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In Situ Synthesis of CdTe/CdSe Core−Shell Quantum Dots

Heonjin Seo and Sang-Wook Kim*

Department of Molecular Science and Technology,
Ajou University, Suwon 443-749, Korea

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Quantum dots (QDs) are materials which show quantum confinement effects and have drawn much attention due to the variety of different applications in which they can be used, including biomedical imaging,[1] display devices,[2] photovoltaics,[3] and lasers.[4] Usually, core−shell type QDs are used,[5] because they have reduced surface defects and nonradiative decay. Core−shell QDs are also divided into type-1 and type-2 like bulk semiconductors, depending on their band gap structure. Type-2 core−shell QDs have staggered band offsets,[7b] namely, a higher valence band or lower conduction band in the shell than in the core. As a result, the wavefunctions of the electron and hole exist separately, which leads to many novel properties, for example, the red-shift of the emission and a long decay lifetime. Type-2 QDs have attracted considerable attention as a result of the emission tuning with the core size and shell thickness in the near-infrared regions, which is important for biomedical imaging, because of their deep penetration and the absorption windows of biomaterials.[6] There are many type-2 systems, including CdTe/CdSe, CdSe/ZnTe, InP/GaAs, GaSb/GaAs, and GaAs/AlAs;[7] however, there have been few reports of type-2 QDs prepared using the colloidal method.[7a−d] Among these reports, the CdTe/CdSe type-2 dots reported by Kim et al. are particularly impressive;[7a,b] however, they used highly toxic (CH$_3$)$_2$Cd to make the CdSe shell, which is not suitable for large scale synthesis.[8]

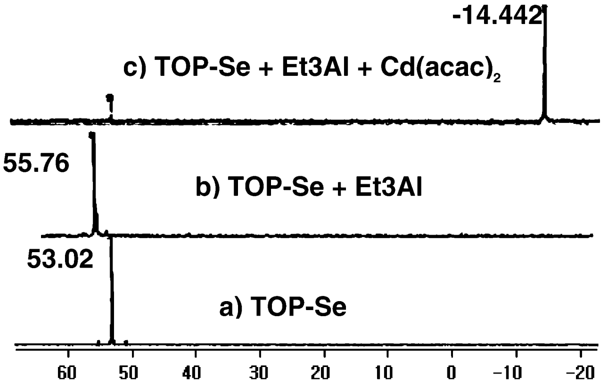
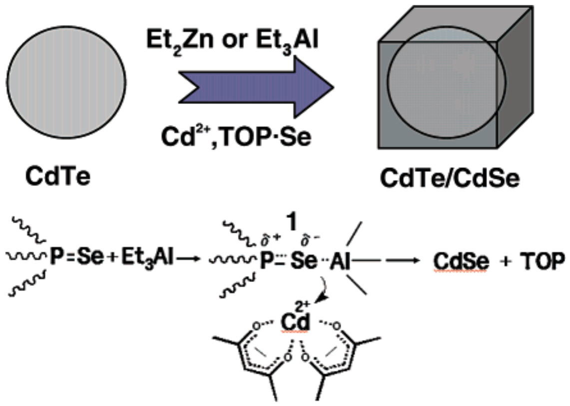


Figure 1. ^{31}P NMR spectrum of (a) TOP−Se, (b) TOP−Se + Et3Al, and (c) TOP−Se + Et$_3$Al + Cd(acac)$_2$ in CdSe synthesis.

Scheme 1. Synthesis of CdTe/CdSe Core−Shell QDs and Proposed Reaction Pathway for CdSe Formation



In this paper, we present an alternative method of the CdTe/CdSe type-2 core−shell structure, which uses alkyl

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* To whom correspondence should be addressed. E-mail: swkim@ajou.ac.kr.

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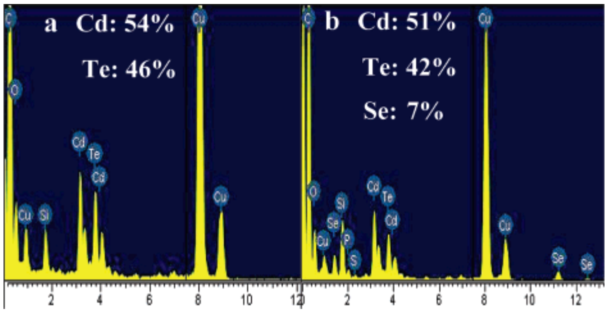

Figure 2. Elemental analysis by EDX of (a) CdTe core and (b) CdTe/CdSe core−shell.

