Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information

Single Enzyme Direct Biomineralization of ZnS, $Zn_xCd_{1-x}S$ and $Zn_xCd_{1-x}S$-ZnS Quantum Confined Nanocrystals

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Figure S1: a) UV-vis absorption and b) corresponding fluorescence emission spectra of buffered (pH=9.0) solutions containing various combinations of Zn acetate ($Zn(Ac)_2$), L-cysteine (L-Cys), the smCSE enzyme incubated for 90 min at room temperature.

Figure S2: Lattice fitting of the ZnS nanocrystal shown in Figure 2b; a) HAADF-STEM image, b) corresponding FFT and c) table of measured lattice spacings and interplanar angles compared with ideal values for sphalerite ZnS viewed along $[11\bar{2}]$ and wurtzite ZnS viewed along $[1\bar{1}0]$ and $[1\bar{1}\bar{2}]$.

Figure S3: SEM-XEDS spectra and calculated mean compositions of $Zn_xCd_{1-x}S$ nanocrystals synthesized with varying ratios of zinc acetate ($Zn(Ac)_2$) to cadmium acetate ($Cd(Ac)_2$).

Figure S4: Tauc plots of $(\alpha h\nu)^{1/2}$ versus photon energy ($h\nu$) showing the band gaps of a) biomineralized ZnS, CdS, and $Zn_{0.73}Cd_{0.27}S$ nanocrystals and b) $Zn_xCd_{1-x}S$ biomineralized nanocrystals of varying composition.

Figure S5: Lattice fitting of the $Zn_{0.73}Cd_{0.27}S$ nanocrystal shown in Figure 4b; a) HAADF-STEM image, b) corresponding FFT image and c) table of measured lattice spacings and interplanar angles compared with ideal values for the sphalerite structures of ZnS, $Zn_{0.73}Cd_{0.27}S$ and CdS viewed along [001].

Figure S6: SEM-XEDS spectra and calculated mean composition of $Zn_xCd_{1-x}S$ nanocrystals synthesized by addition of Na_2S to an aqueous solution of cadmium acetate and zinc acetate in a 4:1 Zn:Cd molar ratio in the presence of L-cysteine.

Figure S7: Lattice fitting of the 3nm diameter $Zn_{0.73}Cd_{0.27}S$-ZnS particle shown in Figure 7b; a) HAADF-STEM image, b) corresponding FFT and c) table of measured lattice spacings and interplanar angles compared with ideal values for wurtzite ZnS, $Zn_{0.73}Cd_{0.27}S$ and CdS viewed along $[21\bar{2}]$.

