



Hydrothermal synthesis of high-quality type-II CdTe/CdSe quantum dots with near-infrared fluorescence

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ABSTRACT

A simple hydrothermal method is developed for the synthesis of high-quality, water-soluble, and near-infrared (NIR)-emitting type-II core/shell CdTe/CdSe quantum dots (QDs) by employing thiol-capped CdTe QDs as core templates and CdCl₂ and Na₂SeO₃ as shell precursors. Compared with the original CdTe core QDs, the core/shell CdTe/CdSe QDs exhibit an obvious red-shifted emission, whose color can be tuned between visible and NIR regions (620–740 nm) by controlling the thickness of the CdSe shell. The photoluminescence quantum yield (PL QY) of CdTe/CdSe QDs with an optimized thickness of the CdSe shell can reach up to 44.2% without any post-preparative treatment. Through a thorough study of the core/shell structure by high-resolution transmission electron microscopy (HRTEM), ultraviolet–visible (UV–vis) absorption spectra, fluorescence spectra, X-ray powder diffraction (XRD) and X-ray photoelectron spectroscopy (XPS), the as-prepared CdTe/CdSe QDs demonstrate good monodispersity, hardened lattice structure and excellent photostability, offering a great potential for biological application.

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1. Introduction

Semiconductor nanocrystals (or quantum dots, QDs), as a new class of very promising materials, have been widely used in biological fields owing to their unique optical properties during the past decade [1–3]. In this area, the near-infrared (NIR) QDs with emission wavelengths between 650 and 900 nm are of particular interest to researchers because the tissue auto-fluorescence and absorption are much more reduced compared to those in other ranges [4,5].

Until now, there have been two strategies to fabricate NIR-emitting QDs. One is to select suitable semiconductor materials with bulk band gap energy lower than the NIR energy to prepare mono-nuclear or alloyed semiconductor nanocrystals by controlling their growth sizes or structure compositions, respectively, such as PbSe, InAs, HgTe, CdHgTe, CdTeS and CdSeTe [6–11]. The other is to fabricate core/shell QDs. Most recently, the synthesis of core/shell (type-I and type-II) NIR-emitting QDs has become an active field; not only do core/shell heterostructure QDs effectively reduce surface defects and nonradioactive decay, but the emission wavelengths of QDs could also be tuned by their sizes and compositions [12–15]. Compared with type-I core/shell QDs, type-II nanocrystals, with the valence band edge or the conduction band edge of the shell material located in the band gap of the core, have many novel prop-

erties, such as the red-shift of the emission and a longer decay lifetime due to the formation of an indirect excitation [12–15]. Thus far, there have been reported many type-II systems, including CdTe/CdSe, ZnTe/CdTe (CdSe, CdS), CdSe/ZnTe and ZnSe/CdS [13–18], and most of these QDs are prepared through organometallic routes. However, for biological applications, additional surface modification is required to disperse the QDs in aqueous phase, for example, wrapping an amphiphilic polymer around the QDs or exchanging original hydrophobic ligands with thiols. Moreover, these further processes often lead to the increment of QD size and the as-prepared QDs usually have a significant decrease of photoluminescence quantum yield (PL QY). As a result, direct aqueous synthesis of type-II core/shell NIR-emitting QDs has become an attractive and challenging task in QD research. Recently, Zhu et al. have obtained NIR-emitting CdTe/CdSe QDs in aqueous solution, and then the as-prepared QDs were applied for ultrasensitive Cu²⁺ sensing [19]. Subsequently, Yan and his co-workers successfully synthesized water-soluble L-cysteine-capped CdTe/CdSe QDs with NIR fluorescence by successive ion-layer adsorption and reaction (SILAR) for bioimaging applications [20]. However, their methods are considerably complicated, because they are time-consuming and the PL QYs of the QDs are much lower than those synthesized in organic phase. Therefore, it is desirable to develop a facile method for the preparation of high-quality type-II core/shell NIR-emitting QDs in aqueous medium.

