

Synthesis of Aqueous CdTe/CdS/ZnS Core/shell/shell Quantum Dots by a Chemical Aerosol Flow Method

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Abstract This work described a continuous method to synthesize CdTe/CdS/ZnS core/shell/shell quantum dots. In an integrated system by flawlessly combining the chemical aerosol flow system working at high temperature (200–300°C) to generate CdTe/CdS intermediate products and an additional heat-up setup at relatively low temperature to overcoat the ZnS shells, the CdTe/CdS/ZnS multi-shell structures were realized. The as-synthesized CdTe/CdS/ZnS core/shell/shell quantum dots are characterized by photoluminescence spectra, X-ray diffraction (XRD), energy-dispersive X-ray spectra (EDS), transmission electron microscopy (TEM), and high-resolution transmission electron microscopy (HRTEM). Fluorescence and XRD results confirm that the obtained quantum dots have a core/shell/shell structure. It shows the highest quantum yield above 45% when compared to the rhodamine 6G. The core/shell/shell QDs were more stable via the oxidation experiment by H₂O₂.

Keywords Chemical aerosol flow · CdTe/CdS/ZnS · Aqueous · Core–shell · Quantum dot

Introduction

In recent years, colloidal semiconductor nanocrystals or quantum dots (QDs) have attracted great scientific and technological interest due to their unique size-dependent properties [1–3]. By changing the size or composition of the QDs, their optical properties can be easily tuned to suit for various requirement [4, 5]. In the biological labeling especially [6, 7], numerous successful efforts have been made by using the QDs as the fluorescence agent. The organometallic synthesis of CdSe and CdTe QDs provides a good method to synthesize high quality QDs, which were synthesized using high boiling point solvents such as trioctylphosphine (TOP), trioctylphosphine oxide (TOPO) and so on. However, they were hydrophobic and need time consuming operation to convert into water soluble dispersions. The high toxicity of precursors and high price also limit their wide application. Aqueous colloid approaches become more attractive because they are much cheaper and suitable for biological studies.

Aqueous CdTe [CdTe (aq)] QDs with high fluorescence can be synthesized using a metal salt and NaHTe with mercaptan acid as the stabilize agent [8, 9]. It provides a simple way to generate aqueous QDs. But several hours to several days' reaction time is needed. Chemical aerosol flow (CAF) synthesis of QDs [10] was first published by Suslick et al. and has been widely used to generate many kinds of nanoparticles, including mesoporous silica [11, 12], mesoporous carbon [13, 14], semiconductor nanocrystals [10, 15, 16], and other nanomaterials [17–19]. It provides a simple and fast way to continuously synthesize

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nanoparticles. In our previous work, we used the modified CAF method to generate CdTe/CdS core/shell quantum dots in several seconds [20]. The QDs showed high stability, high quantum yield and have large scale. But for bioapplication, the cadmium-based QDs would release toxic Cd^{2+} when used in the cell or tissues [21]. Capping a shell of ZnS not only can decrease the toxicity of cadmium but also can increase the quantum yield [21], forming a core/shell or core/shell/shell structure with CdTe cores inside and ZnS shells outside is a good method to solve this problem.

With successive ionic layer adsorption and reaction (SILAR) [22] method, high quality of core/shell and multishell quantum dots can be synthesized [23–27] in organic media. Unfortunately, this method was complex, and it is hard to be carried out in aqueous solution. Synthesis of core/shell QDs especially core/shell/shell QDs in aqueous solution is a hard work as the surface stabilizers were fragile and sensitive to the environment. Many efforts have been made to obtain high quality core/shell in water [28]; however, only a few works pay attention to the synthesis of the CdTe/CdS/ZnS core/shell/shell quantum dots. Because of the large lattice mismatch between CdTe and ZnS (16.4%), it is hard to epitaxially grow ZnS shells on CdTe cores. A shell of CdS between CdTe and ZnS can work as a transition shell because the band gap and lattice contact of CdS is just between that of CdTe and ZnS. Using microwave irradiation method, high quantum yield CdTe/CdS/ZnS quantum dots can be obtained [29], but multistep was needed, the process was extremely troublesome, and the yield was low. So developing a low cost, simple, continuous way for preparing hydrophilic QDs with a shell of ZnS capped is an urgent need.

