

Supporting Information

***In-situ* Optical and Structural Studies on Photoluminescence Quenching in CdSe/CdS/Au Heterostructures.**

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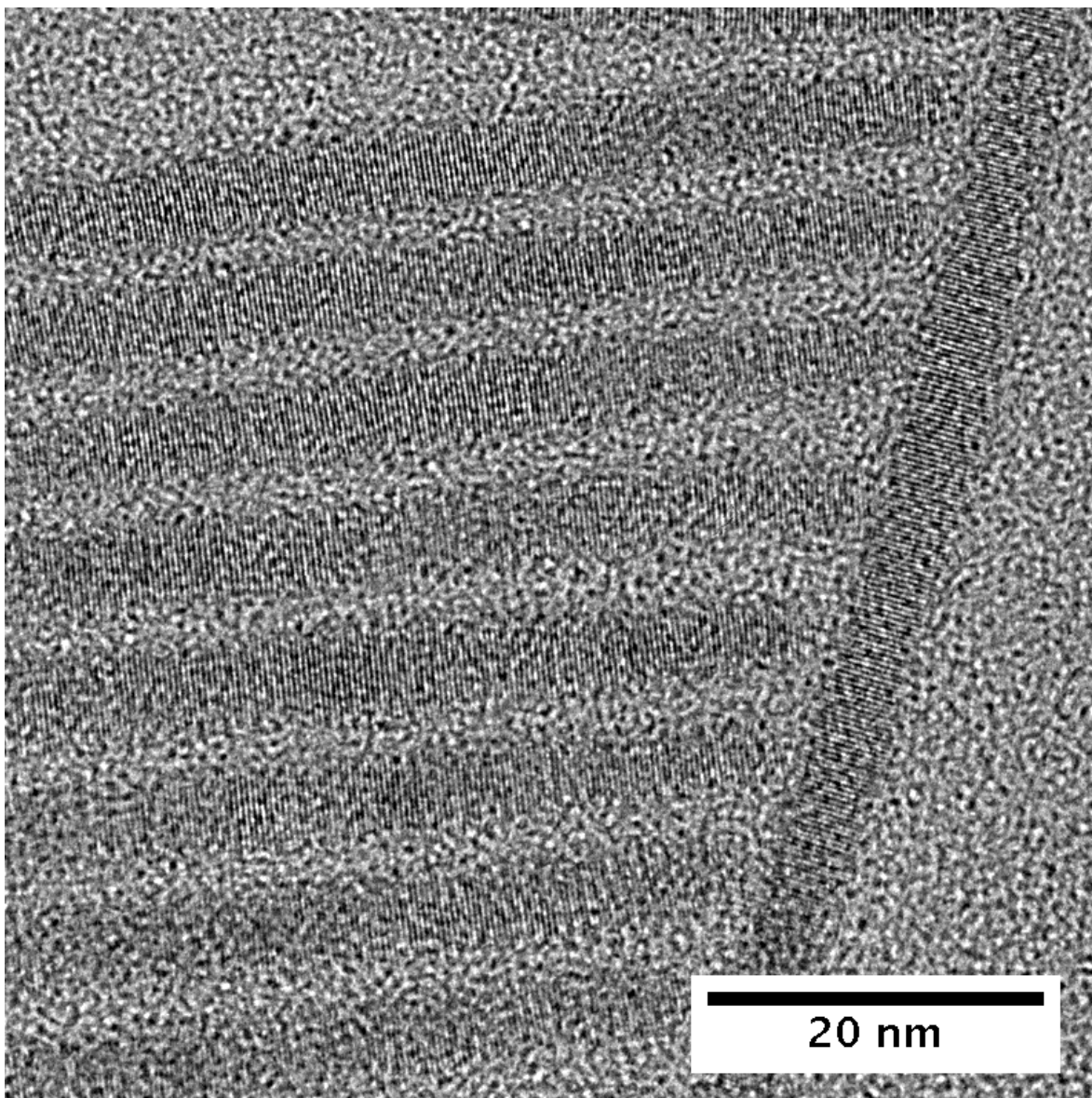


Figure S1. HRTEM image of CdSe/CdS nanorods treated with gold precursor in the darkness (no-UV sample) for 3800 s. No gold domains were formed.

