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Synthesis of CdTe Nanocrystals through Program Process of Microwave Irradiation

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A novel method, the program process of microwave irradiation (PPMI), which commendably integrates good qualities of microwave irradiation and a programmed heating process, is presented to synthesize high-quality CdTe nanocrystals in aqueous solution. Microwave irradiation, which acts as the heating mode of PPMI, is highly favorable for a narrow size distribution and low concentration of surface defects of nanocrystals. On the other hand, two correlative processes (the first process and the second process) are utilized in PPMI to actualize the programmed heating process, which is an effective strategy to improve the quality of nanocrystals. Thus, a series (diameters ∼2−4 nm) of highly luminescent (PLQY ∼ 30−68%) CdTe nanocrystals were rapidly prepared (reaction time ∼ 1−30 min) in aqueous phase through PPMI.

1. Introduction

High-quality semiconductor nanocrystals (NCs), which can be applied in various applications, have been attracting intensive attention due to their special electrical and optical properties.[1] Due to the elegant work of Bawendi,[2] Alivisatos,[3] Peng,[4] and Weller and Rogach,[5] sufficient progress has been made in the synthesis of high-quality nanocrystals through organometallic routes. By contrast, relatively poor spectral properties (low photoluminescence quantum yield (PLQY ∼ 3−10%, increased to 25−30% after further posttreatment), and broad full-width at half-maximum (fwhm)) are often observed in nanocrystals prepared through the conventional aqueous method, despite it being simpler, cheaper, and more environmentally friendly.[6] Many strategies have been developed with the aim of optimizing the spectral properties of nanocrystals directly prepared in aqueous phase. For instance, the hydrothermal method providing higher temperatures was employed to synthesize nanocrystals, which were successfully used as biological labels.[7]

Compared with the conventional heating method, microwave irradiation (MI) has many advantages such as prompt startup, easy heat control (on and off), and low cost. As a result, MI has been widely used in various fields. Especially compared with conventional thermal techniques, microwave dielectric heating can heat material homogeneously due to its penetration characteristic, which is favorable for uniform nucleation and is an essential prerequisite to formation of monodispersed nanoparticles.[8] Besides that, microwaves can penetrate the reaction solution, leading to simultaneous and fast heating.[9] Thus, a successive process of crystal growth by epitaxy can be realized to form nanocrystals in sufficiently short time during the Ostwald ripening stage, which is extraordinarily beneficial for reducing the concentration of surface defects of nanocrystals.[10] Therefore, microwave methodology is considered an effective strategy to prepare high-quality nanocrystals. As a vivid example, MI was applied to the synthesis of CdS nanoparticles as recently as 2002 despite their low PLQY.[10a] Afterward, highly luminescent CdSe NCs (PLQY ∼ 68%) were successfully obtained via MI through an organometallic route.[10b] In addition, water-soluble CdTe NCs, whose PLQY was reported as 60% in the optimum condition, were synthesized through MI as well.[10c]

It is worth mentioning, however, that the growth rate of nuclei is accelerated in the nucleation stage due to the rapid heating of MI. As a result, a high degree of surface disorder of crystal nuclei is likely to be generated, which is greatly adverse to the quality of nanocrystals.[7,11] To overcome this deficiency of MI applied for synthesizing nanocrystals, we herein present a novel method, called the program process of microwave irradiation (PPMI), to prepare high-quality CdTe NCs in the aqueous phase. The optical properties of as-prepared CdTe NCs are further improved, compared with those synthesized via direct MI. In comparison to the PLQY (42.1%) of NCs prepared via direct MI under optimum conditions in our research, the PLQY was enhanced to 68.5% through PPMI amelioration. Meanwhile, the fwhm value was diminished 2−3 nm, implying that narrower size distribution was obtained through PPMI.

