

Rapid synthesis of highly luminescent CdTe nanocrystals in the aqueous phase by microwave irradiation with controllable temperature

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In this paper, we present a new method for rapid synthesis of high quantum yield CdTe nanocrystals in the aqueous phase by microwave irradiation with controllable temperature.

Colloidal semiconductor nanocrystals (NCs), due to their unique optical properties, are currently attracting extensive attention for potential applications in optoelectronics and biolabeling.^{1–3} In recent years, a series of high quality NCs (such as CdSe, CdTe) with high quantum yield (QY ~ 50–80%) and sharp emission spectra have been successfully prepared in organic phases,^{4–6} however, these NCs cannot be directly applied in bio-systems due to their insolubility in water. The aqueous synthesis is an alternative to non-aqueous synthesis, and the as-prepared products have excellent water-solubility, stability and biological compatibility.^{7,8} But, NCs synthesized in the aqueous phase usually possess low quantum yield (3–10%) and also need a long reaction time from several hours to several days.⁷ Microwave irradiation as a heating method is widely used in organic reactions, catalysis, and recently, in the preparation of nanoparticles.^{9–11} These studies demonstrated that microwave irradiation could considerably accelerate the chemical reaction. Unfortunately, no report on the successful preparation of good QY NCs by the microwave irradiation technique has been published to date. In this paper, we describe a rapid synthesis of high-quality CdTe NCs in the aqueous phase by microwave irradiation. At relatively lower temperature (below or equal to 160 °C vs. 300 °C used in organic phase synthesis), various sizes of CdTe NCs with high QY were controllably synthesized by simply varying the temperature and reaction time.

Fig. 1 presents the temporal evolution of the absorption and luminescence spectra of the as-prepared colloidal CdTe NCs grown at four typical temperatures (100 °C, 120 °C, 140 °C, 160 °C). On prolonging the heating time, the growth of the CdTe NCs was clearly evident by the shifts of both absorption and emission spectra to longer wavelength. The emission peaks of CdTe NCs ranged from 505 nm to 733 nm, and the corresponding FWHM (the full width at half maximum) of the band-edge luminescence was from 30 nm to 85 nm ($\lambda_{\text{ex}} = 370$ nm), which indicated the narrow size distribution of the as-prepared CdTe NCs. Fig. 2 expresses the evolutionary emission peaks of CdTe NCs synthesized at different temperatures vs. microwave irradiation time. Since the luminescence of NCs is size-dependent, we can evaluate the growth rate of NCs from the shift of emission peaks. The growth rate at low temperature (100 °C–120 °C) was relatively slow, and the low temperature was well suited to prepare small

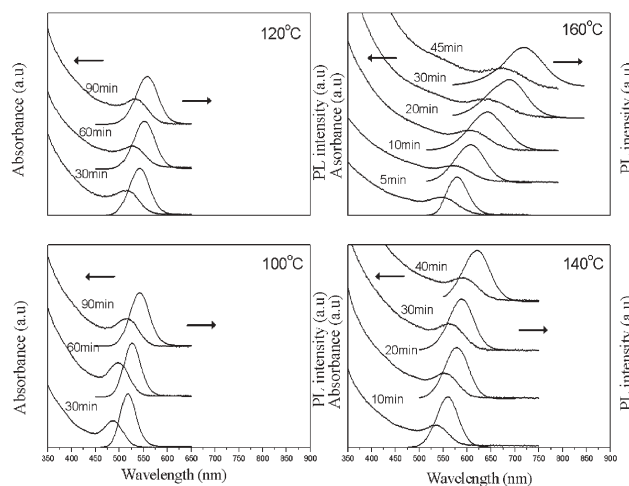


Fig. 1 Temporal evolution of the absorption spectra and corresponding emission spectra of CdTe NCs prepared at different temperatures and different irradiation time. ([Cd] = 1.25 mmol/L, [Te] = 0.625 mmol/L, [MPA] = 3 mmol/L).

