Electronic Supplementary Information

Au-$Cd_{1-x}Zn_xS$ core-alloyed shell nanocrystals: boosting the interfacial charge dynamics by adjusting shell composition

Ying-Chih Pu[a,‡]*, *Wei-Ta Chen*[b,‡], *Mei-Jing Fang*[b], *Yu-Lin Chen*[a], *Kai-An Tsai*[b], *Wei-Hao Lin*[b] *and Yung-Jung Hsu*[b,c]*

[a] Department of Materials Science, National University of Tainan, Tainan 70005, Taiwan

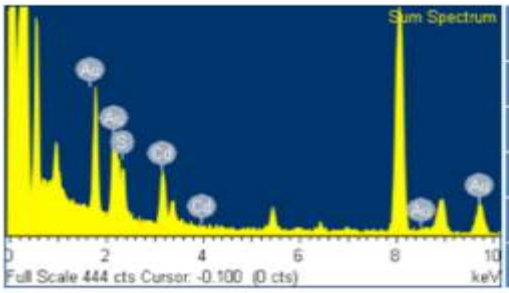
[b] Department of Materials Science and Engineering, National Chiao Tung University, Hsinchu 30010, Taiwan

[c] Center for Emergent Functional Matter Science, National Chiao Tung University, Hsinchu 30010, Taiwan

*Corresponding Author: Y.-C. Pu (ycpu@mail.nutn.edu.tw); Y.-J. Hsu (yhsu@cc.nctu.edu.tw)

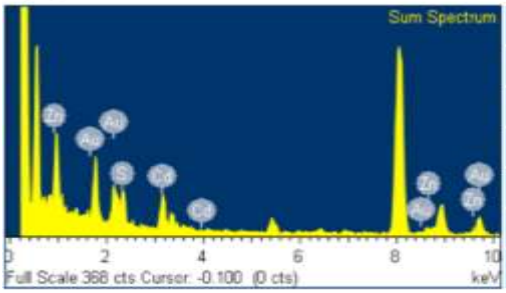
‡These authors contributed equally.

(a)



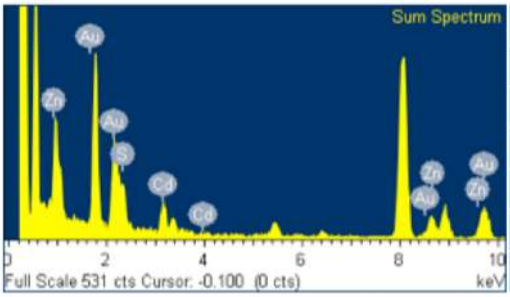
Element	Weight%	Atomic%
S K	11.75	37.99
Cd L	39.31	36.26
Au M	48.94	25.76
Totals	100.00	

(b)



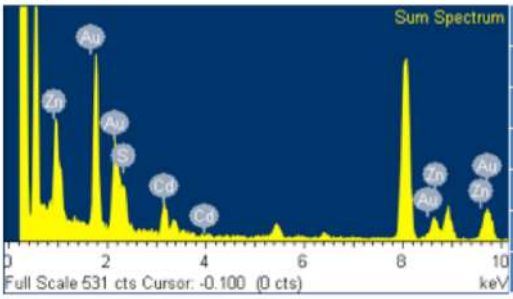
Element	Weight%	Atomic%
S K	13.83	40.33
Zn K	3.22	4.61
Cd L	43.93	36.55
Au M	39.01	18.52
Totals	100.00	

(c)



Element	Weight%	Atomic%
S K	14.63	32.47
Zn K	7.77	11.06
Cd L	27.58	22.83
Au M	50.02	33.63
Totals	100.00	

(d)



Element	Weight%	Atomic%
S K	10.93	34.46
Zn K	9.19	14.20
Cd L	26.80	24.10
Au M	53.08	27.24
Totals	100.00	

Fig. S1 TEM-EDS analysis of (a) Au-CdS, (b) Au-$Cd_{1-x}Zn_xS$_a, (c) Au-$Cd_{1-x}Zn_xS$_b, and (d) Au-$Cd_{1-x}Zn_xS$_c.

Fig. S2 TEM-EDS elemental mapping taken on Au-$Cd_{1-x}Zn_xS$_c.

