Preparation and characterization of CdSe/CdS quantum dots

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Abstract

Monodispersed CdSe quantum dots (QDs) were made via an high temperature heat injection approach by using cadmium oxide and selenium power as precursors, and fatty amines as surface ligands. The injection temperature was changed to investigate the effect on CdSe QDs. The different injection temperature showed an apparent effect on the quantum dots nanocrystal nucleation and growth which is the key controlling the size of resulting CdSe QDs. The CdSe QDs were used as raw materials to prepare CdSe/CdS core-shell QDs at room temperature. CdSe/CdS core-shell QDs has better fluorescence than CdSe QDs.

Keywords

CdSe/CdS, Different injection temperature, High fluorescence.

1. Introduction

In recent years, quantum dots (QDs) have attracted wide attention because of their unique properties as the quantum confinement effect which leads to the tunability of the electronic band structure and optical properties. The common quantum dots are mainly composed of IV, II- VI, IV-VI or III-V elements. For example, II-VI QDs (CdSe, CdTe, ZnSe, ZnTe etc.)[1-4], III-V QDs (InP, InAs)[5, 6], and IV-VI QDs (PbS, PbSe)[7, 8]. CdSe NCs were widely used in the field of solar energy batteries[9], biomarkers[10] and light emitting diodes[11]. In order to realize potential applications, the properties (i.e., emission color, size, fluorescence intensity) of CdSe NCs must be strictly controlled.

In the preparation of quantum dots, the reaction conditions(i.e., injection temperature[12], Ligand species[13], monomer concentration[14]) have effect on preparation of QDs. Among them, Injection temperature of precursor play an important role in determining the nucleation and growth. The injection temperature of the precursor have effects on the activity of the reactants which can control the growth rate of quantum dots.This leads to the size of the quantum dots being controlled.There are defects on QDs surface[15]. QDs surface was modified different kinds of ligands or coated inorganic shells which both will have effect on the fluorescence characteristics of QDs

Monodispersed CdSe quantum dots (QDs) were made via an high temperature heat injection approach by using cadmium oxide and selenium powders as cadmium and selenium sources, and oleylamine as surface ligands. Injection temperature will be the only variable for experiments of studying QDs size. Fluorescence enhancement of QDs by modifying the shell.

2. Experimental details

2.1 Chemical

Cadmiumoxide (CdO, 99.99%), Oleylamine (OLA, 98%), Octadecene (ODE, 90%), Trioctylphosphine (TOP, 99%), Selenium powder (Se, 99.99%), Ammonium sulfide ((NH4)2S, 40%), Cadmium acetate dihydrate (Cd(CH3COO)2 2H2O, 99.99%) were purchased from Aladdin. The acetonitrile, toluene, hexane, N-methylformamide, methanol, anhydrous ethanol were purchased from McLean. All reagents were used as received and no further purified.

2.2 Synthesis of CdSe QDs

The CdSe QDs were synthesized in non-coordinating solvents ODE and the details are shown as followed. CdO (0.0384 g, 0.3 mmol) were mixed with 2 mL of OLA. The reaction mixture was degassed under vacuum for 20 min at room temperature . After that, a Se injection solution containing was prepared by dissolving Se (0.0156 g, 0.2 mmol) powder in 1 ml of TOP in ultrasonic bath. The Se was dissolved by ultrasonic until a clear colorless solution was formed. Then, the solution was heated for under the protection of nitrogen. At different temperature, the Se injection solution was injected quickly into the reaction flask. After the injection, the reaction mixture was then stabilized at the desired growth temperature . Small volume aliquots were taken at same reaction time and placed into 5 mL of N-hexane. The resulting samples were centrifugal purification with methanol for subsequent characterization.

2.3 Synthesis of CdSe/CdS QDs

The CdSe/CdS QDs were synthesized and the details are shown as followed. 2 ml of CdSe QDs, 5ml of N-methylformamide and 40 μL of ammonium sulfide was loaded into a 10 ml beaker and stirring for 5 min until stratification was formed. The solution were centrifugal purification with acetonitrile, toluene for next step. The resulting sample was dissolved in 5 ml of N-methylformamide. After that, Cd precursor solution was prepared as follows. A mixture of 5 mL of N-methylformamide, 366 mg of cadmium acetate dihydrate was loaded into a 10 ml beaker and stirring until completely dissolved. Cd precursor solution were mixed with 5ml of sample solution.