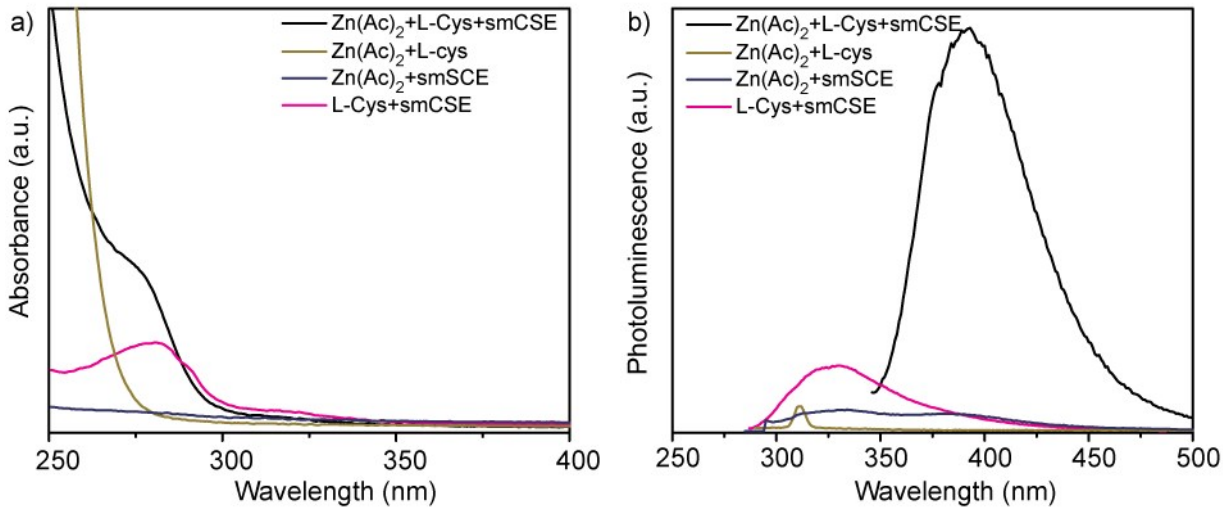
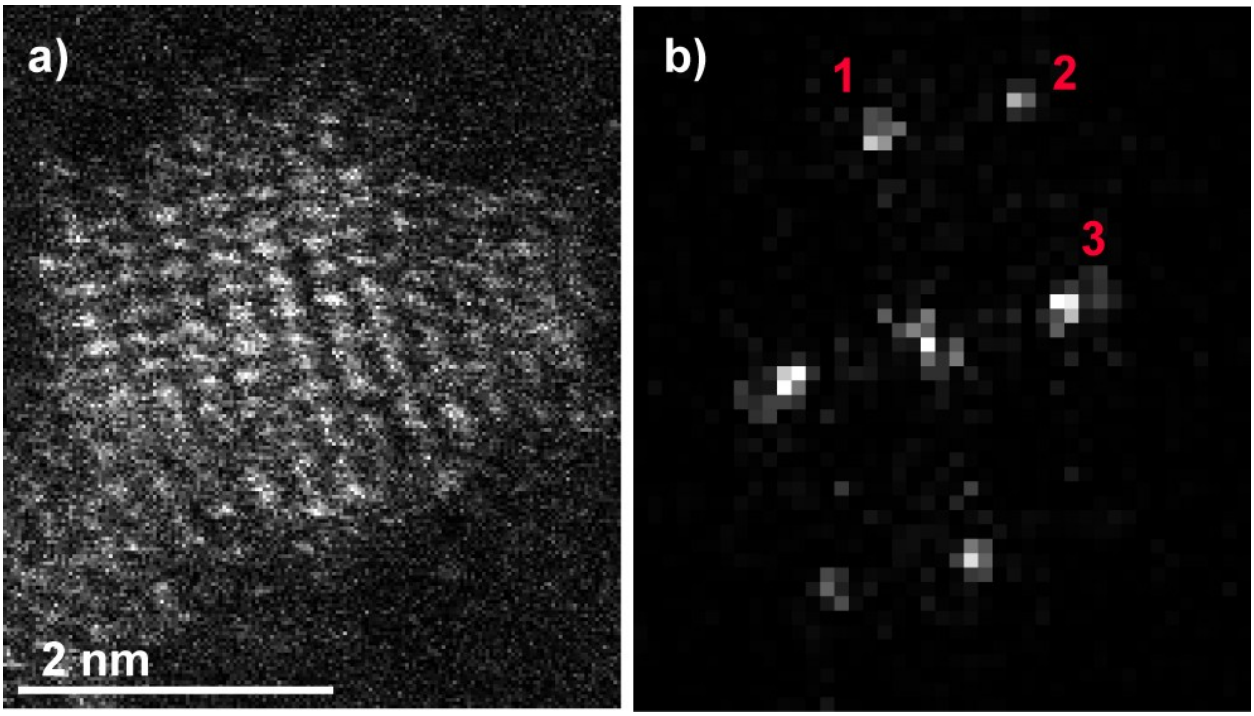


Figure S1: a) UV-vis absorption and b) corresponding fluorescence emission spectra of buffered (pH=9.0) solutions containing various combinations of Zn acetate ($Zn(Ac)_2$), L-cysteine (L-Cys), the smCSE enzyme incubated for 90 min at room temperature. Note that all three components are required to obtain absorbance and photoluminescence consistent with ZnS formation. The absorbance and photoluminescence peaks for the L-Cys+smCSE sample originate from the enzyme.



