

# Synthesis of photoluminescent colloidal CdS nanocrystals via a non-injection method

YAWEI ZHOU, ZHENHUA FANG, WEI ZHAO, XIAOPENG ZHAO\*

*Smart Material Laboratory, Department of Applied Physics, Northwestern Polytechnical University, Xi'an, Shaanxi, 710129, China*

This paper reports a novel method of synthesising CdS nanocrystals (NCs), which 1-octadecene as non-coordinating solvent, cadmium acetate and sulfur as Cd and S sources, and myristic acid as surfactant were used respectively. X-ray powder diffraction, dynamic light scattering and scanning electron microscopy revealed that the as-prepared CdS NCs are highly monodispersed and possess a zinc blende crystal structure. The nucleation and growth stages of the NCs could be automatically separated in a homogeneous system with nucleation initiators, namely, tetraethylthiuram disulfide and 2,2'-dithiobisbenzothiazole. To a certain extent, the size of CdS NCs could be controlled by altering the quantity of nucleation initiators and the reaction time. The photoluminescence spectra of the CdS NCs with narrow photoluminescence emission peaks are dependent on the size of the particles.

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## 1. Introduction

Semiconductor nanocrystals (NCs) are valuable in both fundamental research and industrial development [1,2] due to their physical and chemical properties, which can be attributed to the quantum confinement effect and the large ratio of their surface atoms. CdS is a typical II–VI semiconductor materials, that has two distinct crystalline phases: the cubic zinc blende phase [3–5] and the hexagonal wurtzite phase [6–9]. The direct band gaps of these two crystalline phases are 2.7 and 2.74 eV, respectively [10]. Because of their unique photoelectric properties [11,12], CdS NCs hold potential applications in photoluminescence (PL) [13], electrofluorescence [14], sensor imaging [15], solar cell imaging [16], and photocatalysis [17].

Many methods have been employed for the synthesis of high quality CdS NCs in recent years, including thermolysis of the single-source precursor at high temperatures [18–20] and template-based methods (e.g., liquid crystals [21], micelles [22], polymers [23], DNA [24] and rapid hot injection-based synthesis [25–28]). Among them, the rapid hot injection-based synthesis is the most successful in obtaining CdS NCs with the highest quality, because the injection of room temperature organometallic precursors into well-stirred hot organic solvents could effectively separate the nucleation and growth stages. In this study, we have developed a simple non-injection one-pot synthesis method based on the control of thermodynamics and kinetics of the nucleation process, which can

automatically separate the nucleation and growth stages to obtain high-quality photoluminescent colloidal CdS NCs.

## 2. Experimental setup

**Chemicals and Instruments:** Myristic acid (99.5%; Acros), tetraethylthiuram disulfide (97%; Acros), 2,2'-dithiobisbenzothiazole (99%, Acros), 1-octadecene (ODE) (90%; Acros), sulfur (S) (99.5%; Sinopharm Chemical Reagent), and Cd(Ac)<sub>2</sub> (cadmium acetate dehydrate) (98.5%; Sinopharm Chemical Reagent) were used in this study, all without further purification.

**Synthesis of CdS NCs:** CdS NCs were grown in a Schlenk flask containing Cd(Ac)<sub>2</sub> and elemental S. All chemicals were loaded at room temperature with subsequent growth performed at elevated temperature. In a typical experiment, 0.266 g (0.1 mmol) of Cd acetate hydrate, 0.4567 g (2 mmol) of myristic acid, 5.14 ml of 0.1 M S solution in ODE (0.514 mmol), 1.3 ml of 0.05 M tetraethylthiuram disulfide solution in ODE (65 μmol) and 0.064 g of 2,2'-dithiobisbenzothiazole (192 μmol) were mixed in the Schlenk flask with 30ml of ODE. The reaction was heated up to 120 °C with gentle stirring under vacuum (~50 mTorr). A clear solution was obtained after 1 h. Subsequently, the mixture was slowly heated to 240 °C at a rate of 6 °C/min under a flow of purified argon. The solution turned dark yellow as the

temperature reached 240 °C. After a desired particle size was reached, the growth solution was cooled down and washed twice with  $\text{CHCl}_3$ , toluene and acetone to remove by-products and free ligands, as the synthesised CdS particles were not soluble in either solvent. The washed NCs were dissolved in hexane for further use.