2. Experiment Section

2.1. Materials and Device. Tellurium powder (99%), $CdCl_2$ (99%), and thioglycolic acid (TGA) (99%) were purchased from Aldrich. 3-Mercaptopropionic acid (MPA) (98%) was purchased

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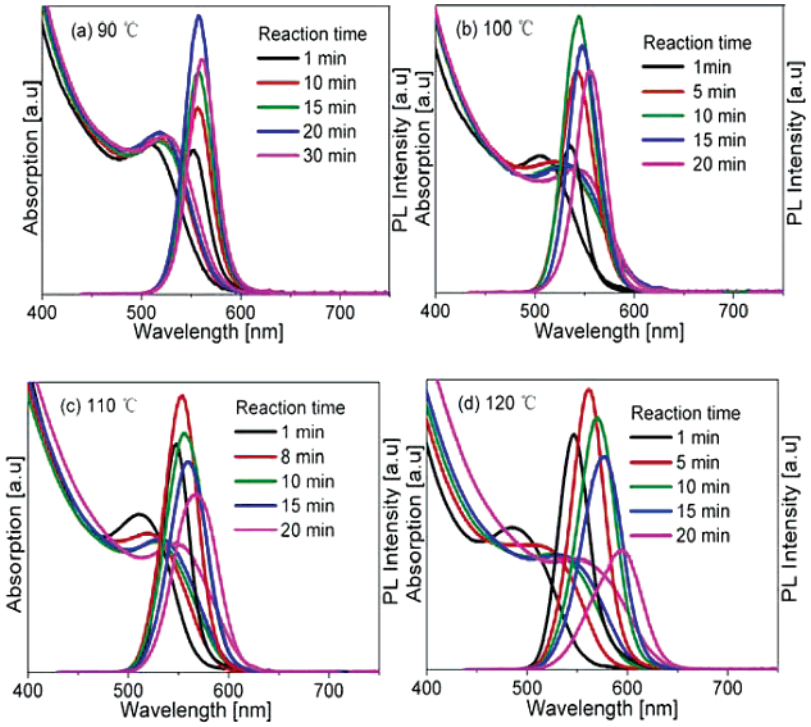

Figure 1. Temporal behavior of absorption and fluorescence of CdTe NCs prepared via direct MI. [Cd] = 1.25 mmol/L; [MPA] = 3.0 mmol/L; [Te] = 0.625 mmol/L.

from Fluka. L-Cysteine (98.5%) and $NaBH_4$ (99%) were purchased from Shanghai Chemical Reagents Company. All chemicals were used without additional purification. All solutions were prepared using Milli-Q water (Millipore) as the solvent. The microwave system (Version 3.5.7) used for synthesizing CdTe nanocrystals was made by CEM of America. Five continued programs are capable of being located to realize program processes accurately. Furthermore, exclusive vitreous vessels with 10 or 100 mL volume are equipped for the system to provide security during reactions demanding high temperature and pressure.

2.2. Experimental Procedure. In a typical procedure, the CdTe precursor solution was prepared by adding freshly prepared NaHTe solution to a N_2-saturated $CdCl_2$ solution at pH 8.4 in the presence of 3-mercaptopropionic acid (MPA) as a stabilizer. The molar ratio of Cd^{2+}/MPA/HTe^- was set as 1:2.4:0.5. A 4 mL volume of CdTe precursor solution was injected into the exclusive vitreous vessel with a volume of 10 mL. A series of high-quality CdTe NCs were prepared under microwave irradiation located by program process. After microwave irradiation, the CdTe NC sample was taken when the temperature cooled to lower than 50 °C naturally. When L-cysteine or TGA was substituted for MPA as the stabilizer, the pH value of the precursor was adjusted to 10.8 or 11.4, and the molar ratio of Cd^{2+}/thiols/HTe^- was accordingly changed to 1:2.4:0.5 or 1:1.0:0.5, respectively. Other manipulations were identical to those when MPA was the stabilizer. All optical measurements were performed at room temperature under ambient conditions without any postpreparative treatment. Samples were precipitated by 2-propanol and dried in a vacuum oven for X-ray diffraction (XRD) characterization. Transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) samples were prepared by dropping the aqueous CdTe solution onto carbon-coated copper grids with the excess solvent evaporated. UV−vis absorption spectra were recorded with a Shimadzu UV-3150 UV−vis−near-infrared spectrophotometer. Photoluminescence (PL) measurements were performed using a Shimadzu RF-6301PC spectrofluorimeter. The PLQY at room temperature was estimated using Rhodamine 6G (ethanol as solvent) as the fluorescence standard (QY = 95%).[12] Transmission electron microscopy and high-resolution transmission electron microscopy overview images were recorded on a JEOL JEM 2011 electron microscope operated at 200 kV. Powder X-ray diffraction patterns were obtained from a Rigaku D/max-γB diffractometer.