2.4 Characterization

All samples were measured with excitation wavelength at 440 nm. CdSe and CdSe/CdS QDs were characterized by transmission electron microscopy (TEM, JEOL2011), UV-visible spectrometer (Lambda 750), luminescence spectrometer (Hitachi U-4100).

3. Results and discussions

3.1 Optical properties of CdSe QDs with different injection temperature

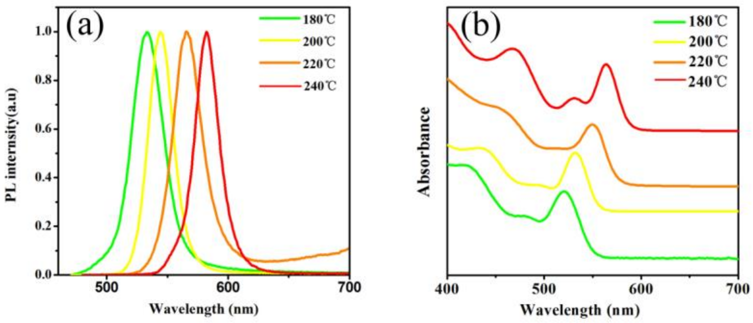

Fig.1. Emission spectra of CdSe QDs with different injection temperature (a). Absorption spectra of CdSe QDs with different injection temperature (b).

Figure 1 (a) and (b) show the evolution of the luminescence and absorption spectra of CdSe QDs grown with different injection temperature. All sample reactions are 3 min.It showed that the emission peak position and band gap absorption of the QDs continuously move to long wavelength with the increase of injection temperature. The emission peak position of CdSe QDs from 525 nm increase to 590 nm.

Preparation of QDs is divided into two processes, the nucleation of monomer and the growth of QDs[16]. In the nucleation stage, the higher the injection temperature is, the faster the precursor convert to active monomer. It will lead to nucleation when the monomer concentration exceeds the threshold. In the growth stage, the higher the temperature is, the stronger the activity of the monomer. There are more probabilities of the reaction of reactive monomers with the core surface of QDs[17]. The growth rate of QDs is more faster.

3.2 Size of CdSe QDs with different injection temperature

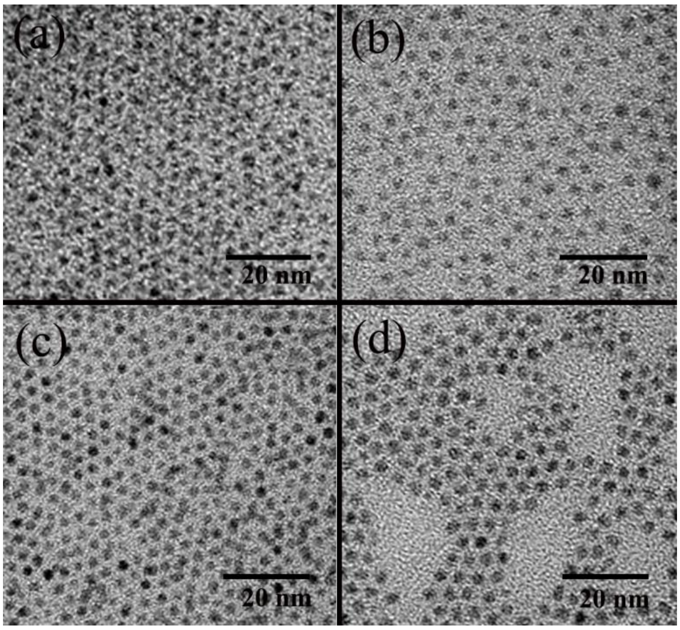

Fig.2. Morphology and Size of CdSe QDs with different injection temperature.
(a),180 oC; (b), 200 oC; (c), 220 oC; (d), 240 oC.

Figure 2 showed that the size of CdSe QDs with four different injection temperature. It is seen from Figure 2 that the size of the CdSe QDs is uniform. With the increase of injection temperature , the size of QDs increases. The size of QDs grow from 3.1 nm to 5.8 nm. This is because high temperatures are more conducive to growth of QDs.

