

# Semiconductor “Nano-Onions” with Multifold Alternating CdS/ CdSe or CdSe/CdS Structure

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“Nano-onions” with multifold alternating CdS/CdSe or CdSe/CdS structure have been synthesized via a two-phase approach. The influences of shell on photoluminescence (PL) quantum yields (QYs) and PL lifetimes are investigated and discussed. It is found that the outmost shell plays an important role in the PL QYs and PL lifetimes of the multishells “onion-like” nanocrystals. The PL QYs and PL lifetimes fluctuate regularly with CdSe and CdS shells. The PL QY increases when the nanocrystals have an outmost CdS shell; however, it decreases dramatically with the outmost CdSe shell. The trend of the change of PL lifetimes is consistent with that of the QYs. The crystal structure and composition of the novel nano-onions are characterized by transmission electron microscopy, X-ray diffraction, and X-ray photoelectron spectra techniques.

## Introduction

Some novel properties of semiconductor nanocrystals can be achieved by coating them with a different inorganic shell. Groups II–VI semiconductor core/shell structured nanocrystals, which are expected to exhibit unique optical and electronic properties, have been successfully synthesized by epitaxial growth. For example, the small lattice mismatch of 3.9% between CdSe and CdS affords the epitaxial growth of the CdSe/CdS core/shell nanocrystals. The photoluminescence (PL) quantum yield (QY) can be sufficiently improved by growing an inorganic shell of the wide band-gap CdS on the CdSe core. The PL QY of CdSe/CdS core/shell nanocrystals can be as high as 60–80% due to the effective passivation of CdSe surface-trapping sites.<sup>1</sup> These type I core/shell nanocrystals with a high PL QY have been widely used in light-emitting diode (LED)<sup>2</sup> biological labeling.<sup>3</sup> Recently, type II core/shell nanocrystals (both the valence and conduction bands in the core are lower or higher than those in the shell) such as CdTe/CdSe and CdSe/ZnTe core/shell nanocrystals have been synthesized.<sup>4</sup> The type II nanocrystals exhibited a relatively long PL lifetime due to

the spatial separation of the charge carriers. These type II nanocrystals are more suitable in photovoltaic applications because of the spatial separation of the charge carriers and a lower PL QY. Moreover, the double-shell semiconductor nanocrystals such as CdS/HgS/CdS,<sup>5</sup> CdSe/CdS/ZnS,<sup>6</sup> CdS/CdSe/CdS,<sup>7</sup> and CdSe/ZnS/CdSe<sup>8</sup> core/shell-1/shell-2 systems have been synthesized and showed improved photoluminescence quantum yields or exhibited some novel properties (e.g., dual emitting in a nanocrystal). Magnetic “nano-onions” with multifold core/shell structures and unique magneto-optical properties have been recently reported (Abe, M.; Takeshi, S. *J. Appl. Phys.* **2005**, *97*, 10M514; Wiggins, J.; Carpenter, E. E.; O’Connor, C. J. *J. Appl. Phys.* **2000**, *87*, 5651; Abe, M.; Takeshi, S. *Phys. Rev. B* **2004**, *70*, 235103).

For CdSe/CdS or CdS/CdSe core/shell nanocrystals, because CdSe (1.7 eV) has a lower band-gap than CdS (2.5 eV), both electrons and holes can be confined in the core or shell, respectively, which will lead to a big change of PL QYs or PL lifetimes. The PL QYs and PL lifetimes can be easily tuned by changing the structure of multishell nanocrystals. The PL lifetime is also very important to luminescent semiconductor nanocrystals in various applications, such as in LED, biological labeling, solar cell, laser, and so forth. However, most work focused on the changing of PL QYs

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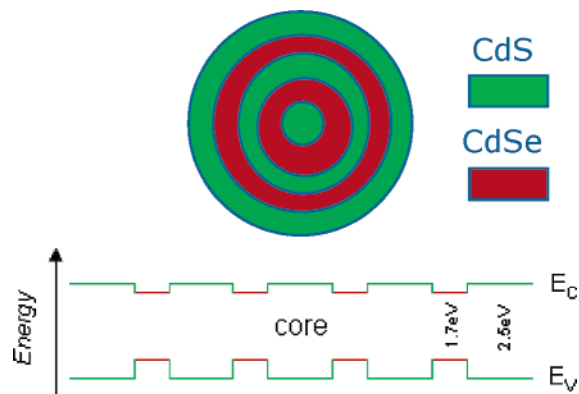
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**Scheme 1. Schematic Illustration (Top) and Corresponding Energy Level Diagram (Bottom) of the Nano-Onions with CdS Cores Capped by Alternating CdSe and CdS Shells**



