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Supplementary Information

Correlation between surface state and band edge emission of white light $Zn_xCd_{1-x}S$ nanocrystals

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Experimental Procedure

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

A series of colloidal ternary semiconductor $Zn_xCd_{1-x}S$ (x=0, 0.2, 0.4, 0.5, 0.7, 0.8, 0.9 and 1, named as Znx) NCs is prepared by thermal pyrolyzed organometallic route. Total amount of 0.3 mmol of CdO and ZnO were mixed with stearic acid (SA), which as complex reagent, in a three-necked flask and then heated to 230 ^{o}C under Ar flow until a clear solution was formed to prepare the cadmium/zinc-SA precursor. The solution was then allowed to cool down to room temperature, and a white solid precipitate was obtained. After cadmium/zinc-SA precursor was formed, the mixture solvent, 15 mmol of TOPO and 24 mmol of HDA, was added into three-necked flask and stirred together under Ar at room temperature for 5 min, then reheated the sample up to 320 ^{o}C to form a transparency solution. At this temperature, S-ODE precursor, which was 1.5 mmol of sulfur dissolved in 4 mL of ODE, was swiftly injected into three-neck flask. The nuclei formed quickly and take out the samples under desire growth time. After the reaction was complete (about 60 min), the mixed solution was swiftly cooled down to 150 oC to stop reaction. Samples were precipitated with hot anhydrous methanol for purification. The precipitate was dissolved in hexane to remove unreacted reagents and excess TOPO or HDA and for further measure.

The optical properties of samples were measured by Fluorescence Spectrophotometer (FL, Hitachi F-7000) and UV-Vis spectrometer (UV-Vis, Jasco V-670 spectrometer), respectively. Relative QY of samples were determined by comparing the area under the curve of FL emission for the $Zn_xCd_{1-x}S$ NCs with that of fluorescent dye (Rhodamine 101 in ethanol). Both of sample and reference are have the same absorbance under the same absorption wavelength. X-ray diffraction (XRD) patterns were recorded on a MacScience Co. Ltd MO3X-HF[22] powder diffractometer with Cu K_α (λ = 1.542 Å) as the incident radiation. Transmission electron microscope (HRTEM, JEOL JEM-2010) was used to analyze the particle size and more than 100 particles was count to measure the size distribution of samples. The compositions of NCs were conducted by X-ray photoelectron spectroscopy (XPS, Thermo VG Scientific Sigma Probe) using an Al K_α radiation was used to study the surface compositions of $Zn_xCd_{1-x}S$ NCs. All binding energies were calibrated with respect to the C 1s line at 284.6 eV. The surface compositions of $Zn_xCd_{1-x}S$ NCs were estimated by calculating the integral of each peak. The exact chemical compositions of the obtained $Zn_xCd_{1-x}S$ NCs were measured by inductively coupled plasma – atomic emission spectrometer (ICP-AES, France Horiba JobinYvon JY2000-2) using a standard HCl/HNO_3 digestion.

The typical XAS spectra of various 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 $\Delta E/E$ better than 1 x 10^{-4} at the Cd K-edge (26711 eV) and Zn K-edge (9659 eV). In general, all NCs were dispersed uniformly on the tape and prepared as thin pellets with an appropriate absorption thickness (μ_x = 1.0, where μ is the absorption edge and x is the thickness of the sample) so as to attain the proper edge jump step at the absorption edge region. In order to acquire acceptable-quality spectra, each XAS measurement was repeated at least twice and averaged for successive comparison. Moreover, 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 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.[36] 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.