TABLE 1: PLQY of CdTe NCs Synthesized via Direct MI under Optimum Conditions

T^a/°C	90	100	110	120
t^b/min	20	10	8	5
PLQY/%	38.3	42.1	34.9	32.6

[a] *T*, reaction temperature. [b] *t*, reaction time.

3. Results and Discussion

3.1. PPMI and Direct Microwave Irradiation (MI). To elaborately demonstrate the advantages of PPMI in contrast to direct MI, we first studied the optimum conditions for preparing CdTe NCs via direct MI (section 3.1.1). Subsequently, optical properties of CdTe NCs synthesized through PPMI and direct MI were adequately compared during varied cases (sections 3.1.2 and 3.1.3).

3.1.1. Synthesis of CdTe NCs via Direct MI. Similar procedures were fully depicted previously.[10c] In our experiment, the reaction temperatures were 90, 100, 110, and 120 °C. UV−PL spectra showed that the PL intensity reached a maximum value in 20, 10, 8, or 5 min based on different temperatures (Figure 1). Less time was required to reach the optimum condition according to higher temperature. The corresponding PLQY values of CdTe NCs are displayed in Table 1.

3.1.2. Synthesis of CdTe NCs through PPMI. The temperatures of the first program process (first process) were 80, 90, 100, and 110 °C. The corresponding time of the first process was from 15 to 120 s. To compare effects between PPMI and direct MI, the reaction temperatures and times of the second