Here we present a layer-by-layer colloidal epitaxial growth of 3-mercaptopropionic acid (MPA)-capped CdTe/CdSe type-II

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core/shell QDs in aqueous solution via hydrothermal technique by using preformed MPA-capped CdTe QDs as core templates and CdCl₂ and Na₂SeO₃ as shell precursors. A CdSe shell is formed on the CdTe core through the reduction of Na₂SeO₃ by NaBH₄. With the increase of the thickness of the CdSe shell on the CdTe core QDs, the fluorescence emissions of the prepared MPA-capped CdTe/CdSe QDs are tunable between 620 and 740 nm. The as-prepared core/shell QDs show a PL QY as high as 44.2% with three layers of CdSe shells, which is much better than previous reports [19,20]. Optical and physical properties have been studied by high-resolution transmission electron microscopy (HRTEM), ultraviolet–visible (UV–vis) absorption spectra, fluorescence spectra, X-ray powder diffraction (XRD) and X-ray photoelectron spectroscopy (XPS). The resulting NIR-emitting QDs are expected to have a great potential for biological application.

2. Materials and methods

2.1. Reagents

CdCl₂·2.5H₂O (99.0%), NaBH₄ (96%) and Na₂SeO₃ (97%) were obtained from Tianjin Chemical Reagent Plant (Tianjin, China), while 3-mercaptopropionic acid (MPA, 99%) and Indocyanine green (IR-125) were purchased from Alfa Aesar (Ward Hill, USA) and TCI (Tokyo, Japan), respectively. All chemicals concerned were of analytical grade or the highest purity available, thus being used as received without being further purified. Besides, all the solutions were prepared with double deionized water (DDW).

2.2. Apparatus

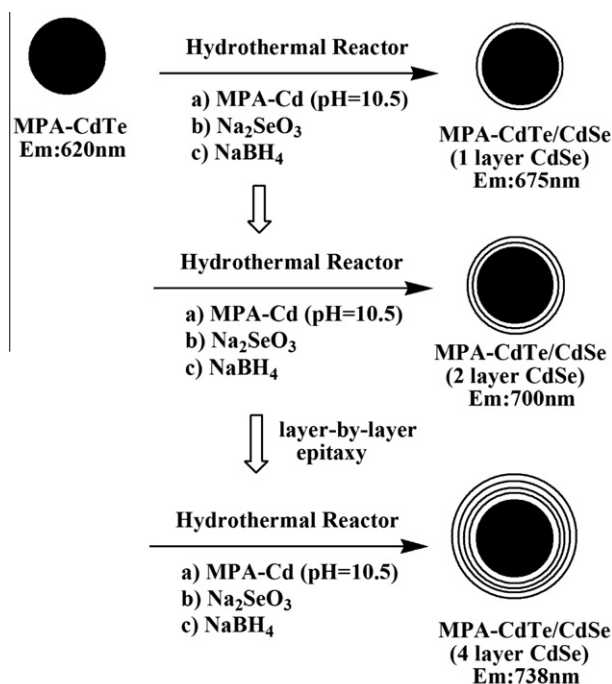
The absorption spectra were acquired on the Nicolet Evolution 300 UV–vis spectrometer coupled with a 1.00 cm quartz cell. Fluorescence measurements of the QDs were performed on a Perkin Elmer Model LS-55 luminescence spectrometer under excitation of 420 nm equipped with a 20 kW xenon discharge lamp as a light source. Measurements of hydrodynamic diameters of the QDs in aqueous solution were acquired on a Zetasizer Nano-ZS90. XRD patterns were taken on a Rigaku D/MAX-RB diffractometer with Cu K α radiation ($\lambda = 0.15406$ nm). XPS data were measured using VG Multilab 2000 X-ray photoelectron spectrometer. HRTEM images were acquired using a JEM-2010FEF transmission electron microscope operating at an acceleration voltage of 200 kV. The PL QY of the as-prepared QDs was determined through comparison using an IR-125 standard organic dye with the excitation wavelength set at 715 nm.

2.3. Synthesis of CdTe QDs

The CdTe core QDs were synthesized in aqueous solution using the method described previously with slight modifications [21]. Briefly, 1.0×10^{-3} mol of CdCl₂·2.5H₂O was dissolved in 50 mL of DDW, and 1.5×10^{-3} mol of MPA was added under stirring, followed by adjusting the pH to 10.5 by putting in dropwise 1.0 mol L^{-1} NaOH solution. Then, trisodium citrate dihydrate (50 mg), Na₂TeO₃ (0.01 mol L^{-1} , 2 mL), and sodium borohydride (NaBH₄, 20 mg) were added with stirring. When the color of the solution turned green, the resulting solution mixture was transferred to a reaction flask, and refluxed at 100 °C in the open air until the particles reached the desired dimension.