c)	Measurement	Sphalerite ZnS $[11\bar{2}]$	Wurtzite ZnS $[1\bar{1}0]$	Wurtzite ZnS $[1\bar{1}\bar{2}]$
Plane 1	d=2.02 Å	1.91 Å $(2\bar{2}0)$	1.91 Å (110)	1.91 Å (110)
Plane 2	d=1.66 Å	1.63 Å $(3\bar{1}1)$	1.62 Å (112)	1.59 Å (201)
Plane 3	d=2.93 Å	3.12 Å (111)	3.10 Å (002)	2.91 Å $(1\bar{1}1)$
<1,2>	32.8˚	31.5˚	31.6˚	33.2˚
<2,3>	54.0˚	58.5˚	58.4˚	56.8˚
<3,1>	86.8˚	90.0˚	90.0˚	90.0˚

Figure S2: Lattice fitting of the ZnS nanocrystal shown in Figure 2b; a) HAADF-STEM image, b) Corresponding FFT image and c) table of measured lattice spacings and interplanar angles compared with ideal values for sphalerite ZnS viewed along $[11\bar{2}]$ and wurtzite ZnS viewed along $[1\bar{1}0]$ and $[1\bar{1}\bar{2}]$.

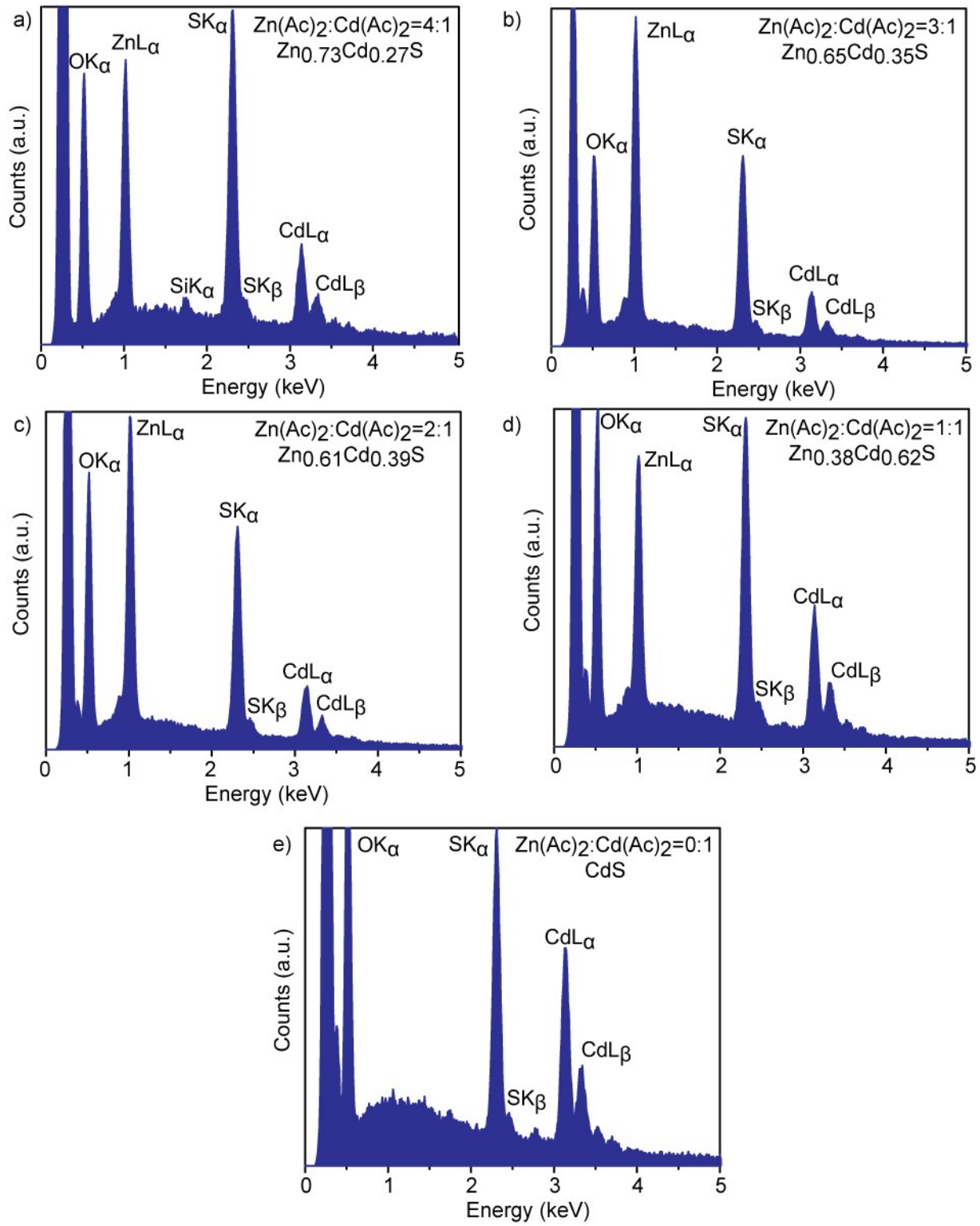


Figure S3: SEM-XEDS spectra and calculated mean compositions of $Zn_xCd_{1-x}S$ nanocrystals synthesized with varying ratios of zinc acetate ($Zn(Ac)_2$) to cadmium acetate ($Cd(Ac)_2$).

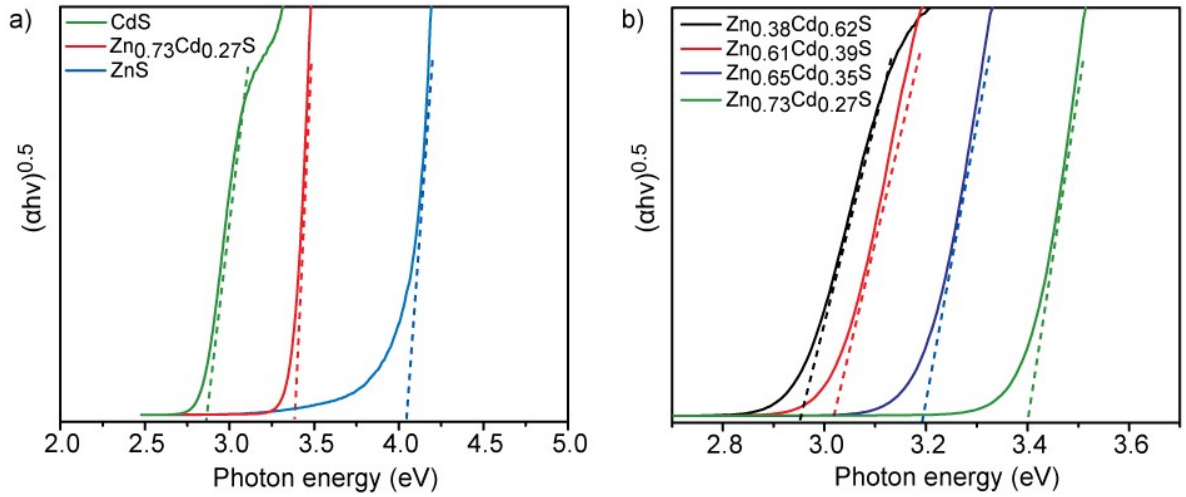
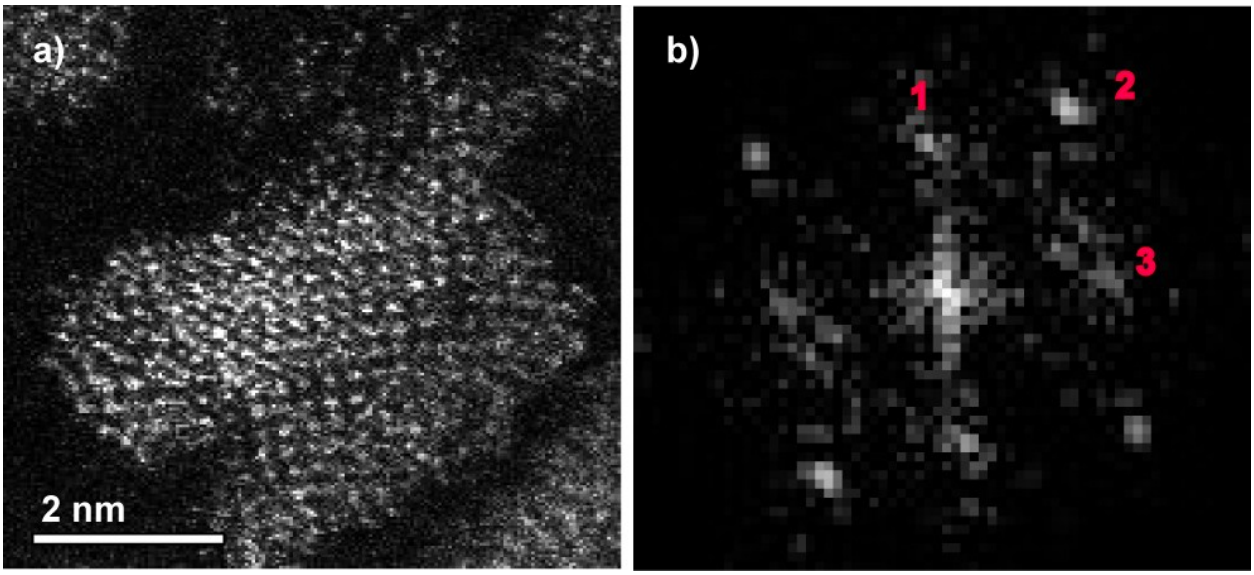


