SUPPLEMENTARY MATERIAL

Alloying buffer layers in colloidal CdSe/ZnS core/shell nanocrystals

Huichao Zhang,[a] Yonghong Ye,[b] Boping Yang,[a] Li Shen,[a] Yiping Cui,[a] and Jiayu Zhang*[,a]

[a] Dept of Electronic Engineering, Southeast University, Nanjing 210096, China.

[b] Dept of Physics, Nanjing Normal University, Nanjing 210097, China

*Corresponding author. E-mail: jyzhang@seu.edu.cn; Fax: +86-25-83790201; Tel: +86-25-83792470-8203

1. Synthesis of the CdSe nanocrystals and CdSe/Cd$_{0.5}$Zn$_{0.5}$Se(1 ML, monolayer)/ZnSe(1 ML) /ZnS (3 MLs) core/buffer shell/shell nanocrystals

Chemicals. Cadmium oxide (CdO, 99.99%), zinc oxide (99.9%) and sulfur (S, 99.98%) were purchased from Aldrich. Selenium (Se, 99.999%, 200mesh), oleic acid (OA, 90%), 1-octadecene (ODE), and octadecylamine (ODA, 98%) were obtained from Alfa Aesar. Tributylphosphine (TBP, 95%) was purchased from Aladdin. All chemicals were used directly without any further purification.

Synthesis process. CdSe nanocrystals (NCs) were synthesized by a general method.[1] For 3.9 nm CdSe NCs, the mixture of 1.2 mmol of CdO, 24 mmol of oleic acid, and 24 g of ODE in a 250 ml three-neck flask was heated to ~240℃ to obtain a colorless clear solution. After this solution was cooled to room temperature, ODA (20 g) was added into the flask. Under argon flow, this mixture was reheated to 310℃. At this temperature, a selenium solution made by dissolving 7.2 mmol of Se powder in 2.5 g of TBP was quickly injected. The solution was maintained at 270℃ during the CdSe growth. When the desired particle size was reached, the reaction mixture was cooled to room temperature, and then CdSe NCs were purified and dissolved in n-hexane for the following shell growth. The particle concentration of the purified CdSe solution was estimated using an

empirical function, which is ~1.7×10^{-3} mmol in total.

The zinc injection solution (0.1M) was prepared by mixing ZnO, OA and ODE, and a clear solution was got at 300℃, under an Ar flow. The cadmium/zinc injection solution (0.1M) was prepared by mixing CdO/ZnO (the molar ratio of Cd to Zn is 1:1), OA and ODE, and a clear solution was got at 300℃, under an Ar flow. The sulfur injection solution (0.1M) was prepared by dissolving sulfur in ODE at 100℃, under an Ar flow. The selenium injection solution (0.1M) was prepared by dissolving selenium in the mixture of TBP and ODE at room temperature (the molar ratio of Se to TBP is 1:16), under an Ar atmosphere. The cadmium injection solution (0.1M) was prepared by mixing CdO, OA and ODE, and a clear solution was got at 250℃, under an Ar flow. The amount of cadmium/zinc, zinc or sulfur precursors required for each layer was determined by the volume increment of every shell and NC's particle concentration. The definition of a monolayer is a $Cd_{0.5}Zn_{0.5}Se$ or ZnSe shell of 0.33 nm along the major axis of a single dot and a monolayer for ZnS shell is 0.31 nm.[2] One-sixth of above CdSe NCs were mixed with 2 g of ODA and 4 g of ODE in a 25 ml three-neck flask. After removal of the hexane under vacuum at 60℃, the mixture was heated to 230℃ under Ar-flow where the shell growth was performed. The core/buffer shell/shell $CdSe/Cd_{0.5}Zn_{0.5}Se$(1 ML)/ZnSe (1 ML)/ZnS(3 MLs) NCs were formed by alternating addition of Cd/Zn-precursor or (Zn-precursor) and S-precursor, respectively. A period of 20 min between each addition was chosen due to the UV-vis and PL spectra showed no further changes after this time period. Core/buffer shell/shell NCs with different shell thickness were synthesized by using CdSe cores with the same size, and the injection quantity of Cd/Zn (or Zn) or S injection solutions are 0.65 ml, 0.89 ml, 1.08 ml, 1.37 ml and 1.79 ml, respectively. According to the TEM measurement, the standard deviations of NCs size is 9% for the CdSe core, and 10%, 10%, 11%, 11%, and 12% for the five core/buffer shell/shell NCs.

