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Fluorescence of CdSe/ZnS quantum dots in toluene: effect of cyclic temperature

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Abstract

Quantum dots (QDs) are the potential material for the application in optical thermometry, and have been successfully applied to solar cells, LEDs, bio-labeling, structural health monitoring, etc. In this paper, we study the fluorescence properties of CdSe/ZnS QDs in toluene under the action of heating-cooling cycles. The experimental results show that, in a heating-cooling cycle, increasing temperature causes red-shift of the emission peak and the decrease of the PL intensity, and decreasing temperature causes blue-shift of the emission peak and the increase of the PL intensity. The surface structures of the QDs likely are dependent on the cycle numbers, which cause the change of the excited energy state of the QDs in toluene. The results presented in this paper reveals the strong effects of cyclic temperature on the photoluminescence characteristics of QDs.

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Keywords: QDs; heating-cooling; photoluminescence; toluene.

1. Introduction

Quantum dots (QDs) have attracted great interests due to their unique optical and electrical properties [1-2], the characteristics of pressure dependence [3], and the potential applications for real-time monitoring [4-5]. In general, QDs become unstable and cannot function properly after exposure to ultraviolet light. There are various factors, such as structures, defects, and temperatures, which determine the stability of QDs. Among these factors, temperature is the most significant factor, which controls the applications and lifetime of QDs.

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There are various studies focusing on the temperature dependence of the photoluminescence (PL) characteristics of QDs for possible applications in optical thermometry and structural-health monitoring. Using CdSe/ZnS QDs nanocoating, Larrion et al. [6] constructed a photonic-crystal fiber temperature sensor, and studied the emission intensity, wavelength, and bandwidth of the emission peaks. Fang et al. [7] investigated the temperature dependence of the optical properties of PbS/CdS core/shell films on three substrates of PMMA, MPA and OA in the temperature range of 5.4 – 295 K. They observed that decreasing temperature caused the increase of the PL intensity and red-shift of the emission wavelength. Al-Agel et al. [8] investigated the PL characteristics of Si QDs prepared at different substrate temperatures (193K, 153K, 123K), and found that the PL intensity of the Si QDs increased with the increase of the substrate temperature. However, there is no work focusing on the effect of cyclic heating and cooling on the fluorescence behaviour of CdSe/ZnS quantum dots in toluene.

In this work, we study the effects of cyclic heating and cooling on the PL responses of CdSe/ZnS core-shell QDs in toluene. The study focused on the variation of the PL intensity and wavelength of the emission peak of the CdSe/ZnS core-shell QDs with cyclic temperature.

2. Experimental details

The CdSe/ZnS core-shell QDs, which were synthesized using a microreaction system [9-12], was collected and dispersed into chloroform to form the CdSe/ZnS core-shell QDs solution. The CdSe/ZnS core-shell QDs solution was purified with acetone centrifugally for three times to obtain CdSe/ZnS QDs, which were then dried in an oven for 1 h to remove the liquid residuals stored in the QDs. The dried CdSe/ZnS QDs were added into toluene to form a QDs-toluene solution. The concentration of the QDs-toluene solution was 10 mg/mL.

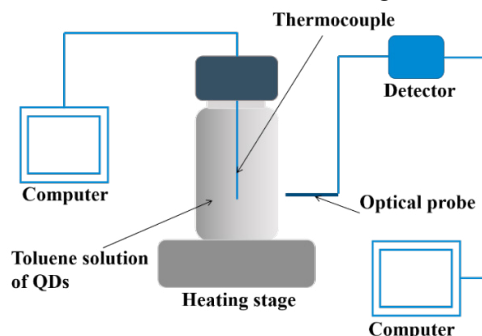


Fig. 1. Schematic of experimental setup for studying the temperature effect on the PL characteristics of the QDs-toluene solution

Figure 1 shows the schematic of the experimental setup used to study the effect of temperature on the PL characteristics of the toluene solution of the CdSe/ZnS QDs under the action of cyclic heating and cooling in a dark environment. Briefly, a glass vial filled with the toluene solution of the CdSe/ZnS QDs was placed on the top of a heating stage, and a thermocouple of K-type was used to measure the temperature of the solution every 10 s. A portable spectrometer (Ocean Optics, QE65-Pro-FL, USA) was used to record the temporal evolution of the PL characteristics of the QDs in the solution every 30 s. Note that the experiments were carried out in a dark environment.