Figure S4: Tauc plots of $(\alpha h\nu)^{1/2}$ versus photon energy (hv) showing the band gaps of a) biomineralized ZnS, CdS, and $Zn_{0.73}Cd_{0.27}S$ nanocrystals and b) $Zn_xCd_{1-x}S$ biomineralized nanocrystals of varying composition.



c)	Measurement	Sphalerite ZnS [001]	Calculated Sphalerite $Zn_{0.73}Cd_{0.27}S$ [001]	Sphalerite CdS [001]
Plane 1	d=2.80 Å	2.70 Å (200)	2.75 Å (200)	2.91 Å (200)
Plane 2	d=1.99 Å	1.91 Å (220)	1.94 Å (220)	2.06 Å (220)
Plane 3	d=2.78 Å	2.70 Å (020)	2.75 Å (020)	2.91 Å (020)
<1,2>	43.0˚	45.0˚	45.0˚	45.0˚
<2,3>	48.0˚	45.0˚	45.0˚	45.0˚
<3,1>	89.0˚	90.0˚	90.0˚	90.0˚

Figure S5: Lattice fitting of the $Zn_{0.73}Cd_{0.27}S$ nanocrystal shown in Figure 4b; a) HAADF-STEM image, b) corresponding FFT image and c) table of measured lattice spacings and interplanar angles compared with ideal values for the sphalerite structures of ZnS, $Zn_{0.73}Cd_{0.27}S$ and CdS viewed along [001].