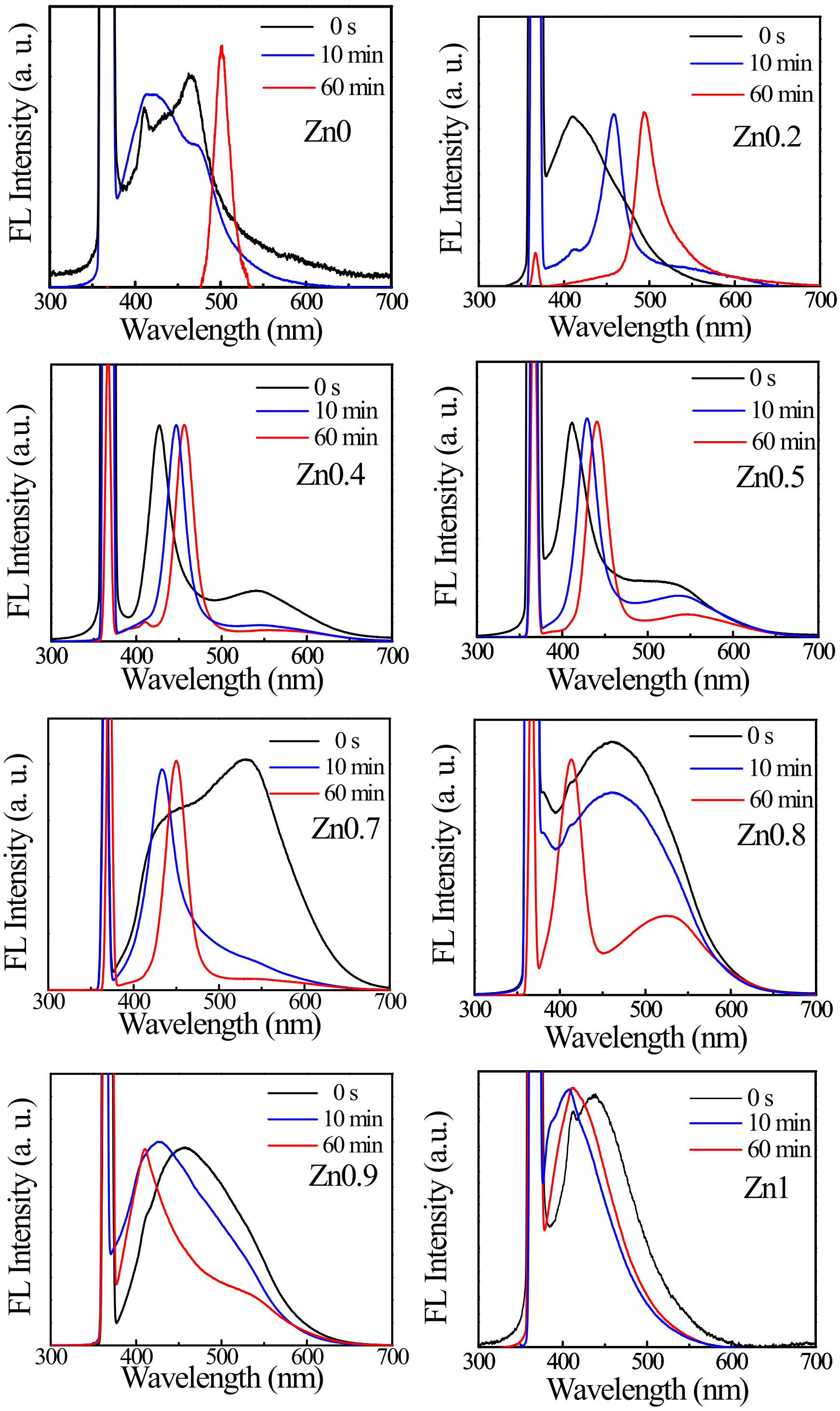

Figure S1 Temporal evolution of Fluorescence spectra of Znx NCs. (λ_{ex}= 365 nm)

