

Synthesis and characterization of small size fluorescent LEEH capped blue emission ZnTe quantum dots

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We report here for the first time the synthesis of LEEH capped very small size (2 nm) ZnTe quantum dots at low temperature (less than 100 °C) using a simple chemical route. The effects of aging and stirring time on the absorption spectra of the quantum dots were investigated. The synthesized nanocrystal (NC) was characterized by PL, TEM, XRD and the formation of very small size quantum dots having FCC structure was confirmed. Further, blue emission from the prepared sample was observed during exposure to monochromatic UV radiation. ZnTe NCs obtained in this study were found to be more stable compared to those presented in literature reports. ZnTe NCs may be considered as a new material in place of CdTe for optoelectronics devices.

Keywords: *photoluminescence (PL); optical absorption; ZnTe Nanocrystals; L-cystein ethyle ester hydrochloride; size quantization effect*

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1. Introduction

Quantum dots (QDs), are semiconducting crystals whose size is very small (usually less than 10 nm). These semiconductor nanocrystals (NCs), exhibit peculiar interesting properties, such as quantum confinement, size dependent optical as well as electrical properties [1–5], and, hence, have a wide range of applications in optoelectronics devices, memory devices, drug delivery systems, biological imaging, sensing and solar cells [6–10].

There are several II-VI semiconductor nanostructures, like CdSe, CdTe, CdS widely investigated for different applications. But the toxicity of Cd makes these NCs not suitable for real applications. ZnTe is another II-VI semiconductor that does not contain harmful elements. Unfortunately, very few investigations are found in the literature for synthesis of ZnTe NCs [11, 12]. This is because the size controlled synthesis of ZnTe

quantum dots is very difficult. Furthermore, these NCs have poor chemical stability due to Te oxidation. However, ZnTe is a direct band gap semiconductor with a band gap 2.26 eV which corresponds to a wavelength of 548.67 nm. So, this is an important material for light emitting diodes, laser diodes and solar cells. Existing methods of synthesis of ZnTe need high temperatures. In addition to this, they have narrower size distribution and poor stability [11].

Herein, we describe the synthesis and characterization of ZnTe QDs having average size as small as 2 nm which, unlike previously reported methods, does not require high temperatures during synthesis. Moreover, the synthesized quantum dots in our case are more stable (approximately 10 days) compared to quantum dots having less than one hour stability mentioned in the literature [11]. We also report, for the first time, blue emission from these quantum dots, when excited with monochromatic UV signal. The resulting NCs are characterized by PL, TEM and XRD measurements, whereas

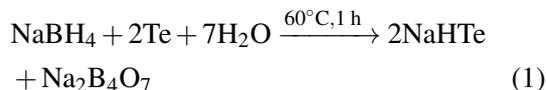
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UV-Vis illumination is carried out to optimize the sample. Further, L-cysteine ethyl ester hydrochloride (LEEH) has been used for the first time in this investigation as a capping agent in the synthesis of ZnTe QDs.

2. Experimental

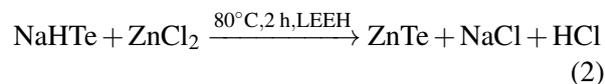
The capped ZnTe NC quantum dots (NCQD) were synthesized by simple chemical root bottom up method. The chemicals used in this process were sodium borohydrate (NaBH_4), a good reducing agent, tellurium (Te) powder and zinc chloride (ZnCl_2) as a source and LEEH as a capping agent. All the chemicals, purchased from Sigma-Aldrich, were of high purity. Deionized water (resistivity $18.2 \text{ M}\Omega\cdot\text{cm}$) was used for the synthesis.

Into 20 mL of deionized water, 189.15 mg of NaBH_4 (0.5 M) and 0.638 mg of tellurium powder (0.5 mM) were added successfully and stirred at 60°C for 1 hour. In this process Te reduced to NaHTe obeying the reaction:



After half an hour of the reaction the solution became light pink which color vanished thereafter. By adding Te directly into water and then adding NaBH_4 , tellurium oxide was obtained which is a stable compound and synthesis of ZnTe did not occur.