2.4. Synthesis and purification of CdTe/CdSe core/shell QDs

Scheme 1 shows the preparation of CdTe/CdSe core/shell QDs with a multishell nanostructure. For the growth of a monolayer



Scheme 1. Layer-by-layer growth of CdTe/CdSe core/shell QDs with near-infrared fluorescence.

(ML) CdSe shell, the precursor solution (1 mL) containing Cd²⁺ (2.0×10^{-6} mol) and MPA (3.0×10^{-6} mol) and Na₂SeO₃ (0.01 mol L^{-1} , 0.1 mL), NaBH₄ (0.001 g) were added into the crude CdTe core solution under continuous stirring, respectively. Then, the mixture was transferred into a hydrothermal reactor and maintained at 150 °C for 45 min. The first layer of CdSe shell came into being with the method described above. Repeating the above procedure resulted in CdTe/CdSe core/shell QDs with increasing shell layers. Finally, the obtained crude products were precipitated for three times by ethanol with centrifugation at 8000 rpm for 5 min and the resultant precipitates were dried at room temperature in vacuum for XRD and XPS characterization.

3. Results and discussion

High-quality NIR-emitting CdTe/CdSe QDs were synthesized through hydrothermal technique by adding a mixture of dissolved shell precursors into the original CdTe core solution. Here NaHSe or KHSe was replaced by an air-stable and commercial Se source, Na₂SeO₃, which was reduced by NaBH₄ in ambient conditions to generate Se²⁻ [22]. Thus the reaction could be carried out in an open air environment, which simplifies operations and saves time. The increased temperature in autoclaves accelerated the growth of nanocrystals accompanied with largely enhancing the synthetic efficiency and improving the PL QY effectively [23]. It is worth mentioning that the reaction temperature and time are two important factors in the formation of the CdSe shell. As previously reported, high temperature or longer reaction time can cause the hydrolysis of thiols and facilitate the formation of alloyed QDs with a decrease of PL QY [10,24]. In addition, sequential injection of precursors in a series of small addition rather than one large addition further facilitated heterogeneous nucleation and the growth of CdSe shell on the CdTe core QDs [19]. The PL QY of as-prepared core/shell QDs can reach as high as 44.2%, which is much higher than some other NIR-emitting QDs synthesized in aqueous phase [19,20].

Fig. 1 provides the HRTEM images of the MPA-CdTe core QDs and MPA-CdTe/CdSe (3ML) core/shell QDs. It is known that HRTEM can make a distinction between crystalline and amorphous mate-

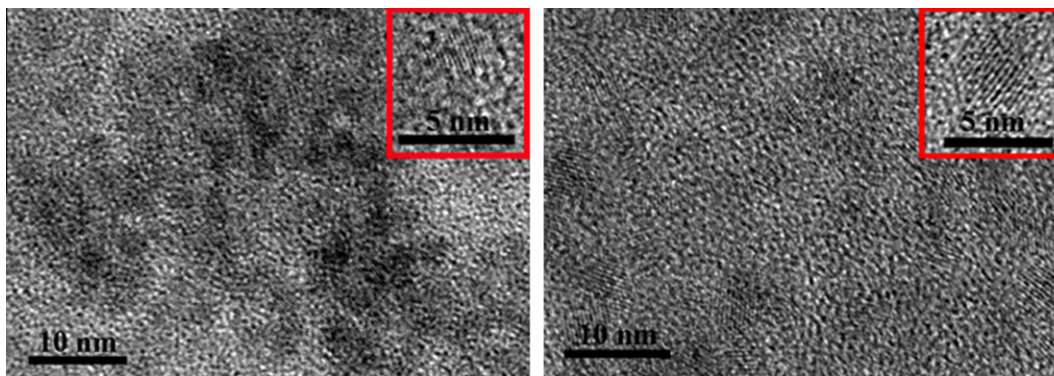


Fig. 1. HRTEM of the as-prepared CdTe core (left) QDs and CdTe/CdSe (right) QDs with 3 layers of CdSe shell.

rials, and can provide lattice information such as crystal type, structure, orientation, and defects. As shown in Fig. 1, the HRTEM images illustrate the nearly spherical and monodispersed QDs and the insets show that the QDs have good crystal structures. The diameters of the nanoparticles were estimated to be 3.1 nm for the CdTe cores and 4.8 nm for CdTe/CdSe QDs after the CdTe cores were covered with three layers of the CdSe shells. These data bolster the theoretical values that the thickness of one layer of CdSe shell was estimated to be about 0.3 nm. Besides, the particle size of the obtained MPA-CdTe/CdSe core-shell QDs is ultrasmall, indicating that the QDs have good prospects for biological application.

