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Effect of preparation conditions on optical properties of CdTe quantum dot dispersed in water

Nguyen Van Hung[1,*], Duong Anh Tuan[1], Trinh Duc Thien[1], Nguyen Dang Phu[1],
Danh Bich Do[1], Pham Van Vinh[1]

[1]*Hanoi National University of Education*
136 Xuan Thuy Road, Cau Giay District, Hanoi, Vietnam

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Abstract. CdTe quantum dots dispersed in water were prepared successfully by the microwave irradiation method. The influence of the pH value of the solution precursor, irradiation time and microwave power on the structure, size and optical properties of CdTe quantum dots was investigated. The fluorescence of CdTe quantum dots studies were illustrated that the samples which were synthesized at pH value of 7 exhibited the best fluorescence. The absorption, fluorescence spectra and TEM images showed that the microwave power and the irradiation time influenced significantly on the size of CdTe quantum dot as well as their optical properties. The fluorescence spectra were red-shift with the increase of the irradiation time and microwave power.

Keywords: CdTe, Quantum dots, optical properties.

1. Introduction

The study and synthesis of quantum dot (QDs) have been the attractive subject in past few decades because of their applications in many fields. Quantum dots belonging to $A_{II}B_{VI}$ group, such as CdS, CdSe, CdTe have potential application to photo devices [1-3], bio sensors [4], bio-label [5-7] and solar cells [8]. In particular, the conjugation of QDs with biomolecules became an increasingly attractive research area after waterdispersed nanocrystals were successfully applied for biological labeling [9-10]. Obviously, water-dispersed nanocrystals with good spectral properties play a critical role in biological applications such as fluorescent labeling [11]. Although nanocrystals with a high photoluminescence quantum yield (PLQY) were obtained through the TOP/TOPO organometallic synthetic approach [12-14], their hydrophobic character rendered them unsuitable for direct use in

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[*] Corresponding author. Tel.: +84-437548442
E-mail address: hung.nv@hnue.edu.vn

biological systems**.** Therefore the search for simple procedures and synthesis in aqueous solution of QDs materials has attracted increasing interest due to the innovative technological applications offered by these materials. Many procedures have been developed with the aim of optimizing the spectral properties of QDs directly prepared in aqueous phase [15-17]. For example, the hydrothermal method providing higher temperatures was employed to synthesize QDs, which were successfully used as biological labels [17]. However, the synthesis of QDs is carried out in an autoclave at high pressure and temperature. This process also takes much time.

Recently, microwave irradiation is an attractive method for synthesis of QDs. The synthesis of QDs by microwave irradiation was first introduced by the Kotov group [18]. Some studies showed that the synthesis of nanocrystals by microwave irradiation was generally quite faster, simpler, and very energy efficient as compared to conventional hydrothermal synthesis [19]. The combination of using water as a solvent to synthesize nanocrystals and applying microwave irradiation as an efficient heating source is a very desirable way to make the synthesis of nanocrystals cleaner and more environment-friendly [20]. In this paper, this microwave irradiation method was used to synthesize CdTe QDs in aqueous phase. According to the grown conditions, CdTe QDs with different particle size and fluorescence energy were obtained. We found the significant effects of microwave irradiation and experimental conditions on the size and optical properties of as-prepared CdTe QDs.

2. Experiment

All chemicals were used without further purification. Sodium borohydride ($NaBH_4$, 99.9%), tellurium powder (99.8%) was purchased from Andrich. Cadmium bromide ($CdBr_2$, 99.9%), 3-mercaptopropionic acid (MPA, 99%) and NaOH 1M were obtained from Shanghai Chemical Reagents Company.

In our experiments, the CdTe precursor solution was prepared by adding freshly prepared NaHTe solution to a N_2-saturated $CdBr_2$ solution at different pH values in the presence of 3-mercaptopropionic acid (MPA) as a stabilizer. The pH of solution was controlled by NaOH. Typically, a 4 mL volume of CdTe precursor solution was injected into the vitreous vessel with a volume of 10 mL. A series of high-quality CdTe QDs were prepared under microwave irradiation process. After microwave irradiation, the CdTe QDs sample was taken when the temperature cooled to room temperature naturally.