Here, we investigated a facial way to directly and continuously synthesize the CdTe/CdS/ZnS core/shell/shell QDs using a modified chemical aerosol flow method. In this integrated synthesis system, the Cd, Te precursors were first carried into the chemical aerosol flow system to result CdTe/CdS core/shell quantum dots. Then, they were brought out into a vessel containing Zn, S precursor solution for coating a shell of ZnS. The obtained core/shell/shell QDs were characterized by X-ray powder diffraction (XRD), transmission electron microscopy (TEM), energy-dispersive X-ray spectrometer (EDS), and PL spectra to confirm the core/shell/shell structure.

Experimental Section

Chemicals

$\text{Cd}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$, $\text{Zn}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$, NaOH, NaBH_4 (99%), tellurium powder (99.8%), thiourea (97%), and 3-mercaptopropionic acid (MPA, 99%) were purchased from Beijing

Chemical Reagent Co., Ltd. All chemicals were used without additional purification. Distilled water was used for preparation of all aqueous solutions.

Precursor Preparation

Briefly, 0.5 mmol Te powder and 2 mmol NaBH_4 were mixed in a tube, and then 2 mL water was added. The reaction mixture was heated at 80°C for 30 min to get a pink NaHTe solution. The NaHTe solution was stored at 4°C for further use. One millimole $\text{Cd}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$, 2.4 mmol MPA, and 100 mL water were mixed, and the pH of the solution was adjusted to 11.5. Subsequently, the NaHTe solution was injected into the mixture, and a clear deep red solution was obtained.

One millimole $\text{Zn}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$, 2.4 mmol MPA, and 100 mL water were mixed, and the pH was adjusted to 11.5. After stirring for 30 min, 2 mmol thiourea was added.

Synthesis of CdTe/CdS/ZnS

In a typical synthetic procedure, the stock solution containing Cd(MPA) complex and NaHTe was carefully transferred to the equipment and nebulized into microdroplets by a 1.7-MHz ultrasonic generator (Yuyue 402AI, Shanghai Yuyue Co. Ltd). The mist was carried to the furnace by a N_2 flow at designed rate through a quartz tube located in a tube furnace kept at appointed temperature, and in the furnace, the solvent evaporated, then the reaction took place, and subsequently CdTe/CdS core/shell quantum dots were obtained; in the following collection and further reaction stage, the synthesized CdTe/CdS QDs were pumped into a three-neck flask containing the Zn and S precursor stock solution with continuous stirring and kept at about 80°C , capping a shell of ZnS was realized in this stage.

Characterization Techniques

Fluorescence spectra were measured at room temperature using a FL-4600 spectrofluorimeter (HITACHI), Powder X-ray diffraction (XRD) measurements were performed on a D8 Focus XRD system (Bruker), and samples for XRD were prepared by dropping a colloidal solution of QDs in water on a glass sheet. EDS data were obtained on a scanning electron microscope S-4300 (HITACHI) system.

Cellular Imaging

Chinese hamster ovary (CHO) cells were grown as a monolayer in a humidified incubator in a 95% air/5% CO_2 atmosphere at 37°C in a dish containing DMEM

supplemented with 10% (v/v) heat-inactivated fetal bovine serum, 100 IU/mL penicillin, and 100 IU/mL streptomycin. The CHO cells were detached mechanically and adjusted to the required concentration of viable cells as determined by counting in a hemocytometer. The CHO cells were plated 24 h before the start of the experiment in chamber slides at a density of 5×10^3 cell/cm². One milliliter QDs was added and incubated with the CHO cells for 30 min. The slides were washed twice with PBS and then examined with a LEICA-Sp5 confocal microscope.

Results and Discussion

As schemed in Fig. 1, CdTe/CdS/ZnS core/shell/shell quantum dots were fabricated in this integrated chemical aerosol flow apparatus through the epitaxial growth stage. In the nebulizer apparatus, the stock solution containing Cd(MPA) complex and NaHTe was misted to microdroplets, carried into the furnace by the 1.5 L/min N₂ flow. CdTe/CdS core/shell quantum dots were directly formed in the furnace. Then, at the end of the furnace, the CdTe/CdS QDs flowed into in a three-neck flask that was kept at 80°C, capping a shell of ZnS was carried out. About 45 min later, CdTe/CdS/ZnS core/shell/shell quantum dots were harvested.

