

LUMINESCENCE STUDY OF CdTe NANOCRYSTALS FOR NANO LEDs

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ABSTRACT - We report the preparation of CdTe quantum dots by chemical route at a temperature of 200 °C followed by their characterizations with XRD, HRTEM, SEM and FTIR. It has been observed that our prepared CdTe quantum dots possess cubic crystallite with size ranging from 3 to 11 nm. Blue shifted sharp absorption edge is observed for the prepared samples. It has been revealed that CdTe quantum dots are of emission (fluorescence) spectra occurring at a wavelength of 600 nm with narrow full width at half maxima. To test the function of CdTe quantum dot assembly as nano LED (nano light emitting device), the electroluminescence is studied and it shows the emission which is almost in the similar wavelength as that of fluorescence. This study infers the possible application of CdTe quantum dots as nano LED with an emission in at around 600 nm. Further, the emission intensity varies with the input bias voltage.

Key Words: CdTe, nanocrystal, luminescence, nano LEDs.

1. INTRODUCTION

During the past decade, the preparation and characterization of materials on the nanometer scale has provided a new physics in reduced dimensions as well as the possibility of fabricating novel material. As a new type of material, semiconductors quantum dots (QDs) present very unique properties. Because of the quantum size effect, the absorption and photoluminescence spectra of the QDs-size semiconductor particles can easily be tuned by varying the particle size [1]. Cadmium telluride (CdTe) is a promising semiconductor with a direct band-gap of 1.49 eV [2]. A few studies have been reported on the development of synthesis of CdTe QDs [3-7]. Recent reports suggest that QDs can be used to produce light of various colors by band gap tuning using particle size effects [1]. CdTe has been regarded as one of the promising candidates for the next generation of light-emitting device (LED) operating at room temperatures with the possibility of tuning the device emission colour [8,9]. Nano LEDs have more advantageous over the more extensively studied conventional LEDs as nano LEDs are of higher quantum efficiency and faster in response speed

[1,10,11]. A few approaches to the fabrication of electroluminescent devices have emerged from the development of colloidal semiconductor QDs.

Here we present a convenient and efficient way to prepare CdTe QDs with chemical route in which, oleic acid is used as a surfactant to stabilize the particles size. Compared to the other solvent (capping agents), oleic acid is cheaper, more environment friendly and more stable in air. The prepared CdTe QDs are characterized by UV-Visible absorption spectroscopy, XRD, high resolution transmission electron microscopy (HRTEM), fluorescence (FL) spectroscopy and FTIR analysis. Significant advances in the preparation of relatively stable, narrowly sized CdTe QDs have been made throughout the synthesis. Over more, the electroluminescence of the samples (CdTe) has been analyzed for their applications as nano light emitting device (LED), which is our original work. This area of research has not been highlighted the way it should have been. Hence, the present study, where the working of CdTe quantum dot assembly as nano LED has been investigated, is very interesting and important.

2. EXPERIMENTAL

Paraffin, oleic acid, methanol and ethanol are purchased from SRL (India) chemicals. Cadmium oxide and tellurium powder are obtained from Merck (India) chemicals. All of them are used without any further purification. Double-distilled (D/D) water has been used throughout the experiment. To prepare CdTe QDs, 1.25 gm of tellurium powder is mixed with 50 ml of liquid paraffin in a beaker by continuous stirring using magnetic stirrer at 200 °C for nearly 2 hours until a dark gray colour appears (tellurium precursor). Then, 2 gm of cadmium oxide, 10 ml of oleic acid and 40 ml of liquid paraffin are mixed in another beaker by continuous stirring by magnetic stirrer at 150 °C for nearly 1 hour until it turns light brown colour (cadmium precursor). Finally, 5 ml of cadmium precursor is quickly added to the tellurium precursor and the content is stirred continuously using magnetic stirrer for nearly 45 min at 200 °C. Next, the sample is kept at room temperature for 10 hours and methanol is added to precipitate CdTe QDs. Finally, the sample is washed with ethanol at 40 °C for characterization. The purpose of washing with ethanol is the removal of other by-products.