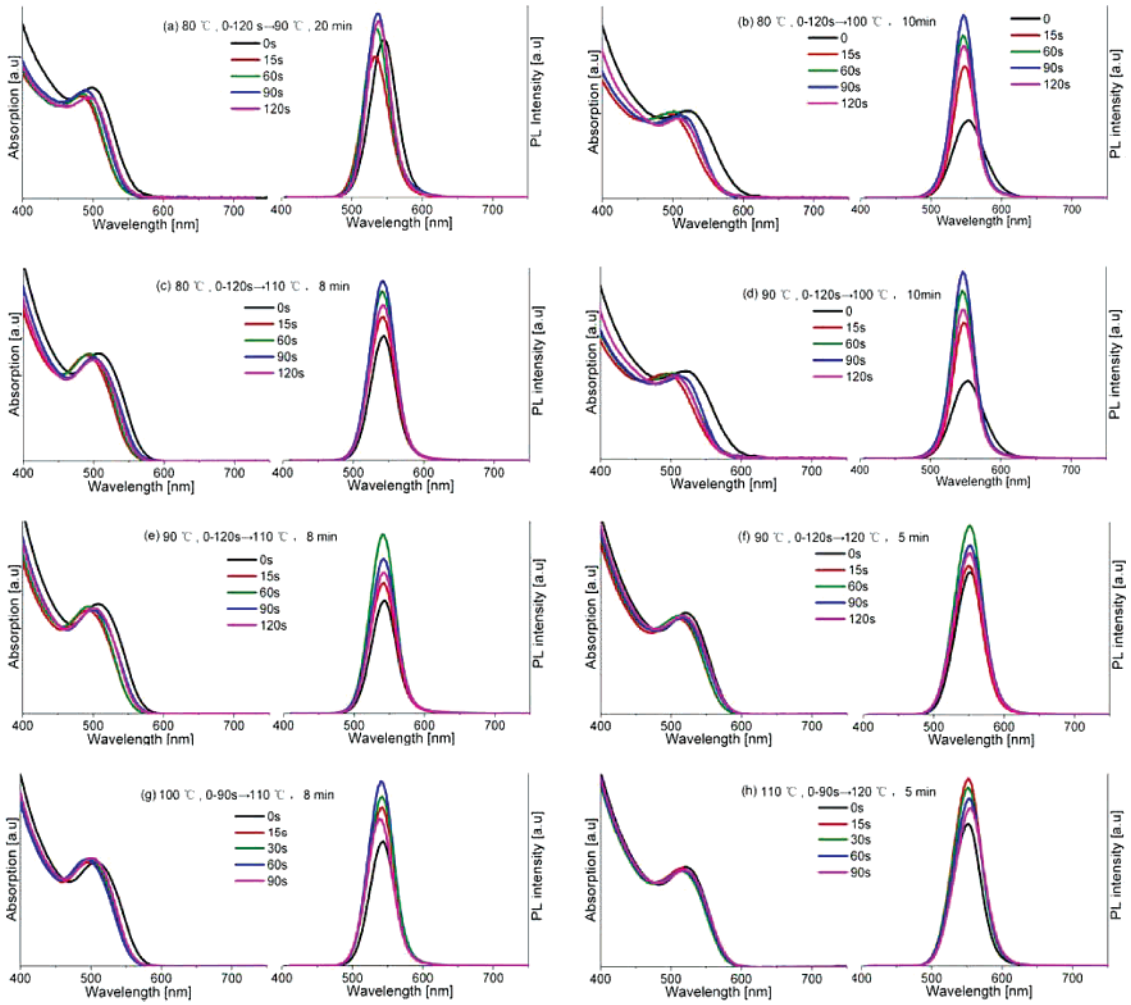

Figure 2. Temporal behavior of absorption and corresponding PL spectra of CdTe NCs prepared through PPMI. Colored lines and black lines stand for spectra of CdTe nanocrystals prepared through PPMI and direct microwave irradiation, respectively. [Cd] = 1.25 mmol/L; [MPA] = 3.0 mmol/L; [Te] = 0.625 mmol/L.

TABLE 2: PLQY of CdTe NCs Synthesized through PPMI under Optimum Conditions and Increasing Percent of PLQY Compared with Direct MI

	(a)	(b)	(c)	(d)	(e)	(f)	(g)	(h)
T^a of first process/°C	80	80	80	90	90	90	100	110
t^b of first process/s	90	90	90	60	60	60	30	15
T of second process/°C	90	100	110	100	110	120	110	120
t of second process/min	20	10	8	10	8	5	8	5
PLQY/%	41.3	63.8	51.2	68.5	55.6	50.3	47.2	41.9
increasing percent[c]/%	7.8	51.5	46.7	62.7	59.3	54.2	35.2	28.5

[a] *T*, reaction temperature. [b] *t*, reaction time. [c] Increasing percent = (PLQY of CdTe NCs synthesized through PPMI − PLQY of CdTe NCs synthesized via direct MI)/PLQY of CdTe NCs synthesized via direct MI.

program process (second process) were regulated the same as the optimum conditions applied in direct MI (Table 1). Figure 2 shows that the spectral properties of CdTe NCs synthesized through PPMI (colored lines) were greatly improved in contrast to those synthesized via direct MI (black lines). Moreover, as shown in Table 2(b)−(f), a high PLQY (50.3−68.5%) was achieved when the relatively low temperatures (80−90 °C) of the first process and relatively high temperatures (100−120 °C) of the second process were selected, respectively. In comparison to direct MI, the increasing percent of PLQY of CdTe NCs synthesized through PPMI was up to 62.7% in the optimum condition (Table 2, (d)). These results evidently demonstrate that the quality of CdTe NCs can be tremendously improved through PPMI compared with direct MI. By contrast, relatively low increasing percents (7.8−35.2%) were obtained when both the first and second processes were performed at low temperatures or high temperatures (Table 2, (a), (g), and (h)). On the other hand, due to the lower quality NCs with more surface defects being primarily dissolved during the second process of PPMI, the positions of PL maxima of CdTe NCs prepared through PPMI presented a slight blue shift (1−3 nm), and the value of fwhm diminished 2−3 nm compared with those prepared via direct MI.[6]

