

Supporting Information

Heterojunction of Zinc Blende/Wurtzite in $\text{Zn}_{1-x}\text{Cd}_x\text{S}$ Solid Solution for Efficient Solar Hydrogen Generation: X-ray Absorption/Diffraction Approaches

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Table S1. Summary of crystal data and refinement results of $\text{Zn}_{1-x}\text{Cd}_x\text{S}$ at room temperature with zinc blende unit cell (Space Group: $F\bar{4}3m$)

No.	ZnS	$\text{Zn}_{0.84}\text{Cd}_{0.16}\text{S}$	$\text{Zn}_{0.58}\text{Cd}_{0.42}\text{S}$	$\text{Zn}_{0.52}\text{Cd}_{0.48}\text{S}$	$\text{Zn}_{0.45}\text{Cd}_{0.55}\text{S}$	$\text{Zn}_{0.18}\text{Cd}_{0.82}\text{S}$	CdS
a=b=c (Å)	5.39109(38)	5.48717(50)	5.56952(50)	5.6042(17)	5.6946(21)	5.77648(86)	5.84509(80)
V (Å ³)	156.686(33)	165.214(45)	172.764(47)	176.01(16)	184.67(20)	192.748(83)	197.960(82)
Position (Zn/Cd)	(x, y, z : 0, 0, 0)						
Beq (Å ²)	0.648	0.662	0.441	0.588	0.336	0.368	0.541
Position (S)	(x, y, z : 0.25, 0.25, 0.25)						
Beq (Å ²)	0.945	0.748	0.601	0.791	0.764	0.764	0.778
Rp%/Rwp%	3.27/4.77	2.69/ 3.60	2.88/ 4.50	5.37/ 8.62	3.58/4.73	3.33/4.57	4.05/4.91
χ^2	1.82	1.25	1.81	3.07	2.01	2.04	2.15
Zn/Cd-S (Å) x4 average	2.334(4)	2.376(2)	2.411(7)	2.426(7)	2.465(8)	2.501(3)	2.531(2)
Crystal size (nm)	6.6	5.3	4.3	4.2	4.2	4.1	3.8

Table S2. Summary of crystal data and refinement results of $\text{Zn}_{1-x}\text{Cd}_x\text{S}$ ($x = 0.48, 0.55, 0.82$ and 1)) at room temperature with wurtzite unit cell (Space Group: $P6_3mc$)

NO.	$\text{Zn}_{0.48}\text{Cd}_{0.52}\text{S}$	$\text{Zn}_{0.45}\text{Cd}_{0.55}\text{S}$	$\text{Zn}_{0.18}\text{Cd}_{0.82}\text{S}$	CdS
a=b (Å)	4.02547(54)	4.07914(51)	4.10130(23)	4.1456(22)
c (Å)	6.52068(93)	6.60012(43)	6.67431(34)	6.7345(69)
V (Å ³)	91.507(86)	95.108(87)	97.225(48)	99.45(20)
Position (Cd)	(0.3333,0.6667, 0)			
Beq (Å ²)	0.474	0.561	0.446	0.475
Position (S)	(0.3333,0.6667, 0.377)			
Beq (Å ²)	0.864	0.884	0.689	0.784
Zn/Cd-S (Å) x 1	2.458(3)	2.491(1)	2.516(2)	2.538(9)
Zn/Cd-S (Å) x 3	2.458(6)	2.488(2)	2.506(2)	2.532(7)
Mean of Zn/Cd-S	2.458(6)	2.489(2)	2.510(2)	2.534(9)
Hexagonal:cubic ratio (%)	0.5	7.3	2.0	3.8

Table S3. Elemental compositions of $\text{Zn}_{1-x}\text{Cd}_x\text{S}$ samples with various x values.