**Measurement and characterisation:** The specimens for scanning electron microscopy (SEM) were prepared by evaporating a few drops of a hexane solution of CdS nanoparticles on low-background quartz plates in a vacuum desiccator. SEM was performed using a JEOL JSM-6700F high-resolution field-emission scanning electron microscope. The X-ray powder diffraction (XRD) samples were prepared by evaporating the hexane solution of CdS NCs in a vacuum desiccator, and the XRD patterns were recorded at room temperature with a D/Max-3C automatic X-ray diffractometer using  $\text{CuK}\alpha$  radiation in the  $\theta$ - $\theta$  mode. The generator was operated at 40 kV and 40 mA. The size distributions of CdS NCs were determined using a Zetasizer Nano ZS90 dynamic light scattering system (Malvern Instruments). The PL spectra were recorded on a F-7000 Fluorescence Spectrophotometer (Hitachi High-Tech) equipped with a 450 W Xe lamp as the excitation source at the excitation wavelength of 370 nm and a data sampling increment of 2 nm.

### 3. Results and discussion

**XRD:** XRD pattern of as-obtained CdS NCs was shown in Fig. 1. All peaks could be indexed to the bulk cubic zinc blende CdS (according to the JCPDS card). CdS is known to exhibit a cubic zinc blende phase and a hexagonal wurtzite phase. Although these crystal phases could produce similar XRD results in NCs, the XRD pattern suggests that the particles are zinc blende structures. The (200) diffraction is clearly shown at  $30.8^\circ$ , which was not detected in the wurtzite phase. Furthermore, peaks between the (220) and (311) diffraction peaks were not detected. Moreover, the broadening of peaks indicates that the crystal size of CdS NCs is rather small. The average crystal size of the as-prepared CdS NCs is 17.8 nm using the Scherrer's equation according to the XRD patterns in the Fig. 1, which is in good agreement with the results of CdS NCs grading analysis and the SEM.

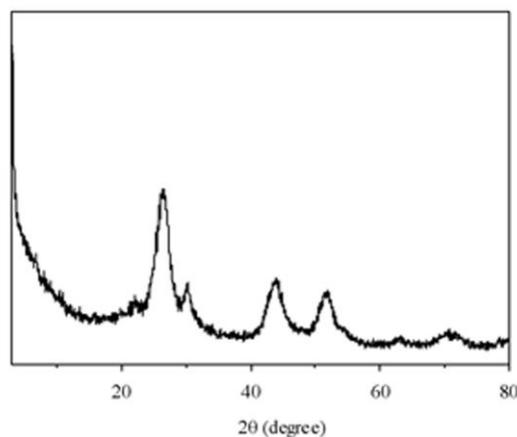


Fig. 1. XRD pattern of CdS NCs.

**Dynamic Light Scattering:** Fig. 2 shows the narrow size distribution of particles synthesised at 240 °C for 20 min and 30 min. The average particle size of CdS NCs synthesised for 20 min was 18 nm, whereas that of CdS NCs synthesised for 30 min was 22 nm. When the temperature reached 240 °C, the average radius of NCs increased with increasing reaction time. The average particle sizes shown in panels (a) and (b), demonstrate that the size distribution of CdS NCs decreased as temperature increased, indicating that no new nucleation occurred during particle growth and that the concentration of NCs in the reaction solution remained nearly unchanged with increasing reaction time. These results demonstrate that the nucleation and growth stages are clearly separated under the proposed non-injection-based synthesis, rendering the growth of CdS NCs controllable.

**Morphology of CdS NCs:** Fig. 3 shows the SEM image of CdS NCs synthesised at 240 °C for 20 min. It demonstrates that the particles are highly monodispersed spherical CdS NCs. The average crystal size of the as-prepared CdS NCs was 20 nm, which is in good agreement with the results of CdS NCs grading analysis.

**PL Spectrum:** Fig. 4 shows the room temperature PL spectra of CdS NCs synthesised at 240 °C for 10, 20 and 30 min at the PL excitation wavelength of 370 nm. The sharp PL spectra with the full width at half-maximum of 50 nm indicate a narrow size distribution of the NCs formed in ODE. With increasing reaction time, the corresponding PL emission peak position red-shifted from 460 to 470 nm, indicating an increase in the average size of the as-prepared CdS NCs. The emission peaks of CdS nanoparticles with different size 16 nm, 18 nm and 22 nm are shown at 460 nm, 464 nm and 470 nm. However, the PL spectra contained a noticeable emission peak at approximately 570 nm, that reached the surface-trap emission

