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Single-sized colloidal CdTe nanocrystals with strong bandgap photoluminescence†

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One brand-new colloidal ensemble of single-sized CdTe nanocrystals, exhibiting a sharp first excitonic absorption peak at 427 nm and bright bandgap photoluminescence at 427 nm with narrow full width at half maximum (FWHM) of only *ca.* 10 nm, was synthesized in 1-octadecene (ODE) via a non-injection one-pot approach which features high synthetic reproducibility with potential for industrial scale production.

Photoluminescent (PL) colloidal semiconductor quantum dots (QDs) have attracted extensive interest in both fundamental research and technological applications in recent years, due to their unique optical properties such as broad absorption and narrow emission with peak positions tunable with their sizes and bandwidth controllable to a certain degree with their size distribution.¹ Significant progress has been made to achieve various high-quality QDs with narrow size distribution; with a certain control, the size distribution can be as tight as 5%.² Such regular QD ensembles exhibit both homogeneous and inhomogeneous broadening of their bandgap photoluminescence, whereas in theory the narrowest bandwidth can only be achieved with single-sized ensembles where there is little inhomogeneous broadening.³ There is an outstanding need for such single-sized ensembles, namely magic-sized quantum dot (MSQD) ensembles, with bandgap photoemission, for both fundamental photophysical studies of the single-dot properties and many potential applications where narrow emission provides high energy density at a specific wavelength. Recently, with a low-temperature injection method, the sequential growth of CdSe MSQDs was observed exhibiting emission with broad bandwidth.⁴ Also, blue-emitting CdSe MSQDs were claimed to exhibit bandgap emission but with typical full width at half maximum (FWHM) of 17–20 nm which is well beyond the PL FWHM of a single dot.^{3,5} Most recently, we reported three colloidal CdSe MSQD ensembles exhibiting strong bandgap photoemission at room temperature with narrow FWHM on the order of *ca.* 10 nm.⁶ They were synthesized *via* a non-injection one-pot method developed in

our laboratories. Each of the three single-sized ensembles was synthesized in pure form, with cadmium acetate dihydrate (Cd(OAc)₂·2H₂O) and elemental selenium as Cd and Se source compounds respectively, 1-octadecene (ODE) as a reaction medium, and a fatty acid as surface capping ligands all loaded together in one pot at room temperature. The essence of this methodology is the slow release of Cd ions into the reaction medium to react with Se ions reduced by the solvent ODE at a certain temperature. The controlled liberation of Cd ions was accomplished using the mixed Cd salt Cd(OAc)_x(OOC-(CH₂)_n-CH₃)_{2-x}. Our non-injection one-pot approach was well-established to accomplish “molecular synthesis” of semiconductor nanocrystals, namely the high-quality CdSe MSQD ensembles exhibiting bandgap emission.

There is little literature on colloidal CdTe MSQD ensembles exhibiting bandgap PL, although the existence of CdTe MSQDs was suggested based on the presence of sharp bandgap absorption.⁷ The lack of an efficient approach to production of pure CdTe MSQDs exhibiting single-dot optical properties including bandgap photoemission has inspired our efforts towards the synthesis of colloidal CdTe MSQDs with bandgap emission. Based on our successful development of colloidal CdSe MSQDs,⁶ we modified our non-injection methodology for the preparation of colloidal CdTe single-sized ensembles.

Here, we report our recent efforts in the synthesis of one colloidal CdTe MSQD ensemble exhibiting bandgap absorption peaking at *ca.* 427 nm and bandgap emission peaking at *ca.* 427 nm with a narrow FWHM of only *ca.* 10 nm. Accordingly, this PL ensemble is named Family 427. Such a narrow bandwidth has never been reported before for any colloidal CdTe QD ensembles.