In our experiment, the intermediate CdTe/CdS QDs synthesized show great stability due to the good crystallization at high reaction temperature, and the in situ

synthesized CdS shells on CdTe cores can play as a buffer layer to further epitaxially grow ZnS shells. So with this facile method, high quality of CdTe/CdS/ZnS core/shell/shell QDs can be synthesized.

As known, in the synthesis of QDs, especially that with core/shell/shell structure, large-scale production is difficult for many methods mainly due to its difficulty to ensure the same temperature and homogeneous mixing in the large volume of solution, which have a great influence on the monodispersity of the nanocrystals. Up to now, large-scale synthesis is still a challenge [23]. Here, in our modified integrated apparatus, the continuous synthesis method makes it possible to realize large-scale synthesis of QDs with core/shell/shell structure. In our experiment, the rate of production can reach as high as 0.1 g/h. As the currently used quartz tube in the furnace only has a diameter of 30 mm, the flow rate is 1.5 L/min. It is easy to improve the production rate using a larger diameter tube or increasing the flow rate. Owing to its continuity, as much core/shell/shell QDs can be synthesized.

CdTe/CdS/ZnS core/shell/shell QDs with different peak position of photoluminescence (PL) can be obtained by changing flow rate and temperature, consistent with our previous description for synthesizing CdTe/CdS QDs [20]. As shown in Fig. 2a, with a flow rate of 1.5 L/min and temperature of 200, 225, and 250°C, CdTe/CdS/ZnS core/shell/shell QDs with PL peak of 525, 554, and 567 nm were synthesized. The flow rates also had an influence on the peak position of PL. With increased flow rate, the PL would be blue-shifted (Data not shown), attributed to shortened reaction time. All the synthesized CdTe/CdS/ZnS core/shell/shell QDs showed high fluorescence (Fig. 2b), whose quantum yields were as high as 45%.

In order to confirm the core/shell/shell structure of the synthesized QDs, several control experiments were carried out, as shown in Table 1 and Fig. 3. For control experiment, the Zn and/or S precursors was absent in the part for ZnS coating. As can be seen, when the Zn precursor and S precursor were added in the three-neck flask simultaneously, the obtained QDs showed a fluorescence peak at

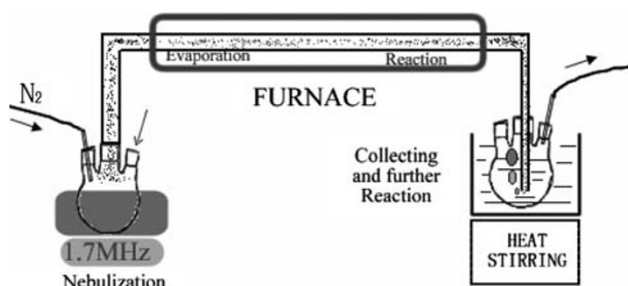


Fig. 1 Apparatus to synthesize the CdTe/CdS/ZnS core/shell/shell quantum dots

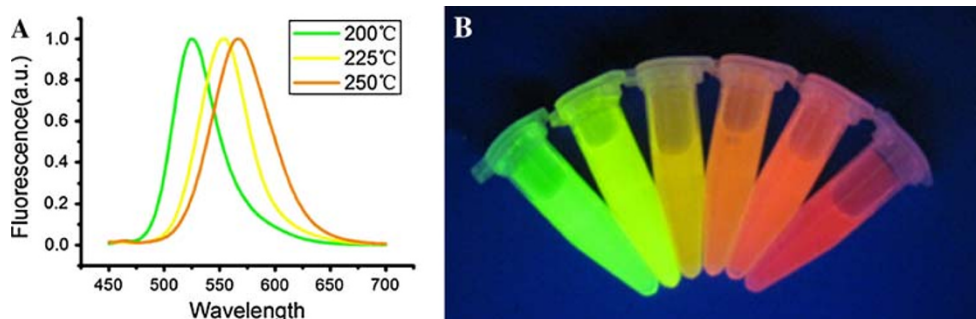
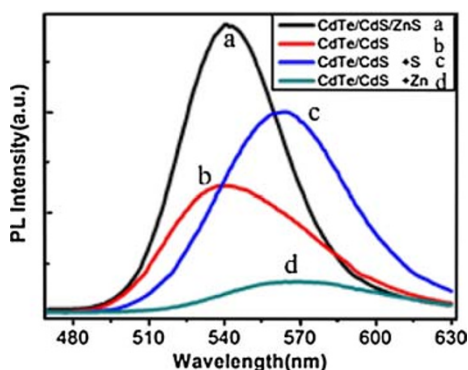