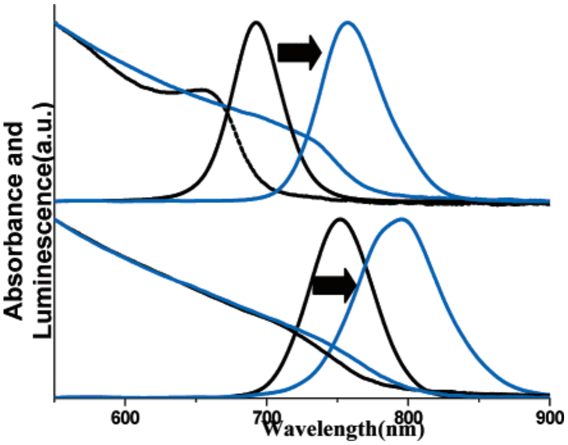

Figure 3. Absorption and emission spectrum of CdTe core (black) and CdTe/CdSe core−shell QDs.

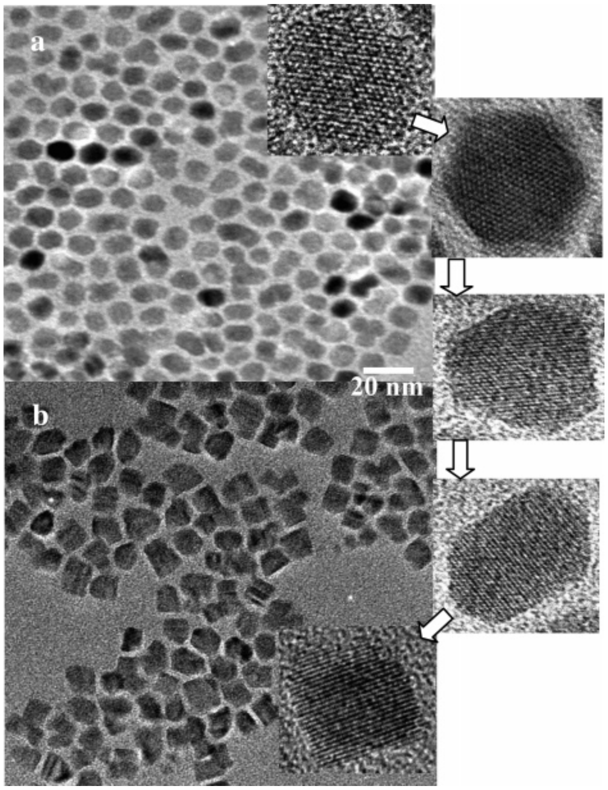

Figure 4. TEM images of CdTe core (a) and CdTe/CdSe core−shell QDs (b).

metals, for example, triethyl aluminum or diethyl zinc as a reducing agent of selenium metals. The synthetic procedure for the CdTe core follows that of ref 7b, with 1.5 equiv of cadmium acetylacetonate and 1 equiv of TOP−Te as the cadmium and tellurium precursors, respectively. Et_2Zn (or Et_3Al) and TOP−Se were added slowly to the core solutions and reacted with excess cadmium cations for the CdSe shell formation. The proposed mechanism of CdSe formation is shown in Scheme 1. The detailed experimental procedures can be found in Supporting Information. Interestingly, we could obtain the rectangular shapes of CdTe/CdSe type-2 dots, not the spherical shape. We suggest that the synthesis proceeds by a mechanism in which the selenide anion, which is activated by Et_2Zn or Et_3Al, reacts with excess cadmium cations. In Scheme 1, Al in Et_3Al attached to Se, which formed metastable adduct **1**. The P atom in adduct **1** was more de-shielded, while the Se was more shielded[9] compared with TOP−Se. Therefore, more anionic Se could react with the Cd cation easily and form CdSe shell and TOP. Our proposed mechanism is proved by ^{31}P NMR spectra. (Figure 1). The model system which we used was composed of TOP−Se (no free TOP), Et_3Al, and $Cd(acac)_2$ in octadecene. After Et_3Al (1.5 equiv of TOP−Se) was added to the vial of TOP−Se and stirred for 5 min in the glovebox, the solution was dropped into $Cd(acac)_2$ solution slowly at 200 °C. The reaction was maintained for 10 min at the same temperature and stopped. The peak of TOP−Se (53.023 ppm) moved to 55.765 ppm in the adduct **1**, which means that the electron clouds near the phosphine became thinner than before as a result of the Lewis acid. Malik et al. reported that the phosphine atom is de-shielded and selenium is shielded when some metal atom is attached to selenium in the trialkylphosphine−selenium complex.[9] When the adduct **1** was added to the cadmium precursor solution at 200 °C, we could observe the disappearance of the adduct and appearance of the phosphine peak (−14.442 ppm) of TOP. In the reaction, ZnSe and Al_2Se_3 were not found. TOP was not formed without Lewis acid. Elemental analysis by EDX (energy dispersive X-ray spectroscopy) showed that the CdTe core consisted of 54% of cadmium and 46% of tellurium, and the core−shell consisted of 51% of cadmium, 42% of tellurium, and 7% of selenium; however, the zinc content was negligible (Figure 2). Figure 3a shows the absorption and emission spectra of the CdTe cores and their core−shells. Red-shifts from 692 to 760 nm and 751 to 802 nm were observed, which are characteristic of type-2 dots. The distinctive peak in the absorption spectra of the initial cores disappeared, and a large Stoke's shift (~50 nm: 802 nm emission) occurred in the type-2 structure. To confirm the suggested mechanism, we conducted two experiments, namely, (1) the aging of the CdTe core for 12 h at 200 °C to exclude the possibility of a red-shift occurring due to core growth and (2) the addition of TOP−Se without Et_2Zn to the CdTe core solution to confirm the role of Et_2Zn. In experiments 1 and 2, the red-shifts of the emission peaks were not observed, which means that the red-shifts are caused by the formation of the CdSe shell and Et_2Zn activated the selenium anion to be attacked easily by an electrophile like as Cd cations. Et_3Al also showed similar results; however, the effect was weaker than that of Et_2Zn. The CdTe cores