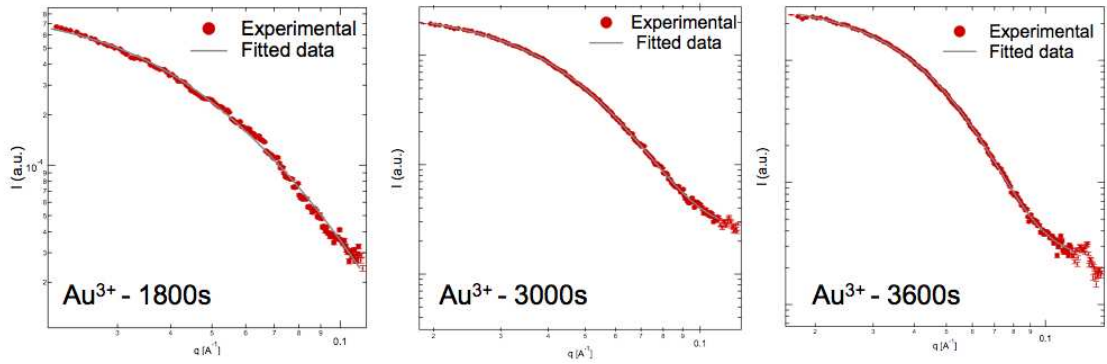


Figure S2. SAXS curve and fit for at 1800s, 3000s and 3800s of reaction time.

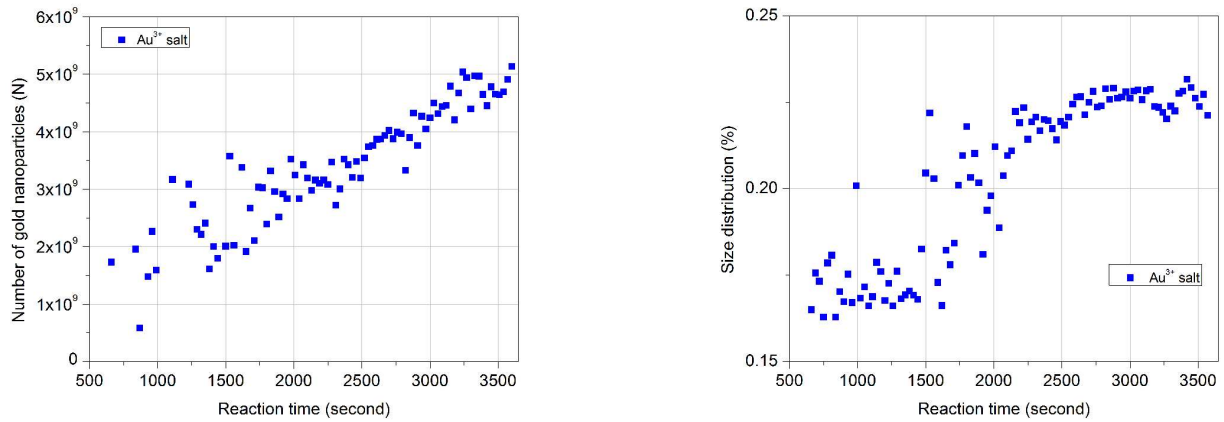


Figure S3. Evolution of Au NP number (left) and size distribution (right) as a function of the reaction time of CdSe/CdS and gold precursor under UV illumination.

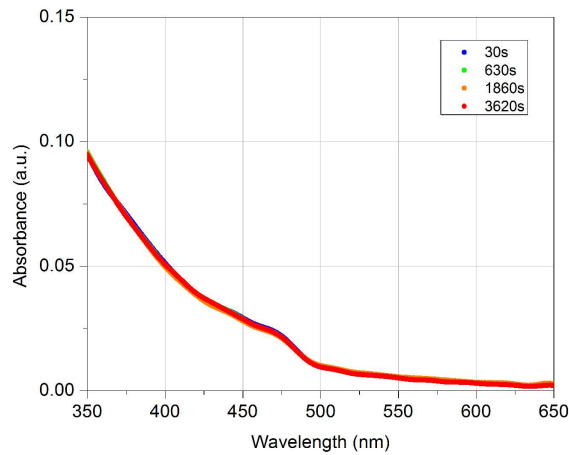


Figure S4. Absorption spectra of CdSe/CdS exposed to gold precursor in the darkness (no-UV sample) as a function of the reaction time.