Crystalline phase of prepared QDs was characterized by X-ray diffractometer D5005 (Siemens). TEM images were recorded on Hitachi S-4800 system. The as-prepared sample was directly used for optical charactization at room temperature under ambient conditions without any postpreparative treatment process. UV-vis absorption spectra were obtained using a JASCO V670 UV-vis-near-infrared spectrophotometer. For Photoluminescence (PL) measurements, we have used a He-Cd laser at $\lambda = 325$nm as an excitation source. The photoluminescence signal was collected and dispersed with a spectrometer model 9490 (SCIENCETECH, Canada) combined with a photomultiplier tube (PMT) detector. Digital lock-in amplification is employed for the PL measurements.

3. Result and discussion

Figure 1 shows XRD patterns obtained from powdered precipitated fractions of CdTe QDs synthesized through microwave irradiation at pH=7, 480 min, 900W . The XRD pattern of the nanocrystalline CdTe powder shows the (1 1 1), (2 2 0) and (3 1 1) planes of the cubic CdTe phase. It is clearly shown that the as-prepared CdTe QDs belonged to the cubic (zinc blende) structure, which was also the dominant crystal phase of bulk CdTe

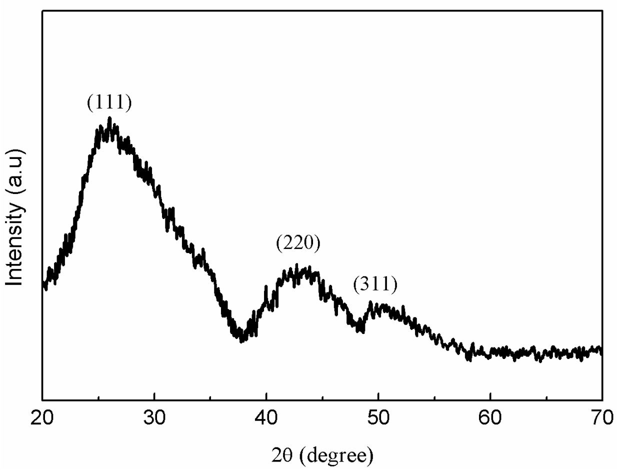


Figure 1. XRD diffractogram of CdTe quantum dots under microwave irradiation for 420 minute at pH=7, 900W

Figure 2 is the TEM images of typical sample irradiated in 5 min and 480 min at pH=7 and power 900W. Particle size of the 5 min and 480 min samples were corresponding to about 2 - 3 nm, 8 – 10 nm, respectively. When irradiation time increased the particle size increased significantly due to the agglomeration and particle growth. In addition, the size distribution of the long time particles was larger than that of the short time samples. Irradiation time was used to change particles size than changing pH in solution and power of microwave

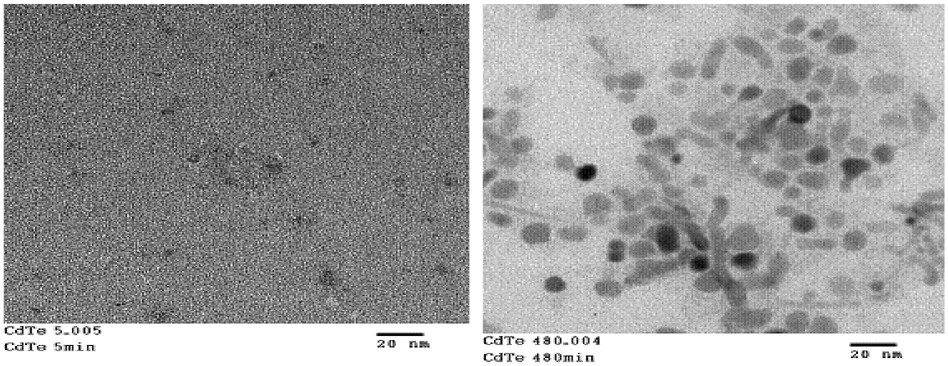


Figure 2. TEM images of CdSe nanoparticles with different time irradiation (left) 5 min; (right) 480 min

