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Surfactant mediated optical properties of cytosine capped CdSe quantum dots

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ABSTRACT

This letter demonstrates the use of one of the nucleobases, 'cytosine' as a new capping agent in controlling the size of the nanoparticles. A size dependent blue shift in optical absorption with enhanced luminescence is observed. Since the calculated density of states do not show any change in the band gap of as-prepared quantum dots after capping, the observed blue shift of the absorption peak can solely be attributed to the so-called size-effect whereas the enhancement in luminescence to surfactant mediated defect passivation. It is expected that the observed properties of the cytosine capped CdSe quantum dots would facilitate a better bio-compatibility of tailor-made nanoparticles for bio-imaging applications.

1. Introduction

In the recent past, synthesis and characterization of II–VI semiconductor materials at nanometer scale have been the focus of several workers. Due to unique optical and electronic properties, CdSe quantum dots (QDs) have been studied and used as biological labels for multiplexed biological detection, imaging and in molecular cell biology [1–5]. Scientific literatures have shown a variety of methods for synthesis of CdSe nanocrystals [6–10]. But these nanocrystals have shown low quantum yields due to the non-radiative recombination of light-generated charge carriers at surface traps caused by surface defects [11,12].

It has been suggested that the passivation of surface defects with ligands or shells of a high band gap semiconductor can reduce the surface trap densities; thereby enhancing the quantum yield of CdSe QDs. Murray and co-workers [6] have achieved the enhancement in the quantum efficiency of CdSe quantum dots by coating them with a higher band gap semiconducting compounds, such as CdS and ZnS. Similarly, CdSe quantum dots embedded in the SiO_2 matrix was found to give a highly intense emission peak in the visible region [5]. In the present study, we follow an alternative route by which passivation of CdSe QDs is achieved employing one of the nucleobases, 'cytosine' that makes the CdSe QDs more biocompatible for its versatility. Cytosine *per se* does not contribute to fluorescence yield [13], as the change in electronic and optical properties of cytosine capped CdSe QDs are insignificant, rather cytosine will only act as a new capping agent for reducing the surface defect density of QDs.

2. Experimental details

2.1. Material and methods

For synthesizing CdSe QDs, 45 mmol of cadmium acetate dihydrate was dissolved in 100 ml of methanol and refluxed through a water condenser for 2 h at 60 °C (solution A). Simultaneously, 140 mM solution of sodium selenide was prepared in 100 ml of methanol while refluxing through a water condenser for 2 h at 60 °C (solution B). Both solutions A and B were mixed while refluxing through a water condenser at 60 °C for 2 h. Thus the prepared solution was maintained at pH 8 and kept for overnight ageing at room temperature. The final product was washed several times with ethanol and double distilled water before vacuum drying at 50 °C. For samples capped with cytosine, the separate solution of cytosine prepared in methanol was added in solution A before adding solution B. Three individual reactions, one without cytosine, second with cytosine in equal amounts of metal ions and third in double amounts of metal ions resulted in sample A, sample B and sample C, respectively.

2.2. Characterizations used

The prepared CdSe nanoparticles were characterized by X-ray diffraction (XRD, Rigaku D/max-2200 PC diffractometer operated at 40 kV/40 mA, using $CuK_{\alpha 1}$ radiation) in the wide angle region of 20°–55° on a 2θ scale, high resolution transmission electron microscopy (HRTEM, model Tecnai 30 G^2 S-Twin electron microscope, operated at 300 kV accelerating voltage). Whereas, a Perkin Elmer make Lambda 35 and LS 55 spectrometer was used for absorption and luminescence studies respectively.

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3. Results and discussions

Fig. 1 shows the X-ray diffraction (XRD) spectra of as-prepared and cytosine capped CdSe QDs. XRD spectra show good agreement with the standard JCPDS file for CdSe (JCPDS number 19-0191, $a = b = c = 6.077$ Å) and can be indexed as the cubic structure having space group $F4_{3m(216)}$. Capping of CdSe QDs with cytosine presumably decreases the crystallinity of the samples, though there is no (noticeable) change in peak positions of capped samples with that of as-prepared samples. Figs 1(b), (c), and (d) show the TEM images of samples A, B and C. All the samples show spherical particles, whereas the CdSe QDs are found enslaved in the cytosine chain for capped samples with a narrow particle size distribution. The size as obtained from XRD and TEM are shown in Table 1.

Table 1
The size and absorption peak position of CdSe QDs.