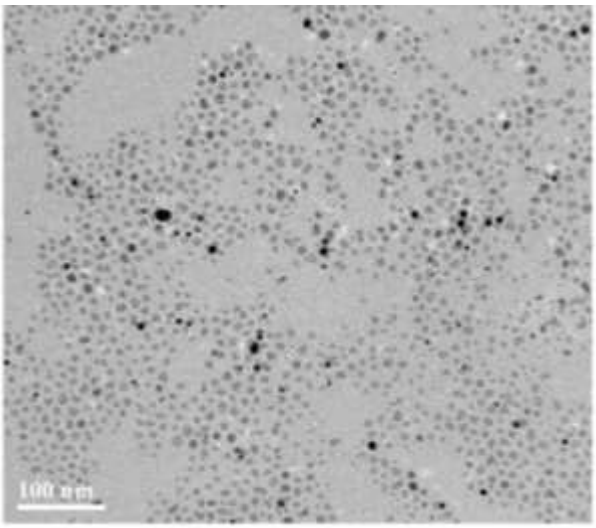


Fig. S3 TEM image of Au-$Cd_{1-x}Zn_xS$ NCs prepared at 270°C for 1 hr.

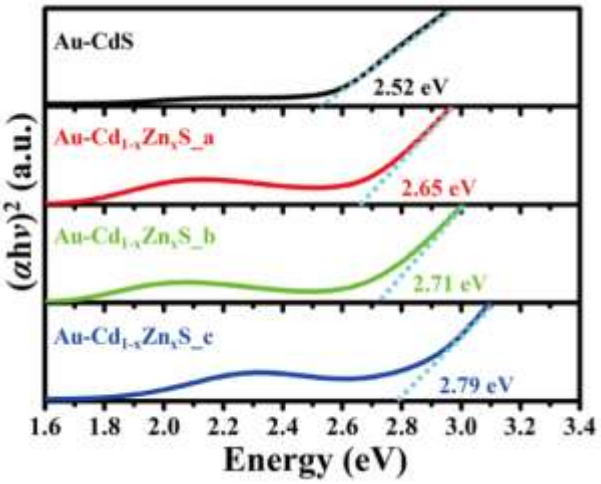


Fig. S4 $(\alpha h\nu)^2$ vs. $h\nu$ plots for Au-CdS and Au-$Cd_{1-x}Zn_xS$ NCs for determination of apparent bandgap.

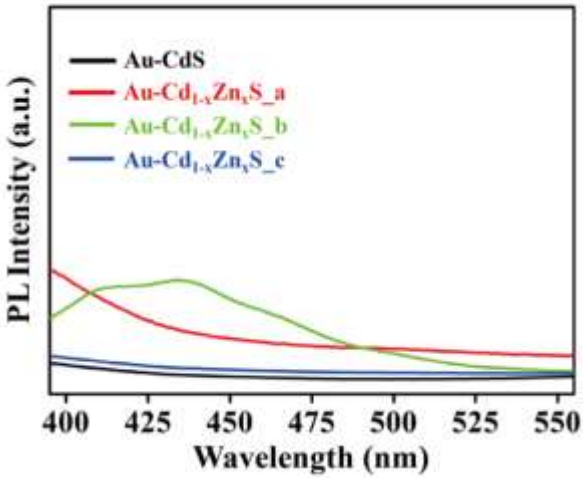


Fig. S5 Steady-state PL spectra for Au-CdS and Au-$Cd_{1-x}Zn_xS$ NCs.

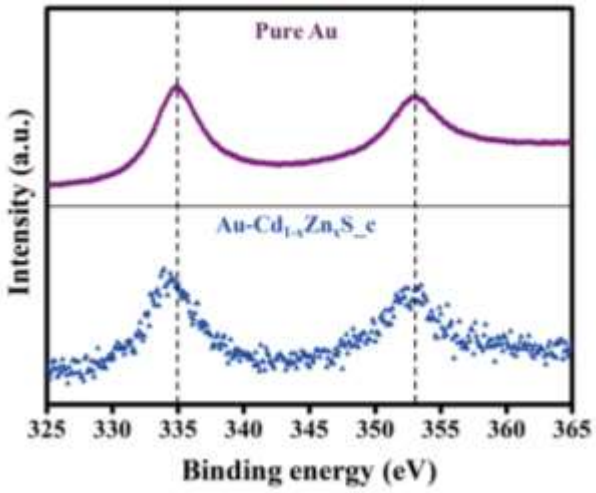


Fig. S6 XPS spectra of Au 4d for pure Au and Au- $Cd_{1-x}Zn_xS$_c.

Table S1 Calculation results of the mole fraction of ZnS for Au-CdS and Au-$Cd_{1-x}Zn_xS$ NCs based on the TEM-EDS examinations.

