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Histidine functionalised CdS quantum dots (QDs) have been synthesised by sonochemical method. Transmission Electron Microscopy (TEM) observation shows that the histidine functionalised CdS QDs are well-defined, nearly spherical particles. The X-ray diffraction pattern indicates formation of cubic phase of CdS/histidine QDs. The absorption spectra confirm quantum confinement of histidine functionalised CdS QDs. The photoluminescence property of CdS/histidine QDs is found better than that of CdS QDs. Histidine functionalised CdS QDs, in which histidine acts as a biocompatibiliser, can find potential applications in the biological fields.

Keywords: semiconductor quantum dot; histidine; biocompatibility

1. Introduction

In the past decade, a variety of semiconductor nanomaterials have shown unique properties and have also attracted great interest from the biological and medical communities [1–4]. Semiconductor nanoparticles are the most intriguing class of fluorescent probes for cellular imaging and *in vivo* cell tracking because of their small size (1–10 nm in diameter), high brightness (20× brighter than most organic fluorophores), good photostability and multiplexing capability [5–6]. Nanoparticles may be harmful for biological systems; therefore, biological capping agents/surfactants are required to attach with nanoparticles. The nature of the surface of the semiconductor nanoparticles has a supreme importance for all biological applications. The photoluminescence intensity and solubility are highly sensitive to the physicochemical characteristics of the surface. Various biomaterials, such as amino acids, dipeptides, and DNA have been investigated as useful biomineralisation substrates due to their unique functionalities, active sites and special biomolecular structure. The surface of the nanoparticles can be made biologically active by the direct attachment of biological agents such as a protein or related structure, such as cysteine or histidine [7]. Amino acids are the building blocks of protein, and some of them play important roles in holding ions in the proper position of protein.

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Among the 20 natural amino acids, histidine, the sole amino acid with pK_a near neutrality [8] usually interacts with ions via its imidazole side chain. To preliminarily explore the biocompatibility of nanoparticles, we herein describe the preparation of histidine stabilised CdS QDs. In this study, we show that histidine functionalised CdS QDs have better photoluminescence and blue-shift in absorption edge as compared to bare histidine functionalised CdS QD.

2. Experimental

The procedure to prepare CdS/histidine QD is as follows: 0.1 M cadmium acetate was mixed with 0.1 M sodium sulphide and 0.2 M histidine. After mixing all the three constituents in the beaker, it was kept in sonochemical bath (33 kHz, 350 W) at room temperature for ultrasonic irradiation time 30 min. The resulting yellow precipitate was then centrifuged and washed with alcohol. To obtain the powder of CdS/histidine QD, the precipitate was then dried at 60°C. To study the effect of histidine on properties of CdS QD, one experiment in the absence of histidine was also performed keeping all other similar conditions.

The crystal structure of CdS and CdS/histidine QDs were characterised by X-ray diffraction (XRD), Rigaku D/MAX-2200 H/PC Cu-Kα radiation. The optical absorption of the CdS and CdS/histidine QDs were examined with a Perkin-Elmer Lambda 35 UV-Vis spectrometer. The photoluminescence study was carried out on Perkin-Elmer LS 55 spectrometer. The transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HR-TEM) image were taken on Tecnai G^2 (FEI company). Quanta 200 FEG fitted with an energy dispersive X-ray spectroscope (EDS; Genesis 2000, EDAX) was used for elemental analysis.

3. Results and discussion

3.1. *Structural study*

Figure 1 shows the XRD pattern of CdS and CdS/histidine QDs synthesised by sonochemical method. Broadening in the X-ray diffraction peaks indicate the formation of nanosize particles. There are mainly three peaks at angles (2θ) of 26.3, 44.0 and 53.5, which could be assigned to the CdS cubic phase (1 1 1), (2 2 0) and (3 1 1) crystal planes, respectively. CdS/histidine QDs have somewhat lower crystallinity in comparison to CdS QD. The average particle size of CdS/histidine and CdS are 1.4 and 4.1 nm, respectively. These average particle size are estimated from the full-width at half-maximum (FWHM) of the diffraction peak, using Scherrer's formula [9].

3.2. *Morphology study*

The morphology of the sonochemically synthesised CdS/histidine is shown in Figure 2. The TEM and HR-TEM image of CdS/histidine shows the presence of nanosize particles. The particles are nearly spherical in shape and have little aggregation. The average size of these QDs are in the range of 2–6 nm.