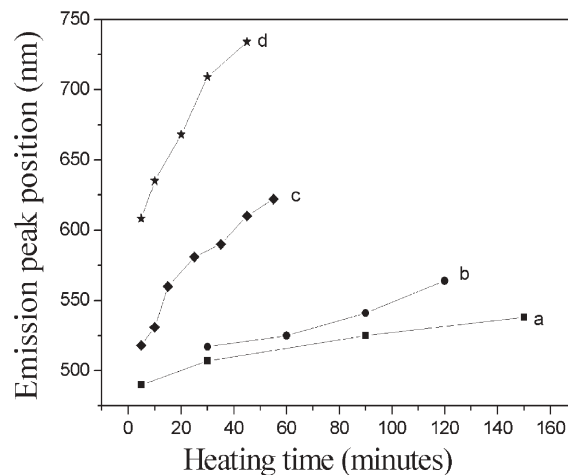


Fig. 2 The PL (photoluminescence) peak position of the crude solution of CdTe NCs during their growth at four different temperatures. In the investigation, the pH, molar ratios and precursors concentrations were fixed. (a. 100 °C, conventional aqueous synthesis; b. 100 °C, microwave irradiation; c. 140 °C, microwave irradiation; d. 160 °C, microwave irradiation).

nanoparticles with emission from green to yellow (500 nm–560 nm) light. At higher temperature, the growth rate was markedly accelerated, and larger sizes of NCs (emission at 550 nm–733 nm)

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were obtained. For example, CdTe NCs with emission at near-IR (733 nm) were synthesized by microwave irradiation at 160 °C within 45 min, however, they generally needed about 2–3 days to be prepared by conventional aqueous synthesis.⁸ Notably, these larger sizes of NCs (emission at 650 nm–733 nm) synthesized by microwave irradiation at higher temperature (140 °C or 160 °C) still contained high QY of around 40%, whereas the same sizes of CdTe NCs synthesized by hydrothermal synthesis only showed very weak or no luminescence.¹² Clearly, high temperature favored an increasing growth rate of NCs, but we found that too high a temperature (more than 200 °C) would lead to a marked decrease in the QY of CdTe NCs, probably due to the decomposition of MPA (3-mercaptopropionic acid) and loss of the stabilizing effect of MPA. Besides high temperature, microwave irradiation itself likely was one key factor affecting the growth rate. We found that even at the same temperature, microwave-assisted synthesis showed much faster growth rates than in conventional aqueous synthesis (same precursor molar ratios, concentrations and pH), but the mechanism is not clear and needs further investigation.

In the current aqueous synthesis, the pH value of Cd precursors was generally fixed at 11.2–11.8.⁸ We found that at such high pH, relatively weak luminescence (QY 3–20%) CdTe NCs were only obtained by the microwave irradiation synthesis. The QY of the as-prepared CdTe NCs was increased with lowering of the pH of Cd precursor solutions from the pH 11.2, but when the pH was over about 8.0, further lowering of the pH led to a slight decrease in the luminescence of CdTe NCs or produced precipitations of CdTe NCs. The CdTe NCs prepared at about pH 8.0 (reaction solution pH was 9.0–9.2) showed a high QY up to 60% (emission peaks at 560 nm–580 nm), but 40–50% QY was more routinely achieved. To our knowledge, this probably is the highest QY of luminescent CdTe NCs achieved in the aqueous synthesis to date. Similar to the results reported in the reference,¹² we also found that the concentrations of precursors played an important role in the controlling of QYs of CdTe NCs, and low precursor concentration was helpful to obtain strongly luminescent CdTe NCs. For example, at the typical precursor concentration (Cd: 1.25 mmol/L, Te: 0.625 mmol/L, MPA: 3 mmol/L), the as-prepared CdTe NCs (emitting from 525 nm to 733 nm) showed QYs as high as 40–60%. The pH-dependent luminescence of CdTe NCs synthesized in the aqueous phase was reported previously,^{13,14} and the QY could be enhanced up to 5 times by decreasing the pH of the colloidal solution to 4.5–5.0. Surprisingly, the luminescence intensity of CdTe NCs synthesized by microwave irradiation nearly kept steady over a wide pH range (5–11) in the presence of MPA, it was possibly owing to the formation of a better surface structure of CdTe NCs under our synthetic conditions.

Fig. 3 (left) shows X-ray powder diffraction (XRD) patterns of CdTe powders (the first absorption peak located at 525 nm). The data showed that the CdTe NCs belonged to the cubic (zinc blende) structure, which was also the dominant crystal phase of bulk CdTe. High-resolution transmission electron microscopy (HRTEM) overview images and a fast Fourier transform (FFT) of a selected area of CdTe NCs (the excitonic absorption peak at 692 nm) are shown in Fig. 3 (right). The existence of lattice planes on the HRTEM image further confirmed the crystallinity of CdTe NCs synthesized by microwave irradiation.

