

Supporting Information:

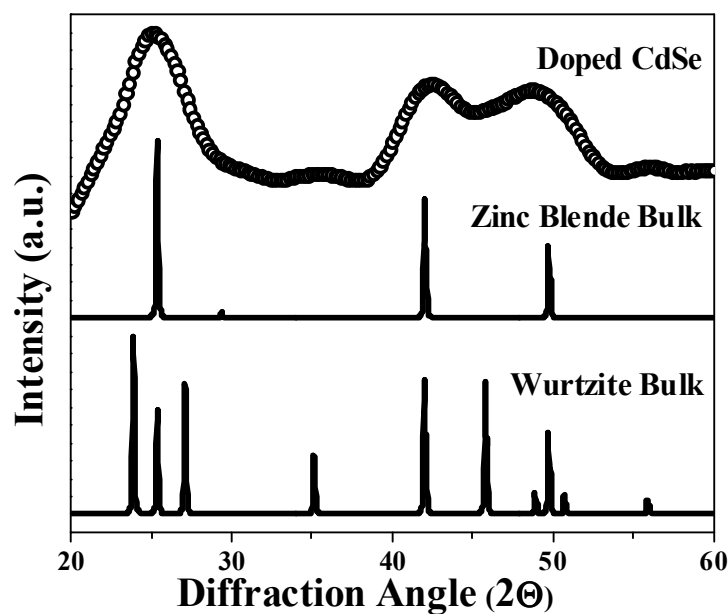
Study of surface and bulk electronic structure of II-VI semiconductor nanocrystals using Cu as a nanosensor

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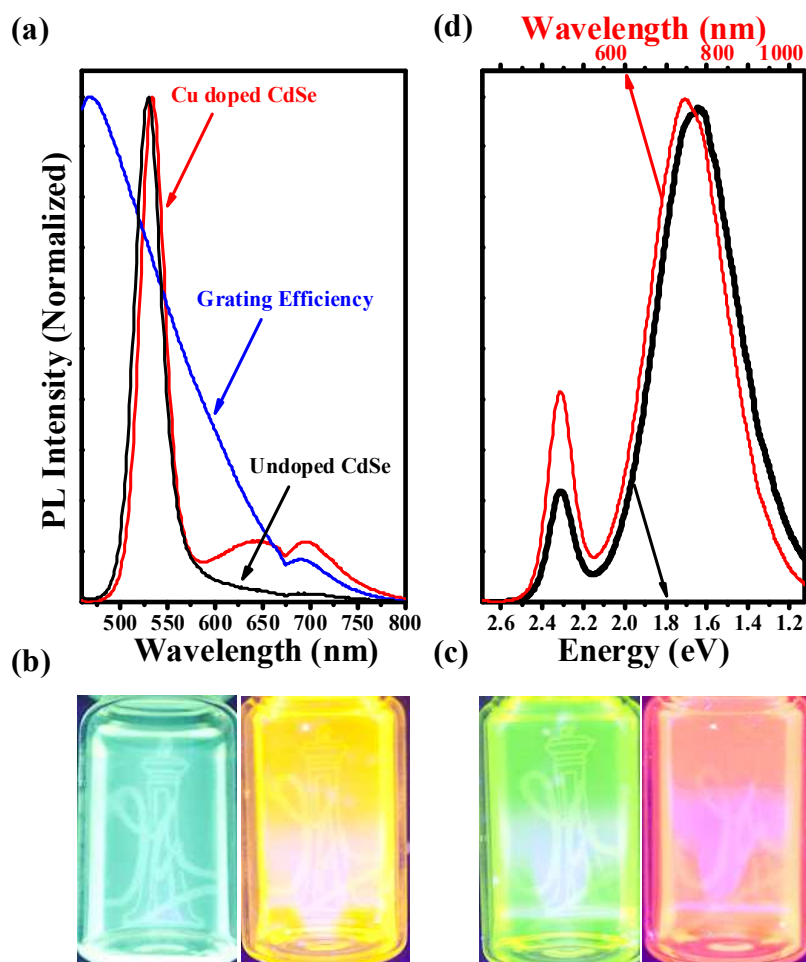
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Supporting Information **Figure S1:** XRD of Cu doped CdSe synthesized using TOPO and octadecyl amine along with other ligands. Also shown in the figure are the bulk XRD patterns of zinc blende and wurtzite CdSe



Supporting Information **Figure S2:** (a) Uncorrected emission spectra of Cu doped and undoped CdSe along with the grating efficiency curve. Digital image of the emission of different sizes of (b) undoped CdSe nanocrystals and (c) Cu doped CdSe nanocrystals. (d) Spectrally and energy corrected emission spectra of Cu doped CdSe nanocrystals.