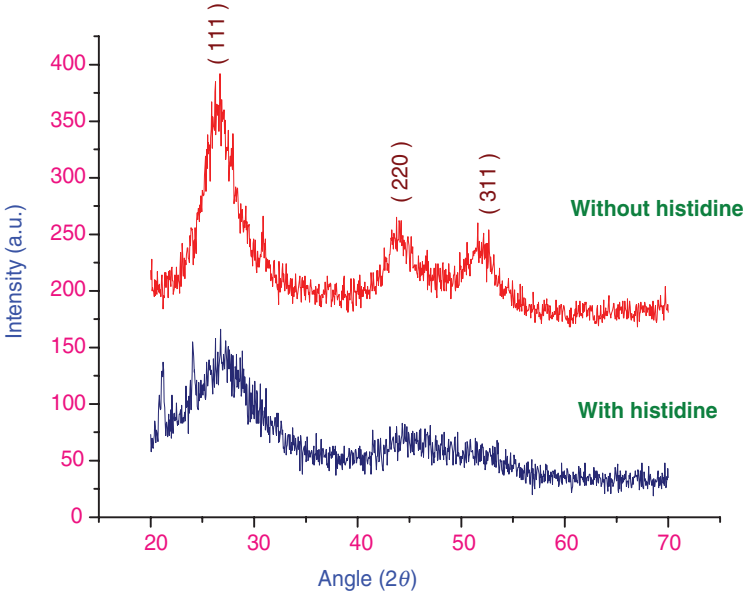

Figure 1. XRD pattern of CdS and CdS/histidine quantum dots synthesised by sonochemical method.

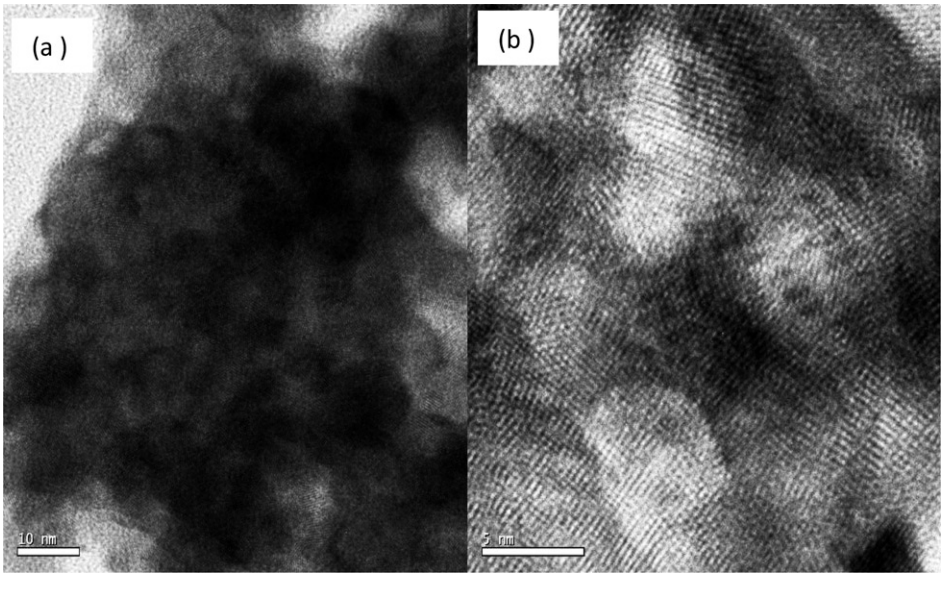

Figure 2. (a) TEM and (b) HR-TEM image of CdS/histidine quantum dots synthesised by sonochemical method.