Fig 3 and Fig 4 presents the UV – Vis absorption and fluorescence spectra of CdTe quantum dots in the range pH from 7 to 12 with the same of the power and time irradiation. In the UV – Vis absorption, the peak position shifted from 520 nm to 536 nm when pH changed from 7 to 12. However, we saw that the peak position was shightly shifted to the longer wavelength. This was the same with the fluorescence spectra in Fig.4 and its intensity also decreased. The highest intensity was found on the samples synthesized at pH value of 7. Therefore, the pH value of 7 was chosen for all experiments.

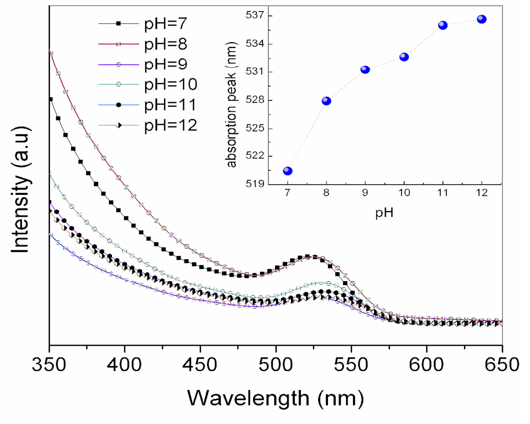


Figure 3. Exciton absorption spectrum of CdTe quantum dots with different pH

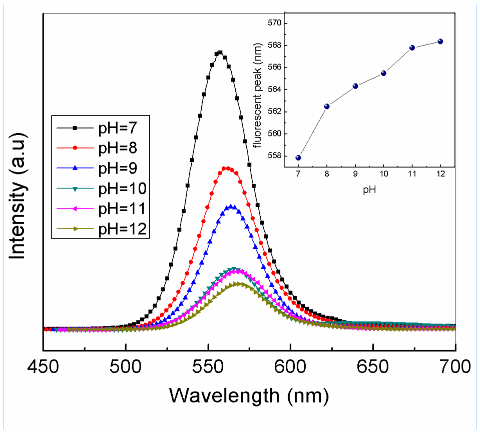
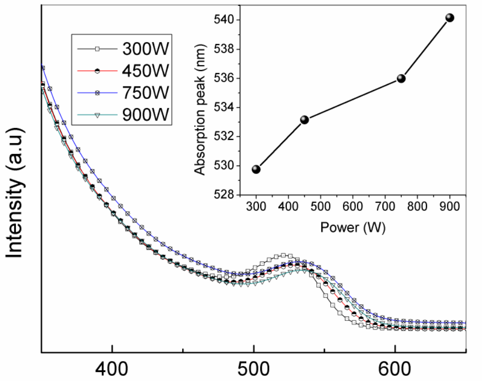


Figure 4. fluorescence spectrum of CdTe quantum dots with different pH

The absorption spectra in Fig.3 showed that the exciton absorption peaks were red-shift from 521 nm to 531 nm. The red-shift was believed due to the increase of QDs size. Indeed, because the bonding between Cd^{2+} and the stabilizer decreases with the increase of pH, the Cd^{2+} and Te^{2-} in solution were easy to bond with the ions in the surface of QDs resulting in the QDs size increase.

As the pH value was fixed at 7, the effect of microwave irradiation on size and optical properties of CdTe QDs was investigated by changing the microwave power or irradiation time. When the microwave power increased, the absorption peaks (Fig. 5) and fluorescent peaks (Fig. 6) position slightly shifted to longer wavelength. However, the flourescent intensity was decreased as microwave power increased. The full width at half maximum (FWHM) of flourescent peaks increased with the increasing of microwave power. This result indicates that the high microwave powver will make the size of QDs become nonuniform.



