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Facile Synthesis of Single-sized Colloidal CdTe Assemblies Exhibiting Bright Band Gap Photoemission

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A facile synthetic strategy to prepare single-sized colloidal CdTe assemblies with bright band gap emission is described in this letter. In contrast to traditional approaches, the preparation of trioctylphosphine telluride (TOPTe) was not required for this synthesis, and our approach follows a one-step reaction. The CdTe magic-sized quantum dot (MSQD) assemblies were sequentially grown in this approach, and the thermodynamic equilibrium of CdTe MSQDs sequential growth was proposed.

The synthesis of high-quality colloidal semiconductor quantum dots has been extensively explored for both fundamental research and for developing applications, such as light-emitting diodes (LEDs),[1] biomedical tags,[2] lasers,[3] and solar cells.[4] These potential applications arise from their size-dependent discrete energy level distribution and also their tunable electronic and optical properties. Both research and application efforts demand high-quality quantum dots (QDs) with narrow size distribution and ideally single-sized assemblies.[5] Single-sized assemblies, namely, magic-sized quantum dot (MSQD) assemblies have well-defined size, structure, and composition with precision at the atomic level. These properties provide persistent fixed absorbance signals during synthesis, which do not undergo red shifts.

Numerous research groups have successfully developed various wet-chemistry synthetic routes to fabricate CdTe MSQDs. Chikan et al.[6] have prepared high-quality CdTe MSQDs by a hot-injection method, and Wang et al.[7] have also acquired these structures by a noninjection one-pot approach. However, the preparation of a fresh TOPTe stock solution was a necessary and vital step in both the hot-injection and non-injection one-pot approaches. The synthesis of TOPTe should be performed in a moisture- and oxygen-free environment by purging the experimental setup with argon (or in a glovebox),[8] which has hindered the synthesis and large-scale production of CdTe MSQDs and also the development of their applications. Simultaneously, the development of synthetic approaches to single-sized QDs with band gap photoemission is still very challenging. Although there were reports on CdS, CdSe, and CdTe nanoclusters or MSQD exhibiting narrow and persistent absorption peaks during synthesis, the resulting MSQDs were not in pure form and/or did not exhibit narrow band gap emission but sometimes broad trap emission.[9]

In this letter, we report a facile and controllable approach for preparing CdTe MSQDs. The methodology leading to the successful synthesis of MSQDs was the innovative noninjection one-pot approach. In this facile synthesis, a freshly prepared TOPTe stock solution was not required as a preceding step, but all chemicals were reacted simultaneously in a one-pot reaction. The obtained CdTe MSQDs exhibit strong UV–visible absorption signals at fixed wavelengths and bright band gap emission with a narrow bandwidth of ca. 10 nm. Their sequential growth from smaller structures (about 1.5 nm) to larger structures (about 2.4 nm) increased with temperature. We also investigated their growth kinetics and determined the thermodynamic equilibrium of CdTe MSQD growth.

The CdTe MSQDs were synthesized by sequential addition of 0.400 g of cadmium acetate dihydrate ($Cd(OAc)_2 \cdot 2H_2O$, 99.5%), 0.450 g of stearic acid (SA, 99.5%), 0.026 g of tellurium (Te), 20.000 g of 1-octadecene (ODE, 90%), and 0.75 mL of trioctylphosphine (TOP, 90%) in a three-neck flask at room temperature. The reaction vessel was degassed, and the mixture was stirred and heated to 120 °C for two hours. The growth temperature was increased to 220 °C under a N_2 atmosphere. At different temperatures, UV–vis absorption and PL spectra were recorded for all aliquots, which were collected from the reaction flask and immediately mixed with 2 mL of cold anhydrous toluene (99.8%).

Figure 1 shows the as-synthesized CdTe MSQDs whose sharp band gap absorption at 427 nm. The bright band gap photoluminescence of family 427 nm CdTe MSQDs appeared at 428 nm with narrow full width at half maximum (fwhm). The fwhm is as narrow as 10 nm. The about 1 nm nonresonant Stokes shift (NRSS) indicates the family 427 nm CdTe MSQDs well-defined structure.