The methodology leading to the successful synthesis of the colloidal CdSe MSQDs had to be modified for the synthesis of the colloidal CdTe MSQDs. Direct employment of our well-established non-injection one-pot approach to the CdSe MSQDs, with Se replaced by Te powder, failed to achieve single-sized CdTe ensembles. We believe that this is related to the relatively low reactivity of Te-ODE as compared to that of Se-ODE, namely Te-ODE is relatively inert in ODE in the 120–220 °C temperature range. An alternative Te precursor with higher reactivity, trioctylphosphine telluride (TOPTe), was considered suitable. With the non-injection approach in ODE, the reactivity of TOPTe matches well with that of the Cd precursor, namely Cd(OAc)_x(OOC-CH₂)_n-CH₃)_{2-x}, which liberates Cd ions slowly at a temperature as low as

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† Electronic supplementary information (ESI) available: Experimental synthesis details, PL spectra of as-synthesized CdTe MSQDs such as Family 500 showing our efforts in the synthesis of large MSQDs, sample preparations for characterization such as TEM and XRD, HRTEM images and one 2D DOSY NMR spectrum of CdTe Family 427 showing the size of 1.5 nm. See DOI: 10.1039/b818967f

120 °C. Such perfect matching of the reactivity in combination with the slow release of Cd ions from the Cd precursor ensures the slow growth which is essential for production of one single-sized ensemble exhibiting bandgap emission.

In a typical synthesis (details in supplementary information†), the Cd precursor solution was made *in situ* by mixing 0.4 mmol Cd(OAc)₂·2H₂O and 0.133 mmol alkylcarboxylic acid in 4 g ODE under vacuum at 120 °C for two hours. The Cd precursor solution was then cooled down to *ca.* 60 °C under argon. Freshly prepared 0.05 mmol TOPTe in 0.1 mmol TOP was added into the Cd(OAc)_x(OOC-(CH₂)_n-CH₃)_{2-x} solution in ODE and the resulting mixture was degassed, stirred and heated to 120 °C for one hour. Aliquots were taken during the growth periods with the growth temperature either kept constant or increased slowly to 240 °C. The feed molar ratios for a typical synthesis were 1acid-to-3Cd and 8Cd-to-1Te with a Te concentration of 1.0×10^{-2} mol kg⁻¹. The temporal evolution of the optical properties of the growing nanocrystals was monitored by absorption and emission measurements. This facile non-injection method features high reproducibility and scale-up capability. It does not require swift hot-injection of precursor(s) followed by fast lowering of temperature to separate the nucleation and growth stages in order to obtain a narrow size distribution; these requirements are necessary in the traditional hot-injection method and make it hard to accomplish in large-scale production.

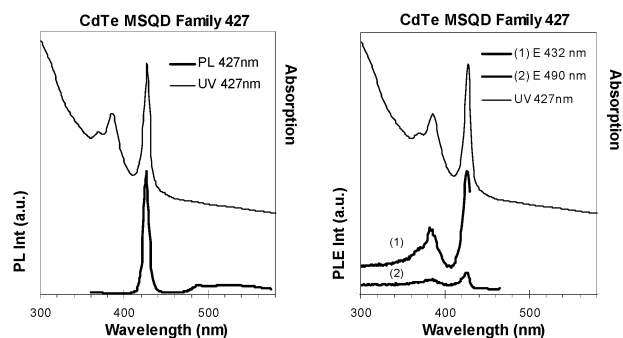


Fig. 1 (Left) Absorption (thin line) and emission (thick line, excitation at 350 nm) spectra of the as-synthesized CdTe MSQD Family 427 dispersed in toluene. (Right) Photoluminescence excitation (PLE) spectra of the MSQD ensemble, with emission at 432 nm (1) and 490 nm (2), together with the absorption spectrum (thin line) for comparison.

Fig. 1 (left) shows the optical properties of the CdTe MSQD ensemble from a typical synthesis batch, with growth at 140 °C. It is obvious that this ensemble exhibits a sharp absorption doublet, together with one narrow and strong bandgap emission. Similar to CdSe MSQDs, the absorption doublet represents two electronic transitions: the lowest at 427 nm is 1S(e)–1S_{3/2}(h) and the second lowest at 386 nm is 1S(e)–2S_{3/2}(h),⁶ thus, the energy separation of the two transitions is *ca.* 308 meV. The FWHM of the bandgap emission is only *ca.* 10 nm, which is approximately one-third of the narrowest width reported so far for the best colloidal CdTe QD ensembles.^{2b,d,8} Moreover, it is noteworthy that the non-resonant Stokes shift (NRSS), the energy difference between the peak positions of the bandgap absorption and

emission, is zero, presumably caused by the large oscillator strength of the exciton.⁹ Such a NRSS also suggests that the CdTe MSQDs possess well-defined structure and relatively perfect surface passivation.