	Mole fraction of Zn/Cd in precursor solution	Atomic ratio of Zn/Cd in $Cd_{1-x}Zn_xS$ shell from TEM-EDS analysis
Au-CdS	0	0
Au-$Cd_{1-x}Zn_xS$_a	1.0 (Zn:Cd = 0.5:0.5)	0.13 (Zn:Cd = 0.11:0.89)
Au-$Cd_{1-x}Zn_xS$_b	4.9 (Zn:Cd = 0.83:0.17)	0.48 (Zn:Cd = 0.33:0.67)
Au-$Cd_{1-x}Zn_xS$_c	9.0 (Zn:Cd = 0.9:0.1)	0.59 (Zn:Cd = 0.37:0.63)

Table S2 Comparison of SPR λ_{max} between experimental and theoretical results.

	Experimental SPR λ_{max}	Theoretical SPR λ_{max}
Au-CdS	612 nm	609 nm
Au-$Cd_{1-x}Zn_xS$_a	600 nm	598 nm
Au-$Cd_{1-x}Zn_xS$_b	586 nm	588 nm
Au-$Cd_{1-x}Zn_xS$_c	580 nm	582 nm

Table S3 Estimated E_g value of the shell for Au-CdS and Au-$Cd_{1-x}Zn_xS$ from absorption spectra and optical bowing function.

	Estimate Eg of $Cd_{1-x}Zn_xS$ shell from UV-vis spectra	Estimate Eg of $Cd_{1-x}Zn_xS$ shell from constituent calculation
Au-CdS	2.52 eV	2.50 eV
Au-$Cd_{1-x}Zn_xS$_a	2.65 eV	2.57 eV
Au-$Cd_{1-x}Zn_xS$_b	2.71 eV	2.76 eV
Au-$Cd_{1-x}Zn_xS$_c	2.79 eV	2.80 eV

[a] $E_g(Cd_{1-x}Zn_xS) = E_g(CdS)(1-x) + E_g(ZnS)x - bx(1-x)$. $E_g(CdS) = 2.5\ eV$; $E_g(ZnS) = 3.7\ eV$; b = 0.6;[1,2] x = 0, 0.11, 0.31 and 0.37 for Au-CdS, Au-$Cd_{1-x}Zn_xS$_a, Au-$Cd_{1-x}Zn_xS$_b, Au-$Cd_{1-x}Zn_xS$_c and Au-$Cd_{1-x}Zn_xS$_d.

Table S4 Calculations of E_{cb} of the shell and ΔG for Au-CdS and Au-$Cd_{1-x}Zn_xS$ NCs.

entry	E_{cb} (V vs NHE)	E_{vb} (V vs NHE)	ΔG (V)
Au-CdS	-1.05	+1.47	-1.55
Au-$Cd_{1-x}Zn_xS$-a	-1.10	+1.55	-1.60
Au-$Cd_{1-x}Zn_xS$-b	-1.12	+1.59	-1.62
Au-$Cd_{1-x}Zn_xS$-c	-1.15	+1.64	-1.65

The E_{cb} of $Cd_xZn_yS_z$ nanocrystals can be calculated by using following formulas:[2, 3]

$$E_{cb} = E^e - X + \frac{1}{2}E_g$$

$$X = \{X_{cd}^x \times X_{Zn}^y \times X_S^z\}^{\frac{1}{(x+y+z)}}$$

$$X_{cd} = \frac{1}{2}(A_{cd} + I_{cd})$$

$$X_{Zn} = \frac{1}{2}(A_{Zn} + I_{Zn})$$

$$X_S = \frac{1}{2}(A_S + I_S)$$

Here, *A* is the electron affinity (A_S = 200 kJ/mol, A_{Cd} = ~0 kJ/mol, A_{Zn} = ~0 kJ/mol), *I* is the ionization energy (I_{Cd} = 866 kJ/mol, I_{Zn} = 904 kJ/mol, I_S = 1000 kJ/mol), E^e = 4.5 eV, E_g is the bandgap determined from $(\alpha h\nu)^2$ vs. hν plots in Fig S3.

References

1. J.-H. Lee, W.-C. Song, J.-S. Yi, K.-J. Yang, W.-D. Han and J. Hwang, *Thin Solid Films*, 2003, **431-432**, 349-353
2. X. Zhong, Y. Feng, W. Knoll and M. Han, *J. Am. Chem. Soc.*, 2003, **125**, 13559-13563.
3. C. Xing, Y. Zhang, W. Yan and L. Guo, *Int. J. Hydrogen Energy*, 2006, **31**, 2018-2024.
4. A. T. Nguyen, W.-H. Lin, Y.-H. Lu, Y.-D. Chiou and Y.-J. Hsu, *Appl. Catal. A- Gen.*, 2014, **476**, 140-147.