and only a few works have reported on the changing of PL lifetimes.<sup>4</sup>

In this work, we have successfully synthesized complex semiconductor “nano-onions” with multifold alternating CdS/CdSe or CdSe/CdS structure. Scheme 1 shows a schematic illustration (top) and the corresponding energy level diagram (bottom) of the nano-onions with CdS cores capped by alternating CdSe and CdS shells. A two-phase approach was developed recently for the preparation of CdSe and CdS nanocrystals in our lab and was exploited here to synthesize the CdSe/CdS or CdS/CdSe “nano-onions” by consequential growth of CdS and CdSe. Cadmium myristate (Cd-MA) and thiourea (selenourea) were used as cadmium and sulfur (selenium) sources, respectively. The two precursors were spatially separated and resolved in toluene and water, respectively. The resulting nanocrystals were capped by oleic acid (OA) and dispersed in toluene.

## Experimental Section

**I. Chemicals.** Cadmium oxide (99.5%), myristic acid (MA, 99.5%), and oleic acid (OA, 90%) were purchased from Aldrich. Thiourea (99%) and selenourea (99.9%) were obtained from Alfa, and coumarin 6 (98%) was purchased from Acrös. Cd-MA was synthesized through the reaction of CdO with myristic acid at 210 °C for 10 min.<sup>9</sup>

**II. Synthesis of “Nano-Onions” with CdS as Core.** The synthesis was done according to our previously reported two-phase approach.<sup>10</sup> For a typical synthesis of alternating CdS/CdSe “nano-onions”, 0.1134 g of Cd-MA, 1 mL of OA, and 10 mL of toluene were added to a Teflon-lined stainless steel autoclave with a volume of 30 mL and heated until Cd-MA was dissolved. Thiourea (0.042 g) was dissolved in 10 mL of water at room temperature, and the solution was then transferred to the autoclave without stirring. The autoclave was sealed and maintained at 180 °C for 70 min, and CdS nanocrystals formed. The autoclave was cooled to room temperature with tap water. Then, about 9 mL of the above crude solution of CdS nanocrystals, 0.0567 g of Cd-MA, and 1 mL of toluene were added to the autoclave and heated until Cd-MA was dissolved, and the solution was then cooled to room temperature. Selenourea (0.013 g) was dissolved in 10 mL of N<sub>2</sub>-saturated water

at room temperature, and the solution was transferred to the autoclave. The autoclave was sealed again and maintained at 180 °C for 40 min for the CdSe shell growth. About 9 mL of the obtained crude solution of CdS/CdSe core/shell nanocrystals, 0.0567 g of Cd-MA, and 1 mL of toluene were added to the autoclave and heated until Cd-MA was dissolved. Thiourea (0.024 g) was dissolved in 10 mL of water, and the solution was transferred to the autoclave. The autoclave was sealed and maintained at 180 °C for 120 min, forming the CdS/CdSe/CdS core/shell-1/shell-2 nanocrystals. The further growth of CdSe and CdS shells was achieved by repeating the above procedures. The as-prepared nanocrystals were precipitated with ethanol and then dispersed in toluene for optical and structural characterizations without any size sorting.

**III. Synthesis of “Nano-Onions” with CdSe as Core.** For a typical synthesis of the CdSe core nanocrystals, 0.1134 g of Cd-MA, 1 mL of oleic acid, and 10 mL of toluene were added to a Teflon-lined stainless steel autoclave and heated until Cd-MA was dissolved, and the solution was then cooled to room temperature. Selenourea (0.013 g) was dissolved in 10 mL of N<sub>2</sub>-saturated water, and the solution was transferred to the autoclave. The autoclave was sealed and maintained at 180 °C for 18 min, and CdSe core nanocrystals formed. The autoclave was cooled to room temperature with tap water. The further growth of CdS and CdSe shells was achieved by procedures similar to those in the synthesis of “nano-onions” with CdS as core.