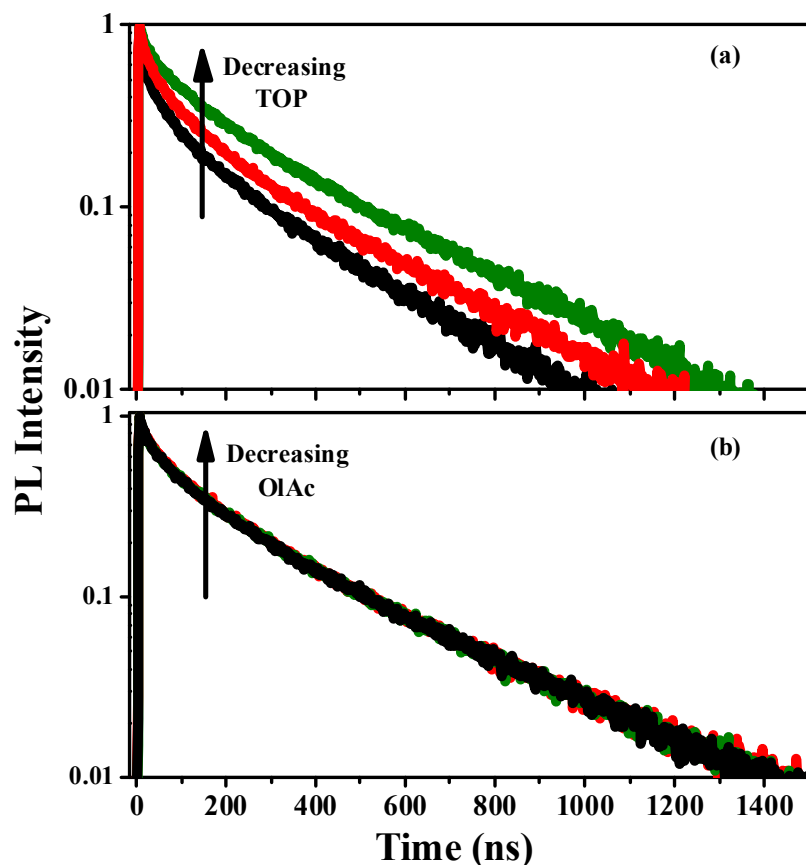
Supporting Information Table S1:

Sl No	Dopant	Host Material	Size	Transition Levels	Transition Energy (eV)	References
1	Eu	ZnS	3-3.5 nm	5D_0 to 7F_2	2.02	Ref 41
		ZnO	Nanopyramids and Dots (31.4 ± 3.9 nm to 16.7 ± 2.1 nm)			Ref 42
2	Mn	ZnO	Nanorods	4T_1 to 6A_1	2.11	Ref 44
		$Cd_{1-x}Zn_xS$	4 nm			R1
		CdSe	2.3 nm			R2
		ZnSe	2.7-5.7 nm			Ref 47
3	Tb	ZnS	3-18 nm	5D_4 to 7F_5	2.27	Ref 41
		CdSe				R3
		ZnS	3.3 ± 0.4 nm			R4
		NaGdF ₄ Tm/Yb @ NaGdF ₄ Tb	3nm Shell			R5

From this table, it is evident that irrespective of the size, shape or composition of the nanocrystal, these atomic levels have the same energy.

Other than the cases already compiled in the main text, it is also seen that the Cu levels are clearly shown in figure 5 of Ref R6 for the case of CdS and ZnS. Since the systems are given side by side within the same manuscript, we compared the numbers and they are given by 1.247 ± 0.047 eV, 0.458 ± 0.023 eV and 0.107 ± 0.013 eV. In other words, the Cu levels are constant in the two systems within an energy of less than 0.05 eV and in most cases, less than 0.02 eV.

Supporting Information **Figure S3**: PL decay curves for the decay of the Cu related emission with **(a)** varying TOP concentration and **(b)** varying OlAc concentration.



References:

- R1. Singh, K.; Kumar, S.; Verma, N. K.; Bhatti, H. S., Photoluminescence Properties of Eu^{3+} -Doped $\text{Cd}_{1-x}\text{Zn}_x\text{S}$ Quantum Dots. *J. Nanopart. Res.* 2009, 11, 1017-1021.
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- R3. Chengelis, D. A.; Yingling, A. M.; Badger, P. D.; Shade, C. M.; Petoud, S., Incorporating Lanthanide Cations with Cadmium Selenide Nanocrystals: A Strategy to Sensitize and Protect Tb (III). *J. Am. Chem. Soc.* 2005, 127, 16752-16753.
- R4. Mukherjee, P.; Shade, C. M.; Yingling, A. M.; Lamont, D. N.; Waldeck, D. H.; Petoud, S., Lanthanide Sensitization in II-VI Semiconductor Materials: A Case Study with Terbium (III) and Europium (III) in Zinc Sulfide Nanoparticles. *J. Phys. Chem. A* 2011, 115, 4031-4041.
- R5. Wang, F.; Deng, R.; Wang, J.; Wang, Q.; Han, Y.; Zhu, H.; Chen, X.; Liu, X., Tuning Upconversion through Energy Migration in Core-Shell Nanoparticles. *Nat. Mater.* 2011, 10, 968-973.

R6. Heitz, R.; Hoffmann, A.; Thurian, P.; Broser, I., The Copper Centre: A Transient Shallow Acceptor in ZnS and CdS. *J. Phys.: Cond. Mat.* 1999, 4, 157-168.