For the synthesis of CdSe/ZnS core/shell NCs, $CdSe/CdS$(1 ML)/$Cd_{0.5}Zn_{0.5}S$(1 ML)/ZnS(3 MLs) core/buffer shell/shell NCs, and $CdSe/Cd_{0.5}Zn_{0.5}Se$(1 ML)/ZnSe(1 ML)/$Cd_{0.5}Zn_{0.5}Se_{0.5}S_{0.5}$(1 ML) /ZnS (2 MLs) core/buffer shell/shell NCs, the similar size CdSe NCs were used as cores. The core/shell NCs (or core/buffer shell/shell NCs) was formed also by alternating addition of Cd/Zn-precursor (or Zn-precursor) and S-precursor (or Se-precursor), respectively. The growth time and growth temperature were same with above synthesis process.

2. PL QY measurements. The PL spectra of a given sample of the CdSe NCs (or $CdSe/Cd_{0.5}Zn_{0.5}Se$(1 ML)/ZnSe(1 ML)/ZnS (3 MLs) core/buffer shell/shell NCs) and an organic dye, whose PL spectrum overlaps significantly with that of the NCs sample, were measured under the same setting of a Edinburgh F900 fluorescence spectrophotometer. The scanning step of the spectrophotometer was set as 0.5 nm. The optical density at the excitation wavelength of the dye and the NCs sample was set to a similar value. The optical density at the first exciton absorption peak of the NCs or the main absorption peak of the dye was below 0.1 in order to avoid any significant reabsorption. The PL QY of the NCs sample was finally obtained by comparing the integrated PL intensities of the NCs and the Rhodamine 6G, which was purchased from Exciton and its PL QY is 95%.[3] The measurement error of the PL QY was reported in the related figures as the error bars.

3. Fitting of PL decay profiles. The PL decay profiles of all the NCs samples could be well-fitted by a triexponential decay $\sum_{i=1}^{3} B_i e^{-t/\tau_i}$ with the reduced chi-square $\chi^2 \leq 1.2$. The noise is of Poissonian statistics for spectra obtained by the TCSPC technique, and the numerical fit with

$\chi^2 \leq 1.2$ is proposed to be acceptable. The residual data shown in Fig. S1 are of random noise distributed around zero, which indicates that the triexponential fit is quite appropriate. The value of τ_{av} is calculated as follows: $\tau_{av}=(B_1\tau_1^2+B_2\tau_2^2+B_3\tau_3^2)/(B_1\tau_1+B_2\tau_2+B_3\tau_3)$. To illuminate the evolvement of τ_{av}, the relative fluorescence intensity of the three decay component ($\Phi_{i(i=1,2,3)}$) is shown in Table 1. The $\Phi_{i(i=1,2,3)}$ value is calculated as follows: $\Phi_{i(i=1,2,3)}=B_i\tau_i/(B_1\tau_1+B_2\tau_2+B_3\tau_3)$, therefore the τ_{av} can be calculated also by equation: $\tau_{av}=\Phi_1\tau_1+\Phi_2\tau_2+\Phi_3\tau_3$.