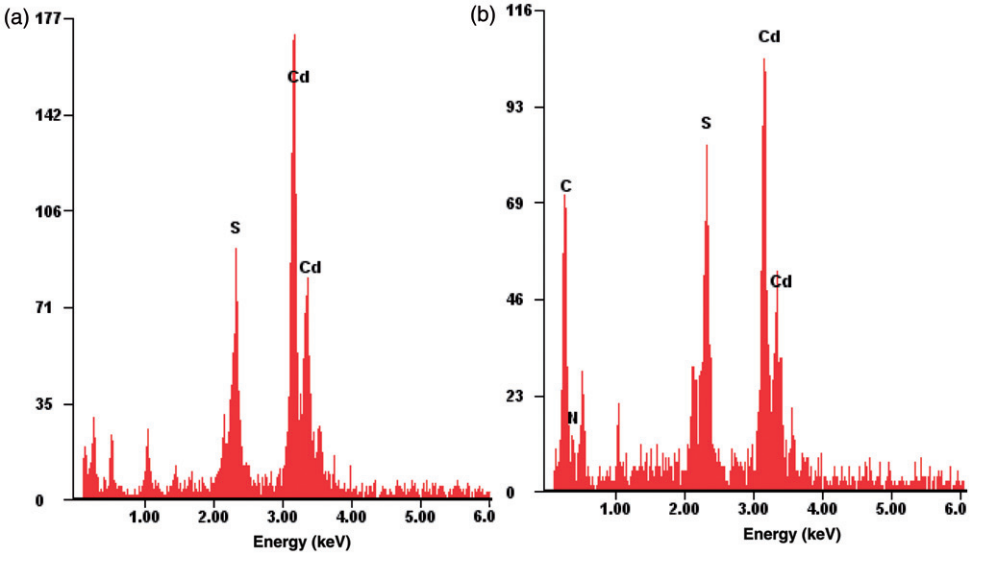

Figure 3. EDAX pattern of CdS and CdS/histidine quantum dots synthesised by sonochemical method.

3.3. *EDAX study*

The elemental composition of the CdS and CdS/histidine QDs was determined using energy dispersive analysis of X-rays (EDAX). The EDAX analysis profile for CdS and CdS/histidine are shown in Figure 3(a) and (b). It can be seen that there is a clean EDAX pattern for CdS QD, without any impurities. The EDAX profile of the CdS/histidine shows the additional signals corresponding to C and N elements, apart from CdS.

3.4. *Absorption spectrum study*

Figure 4 shows the absorption spectra for CdS and CdS/histidine QDs. The significant absorption of UV light at 315 and 376 nm were revealed with 200 and 139 nm blue-shift for CdS/histidine and CdS QD, respectively, when compared with the characteristic absorption of the corresponding band gap of bulk CdS (515 nm), reflecting the quantum confinement effect of the CdS and CdS/histidine QD. The absorption corresponds to the first optically allowed transition between the electronic state in the conduction band and the hole state in the valence band. The particle sizes were estimated from the band-gap values using Brus equation by effective mass approximation [10]:

$$E_{np} = E_g + \left(\frac{\hbar^2\pi^2}{2R^2}\right)\left(\frac{1}{m_e^*} + \frac{1}{m_h^*}\right) - \frac{1.786e^2}{\varepsilon R},$$

where E_{np} is the band gap of the CdS QDs, E_g band gap of bulk CdS, m_e^* effective mass of the electron ($0.19\,m_e$ in CdS) and m_h^* effective mass of the hole ($0.8\,m_e$ in CdS), respectively, R and ε are the radius and dielectric constant of CdS, respectively.

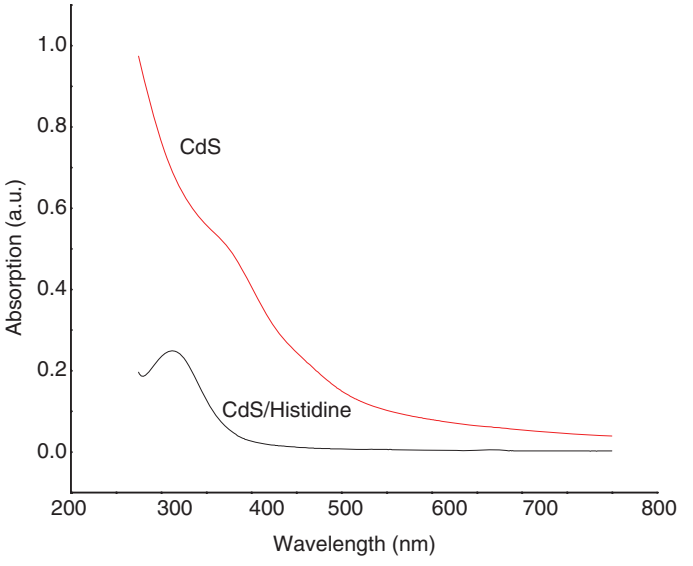

Figure 4. UV/Visible absorption spectrum of CdS and CdS/histidine quantum dots synthesised by sonochemical method.

The simplified expression for the energy E_{np} for CdS QDs of radius R, $E_g = 2.43$ eV and $\varepsilon = 5.7$ is [11]:

$$E(R) = 2.43 + \left(\frac{2.446}{R^2}\right) - \left(\frac{0.3031}{R}\right).$$

Estimated particle size using the above formula was 2.34 and 3.02 nm for CdS/histidine and CdS QDs, respectively. The particle size of CdS/histidine is smaller as compared to CdS because the imidazole ring of histidine captures the Cd ions from the solution and prevents the growth of CdS nanoparticles.