3.1.3. Synthesis of CdTe NCs through PPMI and Direct MI. The temperature and time of the first process were 90 °C and 60 s, respectively. We fixed 100 °C as the temperature of the second process, which was the same as the reaction condition of direct MI. Figure 3 shows that the PLQY of CdTe NCs synthesized through PPMI was always larger than the PLQY

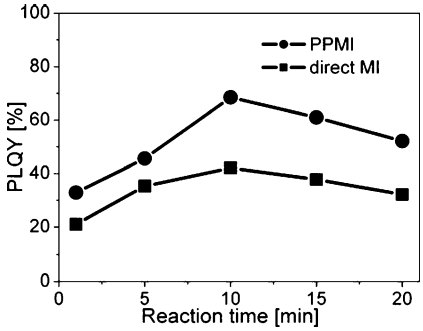

Figure 3. Comparisons of PLQY of CdTe NCs synthesized through PPMI and direct MI at different reaction times.

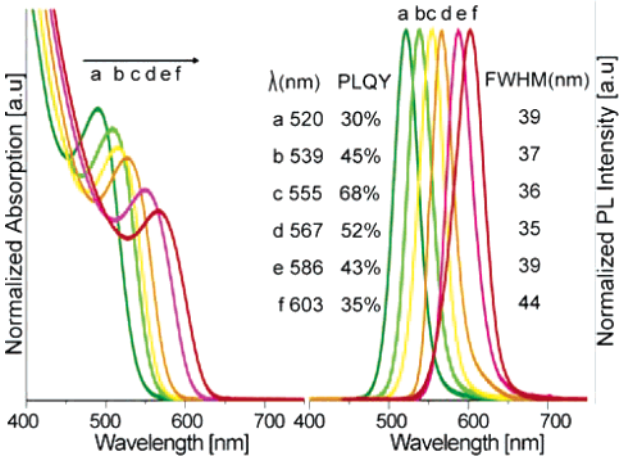

Figure 4. Absorption (left) and fluorescence (right) of CdTe NCs prepared through PPMI. The temperature and time of the first process were 90 °C and 60 s, respectively. The temperature of the second process was 100 °C. a, b, c, d, e, and f stand for spectra of CdTe nanocrystals obtained with 0.5, 5, 10, 20, 25, and 30 min, respectively, as the reaction time of the second process.

of those obtained via direct MI at the same time, though the increasing percent was diverse according to different reaction times. It further demonstrates the tremendous superiority of PPMI in comparison to direct MI.

3.2. Characterization. *3.2.1. Optical Properties.* We have rapidly prepared a series of highly fluorescent CdTe NCs stabilized with 3-mercaptopropionic acid (MPA) in aqueous phase through PPMI. Figure 4 reveals that a clearly resolved absorption of the first electronic transition appeared at ~485 nm and green band-edge emission appeared in only 0.5 min. Merely 30 min were demanded to obtain large CdTe NCs of ~4 nm (luminescence maximum at 603 nm), which was sufficiently time economizing compared with conventional aqueous synthesis (1−2 days demanded). Furthermore, the PL bands were sufficiently narrow (fwhm as low as 35 nm being increased up to 44 nm owing to size fractions of large CdTe NCs). More importantly, the PLQY exceeded 30% during the broad size range of NCs (~2−4 nm) (Figure 4). The PLQY reached as high as 68.5% under the optimum condition, which was comparable with the values of CdTe NCs prepared through the organometallic route.[4a,10b,13] In addition, highly luminescent CdTe NCs capped with thioglycolic acid (PLQY ~ 61%), L-cysteine (PLQY ~ 45%), and other kinds of thiols were synthesized through PPMI as well.

3.2.2. XRD and TEM/HRTEM Characterization. Figure 5 (left) shows XRD patterns obtained from powdered precipitated fractions of CdTe NCs synthesized through PPMI. The as-prepared CdTe NCs belonged to the cubic (zinc blende) structure, which was also the dominant crystal phase of bulk

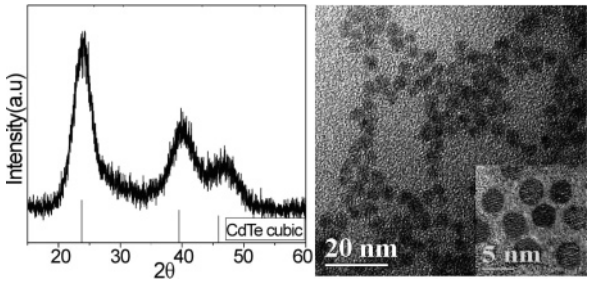

Figure 5. Left: XRD of the CdTe NCs synthesized through PPMI. Right: TEM overview and HRTEM (inset) images of CdTe NCs synthesized through PPMI.