(a) Core (3.9 nm CdSe)
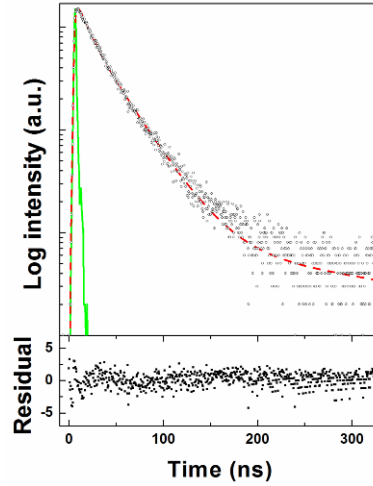
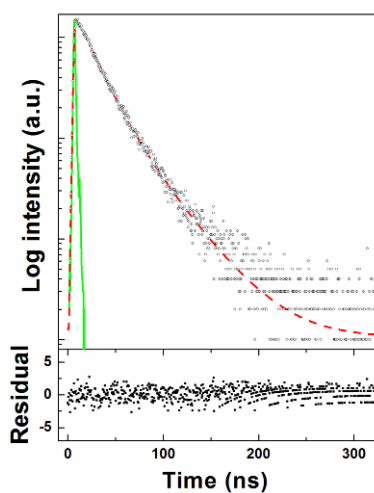(b) 1ML (CdSe/Cd$_{0.5}$Zn$_{0.5}$Se(1 ML) core/buffer shell NCs)
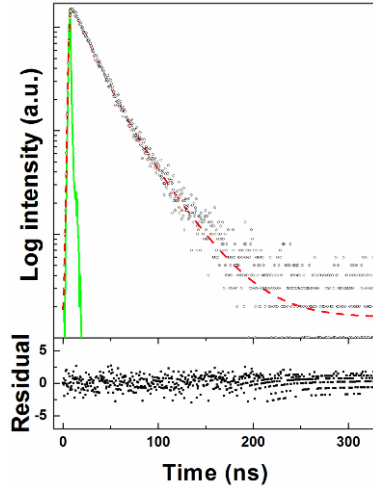
(c) 2ML (CdSe/Cd$_{0.5}$Zn$_{0.5}$Se(1 ML)/ZnSe(1 ML) core/buffer shell NCs)
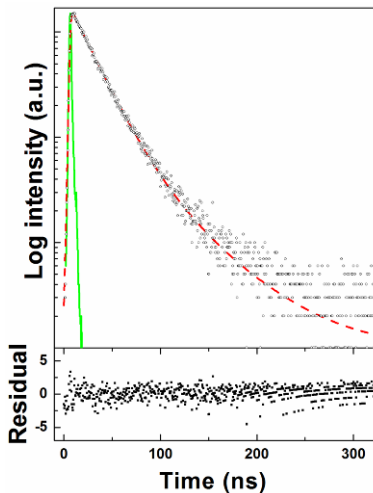
(d) 3ML (CdSe/Cd$_{0.5}$Zn$_{0.5}$Se(1 ML)/ZnSe(1 ML)/ZnS(1 ML) core/buffer shell/shell NCs)
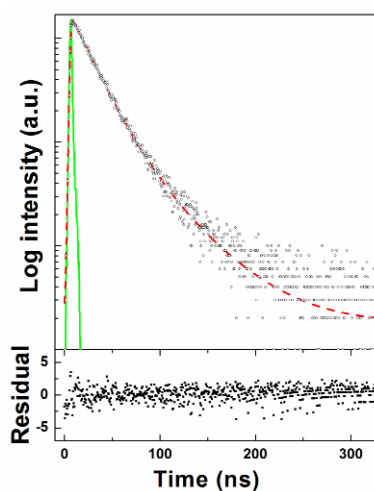
(e) 4ML (CdSe/Cd$_{0.5}$Zn$_{0.5}$Se(1 ML)/ZnSe(1 ML)/ZnS(2 MLs) core/buffer shell/shell NCs)