Sample	Absorption peak (nm)	Band gap (eV)	Size (nm) using	
			Debye Scherrer's equation	TEM
Sample A (as-prepared)	483	2.57	7	8
Sample B (capped)	460	2.70	5	6
Sample C (capped)	438	2.83	3	3

The optical absorption spectra (Fig 2(a)) were recorded by dispersing the samples in double distilled water using double distilled water as reference. The absorption peaks are observed at 483 and 460 nm for as-prepared (sample A) and capped CdSe (sample B),

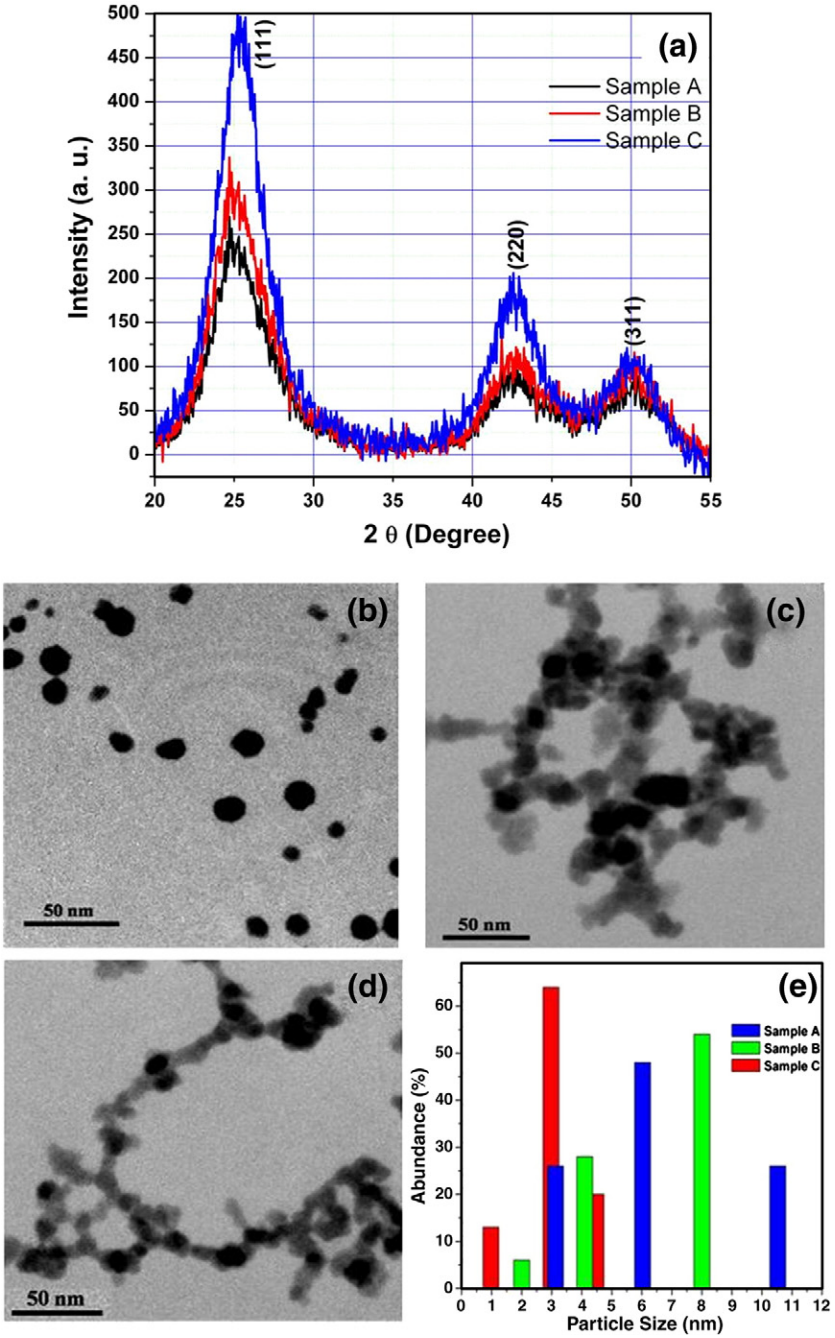

Fig. 1. (a) X-ray diffraction spectra of as-prepared and cytosine capped CdSe QDs. Sample A are the as-prepared QDs and samples B and C are capped QDs. TEM image of (b) as-prepared CdSe QDs with spherical morphology (sample A), (c), (d) capped QDs (samples B and C, respectively) and (e) particle size distribution for all the samples under study.