**IV. Characterization.** Ultraviolet–visible (UV–vis) absorption and photoluminescence (PL) spectra were recorded on a Shimadzu UV-2450 PC spectrometer and a Shimadzu RF-5301 PC fluorometer with a resolution of 1.0 nm, respectively. Room-temperature PL quantum yields were calculated against coumarin 6 in ethanol as a standard (0.78).<sup>11</sup> The absorbances of sample and standard at the excitation wavelength were similar and small (about 0.05) in order to avoid a self-absorbance. Fluorescence lifetimes were measured on a nanosecond laser system. Excitation line was the third harmonic of 1064 nm of Nd:YAG. The fluorescence signal was gathered by Acton 2758 spectrograph with R-928 PMT (HAMAMATUS) and analyzed by the LeCroy Runner 6100 1 GHz digital oscilloscope.

Transmission electron microscopy (TEM) measurements were performed on a JEOL-2010F transmission electron microscope with an acceleration voltage of 200 kV. TEM samples were prepared by dropping about 10 μL of diluted toluene solution onto 400-mesh carbon-coated copper grids and slowly evaporated in air. The particle size and size distribution diagrams were obtained through measuring more than 200 individual nanoparticles carefully. The powder X-ray diffraction (XRD) patterns were recorded on a Rigaku D/MAX-2500 using Cu Kα<sub>1</sub> radiation at 50 kV and 250 mA in the range of 20–60° by step scanning with a step size of 0.02°. X-ray photoelectron spectra (XPS) were measured with VG ESCALAB MK (VG Company, UK) at room temperature by using a Mg Kα X-ray source ( $h\nu = 1253.6$  eV) at 14 kV and 20 mA. The XPS curves were fit, and the peak areas of the Se and S cores were measured by using ORIGIN software. The peak areas and atomic sensitivity factors for each element were used to calculate Se-to-S ratio for the final products.

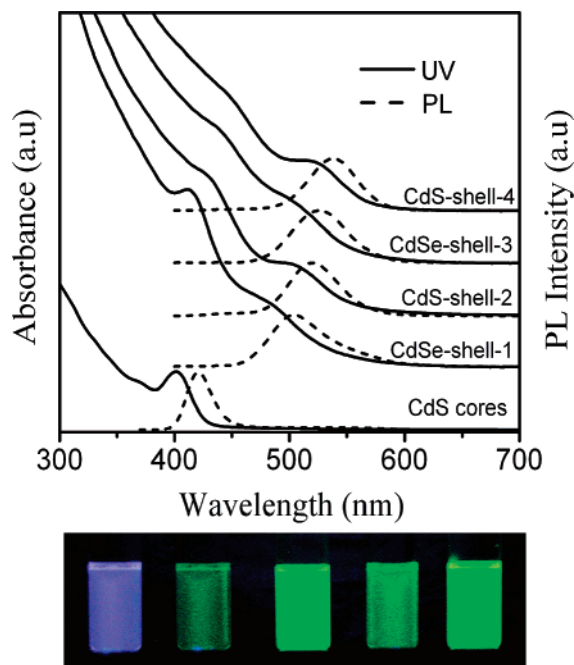
## Results and Discussion

**I. Optical Characterization.** Figure 1 shows the UV–vis absorption and PL spectra (top) of the “nano-onions” with CdS as a core and capped alternately by CdSe and CdS shells

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**Figure 1.** UV-vis absorption and PL spectra (top) of the "nano-onions" with CdS cores capped alternately by CdSe and CdS shells, and the corresponding luminescence image (bottom) for the samples under UV lamp irradiation.