The sizes of family 427 nm CdTe MSQDs is about 1.5 nm according to the following eq 1 described in the literature:[10]

$$D = (9.8127 \times 10^{-7})\lambda^3 - (1.7147 \times 10^{-3})\lambda^2 + 1.0064\lambda - 194.84 \tag{1}$$

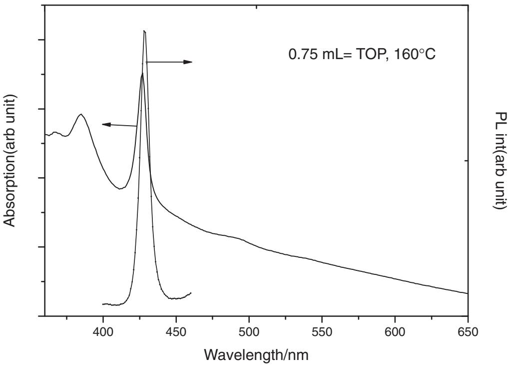

Figure 1. Absorption and emission spectra of CdTe MSQDs in a solution of 20 g of ODE and 0.75 mL of TOP at 160 °C.

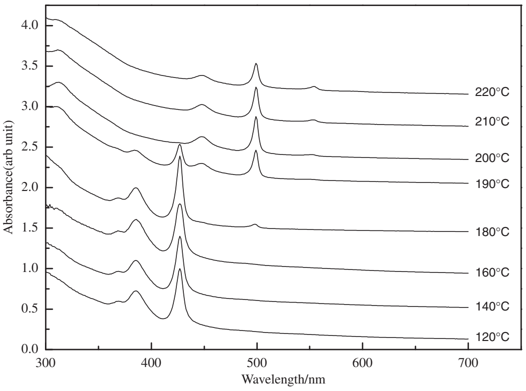

Figure 2. Absorption spectra showing the sequential growth of CdTe MSQDs in a solution of 20 g of ODE and 0.75 mL of TOP.

where D (nm) is the diameter of a given CdTe nanocrystal sample, and λ (nm) is the absorption peak position of the corresponding sample.

The UV–vis absorption spectra of several aliquots were recorded during the synthesis and are shown in Figure 2. Two well-defined peaks appearing at 380 and 426 nm between 120 and 190 °C. Another shoulder appeared simultaneously at longer wavelengths at 180 °C, which developed into a new absorption peak centered at 500 nm. This was followed by another two peaks appearing at 450 and 500 nm at 190 °C. Later, after the first two peaks disappeared, the two new signals became dominant from 200 to 220 °C. Interestingly, as the successors appeared at 550 nm above 200 °C, we predicated that a new family of CdTe MSQDs was being nurtured at the higher temperature.

This sequential growth behavior pointed to a size evolution through different families of increasingly larger CdTe MSQDs. For regular-sized nanocrystals, the spectral positions of the peaks would shift gradually toward longer wavelengths. Also the widths of the signals became broader, because their electronic structures were influenced strongly by the sizes of the nanocrystals.[11] Instead, as shown in Figure 2, the positions of these peaks remained constant over temperature, and only their relative intensities varied. It demonstrated that the nanocrystals obtained were single-sized colloidal CdTe assemblies. For example, according to the eq 1 described above, we found that the size of the family 427 nm CdTe MSQDs was 1.5 nm below 190 °C, and that of family 500 nm was 2.4 nm from 190 to 220 °C. In particular, the peak at the longest wavelength exhibited increasing intensity with respect to those at shorter wavelengths, which eventually disappeared. This indicated that the average size of CdTe MSQDs within each family still remained constant, whereas the relative population of the various families changed in favor of the MSQD with the largest size.

