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Effect of hydrazine hydrate on the luminescence properties of MPA capped CdTe nanocrystals in hot injection method

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ABSTRACT

In this research MPA capped CdTe nanocrystals with sizes around 2.7–3.5 nm were grown in aqueous solution. The process was performed through the reaction of NaHTe with MPA and $CdCl_2$ solution in high temperature. The synthesis was carried out in two different states of standard and modified forms. In the modified synthesis, the hydrazine hydrate material was added to the MPA plus $CdCl_2$ solution before injection. The evolution of the nanocrystals size and PL quantum yield was monitored during the heating time for the growth. The results demonstrated that for the standard synthesis the growth rate was slow. The CdTe nanocrystals with high PL quantum yields were achieved in more than 10 h of heating. In contrast for the modified synthesis the growth rate was considerably higher. In this state a band edge emission with PL quantum yield of about 26% was achieved for the MPA capped CdTe nanocrystals in just 2 h of the heating process.

1. Introduction

Semiconductor nanocrystals (NCs) have attracted a great deal of attention in recent decade. The reason is due to their novel optoelectronic properties created by quantum confinement effects [1–3]. The II–VI and III–V luminescent NCs have been vastly investigated [4–8]. The size dependent luminescent properties [9–13], high photoluminescence (PL) quantum efficiency, proper photostability, narrow band edge emission, variety of methods for the synthesis [14,15] and compatibility with wet chemistry approaches for making the corresponding devices are some of the main advantages. These properties created a wide range of applications from bio-imaging to hybrid organic–inorganic LEDs and lighting [16–20].

There are two main approaches, organometallic [21,22] and aqueous [23], for the synthesis of luminescent semiconductor nanocrystals (NCs). The NCs prepared by the organometalic approach demonstrate a high PL quantum yield [24]. There are several reports on the organometalic synthesis of some well luminescent CdSe, CdTe, CdS and CdTe NCs [25] in recent years. Nevertheless in many cases, the precursors are expensive and toxic in this method. In contrast, the aqueous synthesis approach is much cheaper and safer. But the PL quantum yield of the synthesized NCs is lower than that of the organometalic approach. This is due to the creation of some trap states inside the NCs bandgap and dissipation of incoming energy. Among the II–VI NCs, CdTe has been exceptionally synthesized by the aqueous method with proper PL quantum yield [26]. The prepared NCs demonstrate a narrow band edge emission through the excitation. The aqueous synthesis of the CdTe NCs is performed in presence of some capping agents like mercaptopropionic acid (MPA) and thioglycolic acid (TGA) to retain the nanoscales [27,28]. Nevertheless, the growth rate is rather slow in presence of the MPA molecules and achieves higher PL quantum yield in longer growth times [29].

In this research CdTe NCs are grown in an aqueous solution using MPA as the capping agent. For this process, NaHTe is injected to a solution of $CdCl_2$ and MPA in 80 °C and heated at 100 °C for the growth. The evolution of the NCs size and PL quantum yield is investigated during a long period of heating time. In another approach, hydrazine hydrate is added to $CdCl_2$ plus MPA solution with suitable concentration. The other synthesis stages were performed in high temperature similar to the standard method. The evolution of the NCs size and PL quantum yield is also monitored during heating. The growth rate is observed to be much faster in this state. Finally the results of two different approaches are compared and discussed. It is also tried to show that it is possible to achieve MPA capped CdTe NCs with proper PL quantum yield in very shorter growth times in presence of hydrazine hydrate.

2. Experimental

CdTe NCs were synthesized through the reaction of NaHTe with $CdCl_2$ in presence of mercaptopropionic acid (MPA) as the capping

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agent. The synthesis was performed in two different standard and modified forms. For the standard synthesis 1 mmol of $NaBH_4$ was transferred to a three necked flask. Then 10 mL of DI water was added and solution was purged with Ar for 15 min. Afterwards 0.4 mmol of Te powder was added to the $NaBH_4$ solution. This solution was vigorously stirred for 30 min, transferred to an oil bath at 80 °C and heated for 10 min under the Ar flow. The NaHTe solution of light red color was formed in this stage. In parallel, 0.2 mmol of $CdCl_2$ was added to 40 mL of DI water. Then 30 μl of MPA was added and the solution pH was set to be 9.0. This solution was also purged with Ar to remove the oxygen content. Finally 2 mL of NaHTe solution was slowly injected to the $CdCl_2$ and MPA solution. The molar ratio of Cd:MPA:Te in the reaction solution was 1:1.72:0.4. The solution was heated at 100 °C and refluxed for different times to control the size of CdTe nanocrystals. For the modified synthesis the procedure is totally the same. The only difference is addition of 0.7 mL of hydrazine hydrate to the $CdCl_2$ and MPA solution. The time evolution of the size and photoluminescence quantum yield of different CdTe NCs was investigated. Absorbance spectra were recorded using a Mecasys-optizen system. PL spectra were taken by a Cary Eclipse fluorescence spectrophotometer under excitation with 360 nm UV light. The XRD analyses were performed by a Philips Xpert-pro System using the Cu Kα radiation. PL quantum yields were also calculated in comparison with uranine as a reference material with PL quantum yield of 92%.