Samples	Atomic ratio of Zn/Cd		
	Precursor composition	EDS	ICP-MS
ZnS	1:0	1:0	1:0
$\text{Zn}_{0.84}\text{Cd}_{0.16}\text{S}$	0.8:0.2	0.84:0.16	0.83:0.17
$\text{Zn}_{0.58}\text{Cd}_{0.42}\text{S}$	0.6:0.4	0.58:0.42	0.57:0.43
$\text{Zn}_{0.52}\text{Cd}_{0.48}\text{S}$	0.5:0.5	0.52:0.48	0.55:0.45
$\text{Zn}_{0.45}\text{Cd}_{0.55}\text{S}$	0.4:0.6	0.45:0.55	0.42:0.58
$\text{Zn}_{0.18}\text{Cd}_{0.82}\text{S}$	0.2:0.8	0.18:0.82	0.21:0.79
CdS	0:1	0:1	0.1

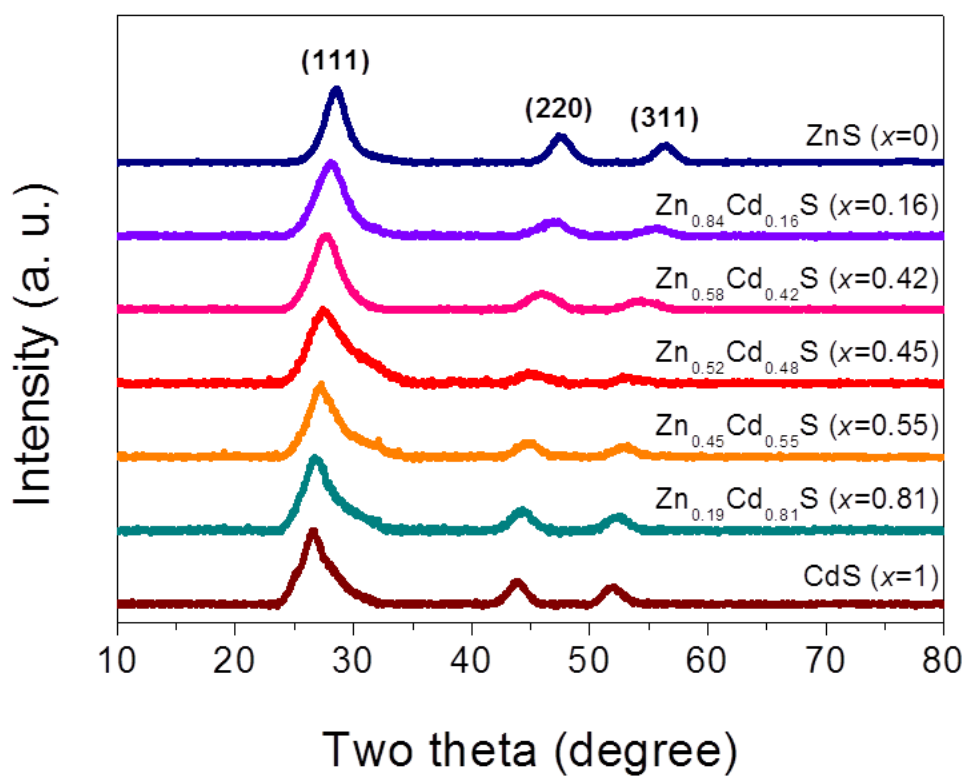
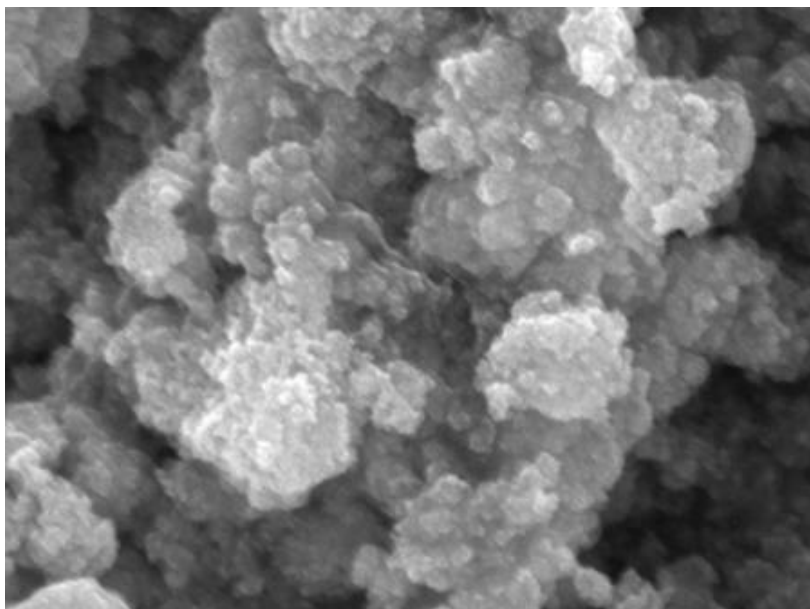
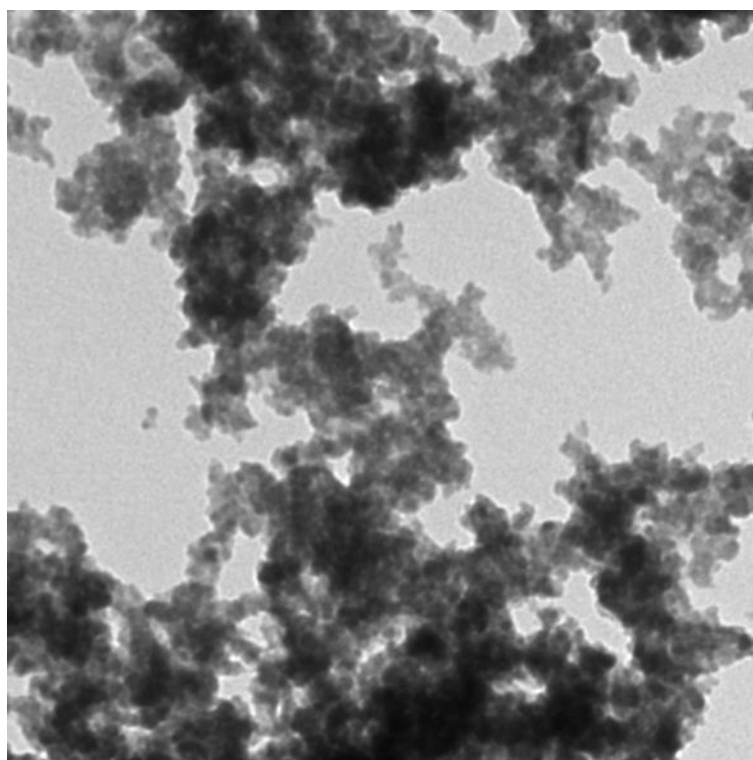