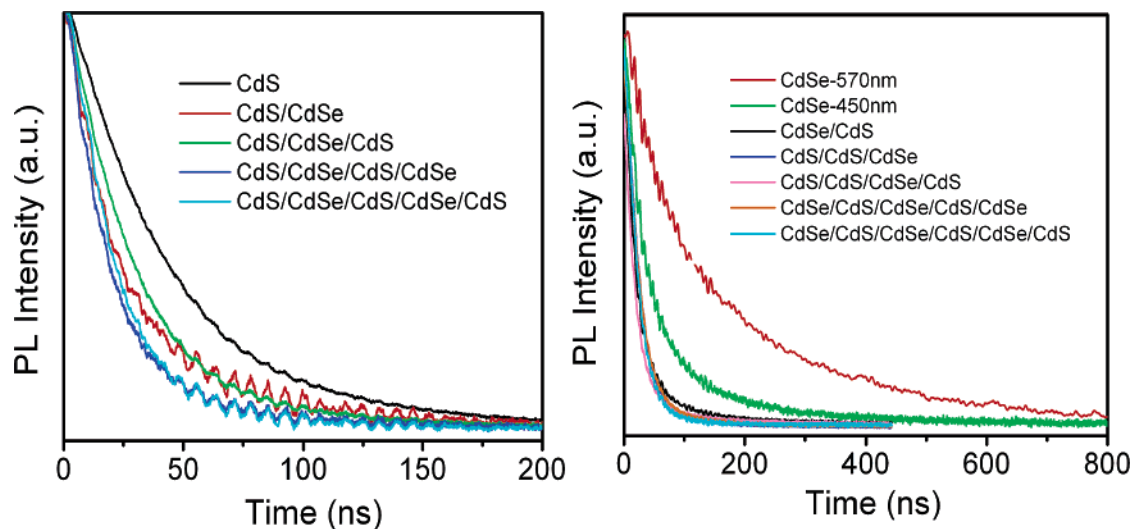
and the corresponding luminescence image (bottom) under UV lamp irradiation. The CdS core nanocrystals exhibit a very sharp first excitonic absorption peak and a strong band-edge emission. The CdS/CdSe core/shell nanocrystals show red-shift absorption and emission spectra as the CdSe shell is formed on the CdS nanocrystals. The very big red shift (~90 nm) in the PL spectrum results from the exciton leakage<sup>12</sup> (i.e., the electron-hole recombination of the excitons is mainly in the CdSe shell because CdSe (1.7 eV) has a lower band gap than CdS (2.5 eV), which leads to energy loss). The first excitonic absorption peak is not evident for CdS/CdSe core/shell nanocrystals, but the second excitonic absorption peak is close to the first excitonic absorption peak of the CdS cores. For CdS/CdSe/CdS core/shell-1/shell-2 nanocrystals, a small red shift (~15 nm) was observed in both UV-vis absorption and PL spectra similarly due to exciton leakage, although the great mass of excitons is confined in the core. The red shift became insignificant for the "nano-onions" with more than two shells. The second excitonic absorption peak will gradually disappear during the growth of more shells; however, the first excitonic absorption peak of the nanocrystals with outmost CdS shell is more evident than that of the nanocrystals with outmost CdSe shell.

The outmost shell plays an important role in the PL QYs and PL lifetimes of the core/multishell structured nanocrystals. The PL QYs and PL lifetimes of the "nano-onions" with CdS as a core fluctuate regularly with CdSe and CdS shells. The PL QYs and PL lifetimes (including the fast and slow components) increase when the nanocrystals are capped by

outmost CdS shell and decrease dramatically when the CdSe shell is formed on the surface of nanocrystals. As shown in Figure 1 (bottom), the PL intensity is higher when the outmost layer of the nanocrystals is CdS. Figure 2 (left) shows the PL decay curves of the "nano-onions" with CdS cores capped alternately by CdSe and CdS shells. All curves fit well by a biexponential function. Table 1 lists the PL QYs and lifetimes of the "nano-onions" during the growth of CdSe and CdS shells. We found that the CdS core nanocrystals have a PL QY of 38% relative to coumarin 6 at room temperature (see Table 1). For the CdS/CdSe core/shell nanocrystals, the PL QY decreases to 4%. The PL lifetimes of CdS/CdSe core/shell nanocrystals are also evidently shorter than those of the CdS cores. That CdSe shell accelerated PL decay of CdS cores can be due to increased rates of electron-hole recombination. A main reason for the decrease in PL QY and PL lifetimes is that both electrons and holes primarily recombine in the CdSe shell instead of in the CdS core, since CdSe has a lower band gap than CdS. This is different from type I and type II core/shell nanocrystals,<sup>4</sup> where both electrons and holes are confined in the core for type I nanocrystals or are spatially separated between the core and the shell for type II nanocrystals. Here, for CdS/CdSe core/shell nanocrystals, the excitons mainly recombine in the CdSe shell and at surface trap sites. When a second shell of CdS is further formed (i.e., CdS/CdSe/CdS core/shell-1/shell-2), the PL QY (32%) and PL lifetimes become higher than those of CdS/CdSe core/shell nanocrystals. Once a CdSe shell is further formed on the CdS/CdSe/CdS core/shell-1/shell-2 nanocrystals, the PL QY (6%) and PL lifetimes decrease again. The 5-fold CdS/CdSe/CdS/CdSe/CdS core/shell-1/shell-2/shell-3/shell-4 nanocrystals show increased PL QY (25%) and PL lifetimes again (see Table 1).