(f) 5ML (CdSe/Cd$_{0.5}$Zn$_{0.5}$Se(1 ML)/ZnSe(1 ML)/ZnS(3 MLs) core/buffer shell/shell NCs)
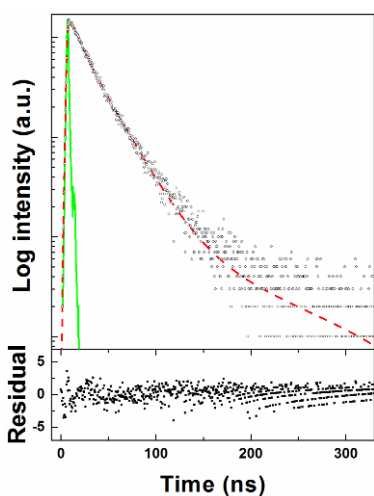

Fig. S1. The PL decay profiles of (a) Core, (b) 1ML, (c) 2ML, (d) 3ML, (e) 4ML, and (f) 5ML, respectively, where the red dashed line is the best-fitted triexponential curve, the green line is the

instrument response, and the black cubic is the residual data (bottom).

4. Fitting of High-resolution XPS spectra. After standard Shirley background subtraction Gaussian-Lorentzian line shapes are used for fitting the Cd3$d_{5/2}$ core-level spectra. It is found that it is necessary to introduce two (or three) components (FWHM ~1 eV, 25% Lorentzian-Gaussian lineshapes without peak asymmetry) to best describe the experimental lineshape. Fig. S1 displays the fitting residuals next to the corresponding Cd3d$_{5/2}$ high-resolution spectrum. From the result of the fits, as displayed in Fig. S1, the binding energies of the three components are determined to be 404.6, 405, and 405.6 eV, respectively.
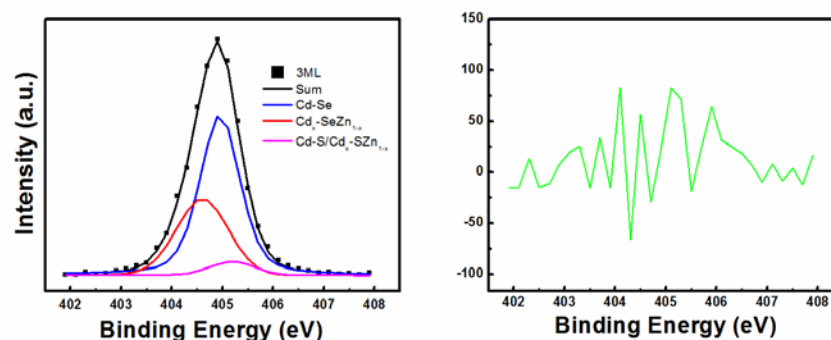
(a) 1ML (CdSe/Cd$_{0.5}$Zn$_{0.5}$Se(1 ML) core/buffer shell NCs)
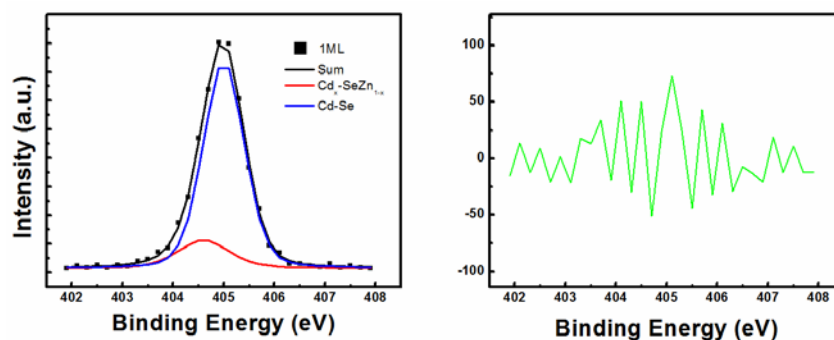
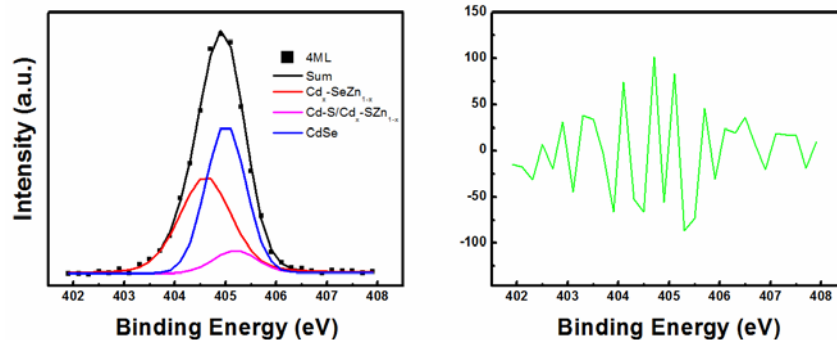(b) 2ML (CdSe/Cd$_{0.5}$Zn$_{0.5}$Se(1 ML)/ZnSe(1 ML) core/buffer shell NCs)
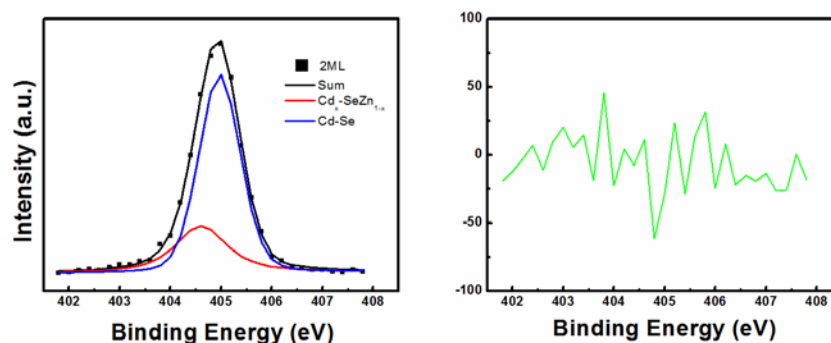
(c) 3ML (CdSe/Cd$_{0.5}$Zn$_{0.5}$Se(1 ML)/ZnSe(1 ML)/ZnS(1 ML) core/buffer shell/shell NCs)