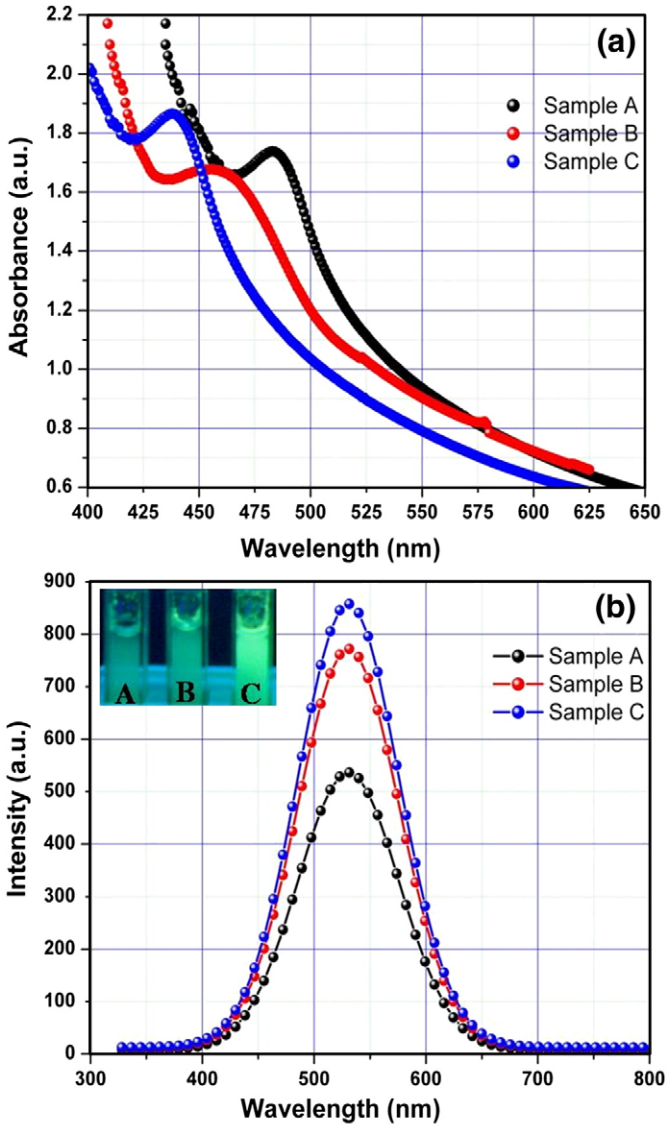

Fig. 2. (a) Optical absorption. (b) photoluminescence spectra of CdSe and CdSe quantum dots capped with different concentration of cytosine. Sample A are as-prepared QDs and samples B and C are capped QDs.

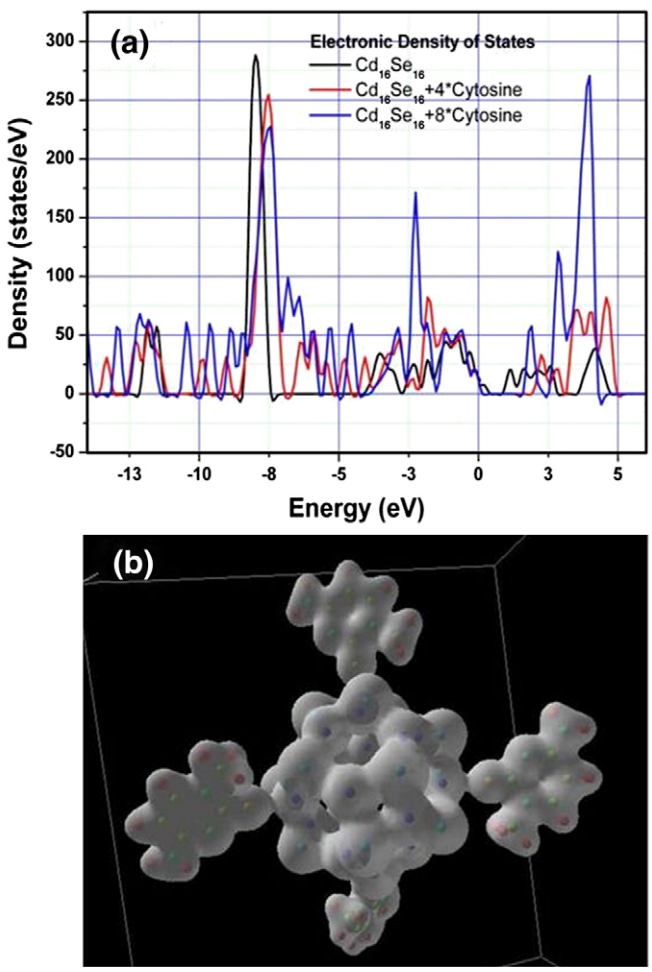

Fig. 3. (a) Density of states of CdSe and capped CdSe QDs. (b) Charge density of capped CdSe QDs. The QD was represented by a 32-atom cluster and capping was performed with either four or eight cytosine molecules. The zero of the energy is aligned to the Fermi energy.