Next, two separate solutions were prepared adding 3.77 mg of ZnCl_2 (2.77 mM) into 10 mL of deionized water and 185.67 mg of LEEH (0.1 mM) into 10 mL of deionized water. These two solutions were mixed together and stirred at 45°C for half an hour. Stirring of this solution and the solution ($\text{NaHTe} + \text{Na}_2\text{B}_4\text{O}_7$) was completed at the same time and the both solutions were mixed immediately and further stirred for 2 h at 80°C . The chemical reaction for the formation of ZnTe NCQD is:



ZnTe QDs sample was studied using UV-Vis absorption spectrophotometer (UV-1800,

Shimadzu). PL measurements were carried out at room temperature using Oriel PL setup (with $\lambda = 355 \text{ nm}$ as incident excitation available from NdYAG laser) to calculate the band gap value.

TEM micrographs of a nanoparticle sample prepared on carbon coated grid were taken using JEOL JEM-2010 Transmission Electron Microscope at 200 kV beam energy. Higher resolution TEM and SAED patterns of the sample were taken to evaluate the particle size and size distribution.

XRD study was carried out using $\text{CuK}\alpha$ radiation of $\lambda = 1.5418 \text{ \AA}$ to investigate the crystal size and geometry of the synthesized QDs.

3. Results and discussion

Fig. 1 presents the XRD (X-ray diffraction) spectra of the optimized ZnTe NC. The diffraction pattern agrees with zinc blende structure (JCPDS Card No. ICSD# 078310). The particle size (diameter) has also been calculated from the XRD spectra using Debye-Scherrer formula:

$$D = k\lambda / \beta \cdot \cos\theta \quad (3)$$

where: β (in radians) is the FWHM of the diffraction peak at an angle θ . The average size of the particle is found to be 1.7156 nm. In the inset of Fig. 1, a well resolved lattice fringes are shown.

High resolution TEM (HRTEM) image of ZnTe QD is shown in Fig. 2a for the optimized sample. The average size of the nanoparticles was

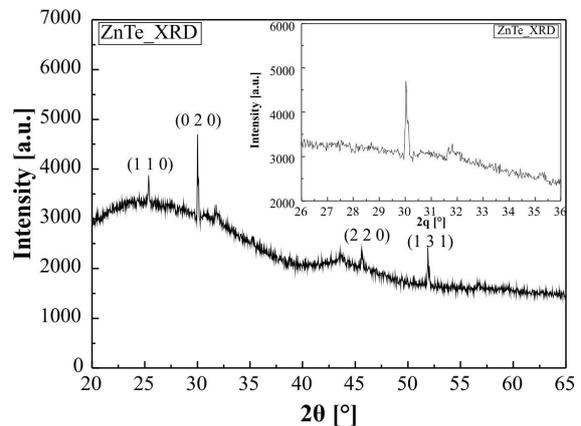
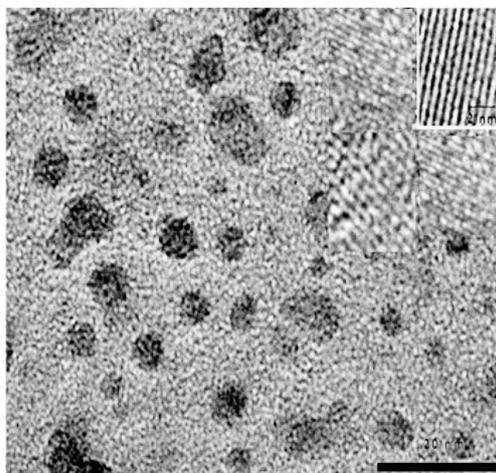
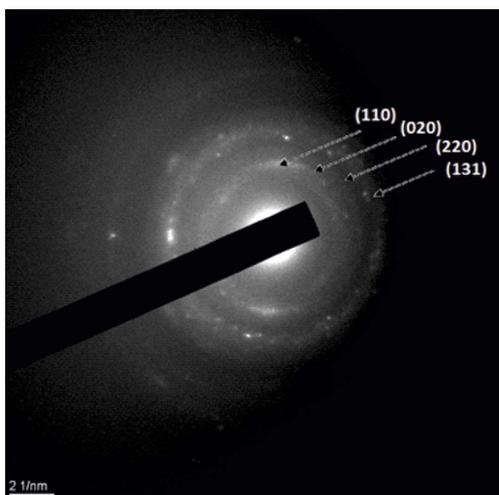