3.5. *Photoluminescence study*

The interesting properties exhibited by semiconductor nanoparticles are attributed to quantum confinement effect [12]. The electronic energy levels are strongly dependent on the size and also on the shape of the nanostructures [13]. CdS and CdS/histidine QDs have interesting and strong photoluminescence properties because of quantum confinement effect. The photoluminescence spectra of CdS and CdS/histidine QDs using an excitation wavelength of 400 nm are shown in Figure 5. CdS QDs have two most intense emission peak at 491 and 506 nm, while CdS/histidine QDs have at 487 and 503 nm. The emission peak at 487 and 491 nm in CdS/histidine and CdS QD is due to excitonic transition. The emission peak at 503 and 506 nm in CdS/histidine and CdS QD is due to deep trap/surface trap emission. It should be noted that the emission peak is also blue shifted from its bulk band gap value. Generally, the photoluminescence in semiconductor nanoparticles are excitonic and trapped emission [14]. The photoluminescence peak is red

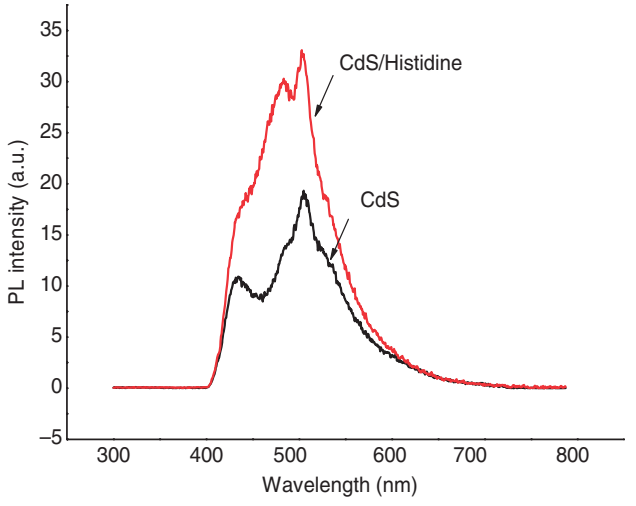

Figure 5. Photoluminescence spectrum of CdS and CdS/histidine quantum dots synthesised by sonochemical method.

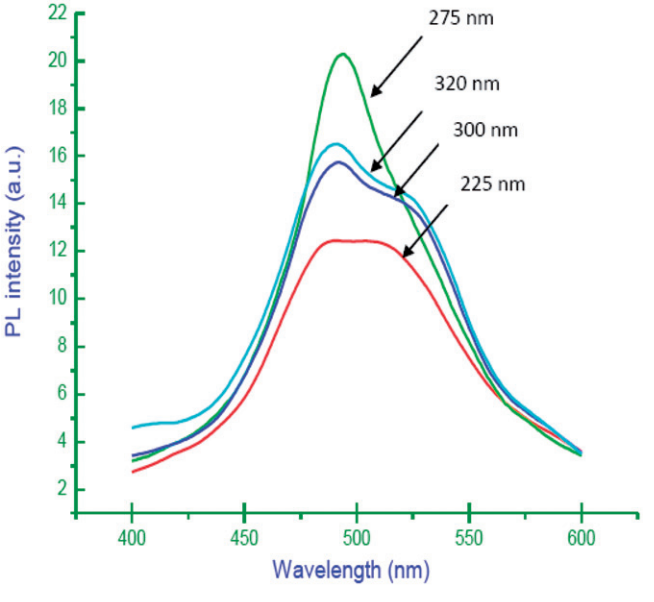

Figure 6. Photoluminescence properties of CdS/histidine quantum dots under different excitation 225, 275, 300 and 320 nm.

shifted with respect to absorption peak, such a large shift, known as Stokes shift [15]. These QDs will also be beneficial in making light emitting diodes (LEDs) as the difference in the absorption and emission states avoid material for self-absorption [16].

Figure 6 shows the room temperature photoluminescence spectra of CdS/histidine QDs synthesised by sonochemical method, under different excitation 225, 275, 300 and 320 nm.