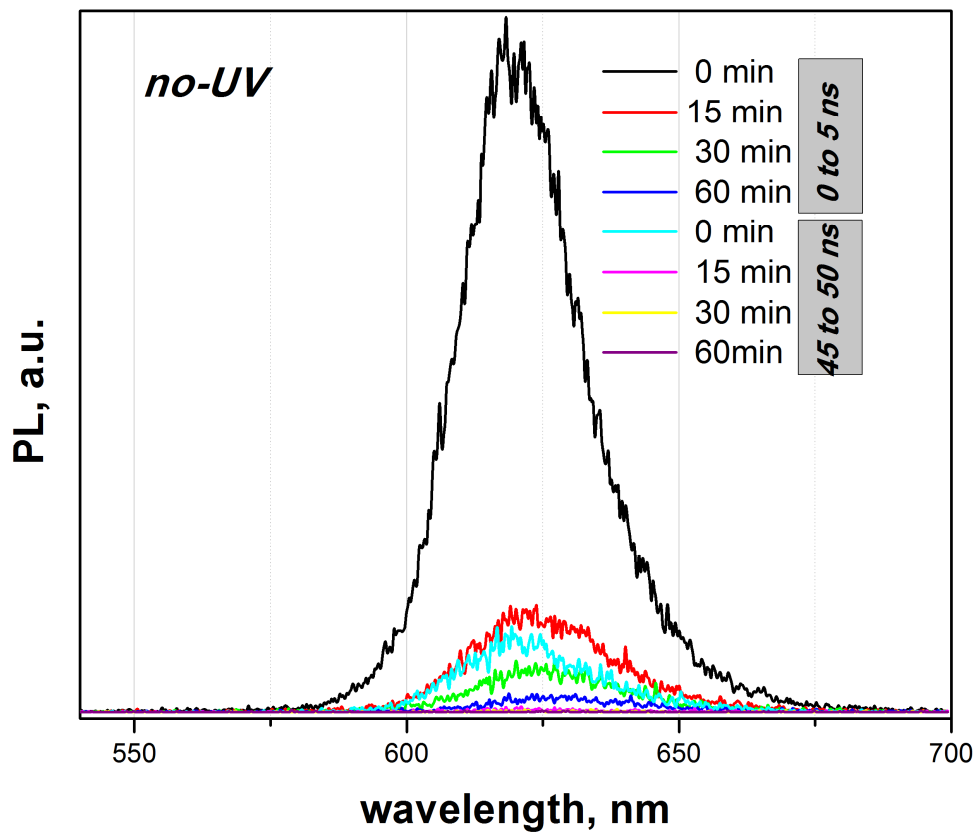


Figure S5. PL spectra of CdSe/CdS exposed to Au precursor under no UV illumination (no-UV sample). The labels on the right indicate reaction progress time and a time range binned.