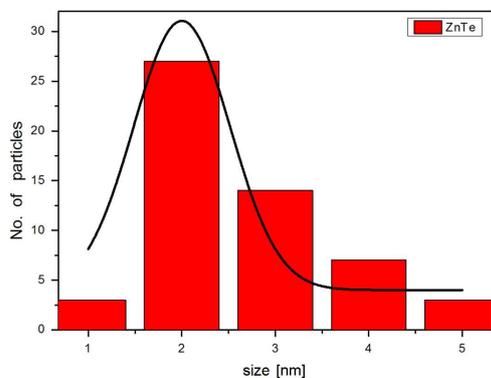
Fig. 1. XRD pattern of ZnTe.



(a)



(b)

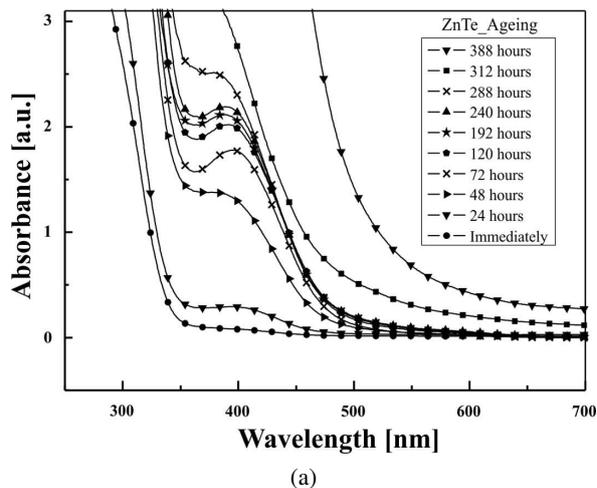


(c)

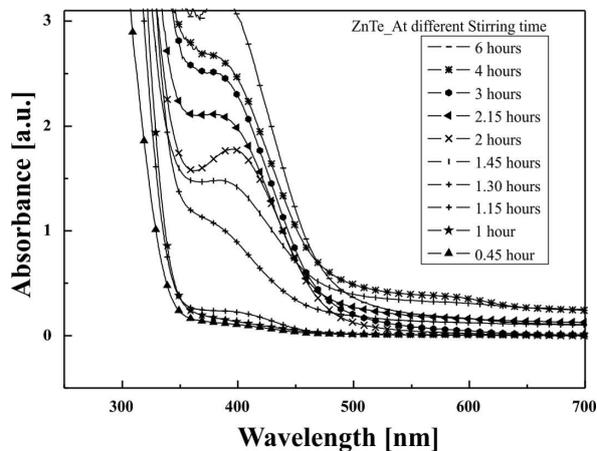
Fig. 2. (a) TEM of ZnTe NC deposited on carbon coated copper grid. The inset shows high resolution lattice image of ZnTe NC; (b) SAED pattern from the region shown in Fig. 2a; (c) size distribution histogram of ZnTe NC.

calculated from this image and was found to be 2 nm. The histogram for size distribution is shown in Fig. 2c. The Selected Area Electron Diffraction Pattern (SAED) in Fig. 2b clearly indicates (1 1 0), (0 2 0), (2 2 0) and (1 3 1) lattice planes and the ratio of the diameters of the rings $d_1^2:d_2^2:d_3^2:d_4^2 = 1:1.33:2.66:3.66$, which indicates the FCC (Zn blend) structure of the prepared sample.

Fig. 3 presents the optical absorption spectra of synthesized ZnTe semiconductor NC. The sample was optimized with respect to stirring time and aging period. Keeping the stirring time constant, that is 2 h, the aging effect was investigated. Similarly the sample was characterized for different stirring times.



(a)



(b)

Fig. 3. Absorption spectra of ZnTe NC showing (a) aging effect; (b) effect of stirring time.

The absorption spectra of the NCs clearly show that the quantum confinement effect depends on the stirring time and aging. A prominent peak appears in the optical absorption if the stirring time is reduced to 2 h, resulting in a strong quantum confinement. Further, with aging (up to 12 days after synthesis) the shoulder remains almost unchanged, except it is pushed up with aging time. But after that the shoulder generally decreases and finally disappears after 16 days. Interestingly, the excitonic peak remains unchanged at 397 nm (3.123 eV) until its disappearance. We have calculated the diameter of the quantum dot [13] and found it to be 1.46989 nm with an uncertainty of 0.041 nm.

