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Synthesis effect, upconversion and amplified stimulated emission of luminescent CdTe NPs

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ABSTRACT

CdTe semiconductor nanoparticles (NPs) have been prepared by the organometallic pyrolysis method and microwave assisted aqueous method. The nanostructure is confirmed by high resolution transmission electron microscopy in addition to absorption and photoluminescence spectra. The CdTe NPs made by the microwave assisted aqueous method exhibit much stronger photoluminescence. Amplified stimulated emission is measured at room temperature and at 10 K. Upconversion luminescence at room temperature is also detected for the prepared samples.

1. Introduction

The field of semiconductor nanoparticles (NPs) has experienced enormous development over the past two decades [1,2]. They show novel optical and electronic properties when they have a size comparable to, or smaller than, the dimensions of the exciton within their corresponding bulk materials. CdTe is one of the most common materials which has special technological importance because it is the only known II–VI semiconductor that can form conventional p–n junctions [3]. Its NPs have been the subject of many scientific and technological applications, including light-emitting diodes (LEDs) [4–6], photosensitive films [7], micro-resonators [8], waveguides [9], and sensors [10], in addition to their biological applications [11,12]. As a result, many of the literature reports deal with synthesis of CdTe NPs of unique properties by engineering the chemical functionality of their surrounding medium [13–24].

In this work, we investigate the effect of preparation method on the optical properties of CdTe NPs. Two approaches have been adopted for preparation. The structure and size of the NPs was examined by the absorption and emission measurements in addition to the high resolution transmission microscopy (HRTEM). The photoluminescence (PL) as well as upconversion luminescence at room temperature are reported for the samples. Stimulated emission is measured at room and low (10 K) temperatures.

2. Experimental

CdTe NPs were synthesized using two methods: (A) the colloidal organometallic pyrolysis in hot surfactant procedure [13] and (B) the microwave-assisted aqueous method [14]. These two methods will be referred to as method “A” and “B”, respectively.

2.1. Method “A”

Solution of Te was prepared by dissolving 0.2 g of Te powder in 5 ml of TOP and heated up to 150 °C until the color of the solution became greenish yellow. 0.2 g of CdO was added to 3 ml of oleic acid and heated up to 170 °C till complete disappearance of the red color of CdO. 2 g of TOPO and 1 g of HDA were added to this reaction mixture and heated at 200 °C. The previously prepared Te solution was quickly injected into the hot mixture and the mixture was left to cool down to 140 °C to allow for the growth of CdTe NPs. Many aliquots samples were withdrawn at different times during the cooling process. The whole synthesis process was carried out under the flow of Ar gas. The separation of NPs was done by mixing them with a mixture of equal volumes of hexane and methanol (1/2, v/v) and then shaking vigorously and the precipitated powder was separated centrifugally. The powder drying process was carried out in an inert atmosphere. The final powder product can be redissolved in a desired solvent (toluene, chloroform, or hexane) for the required measurements. Complete removal of Cd precursors from the final solution was confirmed by UV–vis spectroscopy.

2.2. Method “B”

0.1 g of $NaBH_4$ and 0.1 g of Te powder were added to 3 mL of deionised water. The mixture was left in the dark for ~24 h

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during which hydrogen was released through a small outlet of the flask. White precipitate of sodium tetra-borate was formed; then the NaHTe solution was separated and added to N_2-saturated $Cd(NO_3)_2 \cdot 4H_2O$ solution of pH 11.4. Thioglycolic acid (TGA) was used as a capping material. A solution of Cd^{2+}/TGA/HTe of molar ratio 1:1:0.5 was used to prepare the reaction mixture. Equal volumes of this mixture were exposed to microwaves of different powers for different exposure times, yielding TGA–CdTe NPs of different sizes. Finally, CdTe NPs were precipitated by the centrifugation process.