The size distributions of as-prepared MPA-capped CdTe and CdTe/CdSe core/shell QDs in aqueous solution are presented in Fig. 2. The average hydrodynamic diameters of the MPA-capped CdTe core QDs in aqueous solution are 6.41 nm with narrow size distribution, and CdTe/CdSe QDs with one and three layers of CdSe shell are 7.17 nm and 8.19 nm, respectively, slightly larger than the CdTe core QDs. The hydrodynamic diameter is larger than the size measured by HRTEM. This difference is considering that the size from HRTEM reflects only the inorganic core of the QDs, whereas hydrodynamic diameters include the surface organic molecules and the inorganic core. The small size of the CdTe/CdSe core/shell QDs would facilitate their penetration in biosystem when they were used as fluorescent biological probes.

Shown in Fig. 3 are the typical UV-vis absorption and fluorescence spectra of the original CdTe core QDs and corresponding CdTe/CdSe QDs. It was reported that type-II core/shell QDs have relatively small absorbances near the band edge. The reduced e-h wavefunction overlap results in the weak oscillator strength of type-II QDs as indirect semiconductors due to the spatial separation of the charge carriers [14,25]. As a characteristic of type-II QDs, this has been verified by our results. The distinctive peaks in the absorption spectra of the initial CdTe cores become weak and even vanish at the band edge by increasing the shell thickness. Besides, red-shifts from 620 to 740 nm of the emission wavelength are observed after successively increasing the shell thickness of CdSe on the CdTe cores. Furthermore, it is not found that a blue shift for the fluorescence peak position during the shell growth, which implies that CdTe_xSe_{1-x} alloyed QDs are not formed in the whole process [26]. Also, our findings firmly support the formation of the CdTe/CdSe core/shell structure. The inset presents the picture of as-prepared CdTe/CdSe QDs observed under the radiation with 365 nm ultraviolet light from a UV lamp. As the thickness of CdSe shell increases, the fluorescence of the QDs turns darker because the emission color of the QDs gradually shifts from visible into NIR regions.

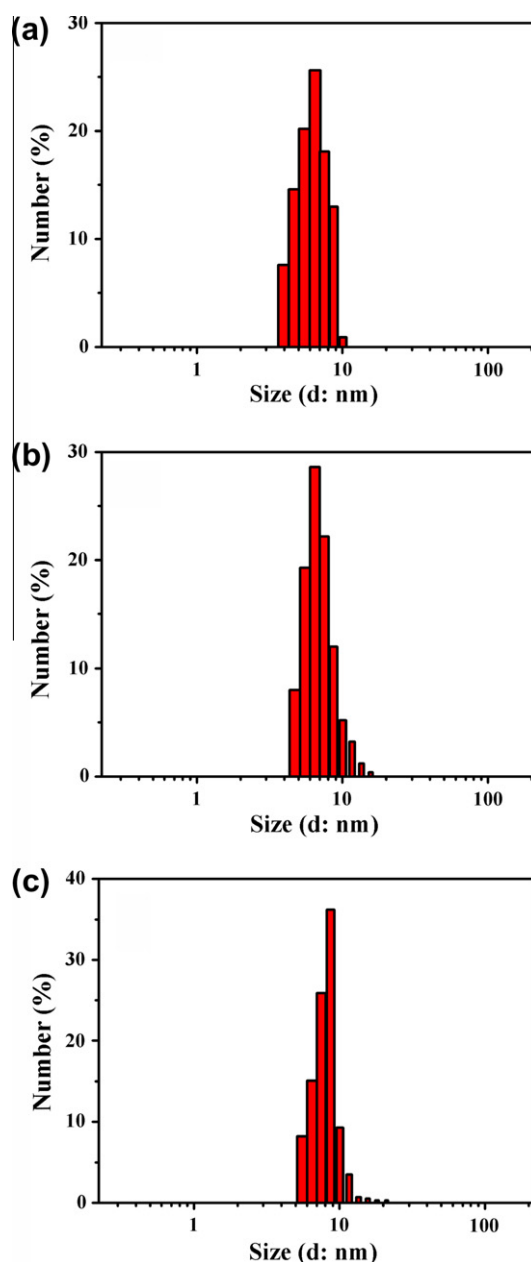


Fig. 2. Size distributions histogram of CdTe core QDs (a), CdTe/CdSe QDs with 1 (b) and 3 (c) layers of CdSe shell.