The literature reports on ZnTe QDs reveal its poor chemical stability due to Te oxidation. For example Lincheneau *et al.* [11] showed ZnTe colloids to be stable only for less than an hour in air in equilibrium solution at room temperature. However, in our case, as it has been shown, ZnTe QDs are stable at least for ten days under the same conditions. The stability of these QDs can be explained by the capping by LEEH. Further, the quantum confinement in our case is more pronounced than that reported by Lincheneau *et al.* [11].

Earlier studies reported luminescence in ZnTe NCs, while recent studies reveal that luminescence is quenched due to surface passivation. However, our sample exhibited spontaneous UV emission upon excitation with monochromatic UV light. However, the emission decayed after ten days due to the increase in size of the QDs.

Photoluminescence measurement was also carried out for the sample which is shown in Fig. 4. The possible band diagram is shown in the inset of Fig. 4.

It may be noted here, that the spectrum shown in Fig. 4 is the emission deconvoluted into two bands at 2.52 eV (491.62 nm) and 5.48 eV (226.25 nm). The high-intensity PL band at 491.62 nm is red shifted by 94.62 nm compared to the exciton appearing at 397 nm (Fig. 3). The PL band appearing at 491.92 nm may be due to the surface trap states arising due to unsaturated dangling bonds within the semiconductor nanocrystal which give a rise to

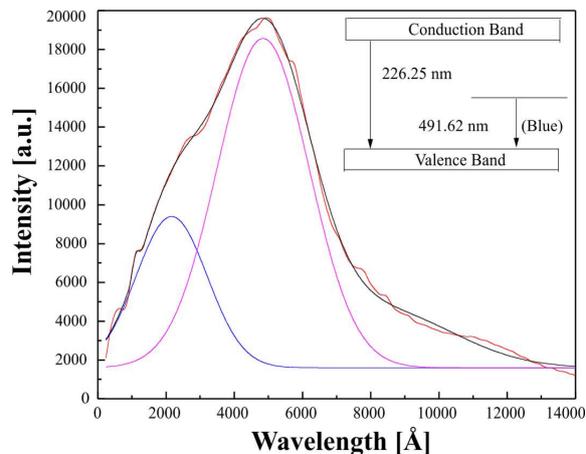


Fig. 4. PL spectrum of ZnTe deconvoluted for two different emissions. The inset shows the possible band diagram.

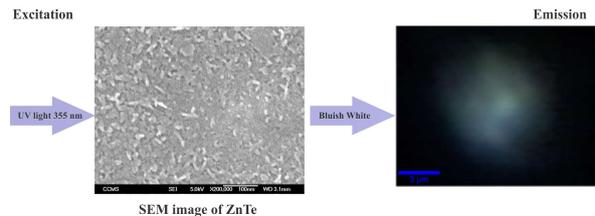


Fig. 5. Optical PL emission excited with monochromatic UV light from ZnTe.

energy levels within the HOMO-LUMO gap (as no care has been taken for surface passivation) [14]. The large wavelength shift compared to exciton position is ascribed to the large nonresonant Stokes shift, where the shift is inversely proportional to the NC size [15]. The optical photograph taken by irradiating the sample with monochromatic UV light corresponds to the blue color as shown in Fig. 5. Emission from the sample kept in a tube illuminated by UV light also showed blue color and was reported here for the first time.

A comparison of average sizes of the QDs from different characterization methods is presented in Table 1.

Table 1. A comparison of average size of the QDs from different characterization methods.

EMA [nm]	GXRD [nm]	TEM [nm]
1.46989	1.8051	2

4. Conclusions

In this paper, we have presented a unique method to synthesize ZnTe NC using LEEH as a capping agent. In contrary to the previous synthesis reported, which involved high temperatures (above 200 °C), herein, the maximum temperature maintained during synthesis was 90 °C. The average diameter of the ZnTe NC was found to be 2 nm and has been reported here for the first time. Further, the prepared sample was stable for 288 h which is the longest period reported in the literature so far. In addition to the above properties, the QDs give blue emission, when excited with monochromatic UV light.

Though ZnTe QDs appear to be less stable and difficult to prepare, they can be considered as an alternate material for cadmium based QDs for LED and LD.

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