2.3. *Techniques*

The nanostructure of the prepared CdTe was characterized by “HRTEM” (Philips CM20 microscope) operating at 200 kV. A drop of dilute solution was deposited on an amorphous carbon–copper grid and left to evaporate at room temperature.

For absorption measurements, the NPs were dispersed in chloroform and absorption spectra were recorded with a Perkin Elmer Lambda 35 spectrometer. Fluorescence emission and excitation spectra were measured using a Perkin Elmer LS55 spectrofluorometer.

Stimulated emission has been studied at room temperature and at lower temperature (10 K). The PL has been measured at different excitation power values of an Ar laser (488 nm). The laser power was varied from 1 mW to 200 mW using power density filters. For lifetime measurements, a nitrogen laser (laser photonics LN1000) of pulse width 800 ps and energy of 0.5 mJ was used as an excitation source.

3. Results

Fig. 1a and b presents the absorption spectra of NPs samples grown at various times via method “A” and at various exposure times and powers for method “B”, respectively. Red shift is observed in the position of the absorption peak (and so their band gaps) as the time or power increases.

For method “A”, the samples were withdrawn after the beginning of heating treatment by 0.5, 6 and 15 min. The absorption wavelength maxima “λ_p” (first excitonic peak) of these samples were found to range from 440 nm to 620 nm corresponding to band gaps “E_g” on the order of 2.82–2 eV.

For method “B”, the samples were obtained after microwave irradiation at 160 W for 5 min and 15 min and at 350 W for 15 min. Absorption spectra of these samples are not as well defined as those of samples obtained by method “A”. The absorption wavelength maxima λ_p range from 500 nm to 570 nm corresponding to E_g $\sim$2.5 eV–$\sim$2.2 eV.

The effect of microwave exposure time and power on the emission spectra of NPs is presented in Fig. 2a and b, respectively. Emissions spectra show a red shift either by increasing the microwave exposure interval at constant power (Fig. 2a) or by increasing the power at constant exposure time (Fig. 2b). The red shift indicates the growth in the NPs size and the narrow emission bands (FWHM of the order of $\sim$40 nm) is an indication for the uniform size distribution.

Fig. 3a and b presents the PL and the absorption of the prepared NPs via methods “A” and “B”, respectively. It can be seen that the two PL bands are located typically close to the absorption thresholds (the so-called band-edge or “excitonic” PL). For method “A”, the average stokes shift is on the order of 27 nm and the FWHM of emission band

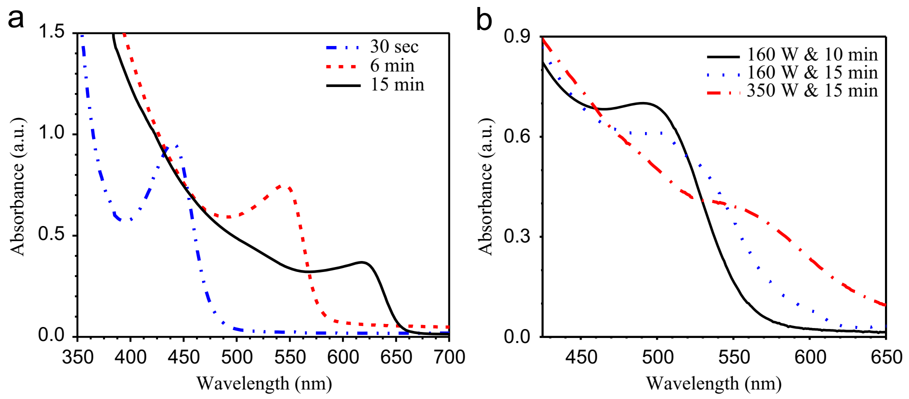

Fig. 1. Absorption spectra of the different sizes of grown CdTe NPs: (a) at various times via method “A” and (b) at various exposure times and powers for method “B”.