Fig. 2 PL spectra of QDs synthesized at different temperature (a). Image of CdTe/CdS/ZnS QDs solution under ultraviolet light

Table 1 Control experiments to confirm the core/shell/shell structure of synthesized QDs

Precursor	A	B	C	D
Zn(MPA) complex	✓	✓	–	–
Thiourea	✓	–	✓	–
Fluorescence wavelength (nm)	541	573	563	541

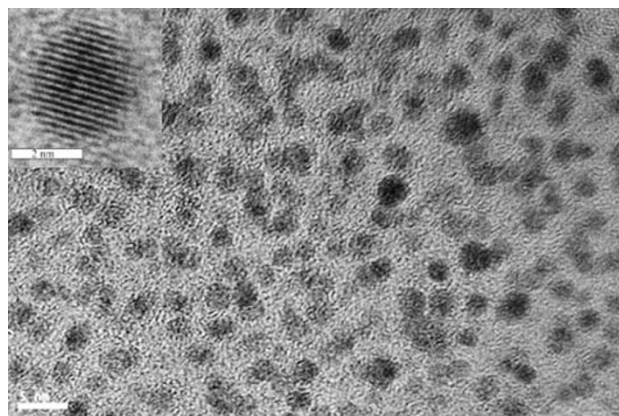
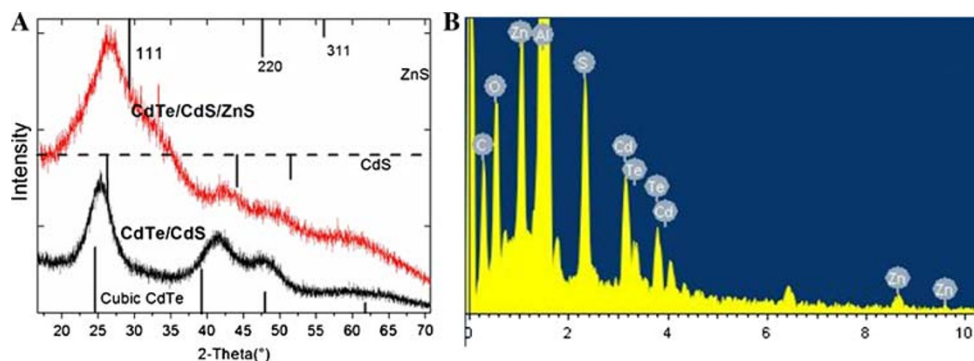
Right character “✓” means they have the precursor in the second part for ZnS coating. While “–” means no precursor was added

**Fig. 3** Fluorescence spectra of different kinds of core/shell QDs

541 nm with high fluorescence intensity. QDs with a weaker fluorescent intensity were obtained when Zn and S precursors were both absent. The results reveal that overcoating a shell of ZnS on the CdTe/CdS greatly enhances the fluorescence intensity. Similarly, when only S precursor was added, the resultant QDs showed a red-shifted PL, because a thicker CdS shell was formed on the outer shell of the QDs. As we know, the CdTe/CdS core/shell QDs have more Cd atoms on its surface. However, when only Zn precursor was added, an aggregated agglomeration with a very weak red fluorescence was obtained. It is deduced that due to the coordination between the Zn^{2+} and QDs, the Zn (MPA) complex acts as a flocculant to aggregate the synthesized QDs in water at the elevated temperature. From the results, we can clearly see that the coexisted Zn

and S precursor in the second part can form a shell of ZnS on the outside of CdTe/CdS QDs.