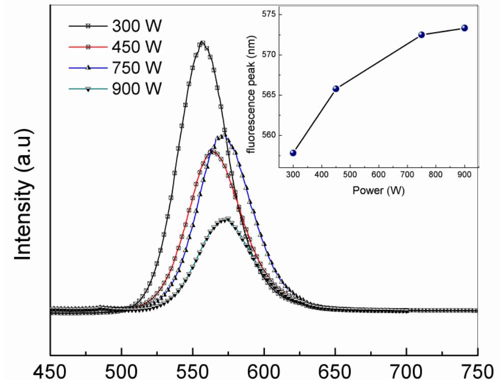
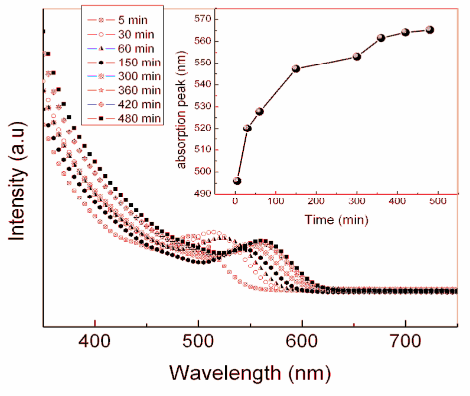


Figure 5. Absorption spectra of CdTe quantum dots with different microwave powers

Figure 6. Fluorescent spectra of CdTe quantum dots with different microwave powers

In order to investigate the influence of irradiation time on properties of CdTe QDs, the irradiation time was varied while the pH value and microwave power were fixed at 7 and 300 W, respectively. Fig. 7 and Fig. 8 show the effect of irradiation time on the optical properties of the QDs.



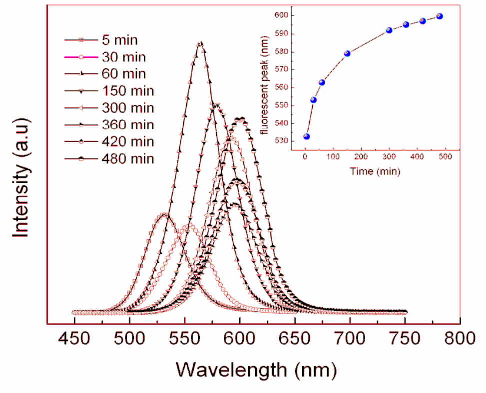


Figure 7. Absorption spectra of CdTe quantum dots with different irradiation time

Figure 8. fluorescence spectra of CdTe quantum dots with different irradiation time

The red-shift of the exciton absorption and fluorescent peaks with the increase of the irradiation time indicated the increase of QDs size. However, the red-shift did not increase linearly with rising irradiation time. Indeed, initially, the crystalline growing rate was fast in the first 100 min. Further, the crystalline growing rate became slowly. The increase in size of QDs approached to the saturation value at the irradiation time of 360 min. The microwave irradiation remarkably accelerated the synthesis rate. The crystalline growing depended on the concentration of the micro crystal present in solution. and the amount of micro crystal decreased with reaction time of ‘Ostwald ripening’ [21]. Beside red-shift, the broader fluorescent peaks were also observed when rising the irradiation time. This indicated the QDs size was not uniform. The optimum time for QDs to crystallize is 100 min.

4. Conclusion

The water-dispersed CdTe quantum dots were synthesized successfully by using the micr0wave irradiation method. The pH, microwave power and irradiation time influenced significantly on the QDs size as well as the optical properties. The fluorescent spectra were red-shift while their peaks intensity decreased and FWHM broadened when the microwave power increased from 300 W to 900 W. The fluorescent spectra were strongly red-shift with the irradiation time in the range from 5 min to 360 min. Further increasing irradiation time, the red-shift increased slowly.

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