From the growth of these different families of CdTe MSQDs with increasing temperature we proposed equations describing the possible thermodynamic equilibrium driving the continuous growth of the CdTe MSQDs. The picture could be imagined by considering that the equilibrium occurred in solution as described by eqs 2–4:

$$\text{Cd precursor} + \text{Te precursor} \rightarrow \text{(Cd–Te) (soluble)} \quad (2)$$

$$\text{Cd precursor} + \text{Te precursor} \rightleftharpoons (\text{CdTe})_m \text{ (solid)} \quad (3)$$

$$(\text{CdTe})_m \text{ (solid)} \rightleftharpoons (\text{CdTe})_n \text{ (solid)} \ (m < n) \quad (4)$$

Equation 2 describes the precursors that formed the (CdTe) monomer.[9c,12,13] Elemental Te, as the Te source, formed the ODE/Te and TOPTe precursor in ODE and TOP. The Cd source, $Cd(OAc)_2 \cdot 2H_2O$ reacted with MA or TOP to form the Cd precursor (such as Cd(OAc)(MA) or a Cd–P complex).[14]

Equation 3 represents the thermodynamic equilibrium between the monomers (such as soluble CdTe) in the solution phase and the nuclei (particularly solid $(\text{CdTe})_m$) in the solid phase. This formula also denotes the thermodynamic equilibrium of the nucleation and dissolution processes. The continuous nucleation led to the formation of MSQDs.

Equation 4 represents the thermodynamic equilibrium between the smaller and larger CdTe MSQDs. In polar media (as observed when TOP was present in solution), the size evolution of the CdTe MSQDs could result from competition between the attachment and detachment of single atoms to its surface.[9b] As media, TOP increased the polarity of the solution, which promoted an equilibrium imbalance toward the right. Thus, once the CdTe MSQDs had grown to a critical size, they became so stable that no atoms could detach from the MSQDs so that they could grow to a larger size. However, if the sizes of CdTe MSQDs were smaller than this "critical size," CdTe MSQDs would shrink to form even smaller MSQDs or magic-sized nuclei. No intermediates were observed between these two magic sizes. If CdTe MSQDs were considered ideally as units similar to conventional quantum dots, CdTe MSQD sequential growth described by eq 4, would also obey an Oswald-ripening process.[15]

An experiment that supports our equilibrium was carried out. A synthesis of CdTe MSQDs was performed, the sample was redissolved in the same mixture of surfactants used for the synthesis of MSQDs, and the mixture was heated at 180 °C. The conditions were similar to those used for the synthesis of MSQDs but no free monomers. The absorption spectra on aliquots taken from this mixture did not show any shift in positions, indicating no further evolution in the size of MSQDs. The result indicated that MSQDs were stable and that no shrinking or ripening occurred. That was to say that no aggregation occurred among smaller MSQDs to form the larger. The experiments support our thermodynamic equilibrium of CdTe MSQDs sequential growth.

Transmission electron microscopy (TEM) analysis on aliquots extracted from the growth solution revealed that these MSQDs have roughly spherical shapes and that they are not aggregated. However, more detailed analysis about average sizes and size distributions were strongly limited by the extremely small sizes of such MSQDs.

In conclusion, we have introduced a simple and reproducible strategy to control the sequential growth of CdTe MSQDs. The obtained CdTe MSQDs exhibit strong absorption signals and bright band gap emission with a narrow bandwidth. A freshly prepared TOPTe stock solution, which was vital for traditional CdTe synthetic techniques, was no longer required for this approach. Therefore, this one-step reaction was greatly simplified. This facile synthetic method yielded continuous CdTe MSQD growth with increasing temperature. The properties of the MSQDs could be tuned by simply adjusting the growth temperature. Their sequential growth from smaller structures to larger structures increased with temperature. A thermodynamic equilibrium was proposed to explain the sequential growth of CdTe MSQDs in solution. Our research may advance colloidal semiconductor quantum dot synthesis toward industrialization and provide the impetus for the large-scale application of these nanocrystals.

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