particle size (D) was calculated by using Debye-Scherrer formula [14-15]

$$D = \frac{K\lambda}{\beta \cos\theta}$$

The lattice constants were measured using the following formula

$$d(hkl) = \frac{a}{\sqrt{h^2 + k^2 + l^2}} \text{ (or) } a = d\sqrt{h^2 + k^2 + l^2}$$

The calculated crystalline size is approximately 3 nm and the lattice parameter value is approximately 3.3320 Å for both QD samples, and it is in agreement with the standard value of CdS. Hence, peak broadening and obtained results were confirmed that the prepared samples are in quantum dots scale-range.

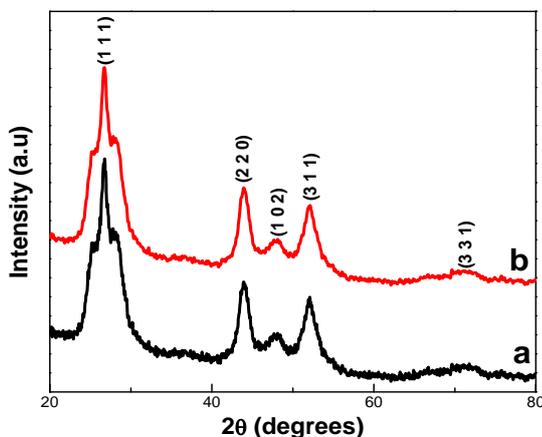


Figure 1. XRD patterns of (a) uncapped CdS and (b) polymer capped CdS QDs.

**3.1.2. TEM:**

Figure 2 shows the TEM images of (a) uncapped CdS and (b) polymer capped CdS QDs. The uncapped CdS QDs shows a clear arrangement of spherical shaped particles with little agglomeration, due to embedded powder samples on the copper grid. Also polymer capped CdS QDs shows a spherical shaped particles nature, however, cluster like surface morphology was observed. It is because of the formation of mono-dispersed QDs were embedded inside the polymer matrix medium which confirms the capping effect of L-Cysteine. Hence, the obtained particles sizes were 3-5 nm and it is good agreement with the calculated crystalline size from the XRD results.

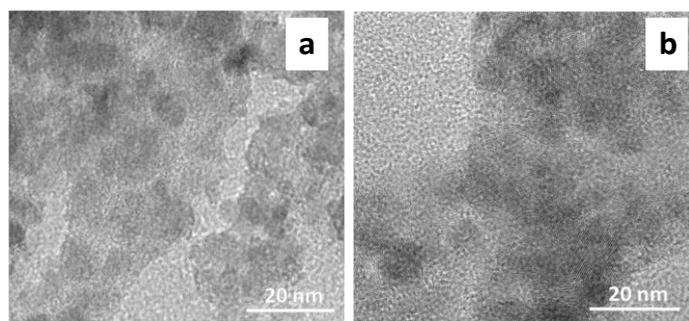


Figure 2. TEM images of (a) uncapped CdS QDs and (b) polymer capped CdS QDs.

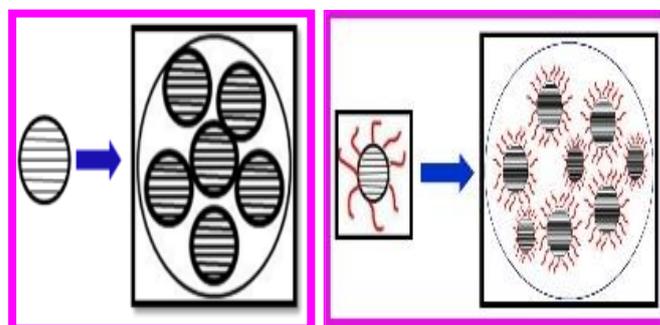


Figure 3. Schematic representation for formation of (left side) uncapped CdS and (right side) polymer capped CdS QDs.

Actually, the polymer capping prevents the uncontrolled growth and agglomeration of the particles. Here, the QD's are formed inside the polymer matrix medium (embedded) and therefore QD's nucleated within the polymer cavities continued to grow until the "steric stabilization of QD's" was obtained. Hence, the cavity walls were physically restrict the particles growth and then smaller sized crystallites within the polymer medium are possible [16-17], shown in figure 3.

### 3.1.3. FTIR:

Figure 4 shows the FTIR spectra of (a) uncapped CdS and (b) polymer capped CdS QDs. The peaks in the range of 500-800  $\text{cm}^{-1}$  confirms Cd-S binding mode and also the Cd-S stretching mode were below 700  $\text{cm}^{-1}$  [18].

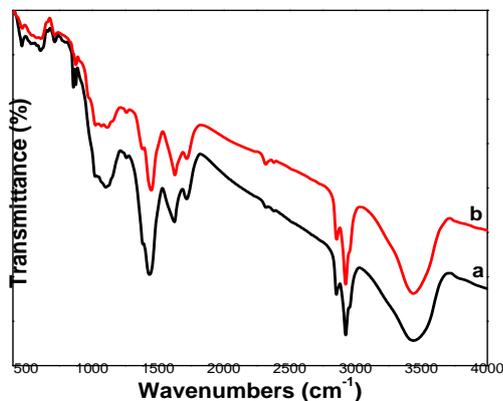


Figure 4. FTIR spectra of (a) uncapped CdS and (b) polymer capped CdS QDs.