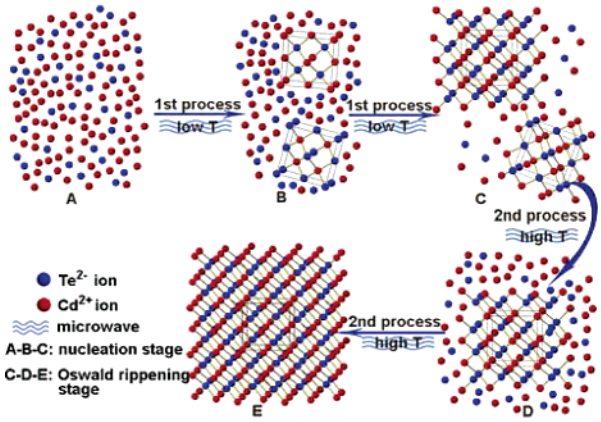

Figure 6. Schematic model of program process of microwave irradiation (PPMI). (B) Two nuclei; (C) large nanocrystal (top) and small nanocrystal (bottom); (E) ideal nanocrystal. *T* is temperature. To simplify the model and make it easier to comprehend, the effect of thiol is ignored.

CdTe. In the TEM and HRTEM images, the as-prepared CdTe NCs appear as spherical particles with excellent monodispersity (Figure 5 (right)).

3.3 Theoretical Mode of PPMI. As mentioned in section 3.1, the processes of PPMI are divided into two consecutive stages: the first program process (first process), which is favorable for nanocrystals forming in nucleation period, and the second program process (second process), which is available for nanocrystals growing in the Ostwald ripening stage. As illustrated by the schematic model of PPMI (Figure 6), nuclei were formed slowly and uniformly at low temperature (80−90 °C) in the first process, which is favorable for surface ordering and monodispersity improving (A → B).[4b,11] When the reaction time of the first process reached some value, the cadmium monomer concentration descended to a critical threshold and the nucleation stopped (B → C).[7] The Ostwald ripening stage took place while continuing to prolong the reaction time, during which further nanocrystal growth occurred through dissolution of small nanocrystals with less stability due to their larger surface-to-volume ratio.[14,15] The average surface disorder and the amount of surface defects of nanocrystals increased, provided that low temperature was maintained.[4a,7] As a result, a relatively higher temperature (100−110 °C) was demanded to preserve the steady growth of larger nanocrystals in favor of a narrow size distribution. Thus, the reaction temperature was raised while the program stepped into the second process (C → D). Moreover, the growth rate of nanocrystals was accelerated at high temperature, which is favorable for reducing the concentration of surface defects of nanocrystals (D → E).[8,11] Therefore, PPMI is extremely favorable for synthesizing high-quality nanocrystals with a low concentration of surface defects and a narrow size distribution.

4. Conclusion

In conclusion, we have reported here a novel method, the program process of microwave irradiation (PPMI), which commendably integrates good qualities of microwave irradiation and a programmed heating process. As discussed above, microwave irradiation, which acts as the heating mode of PPMI, is highly favorable for a narrow size distribution and a low concentration of surface defects of nanocrystals. On the other hand, two correlative processes are utilized in PPMI to actualize the programmed heating process, which is an effective strategy to improve the quality of nanocrystals. Therefore, a series of highly luminescent CdTe nanocrystals were rapidly prepared in aqueous phase through PPMI. It should probably be emphasized that PPMI may be considered a significant approach to directly prepare high-quality nanocrystals in the aqueous phase because it is extremely convenient, rapid, and free of complicated vacuum manipulation or expensive chemical reagents.

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