Figure S1. In-house XRD patterns of $\text{Zn}_{1-x}\text{Cd}_x\text{S}$ samples with various x values.



— 100 nm

Figure S2. SEM image of CdS sample.



— 100 nm

Figure S3. TEM image of CdS sample.

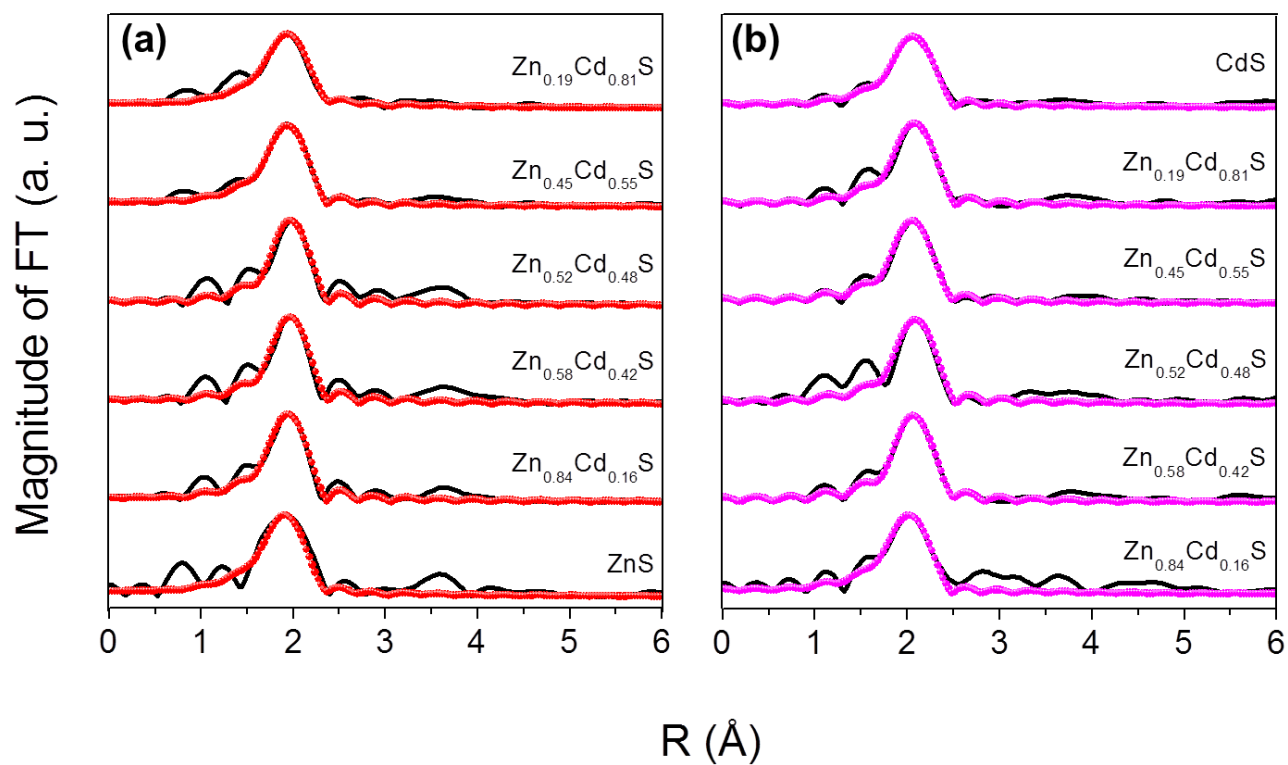


Figure S4. Fourier transform of k^3 -weighted EXAFS spectra for (a) Zn K -edge and (b) Cd K -edge of various $\text{Zn}_{1-x}\text{Cd}_x\text{S}$ samples, where solid and red open circular lines represent the experimental and fitting curves, respectively