The FTIR spectrum of L-Cys capped CdS QDs were not shown -S-H group vibration at 2550-2670  $\text{cm}^{-1}$  when compared with the FTIR spectrum of L-cysteine [19]. Therefore, it is believed to be the nature of interaction between L-cysteine and CdS QD were obtained through sulfur bond, and other stretching vibrational modes also [20-22].

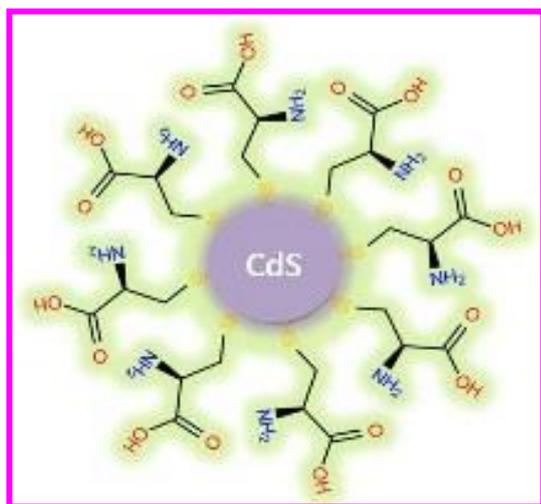


Figure 5. Schematic representation of L-Cys capped CdS QDs.

## 3.2. Optical analysis:

### 3.2.1. UV:

Figure 6 shows the UV-VIS absorption spectra of (a) uncapped CdS and (b) polymer capped CdS QDs. A blue shifted absorption nature were obtained, due to the decreased particles size with increased bandgap energy

when compared with bulk CdS ( $E_g=2.42$  eV), because of quantum confinement effect.

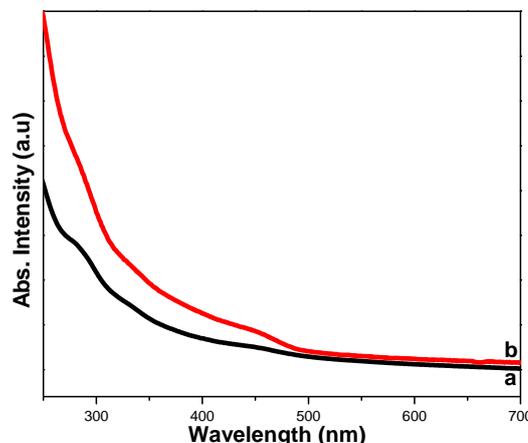


Figure 6. UV-VIS absorption spectra of (a) uncapped CdS and (b) polymer capped CdS QDs.

Moreover, absorption peak/band nature was not observed in the obtained absorption spectrum and it is believed to be the wider distribution of particles [23]. Hence, the bandgap energy values were calculated using the relation

$$E_g = \frac{h\nu}{\lambda_{abs}}$$

The calculated bandgap energy values were approximately 3.3 eV from their corresponding absorption edge ( $\lambda_e=375$  nm). Hence, the diameter of particle ( $2R$ ) was calculated using Henglein's empirical formula [24] corresponds to the absorption edge ( $\lambda_e=375$  nm) of CdS QDs. Their sizes were approximately 5 nm which is matched with the calculated particle size using XRD and TEM results.

### 4.2.2. PL:

The photoluminescence spectra were used to know the emission behavior of QDs excited at their corresponding bandgap energy value (3.3 eV, 375 nm). The uncapped CdS QDs shows a broad greenish-yellow emission band which was maximum emission at 528 nm. It was blue-shifted emission nature when compared with bulk CdS crystal emission (600-650 nm, red emission), due to the recombination of electrons/holes in trap states or defect states or sulphur vacancy on the surface of crystals [25-27]. Whereas the capped CdS QDs shows a broad greenish-yellow emission band while their emission behavior were quenched and shifted. It was due to the surface passivation effect which enhances the blue emission; because small

sizes of QD's surface were covered by the formed polymer and therefore, defect/vacancy states were reduced [28-29].

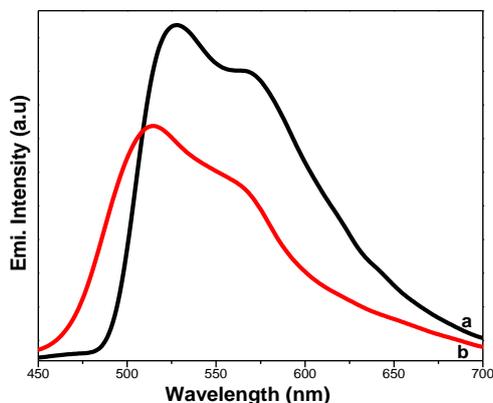


Figure 6. PL emission spectra of (a) uncapped CdS and (b) polymer capped CdS QDs.

### Conclusion:

We have successfully prepared uncapped and polymer capped CdS QDs under room temperature by using environmental friendly novel synthesis route. Further their structural and optical properties were investigated through XRD, TEM, FTIR, UV-VIS and PL techniques. From the XRD analysis, a cubic-hexagonal crystal structure was observed. From the HRTEM analysis, a well grown spherical shaped surface morphology was observed with their sizes 3-5 nm. From the FTIR analysis, the interaction between L-cysteine and CdS QD were confirmed. From the UV analysis, an enhanced absorption nature was observed due to the quantum confinement effect. From the PL analysis, a blue-shifted emission behavior was observed due to the small-sized particles. Hence, the prepared CdS QDs are suitable for opto-electronic as well as bio-imaging applications.

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