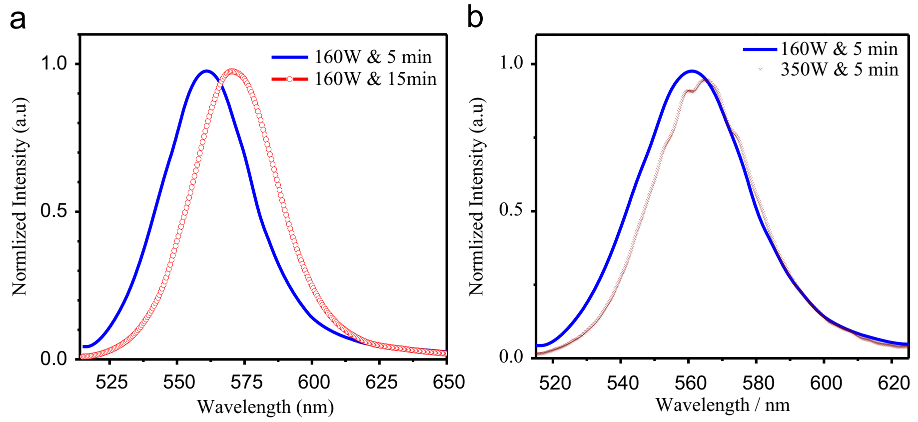

Fig. 2. Effect of microwave exposure time (a) and power (b) on the emission spectra of the CdTe NPs prepared by method “B”.

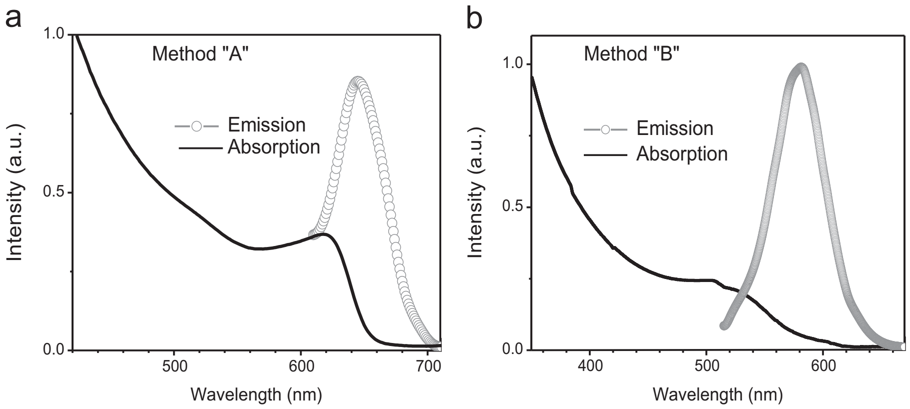

Fig. 3. Absorption and normalized PL spectra of CdTe NPs prepared via methods “A” and “B”.

