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Supporting information

The effect of surface structures and compositions on the quantum yields of highly effective $Zn_{0.8}Cd_{0.2}S$ Nanocrystals

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1. Experimental Procedure

1.1 Preparation of $Zn_{0.8}Cd_{0.2}S$ NCs

Cadmium oxide (CdO, 99.998 %) and stearic acid (SA, 99 %) were obtained by Alfa Aesar. Zinc oxide (ZnO, 99.999 %), sulfur powder (S, 99.98 %), decene (DE, 94%), tetradecene (TDE, 92%), octadecene (ODE, 90 %), hexadecylamine (HDA, 90 %), and trioctylphosphine oxide (TOPO, 90 %) were purchased from Sigma-Aldrich. Hexane (99.7 %) and methanol (99 %) were gotten from Mallinckrodt Chemicals. All chemicals were used as received without purification.

The colloidal ternary semiconductor $Zn_{0.8}Cd_{0.2}S$ named as $Zn_{0.8}$ NCs were prepared by thermal pyrolyzed organometallic route. Total amount of 0.24 mmol of ZnO and 0.06 mmol of CdO were mixed with 2.4 mmol of SA in a three-necked flask under Ar purge. The mixture was heated to 230 ^{o}C under Ar flow until the clear solution was obtained and the Cd/Zn-SA precursor was formed. Then the solution was cooled down to room temperature, and a white solid precipitate was obtained. The amount of 15 mmol of TOPO and 24 mmol of HDA were added into a three-necked flask and stirred together under Ar flow, and then the solid precipitate was reheated up to 320 ^{o}C. At this temperature, S-DE ,S-TDE or S-ODE precursors, which were 1.5 mmol of S dissolved in 4 mL of DE, TDE or ODE, respectively, were rapidly injected into a three-neck flask and reacted for 10, 30 or 60 minutes. The mixed solution was swiftly cooled down to 150 ^{o}C to stop reaction. After purification, the precipitate was dissolved and dispersed in hexane to remove unreacted reagents for further measurement.

1.2 Characterization of NCs

The optical properties of the prepared NCs were measured by fluorescence spectrophotometer (FL, Hitachi F-7000) and ultraviolet-visible spectrometer (UV-Vis, Jasco V-670 spectrometer). Relative quantum yields (QYs) of the $Zn_{0.8}$ NCs were determined by comparing the area under the curve of FL emission with that of fluorescent dye (Rhodamine 101 in ethanol).[S1] The concentration of the QDs and the Rhodamine 101 dye were adjusted to the same optical density at the excitation wavelength. The standard QY of Rhodamine 101 is 98 %. The QYs of $Zn_{0.8}$ sample was calculated by the following equation:

$$QY_s = QY_r \frac{F_s}{F_r} \frac{A_r}{A_s} \frac{n_s^2}{n_r^2}$$

where F_s and F_r are the integrated fluorescence emissions of the sample and the reference, respectively, A_s and A_r are the absorbances at the excitation wavelength of the sample and the reference, respectively, n_s and n_r are the solvent refractive index of the sample and the reference, respectively, and QY_s and QY_r are the QY of the sample and the reference, respectively. X-ray diffraction (XRD) patterns were recorded on a MacScience Co. Ltd MO3X-HF22 powder diffractometer with Cu Kα (λ = 1.542 Å) as the incident radiation. Transmission electron microscope (HRTEM, JEOL JEM-2010) was used to analyze the particle size distribution and the morphology. The surface compositions and the functional group of capping ligands of NCs were investigated by X-ray photoelectron spectroscopy (XPS, Thermo VG Scientific Sigma Probe) and Fourier-transform infrared spectrometer (FTIR, JASCO FT/IR-6100) respectively.