Similar red shifts in the UV-vis absorption and PL spectra (see Figure 3, top) are also observed for the "nano-onions" with CdSe cores capped alternately by CdS and CdSe shells during the growth of CdS and CdSe shells. Figure 3 (bottom) shows the luminescence image of these nanocrystals. Similar to the "nano-onions" with CdS cores, the PL intensity is higher when the outmost layer of the nanocrystals is CdS. As shown in Table 1, the PL QYs of the "nano-onions" with CdSe cores exhibit a behavior similar to those of nano-onions with CdS cores. The QYs of nanocrystals with outmost CdS shell are remarkably higher than those of nanocrystals with outmost CdSe shell. The luminescence of the CdSe core nanocrystals (~1.5 nm in diameter) shows both a sharp band edge emission and a wide trap emission due to the exciton recombination at surface trap sites. The trap emission is substantially removed when the CdS shell is formed on the CdSe cores. The total PL QY for CdSe core nanocrystals is only about 7%. Coating with a CdS shell results in a PL increase of about 10 times to a QY of 78% due to the eliminating of defect states. Once a CdSe shell is formed on the CdSe/CdS core/shell nanocrystals, the PL QY decreases back to 4%. The PL QY changes to 30, 7, and 19% when a shell of CdS, CdSe, and CdS is further grown as the outmost layer.

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**Figure 2.** PL decay curves ( $\lambda_{\text{exc}} = 355$  nm, measured at the emission maximum unless otherwise stated) of the “nano-onions” with CdS cores (left) capped alternately by CdSe and CdS shells and the “nano-onions” with CdSe cores (right) capped alternately by CdS and CdSe shells.

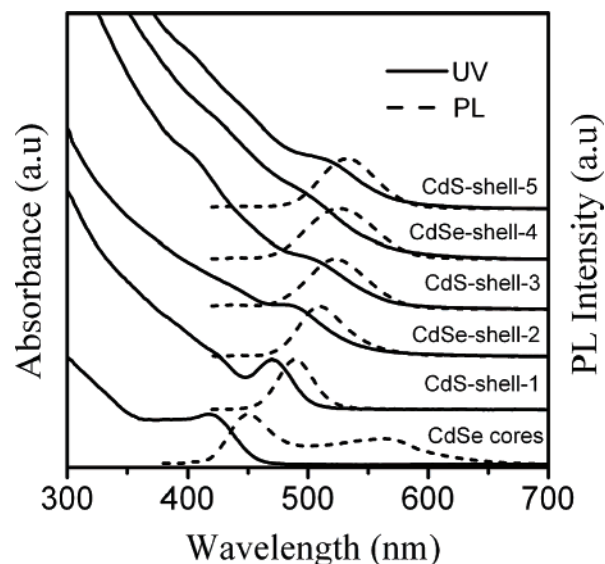
**Table 1.** PL QYs and Lifetimes of the “Nano-Onions” with CdS Cores Capped Alternately by CdSe and CdS Shells and the “Nano-Onions” with CdSe Cores Capped Alternately by CdS and CdSe Shells

	core	shell-1	shell-2	shell-3	shell-4	shell-5
	CdS	CdSe	CdS	CdSe	CdS	
QY (%)	38	4	32	6	25	
$\tau 1^a$ (ns)	37.8	17.8	25.6	14.1	22.4	
$\tau 2^b$ (ns)	151.2	74.7	104.8	45.4	171.2	
	CdSe	CdS	CdSe	CdS	CdSe	CdS
QY (%)	7	78	4	30	7	19
$\tau 1^a$ (ns)	26.9	27.9	25.2	27.2	21.7	25.1
$\tau 2^b$ (ns)	80.2					

<sup>a</sup> Fast component. <sup>b</sup> Slow component.