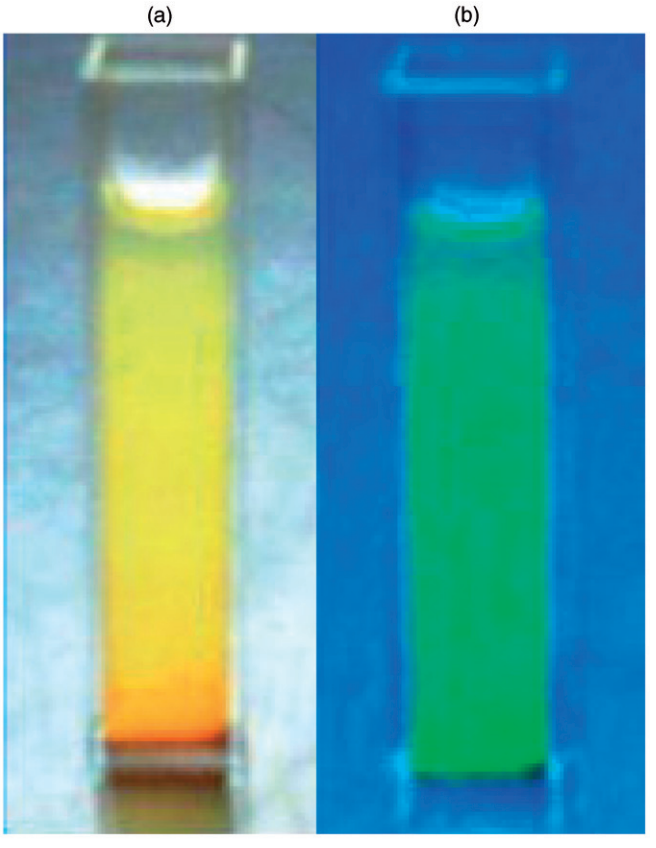

Figure 7. CdS/histidine quantum dots dispersed in water: (a) in daylight, (b) in UV light.

Among the spectra excited at 225, 300 and 320 nm, two peaks at ~490 and ~518 nm for each spectrum are distinguishable. The peaks at ~490 nm of each curve seem independent of excitation wavelength. With the excitation wavelength at 275 nm, there is one emission peak at ~490 nm. Despite the 275 nm excited spectrum, the position of CdS nanoparticles band edge emission remain unchanged with excitation wavelength of 225, 300 and 320 nm, which indicates the narrow size distribution of as-prepared CdS nanoparticles using histidine. Besides band gap emission between 450 and 500 nm, CdS nanoparticles are likely to have green emission ~518 nm related to deep trap/surface trap emission. Figure 7 shows photoluminescence emission from CdS/histidine QDs dissolved in water placed in daylight and UV light, respectively.

3.6. *Functionalisation mechanism*

Histidine is an amino acid, it has a basic structure of a molecule with an NH_2 (amine group) on one end and with a COOH group (carboxyl group) on the other end; there is a carbon atom between these end groups and bound to the carbon atom are a hydrogen

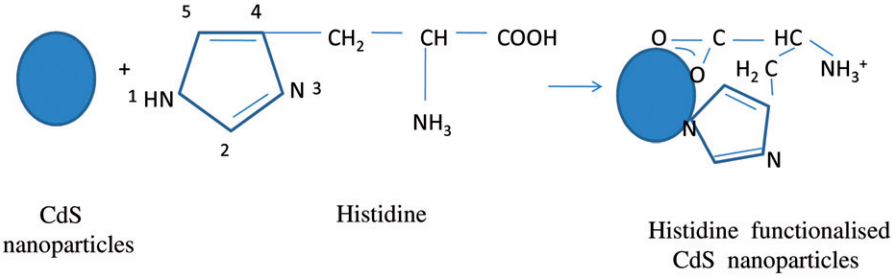

Figure 8. Schematic representation of histidine functionalised CdS quantum dot.

atom and a side group. Histidines differ by other amino acids in possessing imidazole side chain [17]. The schematic representation of Histidine functionalised CdS QD is shown in Figure 8. When the imidazole attached on the CdS QD surface, the N_{1-} group of the imidazole is involved in the coordination of the histidine with the CdS QD surface. The carboxyl group of histidine also binds the CdS QD surface. In this way, with histidine, biocompatible CdS QD can be made by coating and stabilising with their carboxyl and N_{1-} of imidazole binding to the surface.

4. Conclusion

CdS/histidine QDs have been successfully synthesised via a simple sonochemical method. The CdS QDs are functionalised with carboxyl and N_{1-} of imidazole of histidine. The absorption spectra of CdS/histidine QDs show blue shift as compared to bulk CdS. The absorption spectra confirm quantum confinement. The histidine functionalised CdS showed band edge photoluminescence and enhances intensity as compared to bare CdS. QDs CdS/histidine have promising applications in biolabel and *in vivo* image fields because of their photoluminescence and biocompatibility.

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