The typical X-ray absorption spectra (XAS) of the prepared NCs were obtained in fluorescence mode at the BL01C1 beamline at the National Synchrotron Radiation Research Center (NSRRC). The incident beam was monochromated using a double crystal monochromator equipped with Si (111) crystal. Si monochromator was employed to adequately select the energy with a resolution ΔE/E better than 1 x 10^{-4} at the Cd K-edge (26711 eV) and Zn K-edge (9659 eV). In general, all NCs were collected uniformly on the tape with an appropriate absorption thickness (μ_x = 1.0, where μ is the absorption edge and x is the thickness of the sample) in order to reach the proper edge jump step at the absorption edge region. In addition, the ionization chamber filled with different mixing gases such as Ar, N_2, He or Kr was used to detect the intensities of the incident beam (I_o), the florescence beam (I_f) and the beam finally transmitted by the reference foil (I_r). For the extended x-ray absorption fine structure (EXAFS) analysis, the backgrounds of pre-edge and post-edge were subtracted and normalized with respect to the edge jump step from the XAS spectra ($\chi(E)$). The normalized $\chi(E)$ spectra were transformed from energy to k-space and further weighted by k^3 to distinguish the contributions of back scattering interferences from different coordination shells. Subsequently, the extracted k^3-weighted spectra in k-space ranging from 3.0 to 12.9 and 3.3 to 13.0 $Å^{-1}$ for the Cd K-edge and Zn-edge were Fourier transformed into r-space, respectively. The phase correction was set on all spectra in the r-space. Finally, the filtered EXAFS data of Cd K-edge were analyzed by a nonlinear least-squares curve fitting method in the r-space ranging from 1.0 to 2.7 $Å^{-1}$ depending on the bond to be fitted. The reference phase and amplitude for the Cd-O coordination were initially acquired from a CdO powder. Normally, the backscattered amplitude and phase shift functions for specific atom pairs were theoretically estimated by manner of utilizing the FEFF7 code. In addition, the reduction amplitude (S_{02}) value for Cd was fixed at 0.83 in order to determine various structural parameters for each bond pairs.

Reference

[S1] W. S. Song and H. Yang, Chem. Mater., 2012, 24, 1961.

Table. S1 The wavelength of emission peaks and the QYs for $Zn_{0.8}CdS$ NCs.

Sample	Band edge (nm)	Surface state (nm)	R_A	QY (%)
$Zn_{0.8}$ –DE-10	412	509	0.55	99.0
$Zn_{0.8}$ –DE-30	428	540	0.56	50.4
$Zn_{0.8}$ –DE-60	435	550	0.50	25.3
$Zn_{0.8}$ –TDE-10	395	500	0.81	72.6
$Zn_{0.8}$ –ODE-10	381	500	0.88	55.4

$$R_A = \frac{\text{Area Surface state}}{\text{Area Sample}} \quad (\text{Area}_{\text{Sample}} = \text{Area}_{\text{Band edge}} + \text{Area}_{\text{Surface state}})$$

Table. S2 The surface compositions and binding energies of $Zn_{0.8}$ NCs.

Sample	Surface compositions Zn : Zn^{2+} : Cd	Binding energy (eV)		Quantum yields (%)
		Cd $3d_{5/2}$	Zn $2p_{3/2}$	
$Zn_{0.8}$ -DE-10	41.5 : 20.5 : 38.0	403.6	1022.0	99.0
$Zn_{0.8}$ -DE-30	20.6 : 28.4 : 51.0	404.8	1023.3	50.4
$Zn_{0.8}$ -DE-60	14.0 : 25.0 : 61.0	405.1	1023.3	25.3
$Zn_{0.8}$ -TDE-10	33.1 : 23.9 : 43.0	404.3	1022.7	72.6
$Zn_{0.8}$ -ODE-10	28.0 : 32.0 : 40.0	405.1	1023.7	55.4

Table S3. The detailed EXAFS fitting parameters of the Zn K-edge and Cd K-edge for the $Zn_{0.8}$ NCs.

Zn K-edge

Sample	Path	CN	CN ratio	R (Å)	σ^2 ($x10^{-3}$) (Å^2)	ΔE_0 (eV)	QY (%)
$Zn_{0.8}$-DE-10	Zn-O	1.2	0.44	1.95	3.08	1.06	99.0
	Zn-S	1.5		2.29			
$Zn_{0.8}$-DE-30	Zn-O	1.9	0.68	1.95	3.08	2.21	50.4
	Zn-S	0.9		2.34			
$Zn_{0.8}$-DE-60	Zn-O	2.0	0.83	1.96	3.08	0.88	25.3
	Zn-S	0.4		2.29			
$Zn_{0.8}$-TDE-10	Zn-O	1.5	0.47	1.94	3.08	2.22	72.6
	Zn-S	1.7		2.31			
$Zn_{0.8}$-ODE-10	Zn-O	1.2	0.50	1.97	3.08	0.26	55.4
	Zn-S	1.2		2.29			