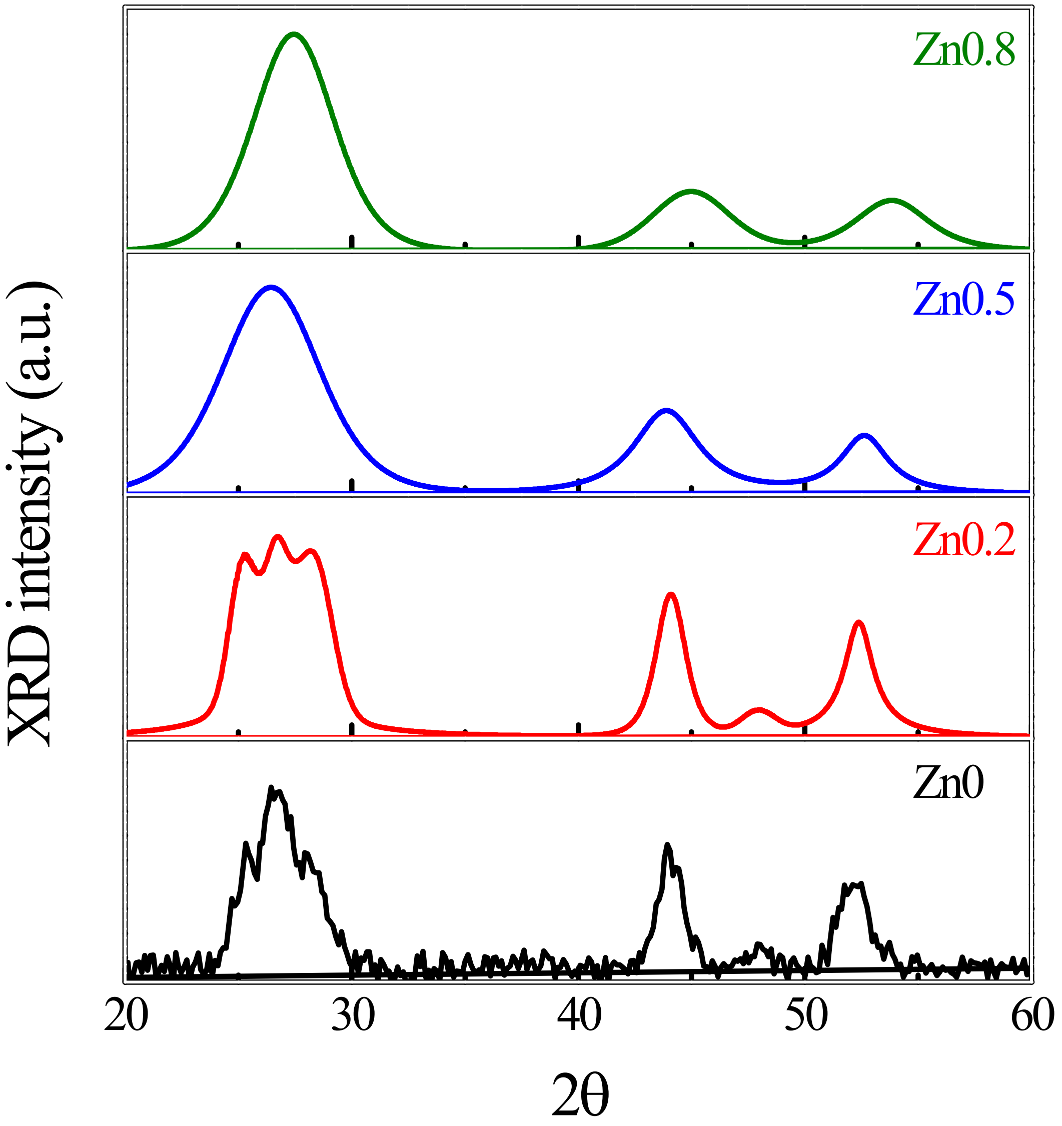

Figure S2 XRD patterns of Znx NCs

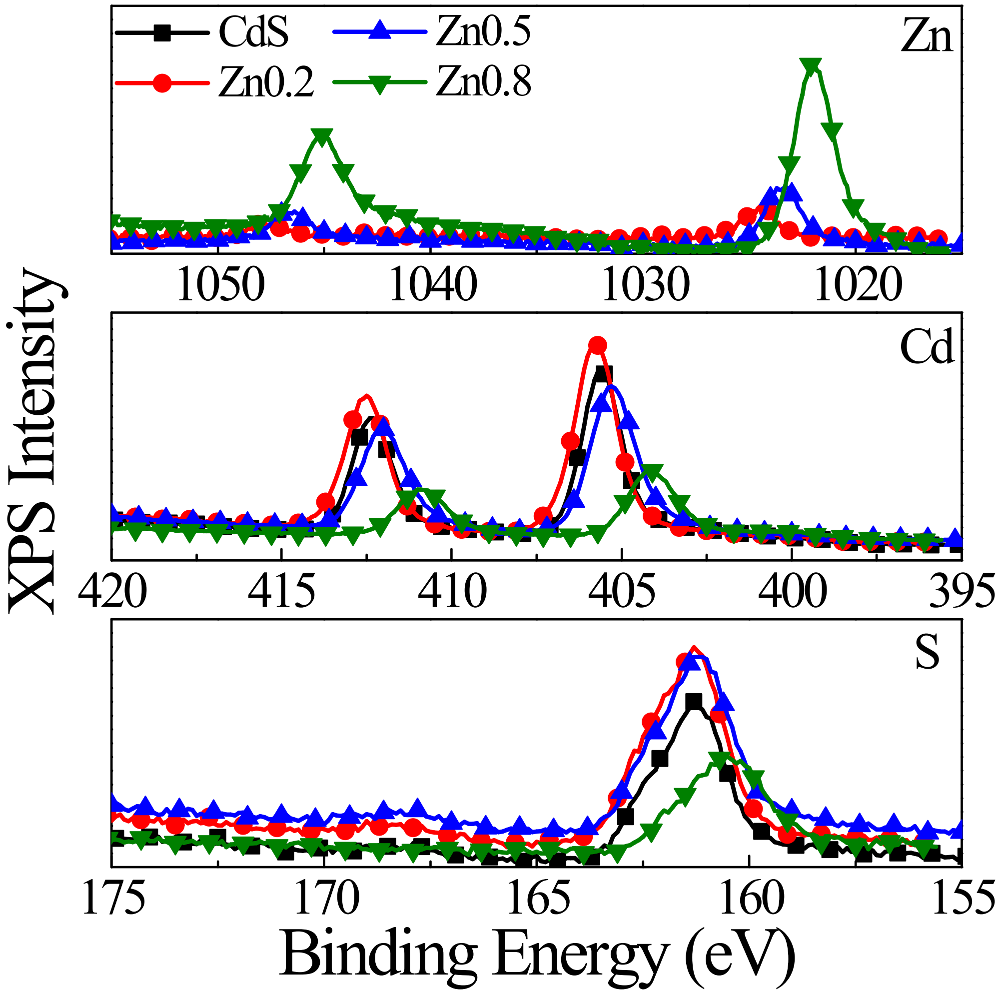

Figure S3 XPS spectra of Znx NCs

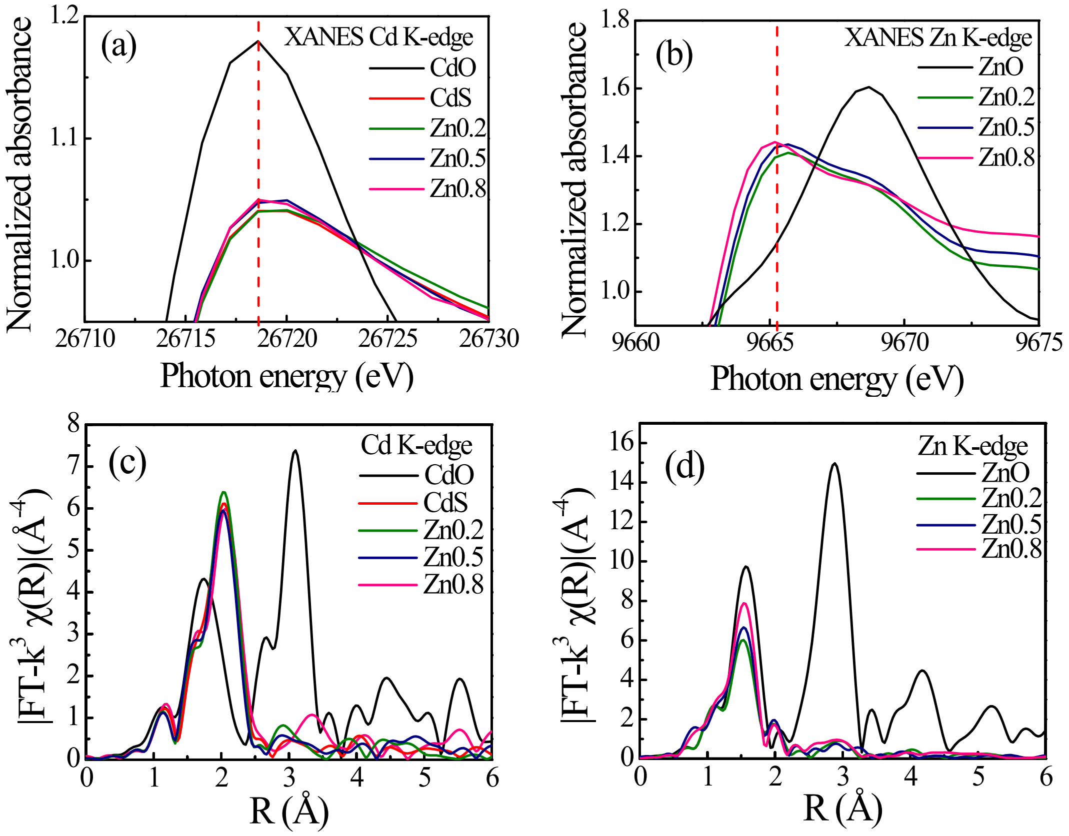

Figure S4 The XANES patterns of $Zn_xCd_{1-x}S$ NCs at (a) Cd K-edge and (b) Zn K-edge, the Fourier Transformed radial structure functions of $Zn_xCd_{1-x}S$ NCs at (c) Cd K-edge and (d) Zn K-edge.

Table S1. Physical and optical properties of $Zn_xCd_{1-x}S$ NCs reacts for 60 min

Nominal composition	Emission wavelength (nm)	Particle size[a] (nm)	QY (%)	Emission range (nm)
CdS	500	-	1	469-540
Zn0.2	493	7.1	4	466-580
Zn0.4	456, 566[*]	-	21	420-700