(d) 4ML (CdSe/Cd$_{0.5}$Zn$_{0.5}$Se(1 ML)/ZnSe(1 ML)/ZnS(2 MLs) core/buffer shell/shell NCs)

(e) 5ML (CdSe/Cd$_{0.5}$Zn$_{0.5}$Se(1 ML)/ZnSe(1 ML)/ZnS(3 MLs) core/buffer shell/shell NCs)
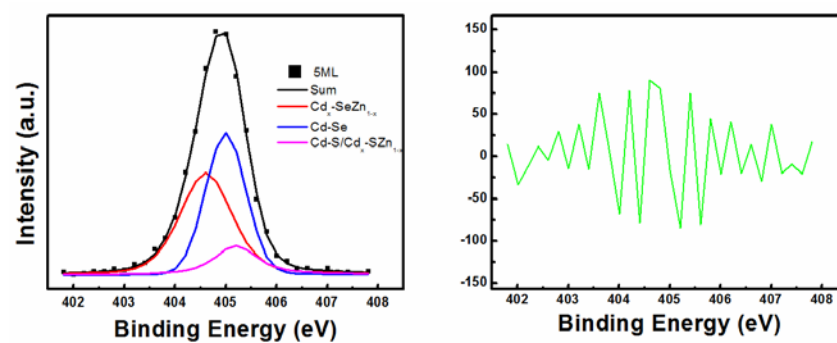

Fig. S2. The fitting result and the residual spectrum of the high resolution core-level Cd 3d$_{5/2}$ spectra of (a) 1ML, (b) 2ML, (c) 3ML, (d) 4ML, and (e) 5ML, respectively.

References:

(1)   H. Zhang, Y. Ye, J. Zhang, Y. Cui, B. Yang, L. Shen, *J. Phys. Chem. C* **2012**, *116*, 15660.

(2)   R. G. Xie, U. Kolb, J. X. Li, T. Basche, A. Mews, *J. Am. Chem. Soc.* **2005**, *127*, 7480.

(3)   L. H. Qu, X. G. Peng, *J. Am. Chem. Soc.* **2002**, *124*, 2049.