CN ratio = $CN_{Zn-O}/(CN_{Zn-O}+CN_{Zn-S})$

Cd K-edge

Sample	Path	CN	CN ratio	R (Å)	σ^2 ($x10^{-3}$) (Å^2)	ΔE_0 (eV)	QY (%)
$Zn_{0.8}$-DE-10	Cd -O	0.4	0.15	2.20	3.08	1.51	99.0
	Cd -S	2.3		2.50			
$Zn_{0.8}$-DE-30	Cd -O	0.8	0.26	2.18	3.08	1.73	50.4
	Cd -S	2.3		2.51			
$Zn_{0.8}$-DE-60	Cd -O	0.9	0.31	2.20	3.08	1.10	25.3
	Cd -S	2.0		2.51			
$Zn_{0.8}$-TDE-10	Cd-O	0.4	0.15	2.17	3.08	1.19	72.6
	Cd-S	2.2		2.50			
$Zn_{0.8}$-ODE-10	Cd-O	0.6	0.19	2.21	3.08	3.50	55.4
	Cd-S	2.5		2.51			

CN ratio = $CN_{Cd-O}/(CN_{Cd-O}+CN_{Cd-S})$

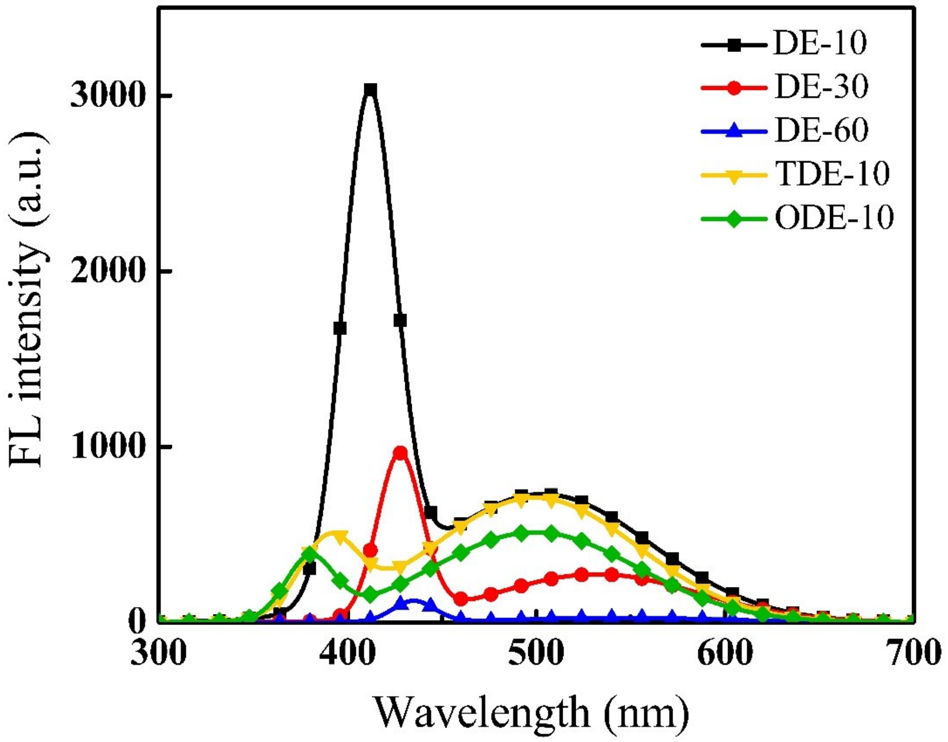


Fig. S1 The quantitative FL emission spectrum of Zn0.8 NCs prepared by DE, TDE and ODE.