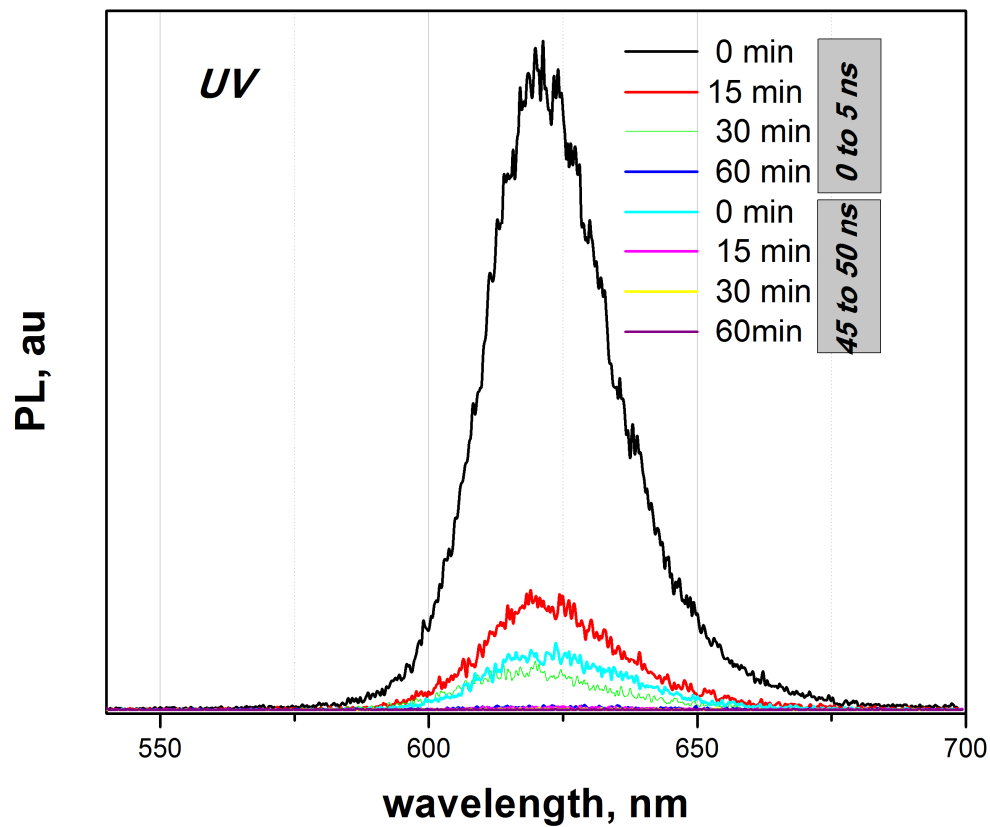


Figure S6. PL spectra of CdSe/CdS exposed to Au precursor under UV illumination (UV sample). The labels on the right indicate reaction progress time and a time range binned.

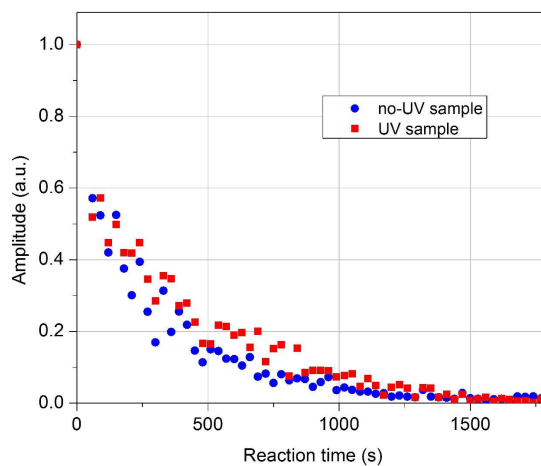


Figure S7. Early amplitudes decay over reaction time for UV and no-UV samples. PL amplitudes were obtained from the fit of PL decay spectra (figure 4) using single exponential function.

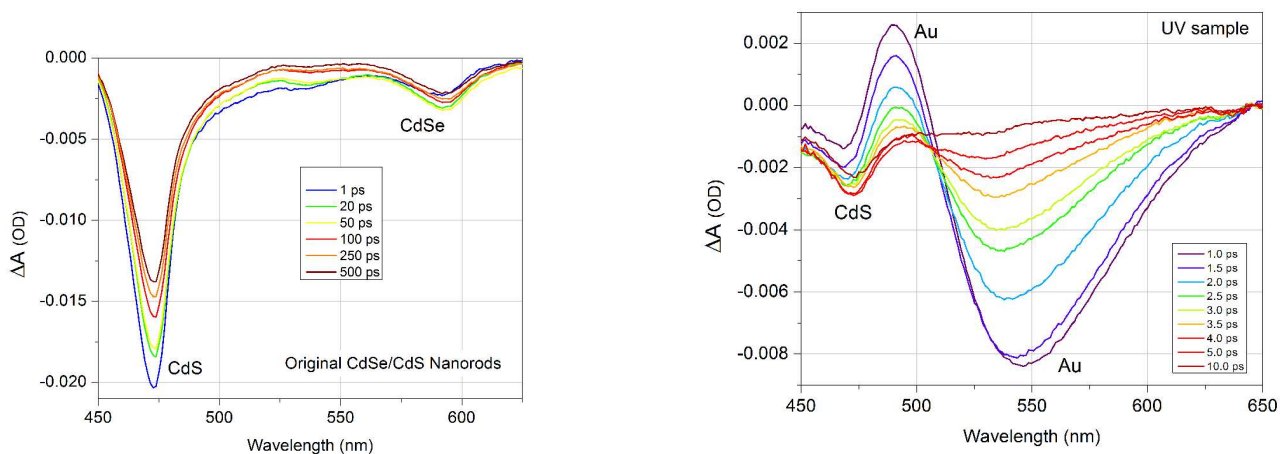


Figure S8. Transient absorption spectra of CdSe/CdS nanorods (left) and UV sample (right) using 420 nm excitation.