3. Results and discussion

CdTe nanocrystals (NCs) were synthesized by injection of clear NaHTe solution to the aqueous solution of $CdCl_2$ plus MPA as the capping agent. The experiments were performed without and in presence of hydrazine hydrate to study the changes in the growth rate and photoluminescence properties. Hydrazine hydrate was added to the $CdCl_2$ and MPA solution and other stages of the experiments were the same.

Fig. 1(a) demonstrates the absorbance and photoluminescence (PL) spectra of a typical CdTe NCs sample prepared at pH 9.0 for $CdCl_2$ plus MPA solution. The sample was heated for 6 h at 100 °C after injection. According to the results the absorption edge of the sample is located around 543 nm (2.28 eV). Here, the turning point of the absorption spectrum in the band edge area is considered as the band edge position and the point which can show the bandgap energy [30–32]. The NCs size, i.e. the diameter could be estimated to be about 3.16 nm from the changes of the NCs band gap compared to that of the bulk [28]. This is performed using the effective mass approximation, i.e. the Brus equation [33–36]. The photoluminescence peak of the CdTe NCs is also located at 546 nm. The correspondence between the absorption edge and the PL peak position can also justify that there is a band-edge emission for CdTe NCs. The full width at half-maximum of the emission is also about 57 nm which is rather narrow. This is mentioned in comparison with other II–VI nanocrystals prepared in the aqueous solution [37–41]. This could confirm the low density of trap states inside the NCs bandgap. Otherwise, there were several paths for the emissive electron–hole recombinations in a wide range of energies which could cause a broad emission. Fig. 1(b) shows the X-ray diffraction pattern of the mentioned CdTe NCs. According to the result, there are three obvious peaks located at 2θ of 24°, 40° and 47°. These peaks belong to the (111), (220) and (311) crystalline planes of cubic phase CdTe NCs (JCPDS data no. 10-459). The NCs size could also be estimated to be about 2 nm using the FWHM of the XRD peaks and Debye–Scherrer formula [42].

Fig. 2(a) demonstrates the evolution of the absorbance of the CdTe NCs during the heating time after injection. The absorption edge of the NCs shows a red-shift and changes from 520 nm at 2 h to 585 nm at 26 h of heating. This could show the slow growth of the MPA capped CdTe NCs during the heating. Fig. 2(b) represents the trend of changes in the NCs bandgap and also the NCs size estimated by effective mass approximation [32–35]. During 26 h of heating, the NCs bandgap changes from 2.4 eV to 2.12 eV. This corresponds to a size change from 2.76 nm to be about 3.53 nm for CdTe NCs.

Fig. 3(a) represents the trend of changes in photoluminescence spectrum of the CdTe NCs during the heating process. It can be seen that the FWHM of the spectrum is nearly constant during the time. The PL peak intensity is also increased by 20 h and decreased in longer heating times. The reason of decrease could be attributed to the weaker effect of quantum confinements for larger CdTe nanocrystals [43–44]. The PL peak position also demonstrates a red-shift as it is represented in Fig. 3(b). According to the results the PL peak position is changed from 540 nm at 2 h to 581 nm at 26 h of heating. This reveals that there is better correspondence between the absorption edge and PL peak position in longer heating times. The reason could be attributed to the improved crystalline quality of the CdTe NCs by heating.

The PL quantum yield (PL Q.Y.) of the MPA capped CdTe NCs was also measured by comparison with uranine as a reference material (PL Q.Y. of 92%). According to the results the PL Q.Y. of the samples reached to 21% at 7 h of heating. Continuing the heating process, the PL Q.Y. of the sample was obtained to be around 32% at the heating times between 10 and 20 h of heating. The whole results could show the nearly slow rate of the growth, slow red-shift of PL peak position and slow rate of increase for the PL Q.Y. of the MPA capped CdTe NCs.

Fig. 4(a) demonstrates a typical absorbance and PL spectrum of a sample prepared in presence of hydrazine hydrate and heated for

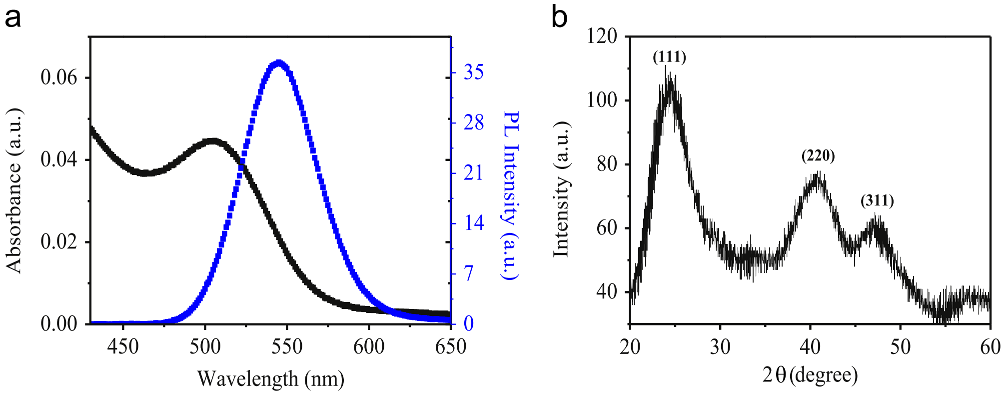

Fig. 1. Absorbance and PL spectra (a) and XRD pattern (b) of the MPA capped CdTe NCs prepared at pH of 9.0. The sample was heated for 6.0 h at 100 °C.