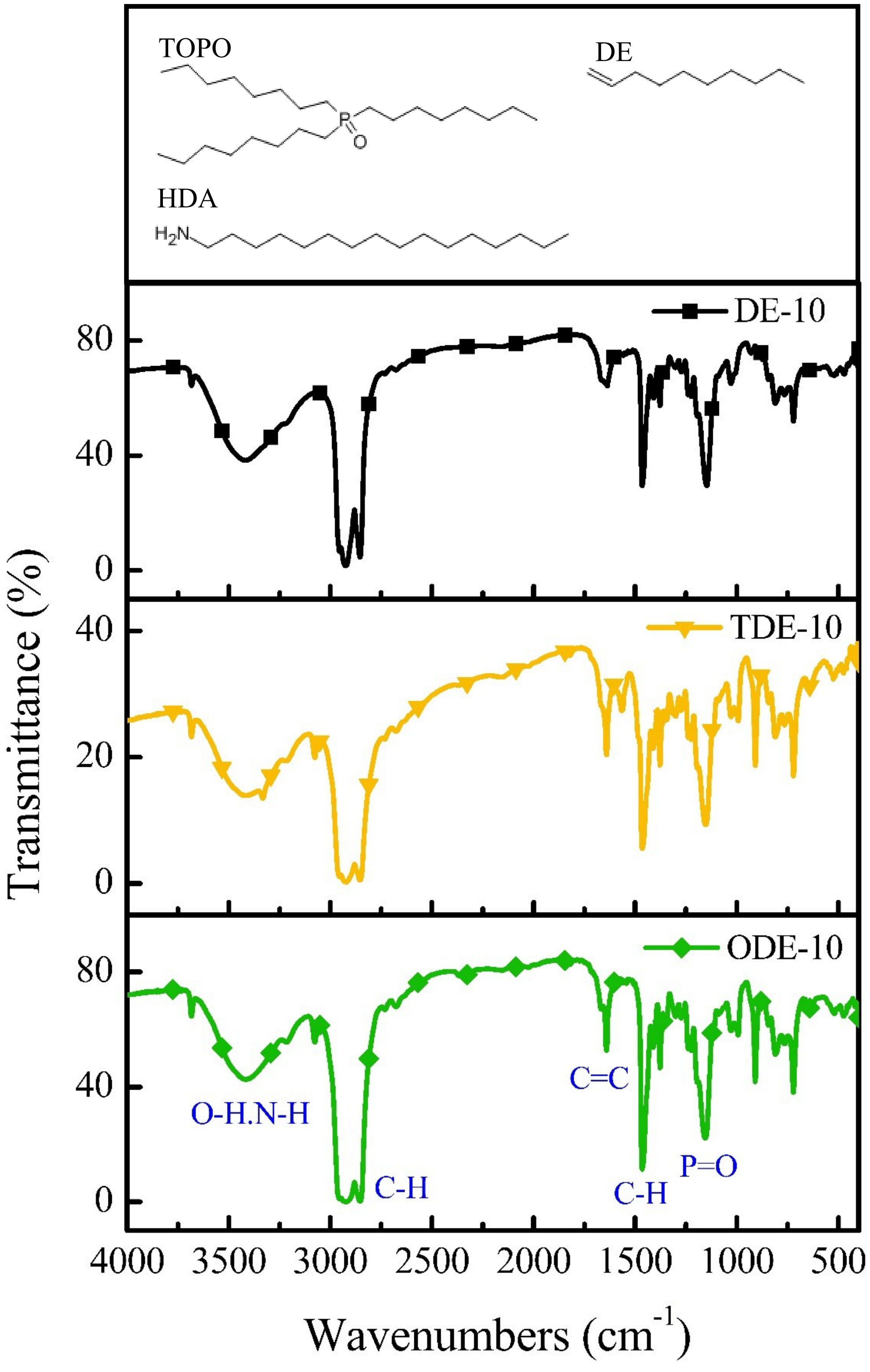


Fig. S2 FTIR spectra of $Zn_{0.8}$ NCs prepared by DE, TDE and ODE.