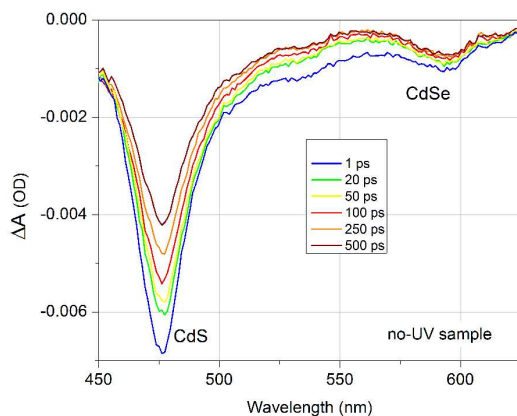


Figure S9. Transient absorption spectra of no-UV sample using 420 nm excitation.

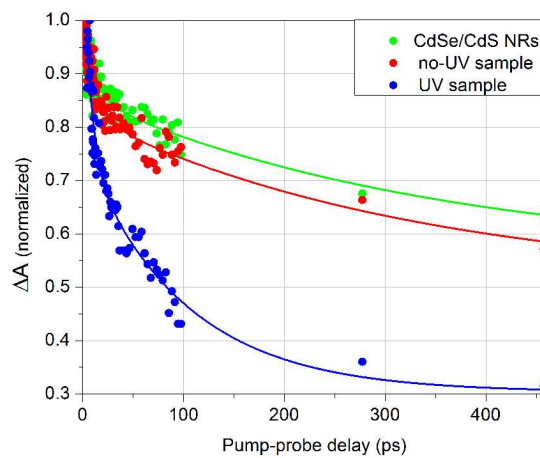


Figure S10. Transient absorption kinetics for CdSe/CdS nanorods, no-UV and UV samples at 476nm.

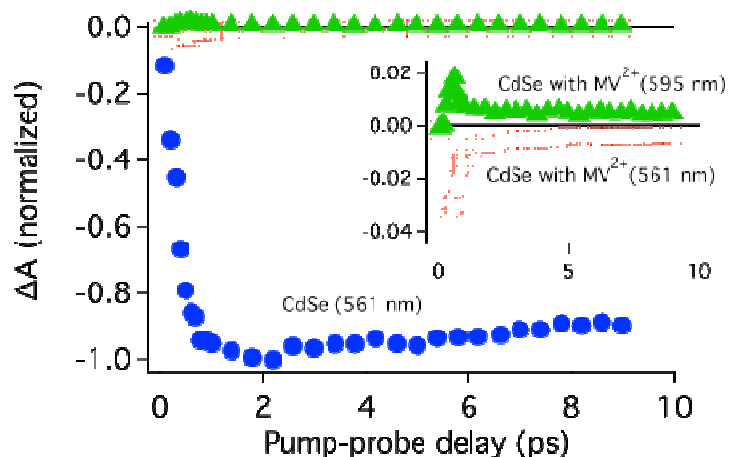


Figure S11. A kinetic trace from transient absorption spectra collected on a CdSe NC sample with lowest energy absorption at 561 nm reveals a relatively flat bleach feature. Addition of methyl viologen (MV^{2+}) eliminates the bleach by pulling the electron observed in CdSe by TA into the electron scavenger (MV^{2+} to MV^+). A photoinduced absorption appears at 595 nm, which corresponds to the formation of MV^+ .¹