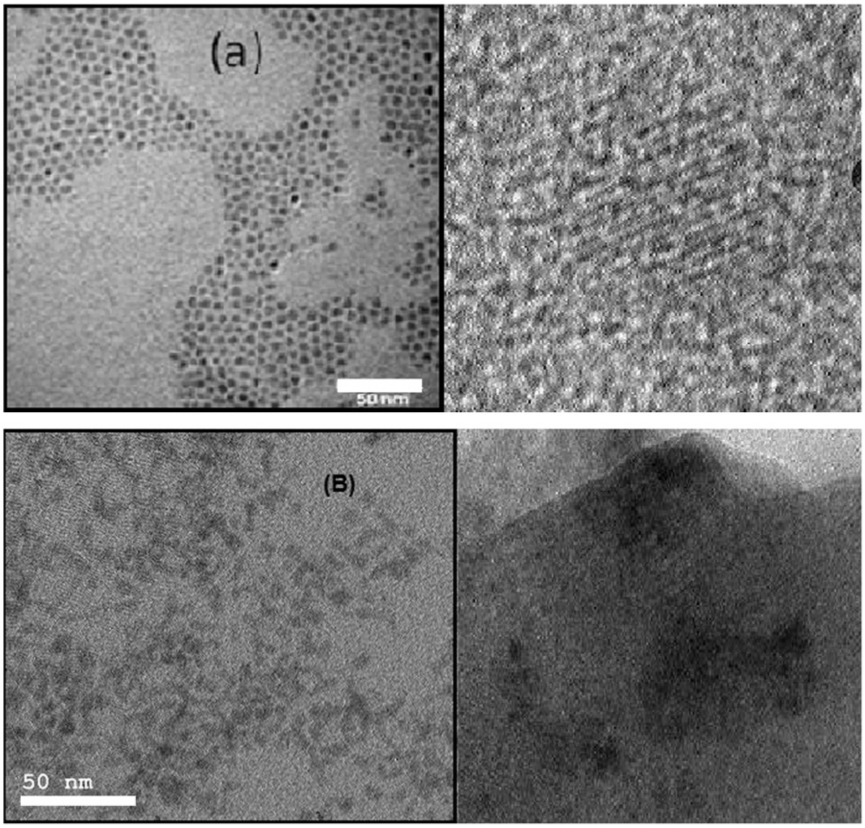

Fig. 4. HRTEM images of CdTe NPs prepared by (a) the organo-metallic pyrolysis method and (b) the microwave assisted aqueous method.

ranges between 27 nm and 50 nm. For method “B”, the average stokes shift is on the order of 70 nm with FWHM of 34–70 nm.

In general, the emission spectra of NPs prepared by method “B” are found to be broader than those of method “A” and the stokes shift is larger. These two observations indicate that method “B” produced NPs of less uniform size distribution but were more likely to be luminescent NPs.

The size of the prepared NPs via both methods was estimated according to the maximum wavelength of the PL band. The size of NPs ranges between ∼2 nm (at 500 nm of green emission)and∼4 nm (at 640 nm of red emission).

Investigations of the nanostructure formation were carried out also via high resolution transmission electron microscopy ‘HRTEM’. The images are presented in Fig. 4a and b for method “A” and method “B” respectively. The nanosize and structure of the prepared CdTe via both methods are confirmed in these images.

Fig. 5 presents a comparison between the PL intensities of CdTe NPs having similar sizes and prepared via methods “A” and “B”. It can be seen that the emission spectrum of method “B” sample shows a much higher intensity with wider FWHM. The PL quantum yield efficiency Q was estimated by comparing the integrated emission band of NPs to that of rhodamine 6G dye in ethanol, as a reference, according to

$$Q_n = Q_d(I_n O_d / I_d O_n)$$

where I is the peak intensity of the emission spectra, O *is* the optical density at the excitation wavelength and the subscripts n and d referred to NPs and dye, respectively. Q_d was obtained according to Photochem CAD database package by Jonathan Lindsey.

The quantum yield of CdTe NPs prepared via methods “A” and “B” was calculated to be ~5% and ~64% respectively. This was unexpected, since NPs of method “B” are capped with the electron donor TGA which is supposed to quench the emission and not to enhance it. This enhancement may be explained as follows: CdTe NPs were passivated with $Cd(OH)_2$ during synthesis in the alkaline media (pH 11.4); therefore, the excess of Cd ions may react with the OH ions, forming a hydroxide layer, which get converted to CdO upon heating by microwave radiation. Since oxides have higher band gap, this may result in enhancement of the emission.

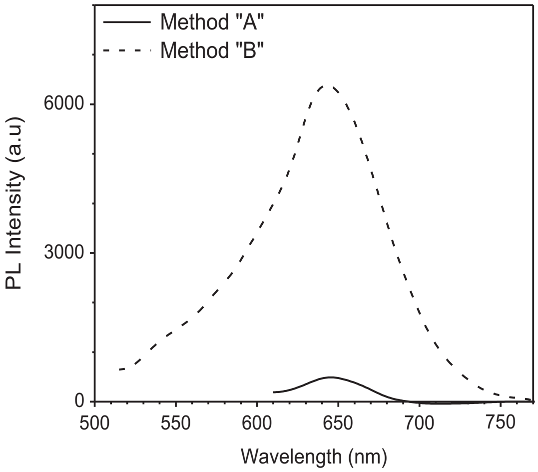

Fig. 5. Comparison between the emission spectra of CdTe NPs, of size 3.8 nm, prepared via method “A” and method “B”.