respectively. Interestingly, the sample C with a larger concentration of cytosine peaks at 438 nm (eg ~2.84 eV). This shows a blue shift in the absorption peak of CdSe QDs as compared to the bulk band gap of 743 nm (i.e. 1.75 eV) [14]. The effect of quantum confinement as a function of size on blue shift in band gap could be easily discerned by inspecting Table 1.

In order to know the mechanism behind the observed shift in the band gap of QDs, electronic structure calculations, based on the density function theory, were performed on $Cd_{16}Se_{16}$ sub nanometer clusters representing a CdSe QD. The cytosine capped CdSe QD is predicted to be stable, capping does not appear to change the electronic structure near the Fermi energy of as-prepared CdSe QD. On the other hand, capping with cytosine introduces the peaks in the valence and conduction bands away from the band gap, as seen in the density of states (Fig. 3). Thus a blue shift in absorption spectra of as-prepared CdSe QDs can be attributed to the quantum confinement effect only.

Fig. 2(b) illustrates the photoluminescence spectra of synthesized CdSe QDs and CdSe QDs capped with different concentrations of cytosine capping for excitations corresponding to the absorption data. The well known green emission from as-prepared CdSe QDs [15] is found shifted from 515 nm to 530 nm in capped QDs. This broad peak in the visible region is associated to the structural defects like interstitials, selenium vacancies and surface traps, although there is a total absence/quenching of excitonic and defect associated emission peak intensities [16]. The enhancement in the bright green luminescence was observed with increasing concentration of cytosine capping. The capped CdSe QDs showed a very strong broad emission around 530 nm due to recombination via surface localized states.

Studies have shown that the luminescence efficiency of nanoparticles strongly depend on the nature of the surface, because of a large surface-to-volume ratio in smaller particles [17]. In the case of as-prepared CdSe QDs, surface states such as dangling bonds are usually involved in non-radiative processes, while Se^{2-} ions provide a critical pathway for the visible emission band. Additionally, the cytosine capping reduces the density of surface dangling bonds and Se^{2-} ions, so the probability of non-radiative transitions is further reduced thereby increasing the probability of visible emission. This could be further understood on the basis of net positive charge of the Cd atom in the Cd–Se–Cytosine bond. Positive centres in CdSe produced an attractive defect potential creating a donor state by pulling conduction band levels into the band gap. Due to the weak attractive potential, the energy level of the donor state created by Cd–Se–Cytosine acts as a luminescence centre for the 530 nm band whereas cytosine capping provides a good coverage of the CdSe surface and acts as an energetic barrier preventing the escape of photo generated

carriers outside the confined CdSe nanoparticles, resulting in enhanced emission intensity.

Moreover, excess cadmium ions would complex on the surface of CdSe, under reflux in methanol, resulting in removal of the surface traps responsible for the enhancement of luminescence. In our case, the CdSe nanoparticles were refluxed again by adding cytosine and therefore the significant changes in the absorption edge (Fig. 2(a)) as well as in the luminescence intensity (Fig. 2(b)) are observed. This illustrates that additional surface modification took place rather than the change in size of the nanoparticle. For the cytosine capped CdSe QDs, refluxing under the reduced barrier helps the formation of cytosine chains to coalesce as a continuous shell on the CdSe surface and remove surface traps, if any which results in the strong emission. Whereas, refluxing under the reduced barrier would give the excess cadmium ions a chance to complex on the surface of the QDs, resulting in further improved luminescence efficiency.

4. Conclusions

A size dependent blue shift in optical absorption with enhanced luminescence is observed from CdSe QDs using the new capping agent 'cytosine'. The mechanism behind the surfactant mediated enhanced bright green luminescence is proposed. The cytosine capped CdSe QDs can be seen as one of the necessary and condemnatory constituent for bio-imaging and bio-sensors after the conjugation of the nanocrystals to biological entities underlying the importance of the current work.

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