The core/shell/shell structure was further confirmed by XRD (Fig. 4a). In the XRD pattern, three peak including (111), (220), and (311) can be clearly seen, which corresponds to the cubic CdTe/CdS and CdTe/CdS/ZnS quantum dots. Figure 4a shows that the scattering peaks of CdTe/CdS quantum dots were just between the bulk cubic CdTe and bulk CdS. This is because of the existence of CdS shell on the edge of CdTe. For the CdTe/CdS/ZnS QDs, the diffraction patterns shift to higher angles due to the growth of ZnS shells. The composition of CdTe/CdS/ZnS QDs was also investigated by energy-dispersive X-ray spectroscopy (EDS) (Fig. 4b). In the EDS pattern, the presence of Zn and S was clearly confirmed, and the atomic ratio of S:Zn: Cd:Te was calculated to be 2.84:1.64:1.38:1. The carbon and oxygen peak showed in the EDS pattern were corresponding to the capping agent of MPA. The TEM and HRTEM of CdTe/CdS/ZnS QDs synthesized with temperature of 200°C and flow rate of 1.5 L/min were shown in Fig. 5. We can see that the CdTe/CdS/ZnS QDs have a narrow size distribution. The average diameter of the QDs is about 2.5 nm. The existence of lattice planes on

**Fig. 5** TEM image for CdTe/CdS/ZnS core/shell/shell quantum dots prepared at 200°C. Inset is the HRTEM image**Fig. 4** a XRD patterns of CdTe/CdS and CdTe/CdS/ZnS and b EDS of CdTe/CdS/ZnS core/shell/shell QDs

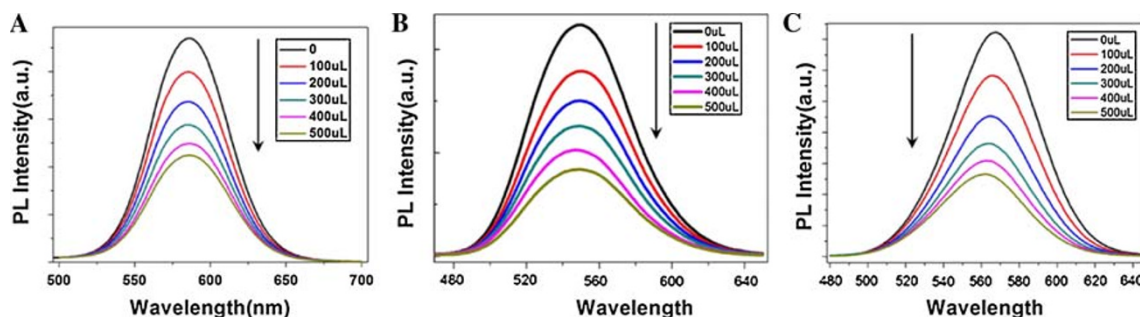


Fig. 6 The fluorescence intensity change of different QDs when added various volumes of 0.03% H_2O_2 solution. **a** CdTe/CdS/ZnS, **b** CdTe/CdS, **c** CdTe(aq)

the HRTEM confirms the good crystallinity of the CdTe/CdS/ZnS QDs.

It was expected that after coating with a ZnS shell, the CdTe/CdS/ZnS core/shell/shell QDs would be more stable, less toxic and have higher quantum efficiency compared to CdTe/CdS quantum dots and CdTe quantum dots. In order to investigate the difference between the three kinds of QDs, CdTe/CdS/ZnS, CdTe/CdS, and CdTe (aq), H_2O_2 was used as an oxidizing agent to examine their anti-oxidation ability via detecting the change of fluorescence spectra (Fig. 6). It is known that when reacted with an oxidizer such as H_2O_2 , a blue shift would be observed due to the oxidation of surface atoms [30, 31]. But if the QDs were core/shell structure, the blue shift would not occur because the thick shell can prevent the oxidation of cores, which determines the PL peak position. Different volumes of

0.03% H_2O_2 were added to equal amount of three kinds of QDs (4 mL). From the results (Fig. 6), we can clearly see that when H_2O_2 solution was added, the fluorescence intensities were all decreased and gave an approximate linear change. The difference is that the PL peak position was almost not changed when ZnS shells existed for CdTe/CdS/ZnS, while there is obviously a blue shift of about 6 nm for CdTe (aq) QDs. Similarly, for the CdTe/CdS QDs, a smaller blue shift of about 2 nm can be seen. This result clearly shows that the CdTe/CdS via CAF has enhanced anti-oxidation ability compared with CdTe (aq). While overcoating ZnS shells on the CdTe/CdS QDs can further enhance this effect. When reacted with H_2O_2 , the surface atoms of CdTe can be oxidized to CdTeO_3 or TeO_2 [31, 32], which causes the decrease in CdTe QDs size and further leads to the blue shift of fluorescence peak. The