Fig. 1 (right) shows the photoluminescence excitation (PLE) spectra with the emission fixed at 432 nm (Curve 1) and 490 nm (Curve 2). The PLE spectra indicate that it is the bandgap absorption that leads to the narrow band emission centered at 427 nm and the red-side emission with a weak but noticeable bump peaking at *ca.* 490 nm. Accordingly, the former is bandgap emission and the latter is weak trap emission.

Fig. 2 shows the evolution of the optical properties of the as-prepared growing CdTe nanocrystals from two synthetic batches with 1MA(myristic acid)-to-3Cd and 8Cd-to-1Te feed molar ratios and [Te] of 1.0×10^{-2} mol kg⁻¹ (a) and 2.5×10^{-3} mol kg⁻¹ (b). Batch (a) is our typical synthesis. The growth temperature was increased from 120 °C to 240 °C. For Batch (a), the formation of CdTe MSQD Family 427 has started at 120 °C, where Cd carboxylate and TOPTe have become reactive leading to the formation of CdTe MSQDs. Continuous growth at 120 °C promoted the formation of the CdTe MSQDs in a relatively pure form with little traceable

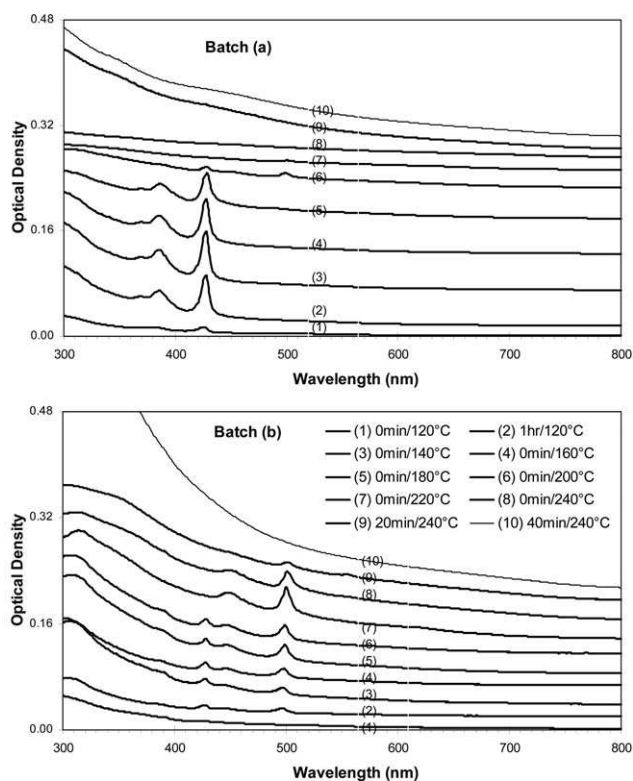


Fig. 2 Temporal and temperature evolution of the optical properties of the as-synthesized nanocrystals from two synthetic batches, with myristic acid (MA) as the capping ligand, a heating rate of 10 °C min⁻¹ from 120 °C to 240 °C, 1MA-to-3Cd and 8Cd-to-1Te feed molar ratios, but [Te] = 1.0×10^{-2} mol kg⁻¹ (a) and 2.5×10^{-3} mol kg⁻¹ (b). The absorption spectra are offset and the spectra from Batch (a) are normalized based on a [Te] feed amount of 2.5×10^{-3} mol kg⁻¹; all the spectra are from 10 µL crude product in 1 mL toluene. Parallel sampling was performed for the two batches with the growth periods and temperature indicated and labelled for Curves 1 to 10.

regular QDs and other MSQD ensembles. It is noteworthy that Family 427 was thermodynamically stable up to 140–150 °C, as long growth periods up to hours preserved the MSQDs very well. However, it decomposed gradually at a temperature higher than 160 °C, and disappeared almost completely at 200 °C, accompanied by the presence of larger MSQD ensembles, *i.e.*, Family 500 and Family 555, with their first excitonic absorptions peaking at *ca.* 500 and 555 nm, respectively.