3. Results and Discussion

Figure 2a shows the temporal variation of the luminescence characteristics of the QDs in the toluene solution for one heating-cooling cycle and the evolution of the corresponding temperature. Increasing temperature causes the decrease of the PL intensity of the QDs, and decreasing temperature leads to the increase of the PL intensity of the QDs in toluene. The QDs in toluene maintain the luminescence characteristics, which is temperature-dependent and partially recoverable for the maximum temperature used in the heating-cooling cycle.

Figure 2b reveals the temporal variation of the PL intensity of the QDs in toluene for single heating-cooling cycles with different maximum temperatures in the same period. The minimum PL intensity of each individual heating-cooling cycle decreases with the increase of the maximum temperature, as expected, since the PL characteristics of

the QDs in toluene is mainly determined by the CdSe/ZnS core-shell QDs. Such behavior suggests that the PL intensity of the QDs in toluene is dependent on the heating/cooling rate. No experiments for the QDs in toluene were performed for temperature larger than 110.6 °C since the boiling point of toluene is 110.6 °C.

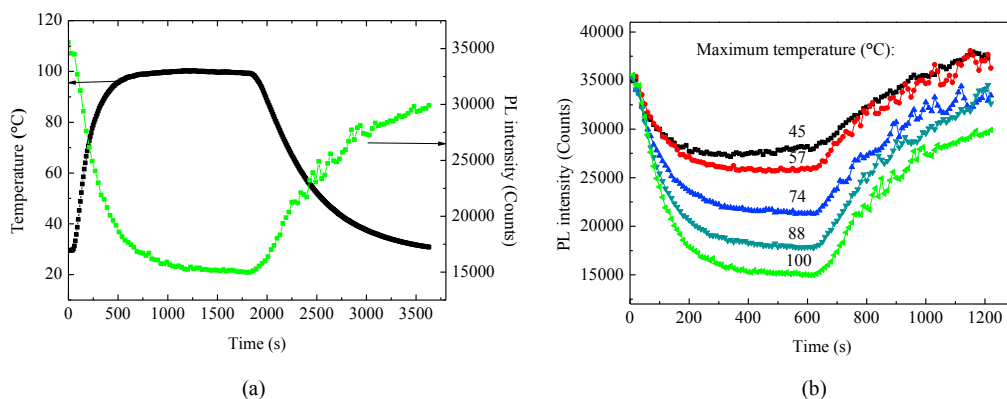


Fig. 2. Temporal variation of the luminescence characteristics of the QDs in toluene for a single heating-cooling cycle: (a) PL intensity with the maximum temperature of ~100 °C, and (b) PL intensity for different maximum temperatures