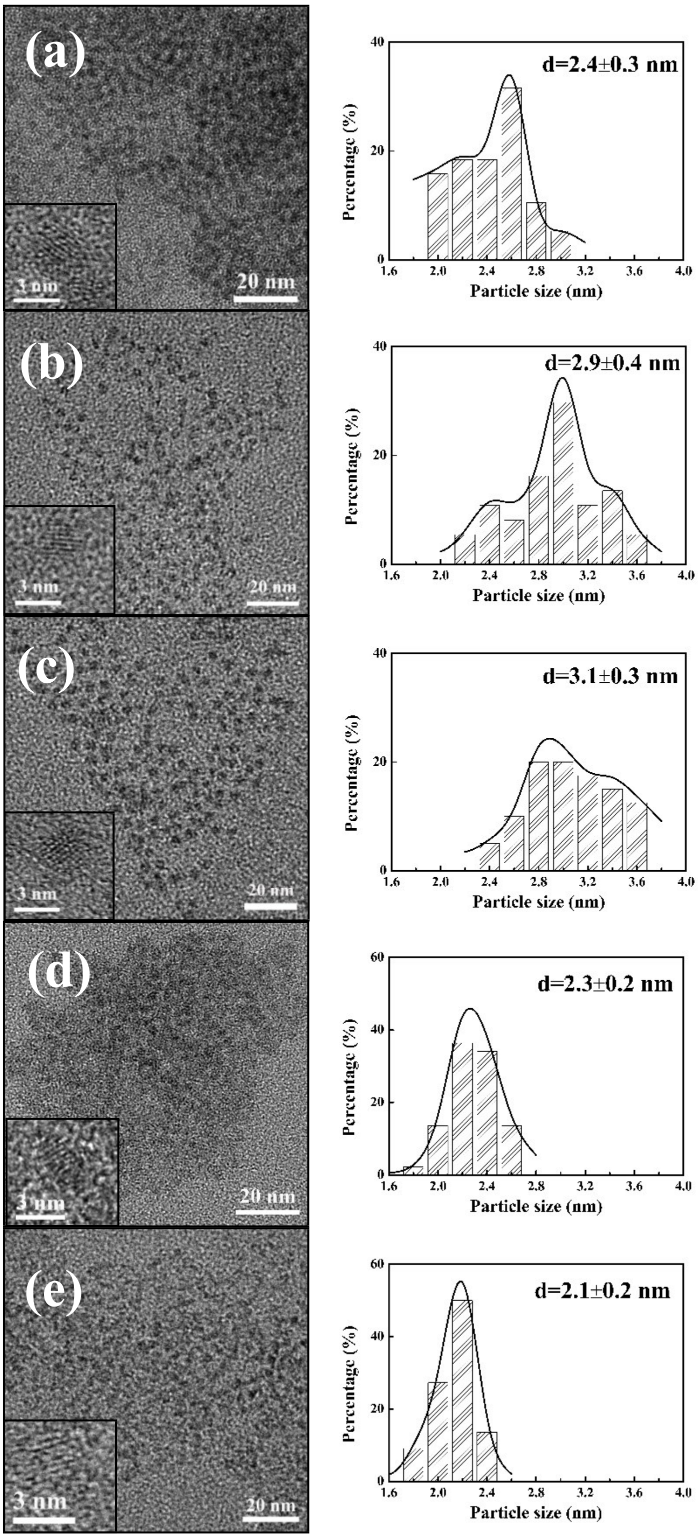


Fig. S3 TEM images and size distribution of $Zn_{0.8}$ NCs. (a) DE-10, (b) DE-30, (c) DE-60, (d) TDE-10 and (e) ODE-10.