The prepared samples are characterized by using UV-visible absorption spectrophotometer (using Perkin Elmer Lambda-25) and absorption spectra are recorded. X-ray diffraction (XRD) measurement is performed with a Bruker X-ray diffractometer (Cu KR radiation, $\lambda = 1.5406 \text{ \AA}$). High Resolution Transmission Electron Microscope (HRTEM) observations are performed by using a Jeol JEM - 2100 transmission electron microscope, operating at 200 kV accelerating voltage, with an interpretable resolution limit of 0.16 nm. For TEM experiments of CdTe samples, a small drop has been dropped onto a carbon coated copper grid, allowing the alcohol to evaporate. High resolution TEM image and selected area electron diffraction (SAED) patterns are obtained in order to evaluate the particle shape, structure and diameter distribution. The surface morphology has been examined using scanning electron microscopy (JSM 6390LV). Fourier Transform Infra Red (FTIR) analysis is carried out on a 'Spectrum two' (Perkin Elmer) spectrometer. Fluorescence (FL) and Electroluminescence (EL) spectra of the samples are recorded (Perkin Elmer LS-45 luminescent spectrometer) to investigate luminescence properties. Optical measurements are carried out at room temperature under ambient condition.

3. RESULTS AND DISCUSSION

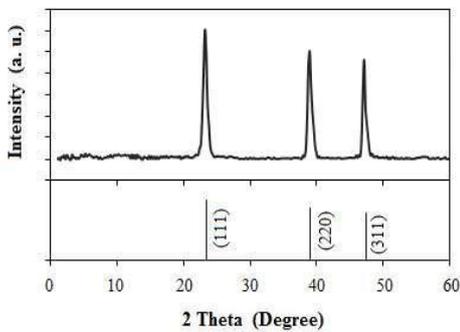


Fig - 1: XRD pattern of CdTe quantum dots.

In order to determine the size and to study the structural properties of the as-prepared CdTe nanocomposites, the XRD analysis has been performed and XRD patterns are depicted in figure 1. By comparison with the data from JCPDS, the diffraction peaks observed at 23.3°, 39.1°, and 47.3° (fig. 3) can be indexed as (111), (220) and (311) planes and it can be ascribed the cubic cadmium telluride crystal. The average crystallite size is estimated from the full width at half maximum (FWHM) of the diffraction peaks using the Debye-Scherrer formula [12]. The average diameter estimates for the CdTe nanocrystals is about 6.8 nm.

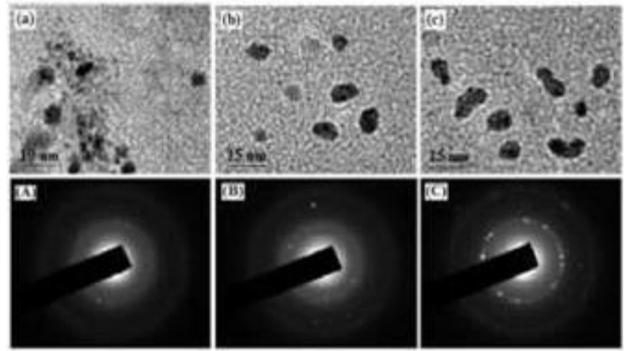


Fig - 2: High-resolution TEM images and SAED patterns of CdTe nanocrystals.



Fig - 3: SEM images of CdTe nanocrystals.

A sight into the structural features and surface morphology of the CdTe QDs has been achieved from the HRTEM images (Fig. 2) and SEM images (Fig. 3). Three samples of CdTe QDs with different concentrations grown in chemical process are presented in figure 2. The diameters of CdTe nanoparticles are determined and it is found of the order of 3-11 nm. The QDs are dispersed well and no aggregation is detected. Size of the QDs gradually increases with increase of Cd-precursor concentration (Fig. 2a, 2b & 2c). An almost-uniform contrast for each particle in the TEM analysis suggests that the electron density is homogeneous within the volume of the particle [13]. TEM images reveal that CdTe QDs are in both nearly spherical and elliptical shapes. The selected area electron diffraction (SAED) patterns (Fig. 2A, 2B & 2C) show good diffraction rings. The intensity of the diffraction rings indicates that the particles crystallized with lattice planes (111), (220) and (311). It's clearly implies the cubic crystalline nature of CdTe QDs. SEM images reveals the smooth surfaces of the nanocrystals.