This report highlights CdTe Family 427, because it is by far the best-developed ensemble in pure form. We have focused some effort on the synthesis of Family 500 and Family 555 in pure form, but have not accomplished this so far with either longer growth periods at 200 °C or at higher growth temperature. Also, we are investigating various synthetic parameters including the nature of the acids, the acid-to-Cd and Cd-to-Te feed molar ratios, and overall reactant concentrations, in order to promote the growth of Family 500 in pure form. One example is shown in Fig. 2b. Batch (b) had the same 1MA-to-3Cd and 8Cd-to-1Te feed molar ratios as Batch (a), but a much lower [Te] concentration of 2.5×10^{-3} mol kg⁻¹. It seems that Batch (b) favoured Family 500 more than Batch (a). The comparison of Fig. 2a and b suggests that a lower concentration favours larger nanocrystals. The effect of the reactant feed concentration on growth kinetics is worthy of attention. Under the same reaction conditions, such as the feed molar ratios and the heating pattern but different reactant feed concentrations, Batch (b) with [Te] of 2.5×10^{-3} mol kg⁻¹ produced Family 500 at *ca.* 220 °C in a relatively pure form, with the presence of a tiny amount of CdTe regular QDs and MSQD Family 555. Family 555 increased in particle number until 20 min of growth at 240 °C, and then decomposed slowly with longer growth periods. Continuing efforts are underway in our laboratories to engineer high-quality pure-form Family 500, Family 555, and so on.

Fig. 3 shows the powder XRD patterns of CdTe MSQD Family 427 and regular wurtzite CdTe QDs. The diffraction peaks are indexed; it seems that the MSQDs have a wurtzite crystal structure, as also suggested by TEM (see supplementary

information†). For CdTe Family 427, the relatively sharp peaks such as (110) and (100) suggest significant aggregation/coalescence along these planes (see supplementary information†). The insert HRTEM image with well-resolved crystal lattice fringes demonstrates the highly crystalline nature of the CdTe MSQDs. The size of CdTe MSQD Family 427 should not be estimated from either TEM or XRD; it has been acknowledged that purification and TEM and XRD sample preparation lead to substantial aggregation/coalescence of such small nanocrystals, as reported for CdSe MSQDs.⁶ Instead, 2D diffusion ordered NMR spectroscopy (DOSY), which is not strongly affected by sample impurities such as ODE and unreacted species and therefore only requires a mild purification process, indicated that the average size of CdTe MSQD Family 427 is *ca.* 1.5 nm, by measuring the diffusion coefficient of the nanocrystals and comparing it with that of methylated β -cyclodextrin (physical size known as 1.4 nm).⁶

In summary, we report the synthesis and characterization of colloidal CdTe MSQDs exhibiting bandgap absorption and emission peaking at 427 nm with a narrow bandwidth of only *ca.* 10 nm FWHM. To the best of our knowledge, the present study is the first regarding the synthesis of CdTe MSQDs exhibiting the narrowest bandgap emission. The CdTe Family 427 was synthesized in pure form *via* a straightforward non-injection one-pot approach, featuring easy handling and large-scale production capability with high synthetic reproducibility. Meanwhile, CdTe MSQD Family 500 and Family 555 with bandgap emission were produced but not in pure form yet, and we are currently focusing our efforts in this direction.

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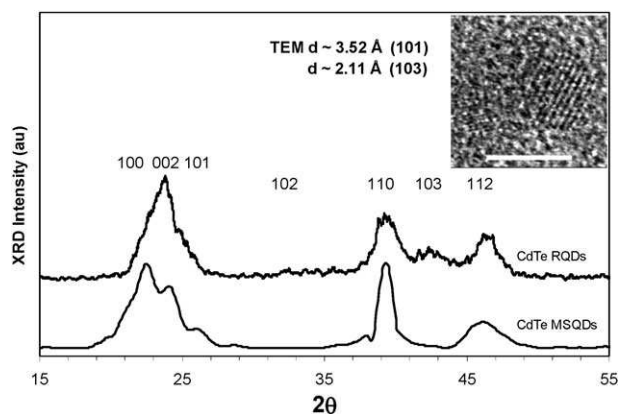


Fig. 3 Powder XRD patterns of regular hexagonal CdTe QDs (top, whose absorption peaks are at *ca.* 685 nm) and CdTe MSQD Family 427 (bottom), with insert of one HRTEM image of the MSQD sample and the scale bar of 5 nm. TEM identified two characteristic d spacings of (101) and (103) planes of wurtzite CdTe.