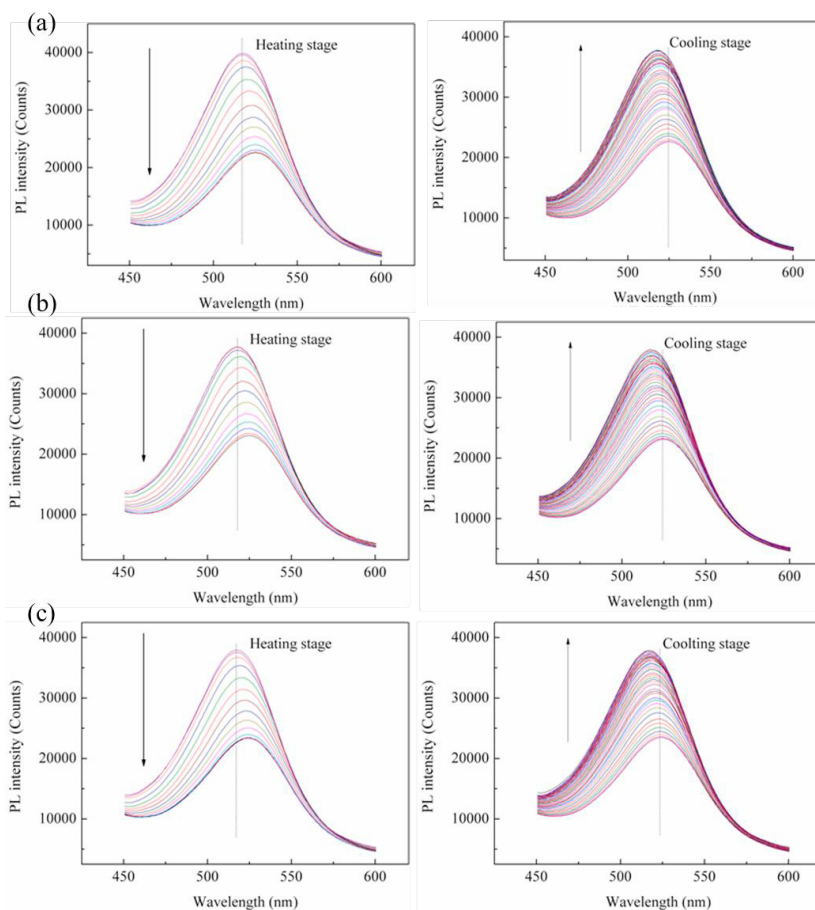


Fig. 3. Fluorescent spectra of the QDs in toluene for the first three heating and cooling cycles with the maximum temperature of ~97 °C: (a) first cycle, (b) second cycle, and (c) third cycle

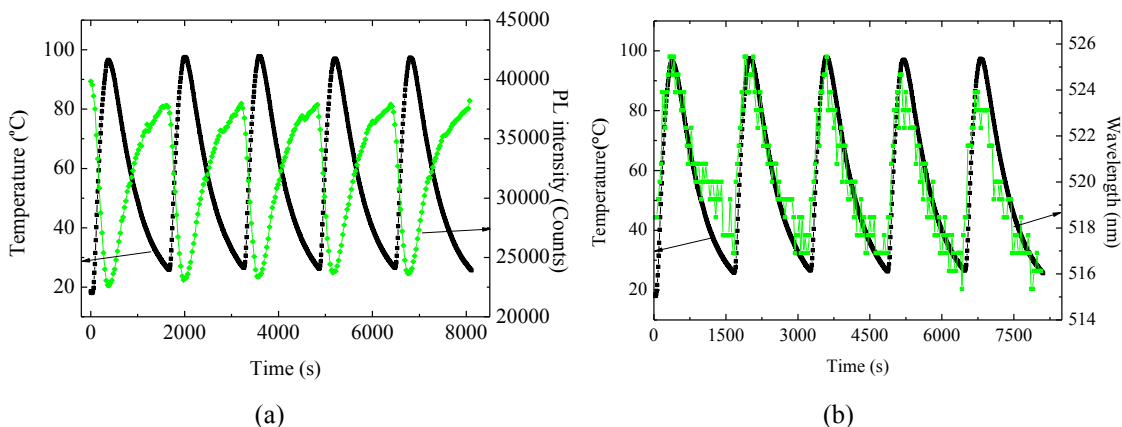


Fig. 4. Temporal variation of the luminescence characteristics of the QDs in toluene during cyclic heating and cooling: (a) variation of the PL intensity with temperature, (b) variation of the wavelength with temperature

Figure 3 shows the fluorescent spectra of the QDs in toluene with the maximum temperature of ~ 97 °C for the first three cycles of heating and cooling. The PL intensity decreases rapidly with increasing the temperature and increases relatively slowly with decreasing the temperature for each individual heating-cooling cycle. Increasing temperature causes red-shift of the PL peak, and decreasing temperature leads to blue-shift of the PL peak.

Figure 4 shows temporal evolution of the PL intensity and the wavelength of the emission peak of the QDs in toluene under the action of cyclic heating and cooling to the fifth cycle. The maximum temperature was ~ 97 °C, and the minimum temperature was ~ 20 °C. According to Fig. 4a, the maximum PL intensity corresponding to the minimum temperature decreases in the first cycle and remains constant to the fifth cycle. The minimum PL intensity corresponding to the maximum temperature increase with the increase of the cycle number. Such a trend is likely due to the change of the surface structures of the QDs, which causes the increase of energy-density levels. It is important to note that there exists UV-induced activation of QDs under continuous irradiation of UV light, which also causes the increase of the PL intensity of the QDs-toluene solution. From Fig. 4b, we note that the wavelength of the emission peak at the maximum temperature remains relatively constant for the first three cycles, and gradually decreases in the next two cycles. The wavelength of the emission peak at the minimum temperature generally decreases with the increase of the cycle number. This result suggests the possible shift of the excited energy state of the QDs in toluene with the increase of cycle number.