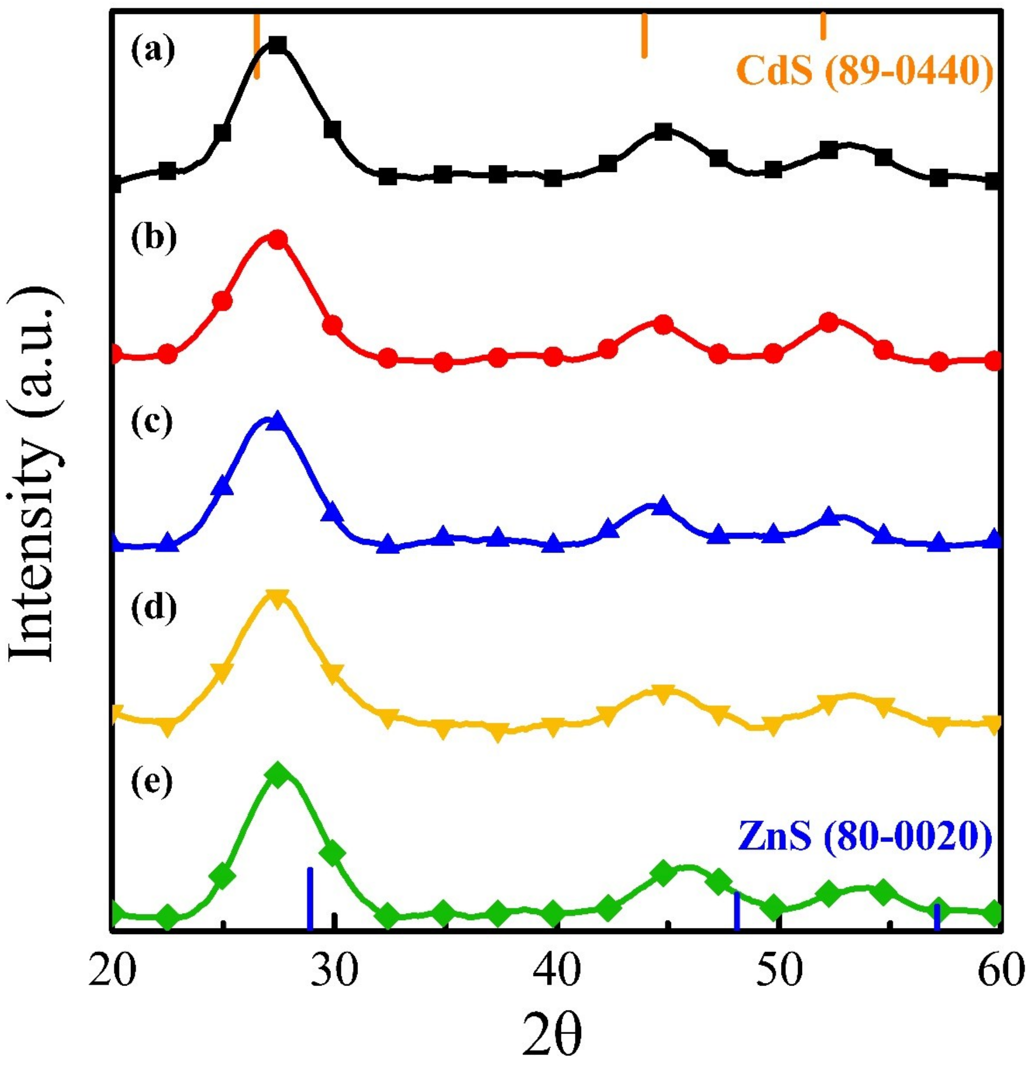


Fig. S4 XRD patterns of various $Zn_{0.8}$ NCs and zinc blende CdS and ZnS reference, (a) DE-10, (b) DE-30, (c) DE-60, (d) TDE-10 and (e) ODE-10.