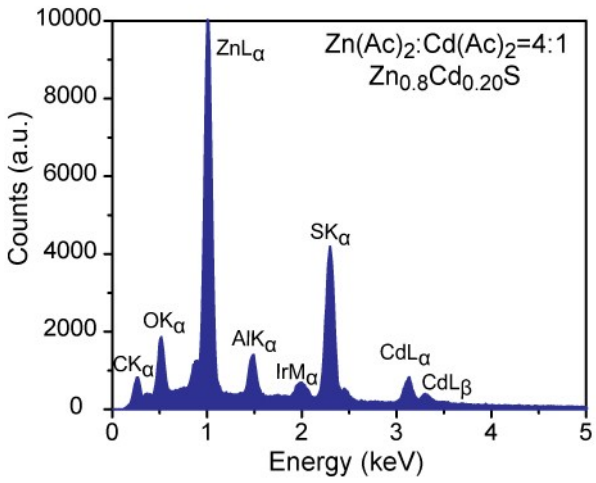
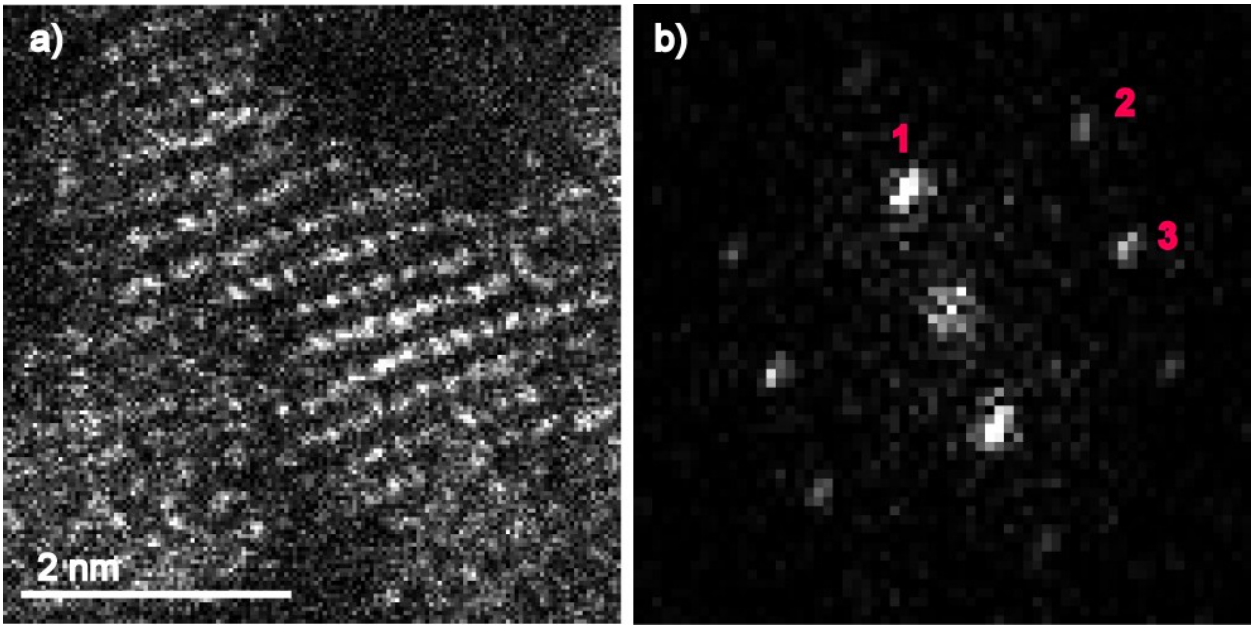


Figure S6: SEM-XEDS spectra and calculated mean composition of $Zn_xCd_{1-x}S$ nanocrystals synthesized by addition of Na_2S to an aqueous solution of cadmium acetate and zinc acetate in a 4:1 Zn:Cd molar ratio in the presence of L-cysteine. In contrast to the biomineralized materials, this shows a close correspondence between the actual and nominal nanoparticle compositions.



c)	Measurement	Wurtzite ZnS $[21\bar{2}]$	Calculated Wurtzite $Zn_{0.73}Cd_{0.27}S$ $[21\bar{2}]$	Wurtzite CdS $[21\bar{2}]$
Plane 1	d=2.95 Å	2.92 Å (101)	2.96 Å (101)	3.16 Å (101)
Plane 2	d=1.66 Å	1.59 Å (021)	1.62 Å (021)	1.73 Å (021)
Plane 3	d=2.02 Å	1.90 Å (120)	1.94 Å $(1\bar{2}0)$	2.07 Å (120)
<1,2>	54.9˚	56.8˚	56.8˚	56.8˚
<2,3>	34.6˚	33.2˚	33.2˚	33.2˚
<3,1>	89.5˚	90.0˚	90.0˚	90.0˚

Figure S7: Lattice fitting of the 3nm diameter $Zn_{0.73}Cd_{0.27}S$-ZnS particle shown in Figure 7b; a) HAADF-STEM image, b) corresponding FFT and c) table of measured lattice spacings and interplanar angles compared with ideal values for wurtzite ZnS, $Zn_{0.73}Cd_{0.27}S$ and CdS viewed along $[21\bar{2}]$.