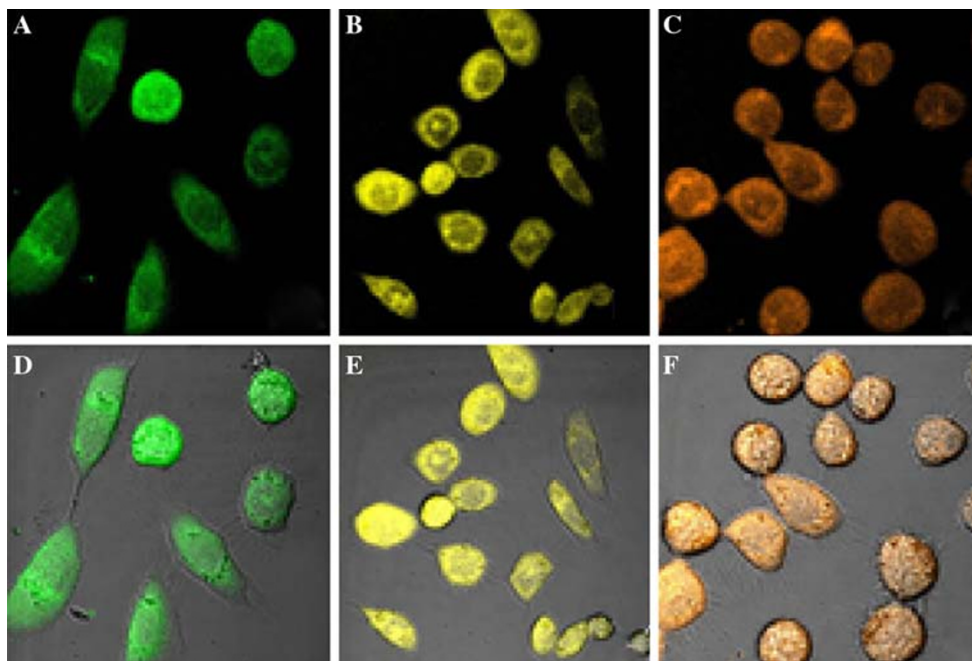


Fig. 7 Labeled CHO (Chinese hamster ovary) with CdTe/CdS/ZnS quantum dots, **a–c** are the fluorescent images of cells. **d–f** are the corresponding co-situated picture of cells and fluorescence

existence of CdS can weaken this effect, while ZnS shells can prevent the blue shift. These results reflect that the overcoating of ZnS shells can greatly enhance its anti-oxide ability and stability.

With ZnS shells on the CdTe/CdS QDs, its toxicity can be greatly decreased. It is more suitable to use it in biological applications such as cellular imaging. To confirm that the QDs can label the cells, we chose three kinds of CdTe/CdS/ZnS QDs (brown, yellow, and green) and added them into the Chinese hamster ovary (CHO) cells. After 30 min incubation, the intracellular distribution of CdTe/CdS/ZnS QDs was observed by confocal microscopy. It can be clearly seen that the QDs penetrate into the living cells and exhibit bright fluorescence (Fig. 7). The distribution of all three kinds of QDs is in the cytoplasm and the nucleus. This observation demonstrates that QDs are gradually transported inside the cytoplasm and eventually to the nucleus. On the basis of these fluorescence images, we consider that the CHO cells are efficiently labeled with QDs and can display multicolor images.

Conclusion

In summary, CdTe/CdS/ZnS core/shell/shell quantum dots were synthesized by chemical aerosol flow method in a continuous system. This method can provide a simple, ultrafast, and continuous way to prepare core/shell/shell quantum dots. Importantly, compared with CdTe QDs prepared directly in aqueous solution and CdTe/CdS core/shell QDs synthesized by chemical aerosol flow method, the CdTe/CdS/ZnS core/shell/shell QDs have enhanced anti-oxide ability and stability. This is significant for further application of aqueous QDs. We also prove that the QDs can achieve multicolor label in living cells. Benefiting from their reduced toxicity, enhanced stability, and increased PLQY, this kind of core/shell/shell QDs has potential for future in vivo fluorescent imaging.

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