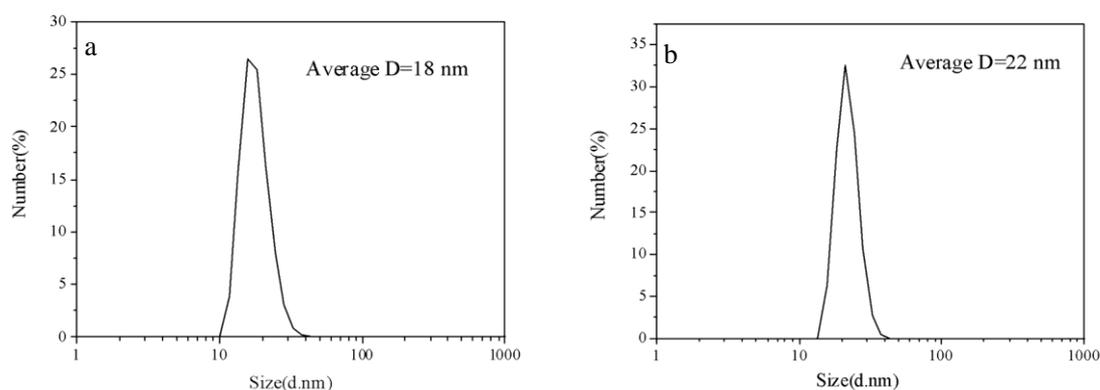


Fig. 2. Size distribution of CdS NCs synthesised at 240 °C for (a) 20 min and (b) 30 min.

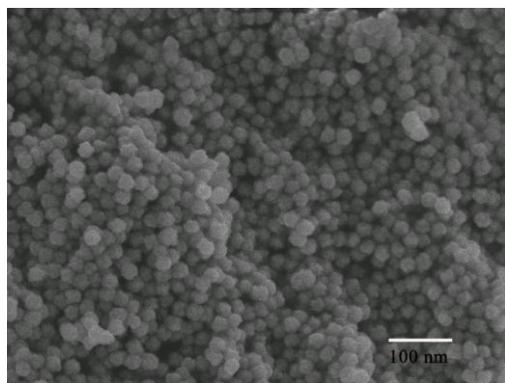


Fig. 3. SEM images of CdS NCs synthesised at 240 °C for 20 min (scale bar represents 100 nm).

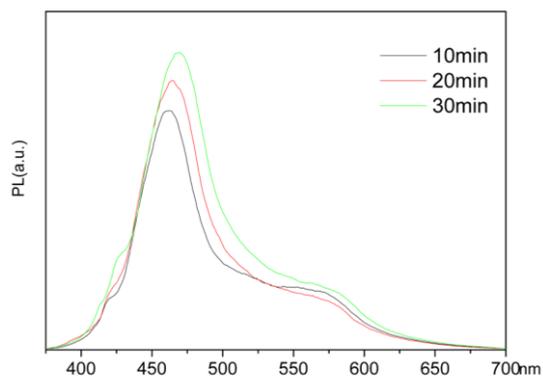


Fig. 4. PL spectra of CdS NCs synthesised at 240 °C for 10, 20 and 30 min.

**Effects of Nucleating Initiators:** Tetraethylthiuram disulfide and 2,2'-dithiobisbenzothiazole play an important role in our proposed synthesis of CdS NCs. These nucleating initiators have been used as vulcanisation accelerators to accelerate the reactivity of the precursors, such as Cd(Ac)<sub>2</sub> and S. In the absence of these initiators, some white precipitate would form when the reaction temperature has reached 240 °C. On the

other hand, increasing the amount of nucleating initiators would accelerate NCs growth, but leave the general nucleation characteristics unchanged. Moreover, the amount of nucleating initiators affects the number of stable nuclei, such that a higher amount of initiators corresponds to a smaller number of stable nuclei formed in the synthesis. With the same amount of precursors, the smaller number of stable nuclei would lead to larger NCs. This method thus allows control of the final particle sizes in the synthesis by changing the amount of nucleating initiators.

#### 4. Conclusions

In summary, we have presented a simple non-injection one-pot method to synthesise high-quality photoluminescent CdS NCs. The XRD results indicate that the CdS NCs have a cubic zinc blende crystalline phase, whereas dynamic light scattering and SEM show that the average size of the CdS NCs is 20 nm. The room temperature PL spectra of the CdS NCs excited at a 370 nm wavelength have typical narrow peaks at approximately 470 nm. The nucleating initiators automatically separate the nucleation stage and the growth stage in a homogeneous system, making it possible to control the growth of the CdS NCs by changing the reaction time and the amount of initiators. This concept of using nucleating initiators to control the kinetics of nucleation and growth can be used in the synthesis of many other metal sulfide and metal oxide NCs.

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\*Corresponding author: xpzhao@nwpu.edu.cn