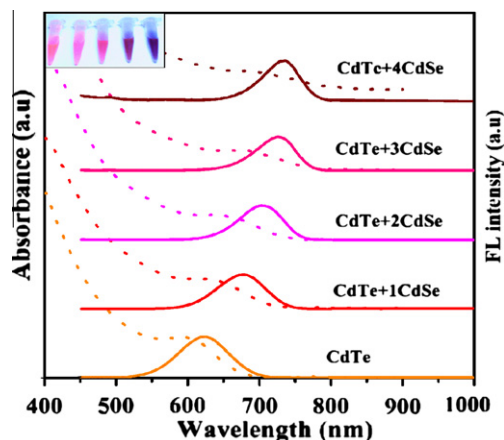


Fig. 3. Temporal evolution of UV-vis absorption (dashed line) and fluorescence spectra (solid line) of the CdTe core QDs and CdTe/CdSe (with 1–4 layers of CdSe shell) QDs. Inset is the photograph of CdTe core QDs and CdTe/CdSe (with 1–4 layers of CdSe shell) QDs irradiation with 365 nm ultraviolet light from a UV lamp.

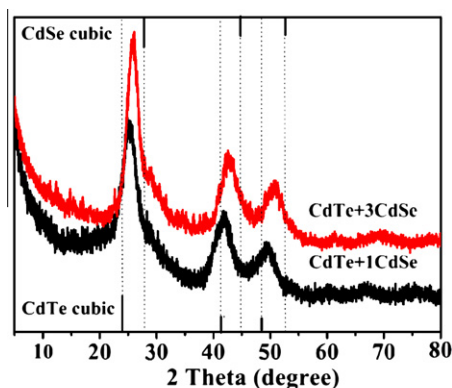


Fig. 4. XRD patterns of CdTe/CdSe QDs with 1 and 3 layers of CdSe shell. The vertical lines stand for the diffraction peaks of cubic CdTe and CdSe.

To further characterize the core/shell structures, their crystallographic properties were investigated by XRD. Fig. 4 presents the XRD patterns of CdTe/CdSe (1ML) QDs and CdTe/CdSe (3ML) QDs. It can be seen that the broad diffractive peaks are typical for nanoparticles and the peak positions of the original CdTe are consistent with those of bulk cubic CdTe structure (not shown). With the growth of the CdSe shell, the peak positions shift slightly toward larger angles as compared with the CdTe core, while the pattern of peak widths and shapes remain almost unchanged, which further demonstrates the formation of a core/shell structure rather than an alloyed structure. A homogeneous alloy would show a significant narrowing of XRD peak widths upon increasing particle size [27,28]. Additionally, no separate CdSe peaks are observed. These results confirm the formation of the heterostructure of CdTe/CdSe.

The elemental compositions of the CdTe core QDs and CdTe/CdSe core/shell QDs with three layers of CdSe shell were analyzed by XPS, which was considered as a powerful tool for identifying the chemical nature of the surface of nanomaterials. As shown in Fig. 5, the binding energies of 405.15, 572.40 eV, respectively, correspond to the Cd 3d and Te 3d levels of the CdTe core QDs. Compared with the original CdTe cores, the surface elemental Cd content of CdTe/CdSe QDs is much higher, which is attributed to the fact that the Cd-MPA precursors have been attached on the CdTe cores, and