Optical amplification and lasing properties of NPs mainly depend on the multi-exciton emission and are also related to the quantum yield efficiency. Therefore, we investigate the amplified stimulated emission (ASE) for CdTe NPs which yields higher quantum efficiencies (method “B”).

The NPs of size 3.1 nm were excited by 488 nm of Ar laser at different powers (from 1 mW to 200 mW). Measurements of the induced fluorescence were obtained for NPs at room temperature and also at a lower temperature (at 10 K to eliminate the thermal and phonon contribution effects). The results are displayed in Fig. 6a and b, correspondingly.

The PL intensity as a function of Ar laser pump power is presented in Fig. 7a and b, for NPs at temperatures 300 K and 10 K, respectively. The figures show that the output PL intensity linearly increases with the pump power via two different rates (two different slopes). The slower rate is attributed to monoexciton emissions. The faster rate was attributed to stimulated emission of multiexcitons which was induced by the high excitation powers. Multiexciton emission is observed with a threshold power of nearly 40 mW. The threshold power was found to depend on the NPs size, quality and on the NPs quantum yield efficiency. Also, the emission spectra at room temperature show a mixing between the monoexciton and the multiexciton emissions. This mixing was attributed to the thermal effect. This is confirmed by the mixing disappearing at 10 K when thermal effect is eliminated and e–h recombination is considered as the only source of photon emission. This means that, population inversion in $1S_e$ state can be achieved at 10 K with a threshold pump power of 40 mW. The multiexcitonic states have been detected at room temperature by exciting the samples with 800 ps pulses of N_2 laser. The measured

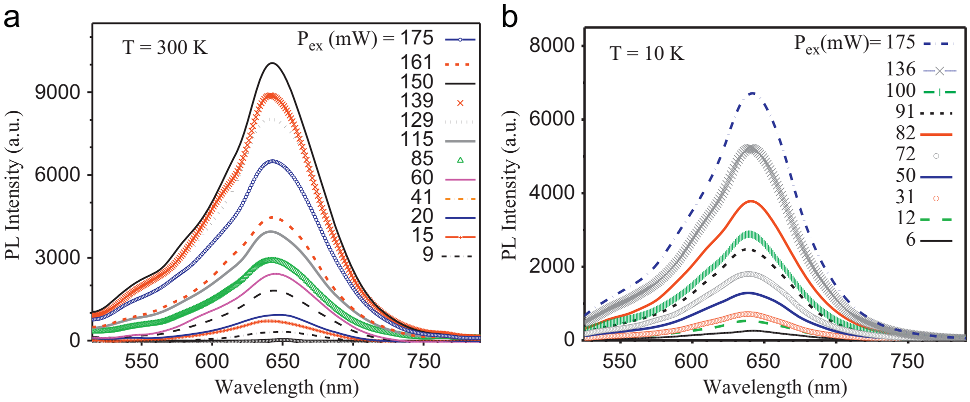

Fig. 6. Photoluminescence spectra of CdTe NPS at different excitation powers (P_{ex}) of Ar laser at temperatures (a) 300 K and (b) 10 K.