Zn0.5	440, 546[*]	3.6	26	416-700
Zn0.7	428, 541[*]	-	42	410-700
Zn0.8	411, 523[*]	3.1	56	380-700
Zn0.9	410, 485[*]	-	27	377-700
ZnS	410	-	-	-

[*] Surface state emission

[a] HRTEM characterization

Table S2 EXAFS fitting parameters of the Cd K-edge and Zn K-edge for the $Zn_xCd_{1-x}S$ NCs.

Cd K-edge

Sample	Path	CN[a]	R[b] (Å)	σ^2(×10^{-3})[c](Å^2)	ΔE_0[d] (eV)
CdO	Cd-O	4.4	2.28	0.008	1.7
	Cd-Cd	7.1	3.33		
CdS	Cd-O	1.2	2.22	0.003	16.0
	Cd-S	4.9	2.39		
Zn0.2	Cd-O	1.1	2.22	0.003	17.6
	Cd-S	4.2	2.39		
Zn0.5	Cd-O	1.3	2.22	0.003	15.8
	Cd-S	4.1	2.39		
Zn0.8	Cd-O	1.6	2.22	0.003	17.1
	Cd-S	4.2	2.39		

Zn K-edge

Sample	Path	CN[a]	R[b] (Å)	σ^2(×10^{-3})[c](Å^2)	ΔE_0[d] (eV)
ZnO	Zn-O	4.8	1.99	0.006	-0.2
	Zn-Zn	9.6	3.21		
Zn0.2	Zn-O	2.1	1.95	0.003	-1.0
	Zn-Zn	0.4	2.28		
Zn0.5	Zn-O	2.1	1.95	0.003	0.4
	Zn-Zn	0.4	2.30		
Zn0.8	Zn-O	2.4	1.95	0.003	17.1
	Zn-Zn	0.3	2.30		

[a] CN: coordination number, [b] R: bond distance, [c] σ^2: Debye-Waller factor, [d] ΔE_0: inner potential correction.

Table S3 ICP, TEM and XPS characterizations of $Zn_xCd_{1-x}S$ NCs.

Samples	Chemical compositions Cd:Zn	d-spacing (nm)	Binding energy (eV)		Surface compositions Cd:Zn
			Cd $3d_{5/2}$	Zn $2p_{3/2}$	
CdS	100:0	0.335	405.7	NA	100:0
Zn0.2	92:8	0.337	405.8	1024.5	95:5
Zn0.5	78:22	0.328	405.3	1023.5	88:12
Zn0.8	66:34	0.323	404.2	1022.0	42:58