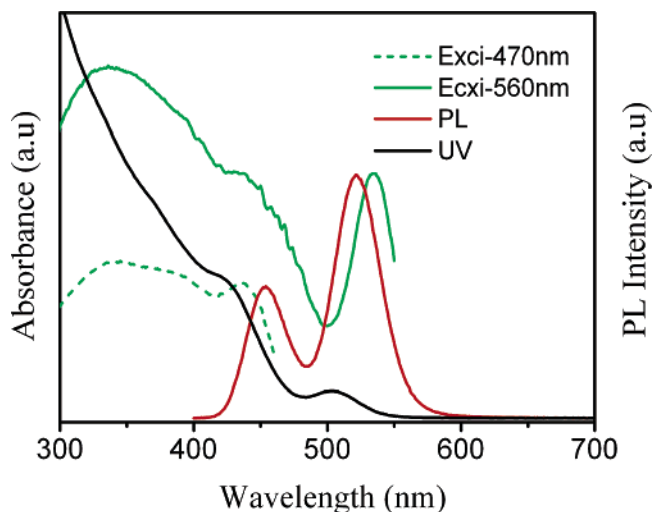
For CdSe core nanocrystals, the PL band edge lifetimes decay biexponentially, with a fast component of 26.9 ns and a slow component of 80.2 ns, while the band edge PL of the CdSe/CdS core/shell nanocrystals exhibit monoexponential decay with a lifetime of 27.9 ns (see Table 1). Different from type II core/shell nanocrystals<sup>4</sup> where both electrons and holes are spatially separated between the core and the shell, for type I CdSe/CdS core/shell nanocrystals, both electrons and holes primarily reside in the CdSe core, which reduces their interactions with surface trap states and improves the PL quantum yields and decreases the PL lifetime. The PL lifetimes of the CdSe/CdS and CdS/CdSe core/shell nanocrystals are shorter than those of the CdSe cores and CdS cores, respectively, because the carriers are confined in the core or shell for the core/shell nanocrystals and resided in the entire nanocrystal for the pure nanocrystals. The trap emission of CdSe cores shows very long PL lifetimes, with a fast component of 79.5 ns and a slow component of 318.5 ns. For other CdSe and CdS shell nanocrystals with CdSe as core, all PL lifetimes decay monoexponentially and they have a small fluctuation. The trend of change of the PL lifetimes is also consistent with the trend of the change of the quantum yields, but the change of PL lifetime becomes small for the nanocrystals with more than two shells.

Moreover, separate CdS or CdSe nanocrystals were not found during the growth of CdS and CdSe shells. It was noticed that when the excess Cd and S precursors were added to solution for the growth of CdS shell onto the CdSe cores,

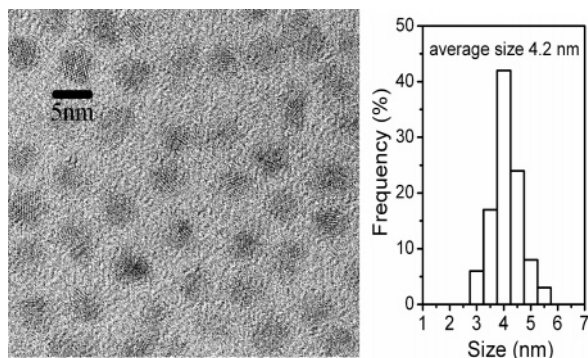


**Figure 3.** UV-vis absorption and PL spectra (top) of the “nano-onions” with CdSe cores capped alternately by CdS and CdSe shells, and the corresponding luminescence image (bottom) for the samples under UV lamp irradiation.

separate CdS nanocrystals were formed in the solution. Once there are separate CdS nanocrystals formed in the solution instead of being coated on the surface of CdSe cores, the emission of CdS nanocrystals should be observed as shown in Figure 4 (red line). The two PL peaks at 453 and 521 nm are associated with emissions of CdS and CdSe/CdS core/shell nanocrystals, respectively. The PL excitation spectra (Figure 4) also indicate that there are two kinds of nanocrystals in the solution. In this work, there are no CdS and/or CdSe emissions observed for all the samples (see Figures 1 and 3), indicating that no separate CdS and CdSe nanocrystals were formed in the solution during the growth of CdS and CdSe shells.



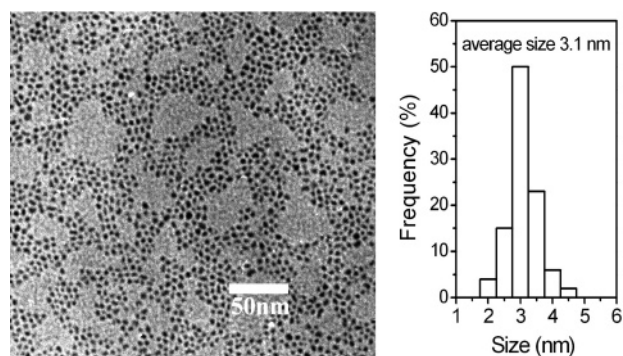
**Figure 4.** UV-vis absorption and PL spectra of OA-capped CdS and CdSe/CdS core/shell nanocrystals, and the excitation spectra of emission at 470 nm (green dashed line) and 560 nm (green solid line), respectively.