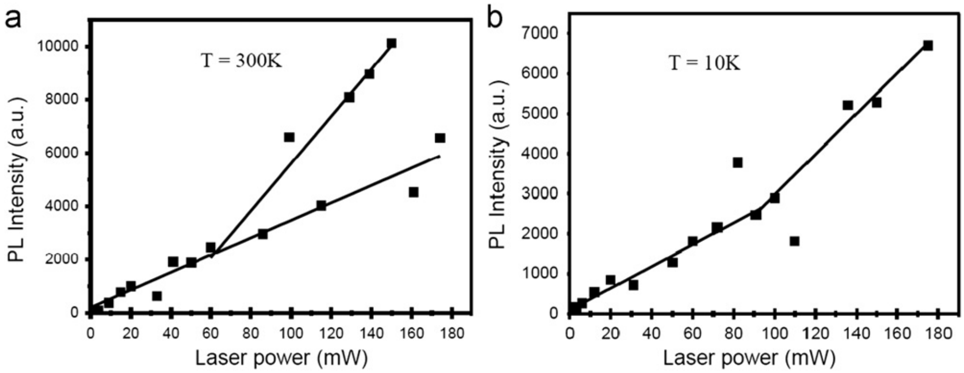

Fig. 7. ASE intensity as a function of pump power at temperatures (a) 300 K and (b) 10 K.

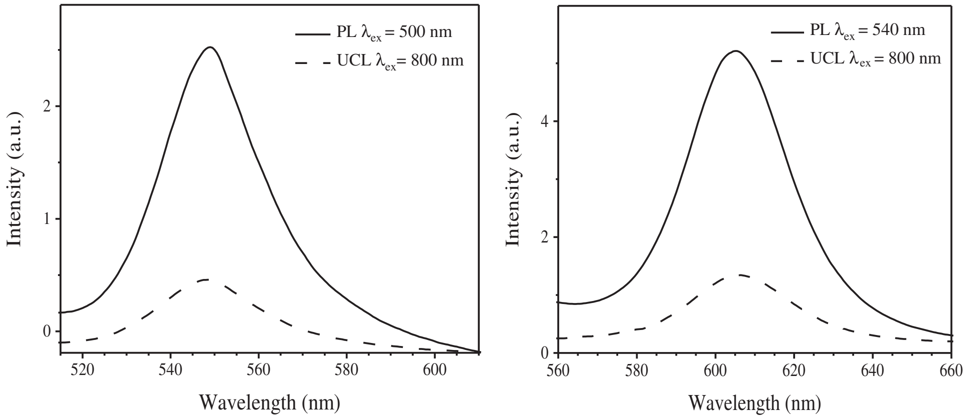

Fig. 8. Photoluminescence of CdTe NPs (solid curves, excitation at 500 nm and 540 nm) and upconversion luminescence (dashed curves, excitation at 800 nm).

lifetimes were 2 ns and 10 ns for multi- and mono-exciton, respectively.

The upconversion luminescence is a nonlinear phenomenon where high energy photons emission can be obtained by pumping the material with low energy photons. It can be detected in a material without the need for the phase matching adaption condition. The upconversion luminescence was examined for two samples of the prepared CdTe NPs. Fig. 8a and b displays the PL (excited at 500 nm and 540 nm) and the upconversion luminescence spectra (excited at 800 nm). It can be noticed from this figure that the spectral band of upconversion and PL peaked at the same wavelength. The upconversion luminescence efficiency was estimated to be of the order of ~5% and attribute to the two photon absorption process [22].

4. Conclusion

CdTe NPs have been prepared via the organometallic pyrolysis method and microwave assisted aqueous method. The results show that the method of preparation affects the optical properties and the quality of the yielded CdTe NPs. The quantum yield of CdTe NPs prepared via the microwave method shows much higher value (~64%) than that of the organometallic pyrolysis method (~5%). The high quantum efficiency values are attributed to the possibility that CdTe NPs are passivated by $Cd(OH)_2$ in the alkaline reaction medium (pH = 11.4). The excess of Cd ions react with the OH ions in the solution, forming the hydroxide. The hydroxide layer could be easily converted to CdO upon microwave heating (oxides have higher band gap). The CdTe NPs made by the microwave aqueous method exhibit strong photoluminescence at room temperature. Amplified stimulated emission is reported with threshold power of ~40 mW. Emission lifetime and upconversion luminescence are also measured for the samples at room temperature.

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