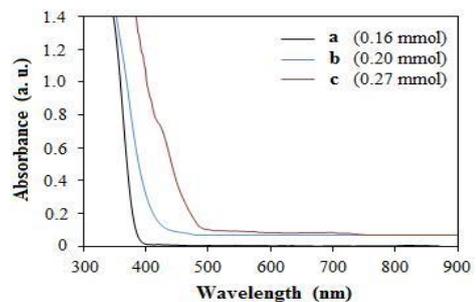


Fig - 4: FTIR spectra of pure OA (curve 1) and OA capped CdTe QDs (curve 2).

FTIR is a prevailing apparatus to study the capping of surfactants to the surface of the nanoparticles. Figure 4 shows the FTIR spectra for pure oleic acid (OA) and oleic acid capped CdTe QDs (OA-CdTe QDs). The prominent features of the spectrum in OA (curve 1) are peaks occurring at 1710 cm⁻¹ and 3004 cm⁻¹ (curve 1). We also observe bands positioned at 2857 and 2928 cm⁻¹ which are designated to symmetric and antisymmetric stretching of CH₂ [14]. The most important differences in the OA-CdTe QDs spectrum (curve 2) from that of pure OA are a shift in the 1710 cm⁻¹ band to 1632 cm⁻¹ which is attributed the existence of C=O stretch and the disappearance of 3004 cm⁻¹ peak. A intense peak is observed at 3060 cm⁻¹ which is assigned to OH stretch and another weak peak is observed at 1910 cm⁻¹ is assigned to COO- stretch in the OA-CdTe QDs spectrum. The FTIR spectra indicated the typical characteristics of CdTe QDs capped with oleic acid.

Fig - 5: UV-Vis absorption spectra of CdTe quantum dots prepared in different concentrations.

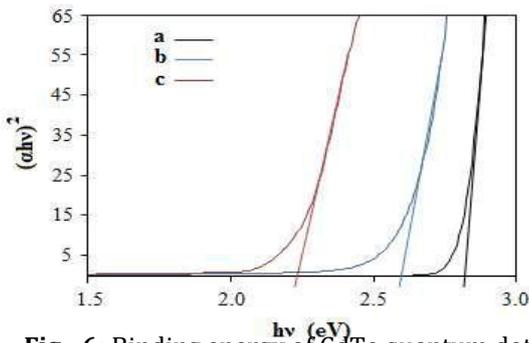


Fig - 6: Binding energy of CdTe quantum dots.

UV-Vis spectrum is a fundamental and widely used approach to determine the band gap energy and other related properties of semiconductors QDs. In the ultraviolet-visible range, the transition of free electrons from valence band to conduction band causes a strong absorption edge. CdTe QDs shows strong absorption in the ultraviolet-visible wave region. This is a clear signature of the formation of CdTe QDs. Figure 5 shows the absorption spectra of CdTe QDs growth in different concentration of Cd-precursor with the same reaction conditions (reaction temperature, stirring rate etc.). The absorption peaks are observed at 397 nm, 432nm and 493 nm for the samples 'a' (0.16 mol), 'b' (0.20 mol) and 'c' (0.27 mol) respectively, which are blue shifted from 827 nm (bulk CdTe), is due to quantum -size effects resulting the formation of quantum dots [15]. The straight-line portions of the absorption coefficient squared (α^2) against energy curves ($h\nu$) are extrapolated [16] to obtain the band gap energy as intercepts with the $\alpha^2 = 0$ line as shown in figure 6. For the as prepared CdTe samples 'a', 'b' and 'c', the band gap energies are obtained 2.82 eV, 2.61 eV and 2.23 eV respectively. From the band gap information of

the size of CdTe QDs are calculated using the effective mass approximation (EMA) method [17]. The value of the particle size is estimated to be 7.7 nm, 8.5 nm and 10.5 nm for the CdTe samples 'a', 'b' and 'c'.

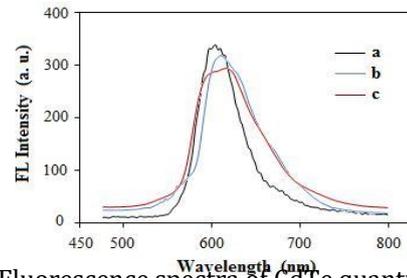


Fig - 7: Fluorescence spectra of CdTe quantum dots.