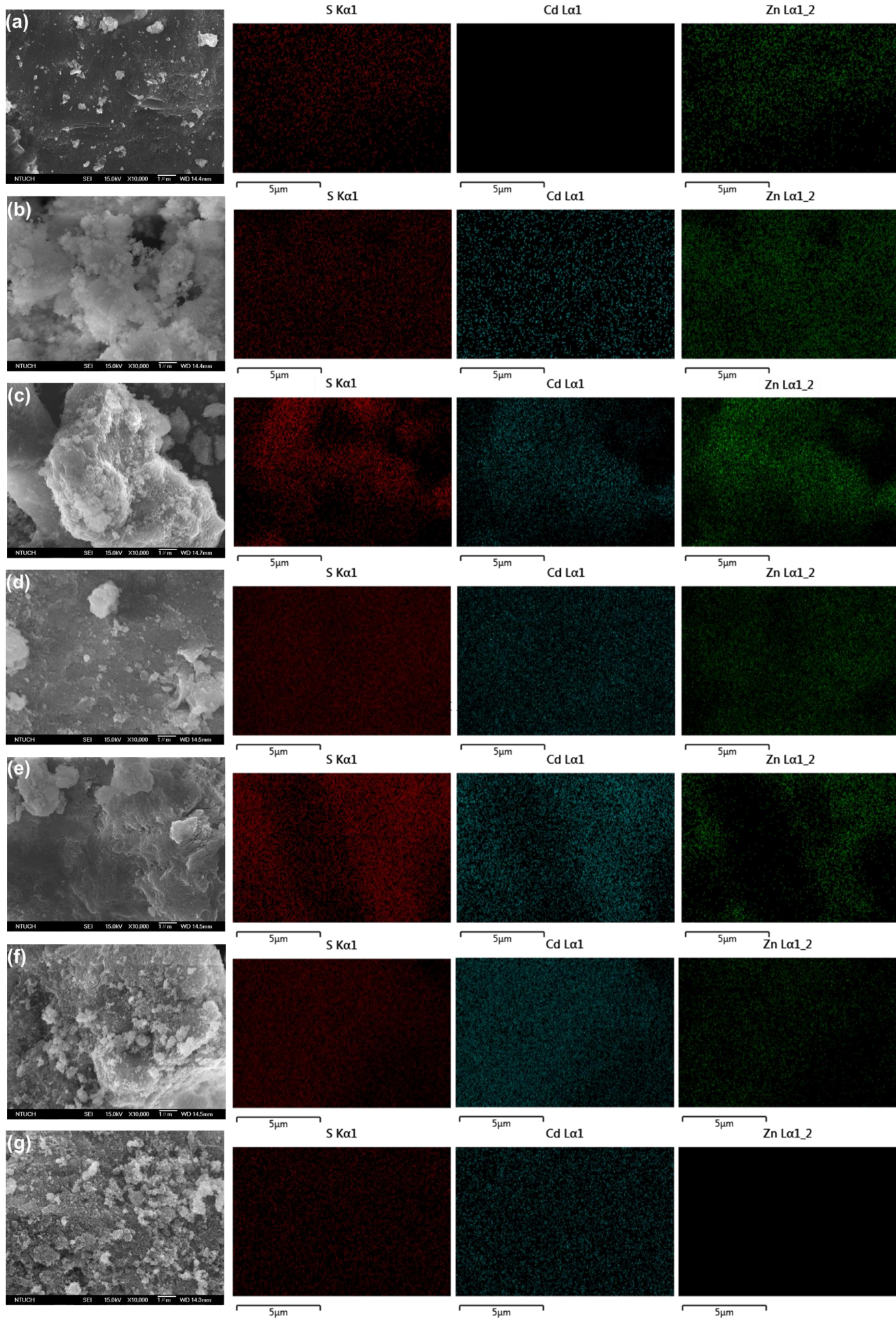


Figure S5. SEM and corresponding EDS mapping micrographs of the $\text{Zn}_{1-x}\text{Cd}_x\text{S}$ samples with various x values: (a) 0, (b) 0.16, (c) 0.42, (d) 0.48, (e) 0.55, (f) 0.81 and (g) 1.0.