3.3 Optical properties of CdSe/CdS QDs

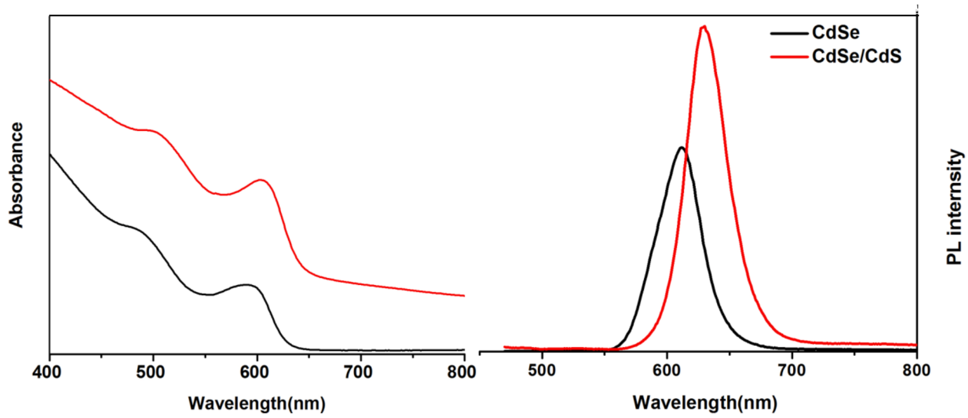

Fig.3. Emission spectra and absorption spectra of CdSe/CdS QDs

It is seen from Figure 3 that the fluorescence peaks and absorption peaks of CdSe QDs coated with CdS shells are red-shifted and increased fluorescence intensity. The large surface-to-volume ratio of QDs causes a large number of crystal defects on the surface of the QDs which leads to a decrease in the fluorescence intensity of the QDs[18]. The inorganic shell can reduce the defects on the surface of the QDs, and therefore its fluorescence intensity increases.

3.4 Size of CdSe/CdS QDs

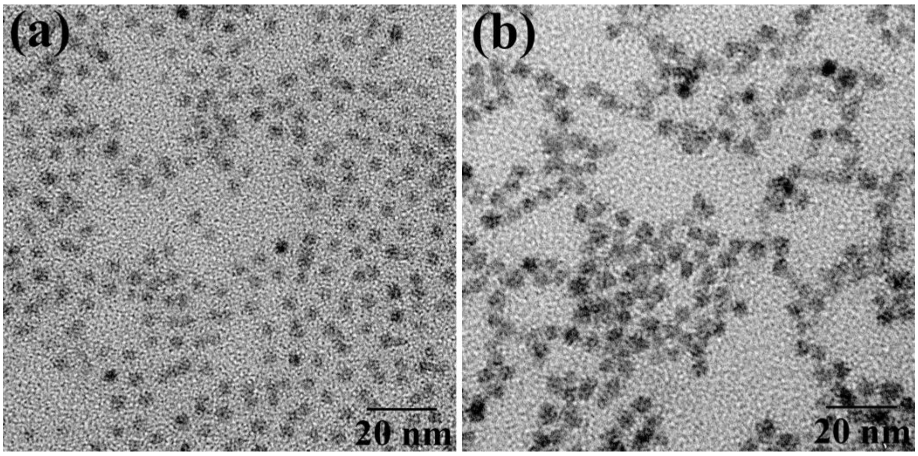

Fig.4. Morphology and Size of CdSe QDs (a) and CdSe/CdS QDs (b).

Fig 4 (b) is coated with a layer of CdS shell on the surface of Fig 4 (a). It can be clearly seen from the Fig 4 that the size of Fig 4 (b) is larger than that of Fig 4 (a). Due to the quantum size effect of QDs, the larger the emission peak position of the QDs , the larger the QDs size. The results of fluorescence spectrum and transmission electron microscopy diagram are consistent.

4. Conclusion

The CdSe QDs were synthesized with different injection temperature as well as oleylamine as ligands in a non-coordination solvent EDO by a simple and convenient method. CdSe QDs with different size and color fluorescence were obtained. CdSe/CdS QDs with higher fluorescence intensity were obtained by coating with CdS shell.These QDs will be potentially applied for bioimaging, sensing and environmental evaluations.

Acknowledgements

This work was supported by (1) the Program for Introducing Talents of Discipline to Universities (“111” plan); (2) The 1st class disciplines of Shandong Province. The Natural Scientific Foundation of China (51473082, 51503112); State Key Project of International Cooperation Research (2017YFE0108300, 2016YFE0110800); the National One-Thousand Foreign Expert Program (WQ20123700111); Key Research and Development Plan of Shandong Province (2017GGX20112).

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