In summary, a new method for the aqueous synthesis of CdTe NCs assisted by microwave irradiation is presented in this

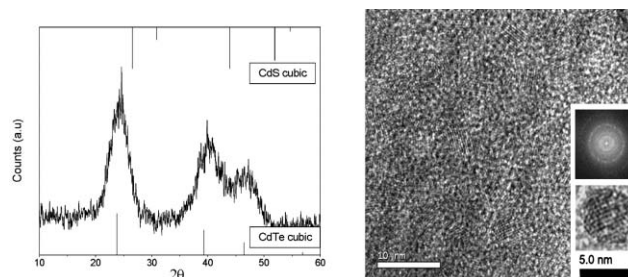


Fig. 3 Left: The powder X-ray diffractograms of the CdTe NCs synthesized by microwave irradiation (the excitonic absorption peak at 525 nm). Right: HRTEM images of CdTe NCs synthesized by microwave irradiation. The inset shows a certain area with a corresponding FFT. (The excitonic absorption peak of NCs at 692 nm).

communication. This method allows the rapid preparation of a series of CdTe NCs emitting at the green to the near-IR spectral window (505–733 nm) at moderate temperatures. Our results illustrated that the as-prepared CdTe NCs possessed strong luminescence (QY 40%–60%) and pH-independent luminescence. Furthermore, our data demonstrated that microwave irradiation with controllable temperature might be an attractive alternative to current syntheses of NCs in aqueous and organic phases.†

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Notes and references

† The microwave digestion system (WX-3000) used for the preparation of CdTe NCs was made by Shanghai Yi-Yao Instruments (Shanghai), and was equipped with controllable temperature units. The temperature can be controlled within variation of ± 2 °C at the set temperature by a thermal sensor in the sealed digestion vessels. The system operates at 2450 MHz frequency, and works at 0–1000 W power. Users can program the reaction temperature and time. The reaction vessel was double walled and consisted of a Teflon inner liner and cover surrounded by a high strength vessel shell of Ultem polyetherimide. CdTe nanocrystals were prepared using the reaction between Cd^{2+} and NaHTe solution. Cd precursor solutions were prepared by mixing a solution of CdCl_2 and MPA as stabilizer in ultrapure water, and then adjusted to different pH values with 1 M NaOH. The typical molar ratio of Cd : Te : MPA was 2 : 1 : 4.8 in our experiments. The solution was deaerated with N_2 bubbling for 30 min. Under vigorous stirring, the oxygen-free NaHTe solution prepared according to the protocol¹³ was injected; 20 ml mixture solution (CdTe precursors) was transferred into a vessel (total volume 60 ml) and placed into the microwave digestion furnace. Under microwave irradiation (300 W), the reaction system reached certain temperature and pressure (the temperature decides the pressure). Various sizes of CdTe NCs with high QY were prepared by controlling microwave irradiation time and reaction temperature. Because the reaction vessel was closed, high temperature and pressure were produced in this system. Noticeably, when the temperature of the vessel was naturally cooled to lower than 90 °C, we opened the cover of the reaction vessel and took the samples. The as-prepared colloid samples were diluted for optical characterizations, and precipitated by 2-propanol⁸ for the XRD characterization. TEM samples were prepared by dropping the aqueous CdTe solution onto carbon-coated copper grids with the excess solvent evaporated. The QY of CdTe NC was measured according to the method described in the references.¹⁵ Briefly, rhodamine 6G (ethanol as solvent) was chosen as a reference standard

(QY = 95%), the absorbance for the standard and the CdTe colloid samples at the excitation wavelengths and the fluorescence spectra of the same solutions were measured respectively. The integrated fluorescence intensity (that is, the area of the fluorescence spectrum) from the fully corrected fluorescence spectrum was calculated. Six different concentration solutions of rhodamine 6G and CdTe colloid solutions (absorbance at excitation wavelength < 0.1) were used in the measurements. The areas of the integrated fluorescence intensity vs. absorbance were plotted. The plot obtained should be a straight line with a gradient M , which was used to calculate the quantum yield according to the following equation:

$$\phi_x = \phi_s \left(\frac{M_x}{M_s} \right) \left(\frac{\eta_x}{\eta_s} \right)^2$$

Where the subscripts s and x denote standard (such as rhodamine 6G) and test samples respectively, ϕ is QY, and η is the refractive index of the solvent. It should be noted that the excitation wavelength for measurements of QY was set at the excitonic absorption peak of the CdTe nanocrystal samples in our experiments.

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