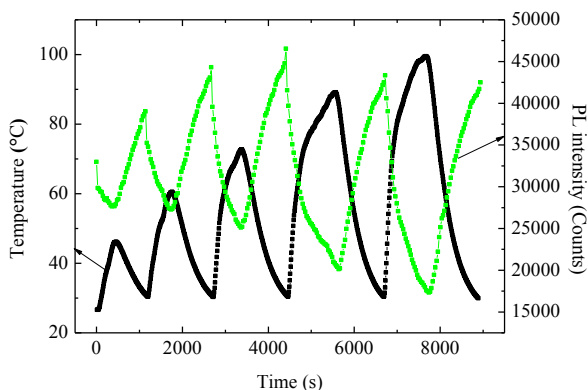


Fig. 5. Temporal variation of the PL intensity of the QDs-toluene solution in air with different maximum temperatures in different heating-cooling cycles

To study the effect of heating and cooling rates on the heating-cooling cycle, different heating rates were investigated in the experiments. Figure 5 shows the temporal evolution of the PL intensity of the QDs-toluene solution with different maximum temperatures in different heating-cooling cycles, corresponding to different heating rates. It is evident that the maximum PL intensity of each heating-cooling cycle increases at the minimum temperature for the first three cycles, and the maximum PL intensity decreases slightly at the minimum temperature from the third cycle to the fifth cycle. The minimum PL intensity at the maximum temperature decreases with the increase of the cycle number. Such results are due to the dependence of the PL intensity on temperature and the UV-induced activation of QDs under continuous irradiation of UV light. Increasing the maximum temperature leads to the increase of the heating rate, and accelerates the quenching of QDs.

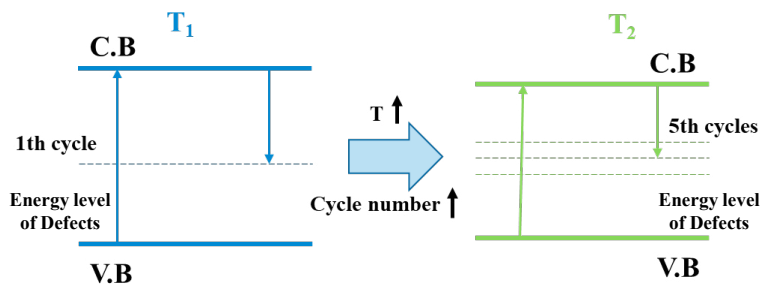


Fig. 6. Schematic energy level of QDs in toluene solution with temperature. C.B and V.B represents the conduction band and valence band, respectively.

From the above experiment results, we can conclude that increasing the cyclic temperature/heating rate causes the decrease of the PL intensity of the QDs-toluene solution and the red-shift of the wavelength of the PL emission peak. Such behaviour can be attributed to the changes of the energy level of the defects on the QDs and the energy gap between valence band and conduction band, as schematically illustrated in Fig. 6. Increasing the maximum temperature causes the decrease of the bandgap of the QDs associated with the decrease of the energy of the conduction band, which results in the increase of the wavelength of the PL emission peak [13]. The decrease of the PL intensity at the maximum temperature with the increase of the cycle number is partially due to that the quenching of the activated QDs, which increases the non-radiative process with the increasing of the density of defects level [14] and reduces the number of QDs for the PL emission.

4. Summary

- 1) Increasing cyclic temperature causes the red-shift of the PL emission peak, and decreasing cyclic temperature causes the blue-shift of the PL emission peak for the CdSe/ZnS QDs in toluene.
- 2) Both the cycle numbers and the heating/cooling rate play important roles in controlling the photo emission of the QDs in toluene. The wavelength of the PL emission peak at the maximum temperature decreases with the increase of the cycle number.
- 3) Increasing the maximum temperature causes the decrease of the PL intensity of the QDs-toluene solution and the red-shift of the wavelength of the PL emission peak.

5. Acknowledgement

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