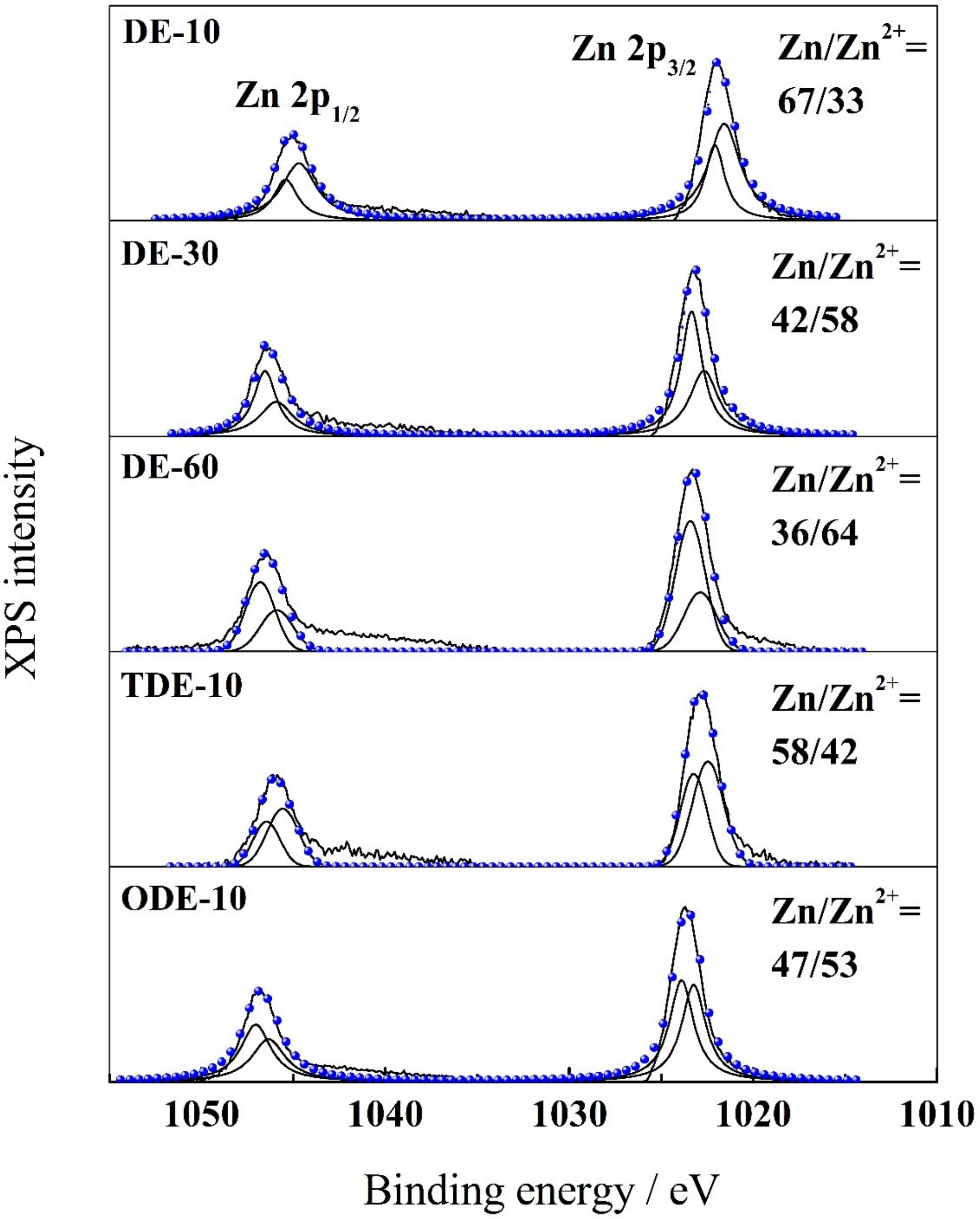


Fig. S5 The XPS fitting results for Zn 2p spectra of $Zn_{0.8}$ NCs.

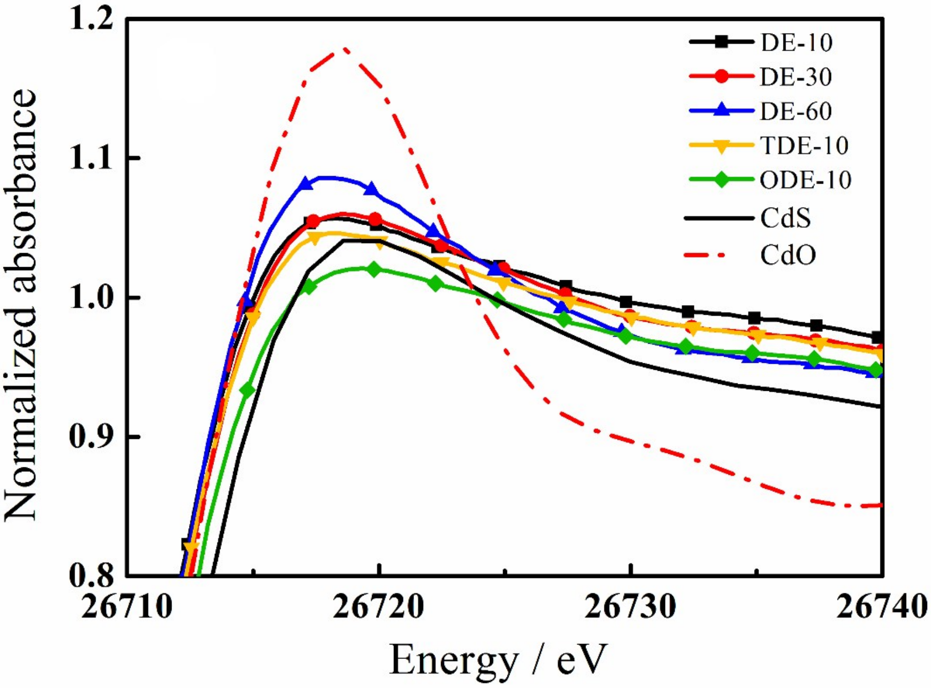
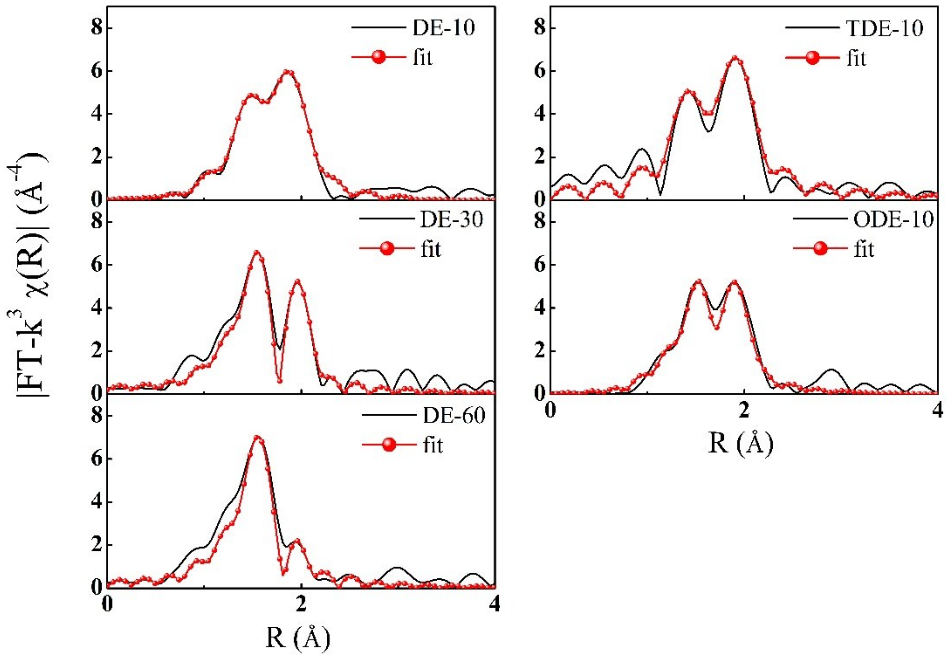