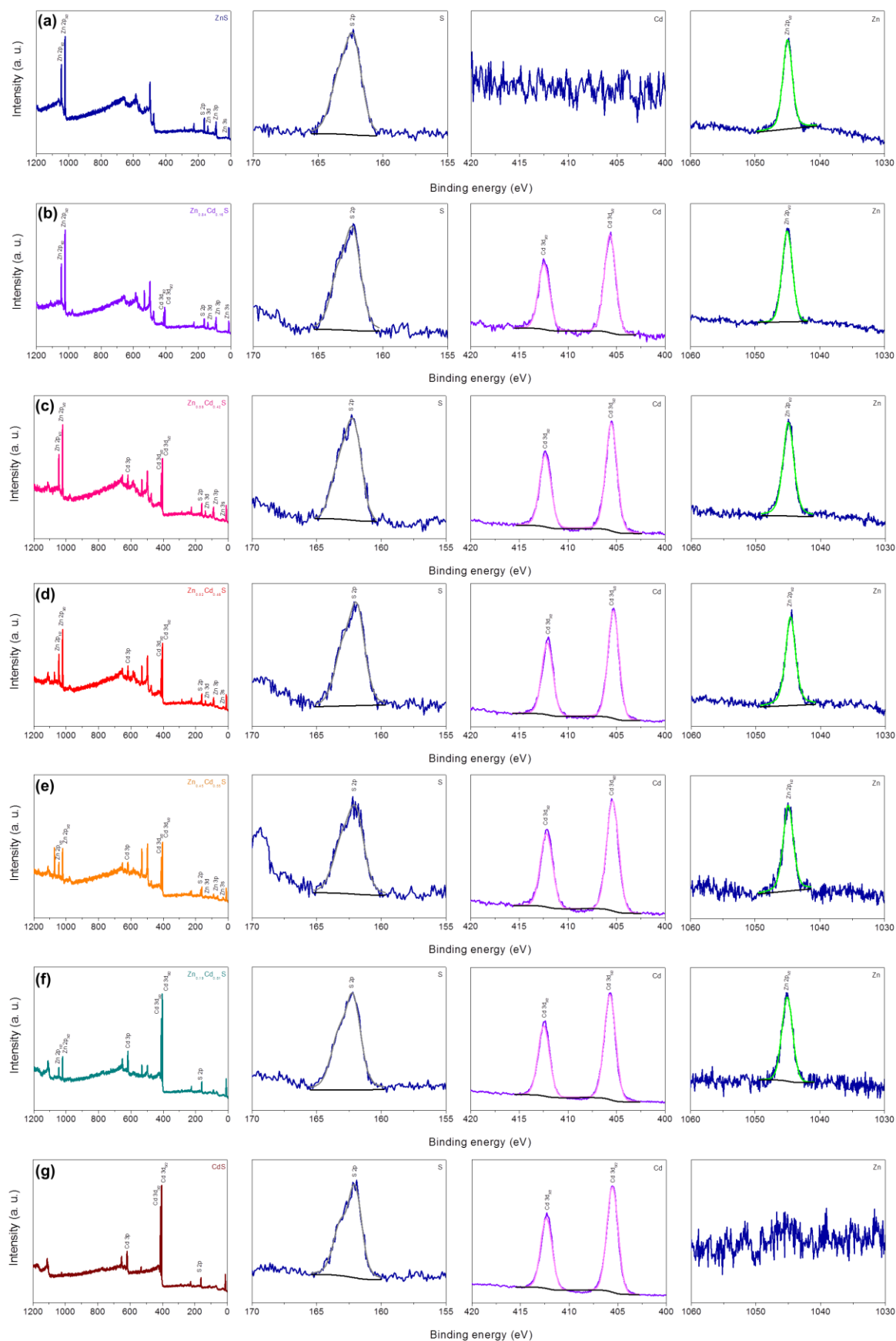


Figure S6. Wide-ranged XP spectra and high resolution of S (2p), Cd (3d) and Zn (2p) XP spectra of the $\text{Zn}_{1-x}\text{Cd}_x\text{S}$ samples with various x values: (a) 0, (b) 0.16, (c) 0.42, (d) 0.48, (e) 0.55, (f) 0.81 and (g) 1.0.