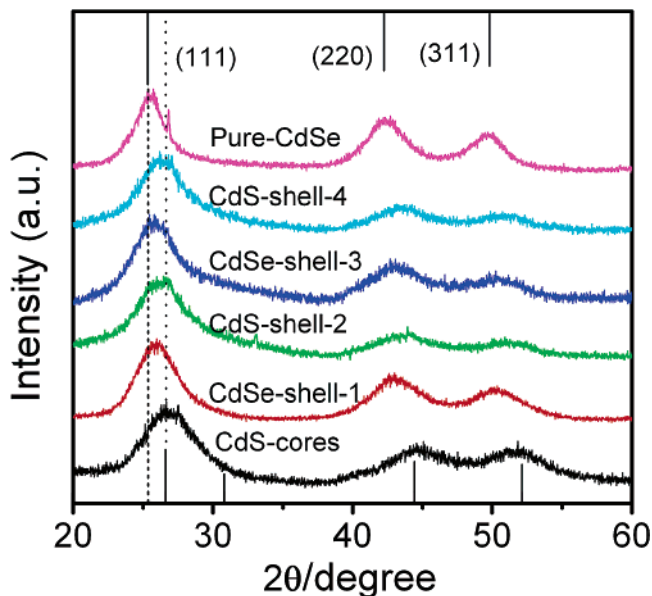
**Figure 5.** TEM image (left) and the corresponding size distribution diagram (right) of the 5-fold "nano-onions" with CdS cores.

**II. Structural Characterization.** Figure 5 shows the HR-TEM image (left) and the corresponding size distribution diagram (right) of the 5-fold "nano-onions" with CdS cores. The nanocrystals have a relatively narrow size distribution, and the average size is 4.2 nm. The CdS cores are about 3.2 nm in diameter calculated from UV-vis absorption spectrum.<sup>13</sup> The average shell thickness of each CdSe or CdS shell is about 0.125 nm. It is difficult to distinguish CdS and CdSe lattices on the HR-TEM image because they all belong to cubic phase and their lattice parameters are very close. Figure 6 shows the TEM image (left) and the corresponding size distribution diagram (right) of the 6-fold "nano-onions" with CdSe as core. The diameter of the final products with CdSe cores is 3.1 nm, and the size of original CdSe cores is about 1.5 nm calculated from UV-vis absorption spectrum.<sup>13</sup> The average shell thickness of each CdS or CdSe shell is about 0.16 nm.

In this work, the thickness of an individual CdSe or CdS shell is less than one monolayer due to two reasons. First, the influence of a thinner shell on PL QY and PL lifetime is more significant than that of a thicker shell. For example, both holes and electrons will mainly recombine in the outmost CdSe shell for the nanocrystals with outmost CdSe



**Figure 6.** TEM image (left) and the corresponding size distribution diagram (right) of the 6-fold "nano-onions" with CdS cores.

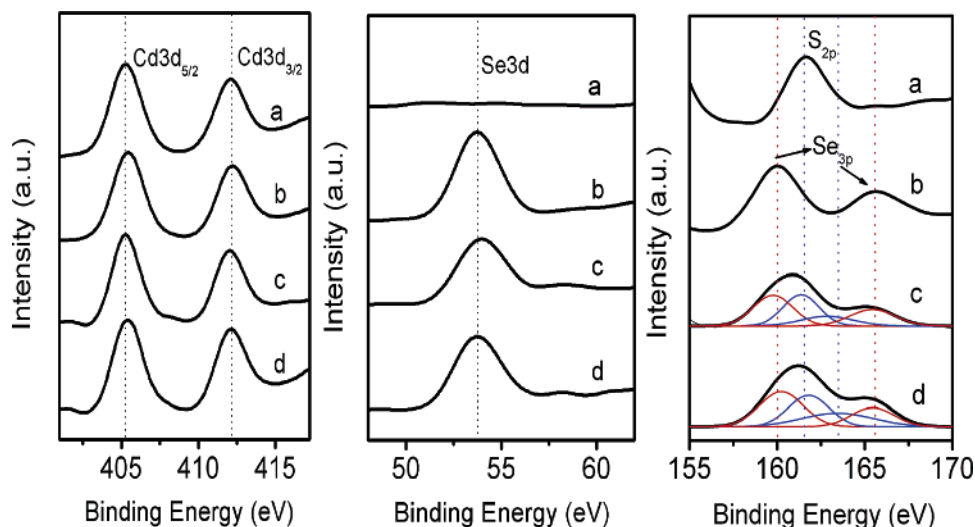


**Figure 7.** XRD patterns of the "nano-onions" with CdS cores capped alternately by CdSe and CdS shells. Vertical lines indicate pure CdSe and CdS reflections (top: zinc blend, CdSe; bottom: zinc blend, CdS).