The fluorescence (FL) emissions spectra of CdTe QDs are obtained at different concentrated Cd-precursor at room temperature are shown in figure 7. The concentration of cadmium (Cd) slightly affects both the peak position and the maximum intensity of FL emission. A strong emission peak is observed at 602 nm which attributes the Cd²⁺ vacancies of the CdTe QDs [18]. The peak is moved towards the higher wavelength (608 nm & 617 nm) with the increase of precursor concentration. However, a decrease in the luminescence intensity has been observed simultaneously at higher Cd-precursor concentration. Moreover, the full width at half maxima (FWHM) of the emission spectra has been gradually increased for higher precursor concentration. It's resulted from the large size and relatively small surface to volume ratio of the prepared QDs [19].

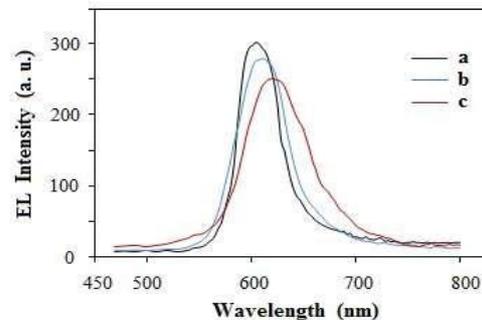


Fig - 8: EL spectra of CdTe quantum dots for samples a, band c.

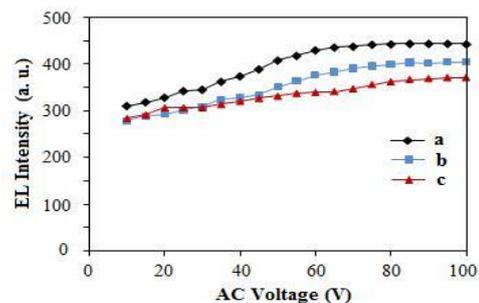


Fig - 9: ac voltage (50 Hz) vs EL intensity characteristic for CdTe QDs.

To test the application of CdTe quantum dots for nano LED, the EL spectra of the as prepared samples have been recorded and are shown in Fig. 8. The EL Peak positions do not shift significantly and have been observed at around 605 nm, 611 nm and 620 nm for the samples 'a', 'b' and 'c' respectively. Literature reports that both types of luminescence (FL and EL) are occurred due to the presence of similar kind of sources in the sample. Here, probably intermediate surface states are responsible for FL and EL emission of the samples and hence occurring in the similar fashion and almost in the same wavelength range from 602-620 nm. The basic difference between EL and FL is that the FWHM of EL is less in comparison to that of FL. The key reason for that FL spectrum is represented by nanoparticles size distribution [20], but in EL, the nanocrystals accept electrons as the voltage is increased and the larger crystallites are charged at low potential than smaller crystallites. So, the width of EL spectrum is smaller. Figure 9 disclose that EL intensity is a function of excitation voltage. It is observed in the figure that above 60 V of operating voltage, the EL curve saturates. This attributed that above 60 V, luminescence efficiency remains same. Hence EL study indicates the possible application of CdTe quantum dots as nano LED with the optical emission range from 605-620 nm.

3. CONCLUSION

In this effort, we have devised a low-temperature procedure for the preparation of CdTe quantum dots of size 3-11 nm with cubic crystalline by a chemical route. The method has the prominent advantage of synthesizing the oleic acid capped CdTe QDs at low cost. The optical properties of the QDs are obtained from UV-Vis and fluorescence spectroscopy. Blue shifted absorption edges are observed which results of increase in band gap and discretization of energy levels due to quantum confinement in nanoparticles. The as prepared CdTe QDs have been manifested very efficient fluorescence and electroluminescence emission in the visible spectral range, especially in orange light emission (605-620 nm). EL studies indicate nonlinear increase in brightness with increasing voltage and saturates at higher voltage. This provides an understanding that assembly of CdTe quantum dots can be used as nano LED to emit orange or near orange colour.

4. ACKNOWLEDGEMENTS

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