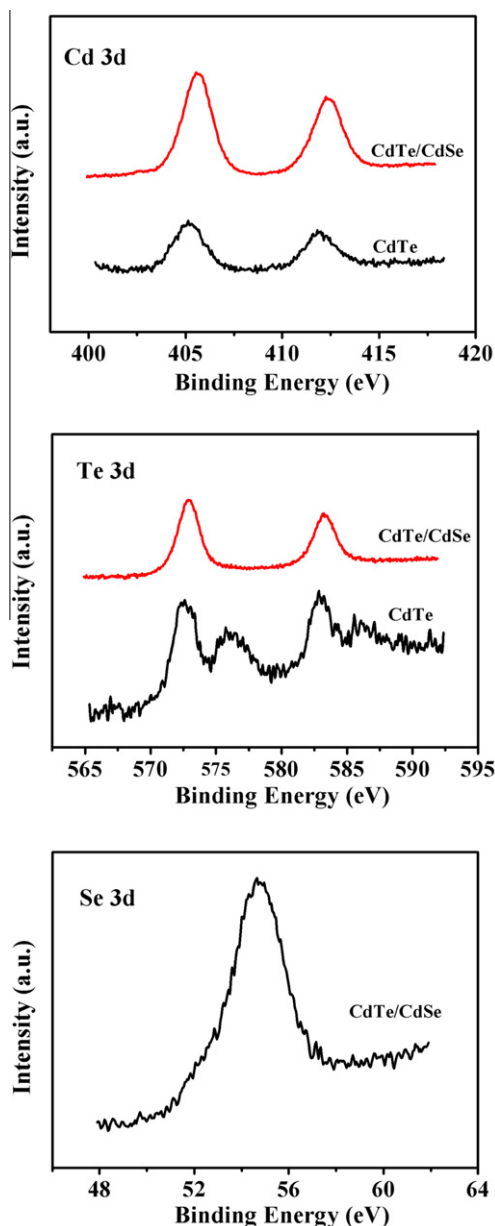


Fig. 5. XPS data of the original CdTe core QDs and CdTe/CdSe QDs with 3 layers of CdSe shell.

the lower content of Te and the existence of Se (Se 3d, 54.80 eV) indicate the formation of CdSe-rich shells.

The photostability of the as-prepared core/shell CdTe/CdSe QDs was carefully investigated by using the Time Driver system on a Perkin Elmer Model LS-55 luminescence spectrometer (Fig. 6). The sample solutions of the original CdTe, CdTe/CdSe (2ML), CdTe/CdSe (4ML) were placed in a small cuvette with a volume of 500 μ L and then irradiated with a xenon ion laser with an intensity of 20 kW/cm². After 6000 s of continuous irradiation, the CdTe/CdSe (4ML) QDs held their fluorescence, and the fluorescence intensity of the CdTe/CdSe (2ML) QDs was slightly reduced, whereas the original CdTe QDs lost about 20% of their fluorescence. The results indicate that the core/shell CdTe/CdSe QDs have better photostability than the bare CdTe QDs. The probable reason is that the shell effectively protects the core QDs from the irradiation and prevents the unsaturated Te atoms on the surface of the core from oxidation under the irradiation [27,28]. Moreover, it is found that

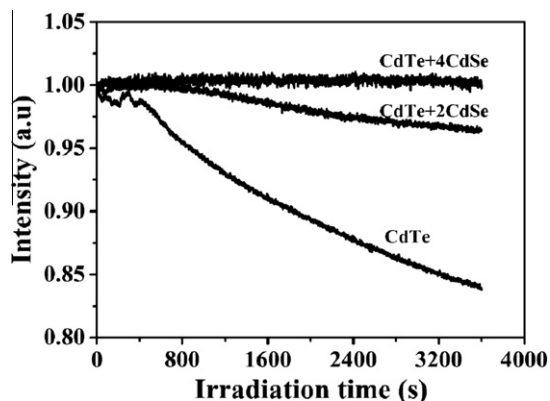


Fig. 6. Photostability of CdTe core QDs, CdTe/CdSe QDs with 2, and 4 layers of CdSe shell.

the thickness of the CdSe shell directly influence the photostability of QDs.

4. Conclusions

In summary, we have employed the hydrothermal technique to develop a simple approach to the preparation of NIR-emitting type-II core/shell CdTe/CdSe QDs. Our as-prepared NIR-emitting CdTe/CdSe QDs exhibit hardened lattice structure, high QY (up to 44.2%) and excellent photostability, which are attributed to the formation of CdSe shells on the CdTe cores through the reduction of Na_2SeO_3 in the hydrothermal route under relatively high temperature. Compared with the previous methods, this strategy is more efficient, convenient and time saving, regardless of the pretreatment and oxidation of Se source. Our preliminary findings indicate that the as-prepared type-II CdTe/CdSe QDs have the potential to construct an alternative probe in vivo imaging and biological targeting.

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