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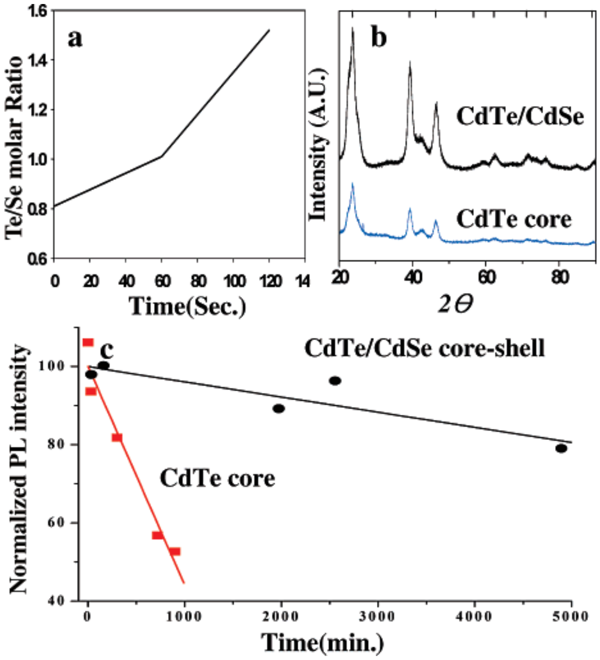

Figure 5. (a) Te/Se mole ratio by depth profile of CdTe/CdSe core–shell QDs and (b) PXRD patterns of CdTe cores (blue) and CdTe/CdSe core–shell QDs (black). Solid ticks are for bulk CdTe with zinc blende structure. (c) Photoluminescence intensity changes of CdTe cores (red) and CdTe/CdSe core–shell QDs (black) under natural light at room temperature.

have a quantum yield of 10–20%, and the CdTe/CdSe core–shells have a slightly improved quantum yield of 15–25%. Figure 4b,c shows the sphere-like CdTe core with a diameter of 8–9 nm and rectangular-like CdTe/CdSe core–shell with a size of ∼10 nm. Various shapes, such as trapezoid and parallelogram, also are observed as metastable states. High-resolution images revealed that most of the particles have a highly crystalline structure. Depth profile experiment with XPS (X-ray photoelectron spectroscopy) was conducted to confirm the core–shell structure. The elemental analysis data of core–shell before sputtering, of 1 and 2 min sputtering, were obtained and are shown in Figure 5a. As the sputtering time increases, the selenium content decreases, which means that these QDs have a tellurium-rich core and selenium-rich shell. Figure 5b shows the zinc-blende powder X-ray diffraction pattern of the CdTe core and CdTe/CdSe core–shell QDs. Most of the peaks coincide with the bulk CdTe structure of zinc blende. In the core–shell QDs, no peak shift was observed as a result of the thin shell thickness (∼0.5–1 nm).

Generally, CdTe QDs show poor photostability because of the easy oxidation of tellurium, especially in the case of large sized QDs. Figure 5c shows the photoluminescence stability data of the CdTe cores and CdTe/CdSe core–shells. The CdTe core sample loses ∼50% of its initial quantum yield within 1000 min, while the CdSe/CdTe core–shell maintains its photostability for more than 2500 min under white light. This improved photostability of the core–shell dots opens up the possibility of their being used in biomedical imaging.

In conclusion, we synthesized CdTe/CdSe core–shell type-2 QDs using alkyl metal (Et_2Zn or Et_3Al) as an activating agent of selenium. During the shell formation process, the sphere-like CdTe core transforms to a rectangular-like shape. The zinc blende structured core–shell QDs show better photostability than the cores, which should enable them to be used in biomedical imaging.

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Supporting Information Available: Experimental details of the synthetic procedure of CdTe core and CdTe/CdSe core–shell QDs (PDF). This material is available free of charge via the internet at http://pubs.acs.org.

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