Fig. S6 The XANES patterns of $Zn_{0.8}$ NCs at Cd K-edge.



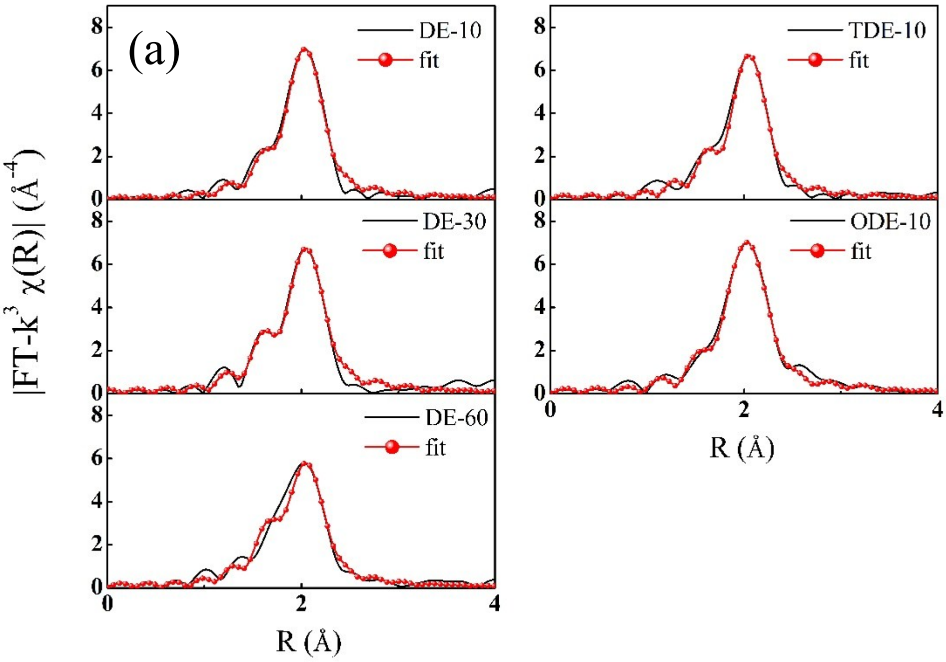


Fig. S7 The Fourier Transformed radial structure functions of $Zn_{0.8}$ NCs at (a) Zn K-edge and (b) Cd K-edge.

(b)