shell. If the CdSe shell is less than one monolayer, the excitons will recombine in a smaller space and have more chances to recombine at surface trap sites. The PL QYs and PL lifetimes will be sufficiently decreased. Second, for multishells "nano-onions", a thicker shell will cause stronger interface strain between the CdSe shell and CdS shell lattice although the lattice mismatch between CdSe and CdS is only 3.9%.

Figure 7 compares the XRD patterns of different stages for the "nano-onions" with CdS cores capped alternately by CdSe and CdS shells. For CdS core nanocrystals, the peak positions match well with the theoretical values of the cubic structure of CdS. For CdS/CdSe core/shell nanocrystals, the peak positions shift toward those for cubic CdSe nanocrystals. When a CdS shell is further formed on CdSe nanocrystals, the peak positions shift back toward CdS values. The peak positions shift to CdSe values again for the CdS/CdSe/CdS/CdSe core/shell-1/shell-2/shell-3 nanocrystals. Finally, the diffraction pattern for the 5-fold CdS/CdSe/CdS/CdSe/CdS core/shell-1/shell-2/shell-3/shell-4 nanocrystals is close to that for cubic CdS structure. Therefore, the XRD diffractions of the multifold "nano-onions" are much closer to those of the pure nanocrystals with the same composition

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**Figure 8.** XPS spectra of pure CdS (a) and CdSe (b) nanocrystals and the final “nano-onions” with CdSe cores (c) and CdS cores (d), respectively. Vertical lines are guides for peak positions of  $S_{2p}$  (blue dot line) and  $Se_{3p}$  (red dot line).

as the shell instead of core. The broadness of the diffraction peaks decreases gradually along with the growth of more shells. The mean nanocrystal sizes obtained from the full width at half-maximum intensity of the (111) cubic reflection according to the Debye–Scherrer formula increase gradually. If there are two kinds of nanocrystals, the peak width should be broader. These results indicate that CdSe or CdS grows on the nanocrystal surface instead of isolated nucleation. Moreover, the nanocrystal sizes obtained from XRD are all smaller than those determined from TEM.

Figure 8 shows the XPS spectra of pure CdS (a) and CdSe (b) nanocrystals and the final “nano-onions” with CdSe cores (c), and CdS cores (d), respectively. All the peaks are calibrated by using C (1s) (284.6 eV) as the reference. The  $Cd_{3d}$  core is split into  $3d_{5/2}$  (405.2 eV) and  $3d_{3/2}$  (412.2 eV) peaks, and the  $Se_{3d}$  core shows a peak at 53.8 eV. All of the observed binding energy values for  $Cd_{3d}$  and  $Se_{3d}$  are nearly in agreement with the reported data in the literature.<sup>14</sup> The peaks at 160.0 and 165.6 eV correspond to  $Se_{3p}$  transitions, and the peaks at 161.7 and 163.5 eV correspond to  $S_{2p}$  transitions. The atomic ratio of Se-to-S is about 0.86 and 0.48 for the “nano-onions” with CdSe and CdS cores, respectively. The experimental ratios of Se-to-S for the “nano-onions” with CdSe and CdS cores are close to those of theoretical values.

## Conclusions

In summary, “nano-onions” with multifold alternating CdS/CdSe or CdSe/CdS structure have been synthesized via a two-phase approach. The core/multishell structured nanocrystals are characterized by UV–vis, PL, TEM, XRD, and XPS techniques. These “nano-onions” exhibit interesting optical properties. The PL QYs and PL lifetimes fluctuate regularly with the CdSe and CdS shells. The hole and the electron can be confined in the core or shell by changing the structure of the “nano-onions”, resulting in a big change in PL QYs or PL lifetimes. The PL QYs are correlated with PL lifetimes, and they have a similar trend of change. These “nano-onions” with tuned PL QYs and PL lifetimes are interesting in LED, biological labeling, solar cells, and other applications.

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