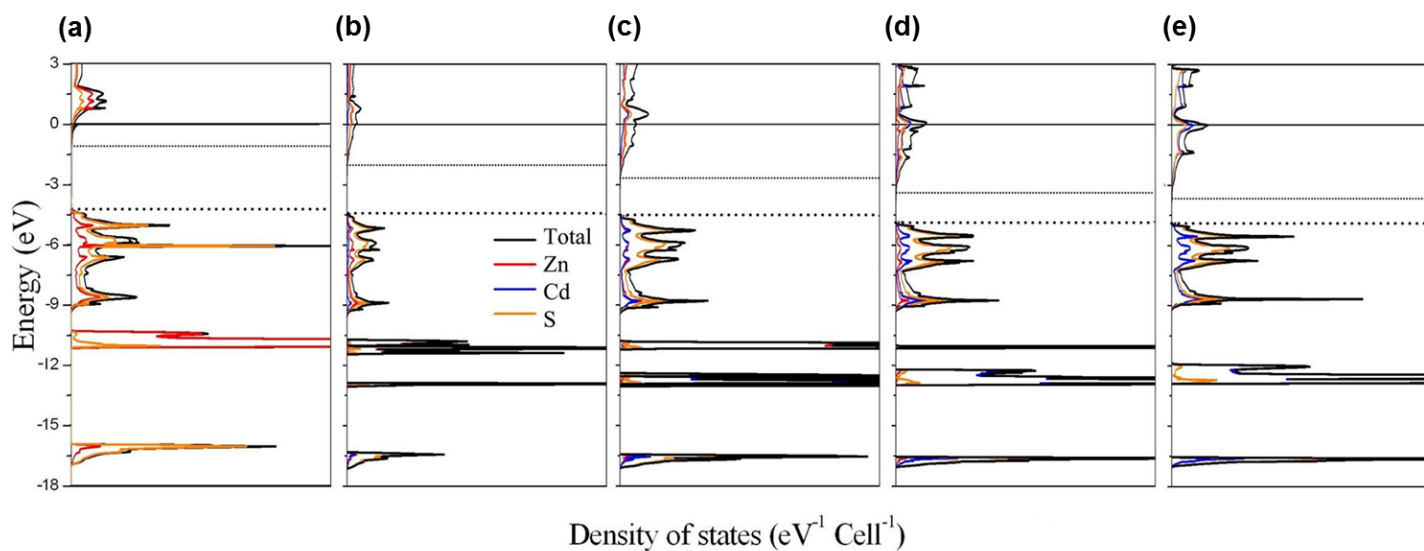


Figure S7. Density of states for (a) ZnS (b) $\text{Zn}_{0.75}\text{Cd}_{0.25}\text{S}$ (c) $\text{Zn}_{0.5}\text{Cd}_{0.5}\text{S}$ (d) $\text{Zn}_{0.25}\text{Cd}_{0.75}\text{S}$ (e) CdS in blende phase.