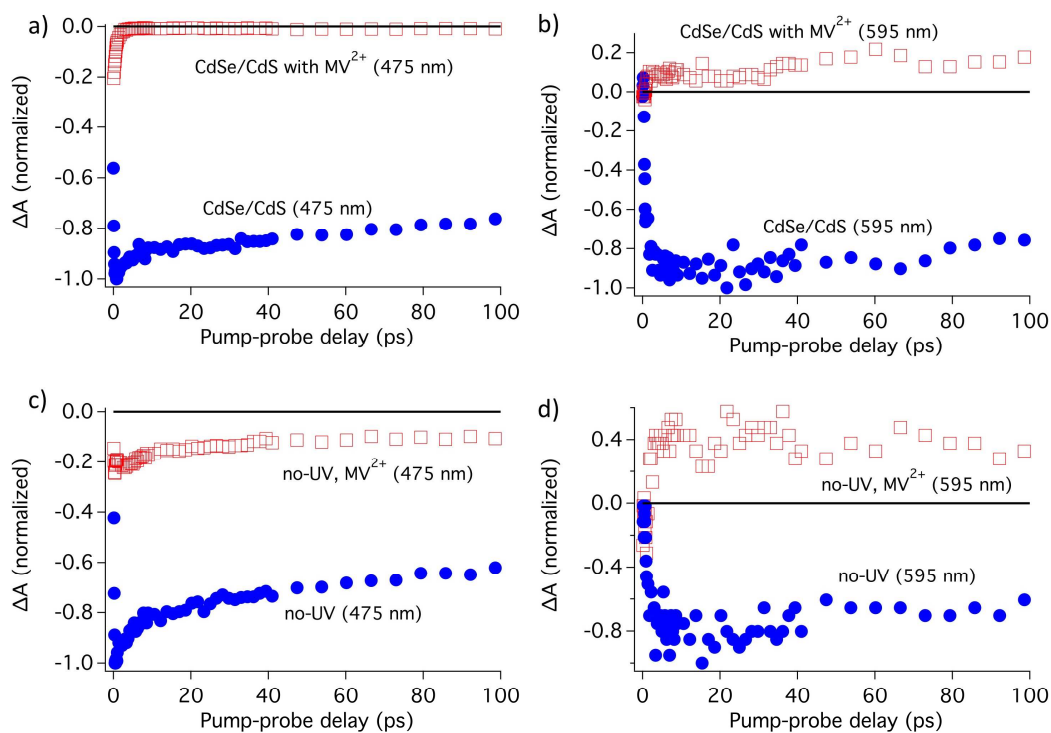


Figure S12. The bleach features present in transient absorption spectra of the CdSe/CdS rods at 475 nm and 595 nm, originating from the CdS and CdSe, respectively, are represented by blue circles in panels a) and b). Addition of methyl viologen (MV^{2+}), an electron scavenger, to the sample reduces the bleach at both wavelengths on a <1 ps timescale, as shown by the red squares. In addition, a slight induced absorption, attributed to the generation of MV^+ from MV^{2+} upon oxidation of CdS/CdSe, appears at 595 nm. In c) and d), kinetic traces of CdS/CdS + Au^+ (no-UV) are shown at 475 and 595 nm. Addition of MV^{2+} to this sample again shows the disappearance of the bleach and the appearance of an induced absorption at 595 nm corresponding to the formation of MV^+ .¹

EXAFS/XANES: The spot size of the incident x-ray beam on the samples was 400 micron by 400 micron. Data collected was processed using Athena software by extracting the EXAFS oscillations $\chi(k)$ as a function of photoelectron wave number k following standard procedures. The theoretical paths were generated using FEFF6 and the models were done in the conventional way using the fitting program called Artemis. Fitting parameters were obtained by modeling the EXAFS data of each sample in R-space until a satisfactory fit describing the system was obtained. Data sets were simultaneously fitted in R-space with k-weights of 1, 2 and 3. The fits reported have R-factor below 0.03. Figure S9 and S10 demonstrate the experimental data and their fits. Paths generated with FEFF6 and used for the fitting of the data are summarized in Table S2.

S_0^2 was obtained by fitting the Au edge data from Au foil spectra and was set to 0.8 for fitting EXAFS of Au spectra from the samples. The data range and fit range for each data set is mentioned for the respective samples. For fitting Au-Au paths in the samples, the Debye-Waller factor (DWF) was set to 0.008 obtained from fitting Au foil and for Au-S paths, it was set to 0.005 obtained by fitting Au precursor solution. R-factor for the fits are 0.03 and below.

Table S1. List of fit parameters obtained by fitting Au edge data of CdSe/CdS samples and Au salt. The Au-Au correlations in the no-UV sample is very similar to that in the Au precursor and very different from metallic Au bonds observed in the UV sample.

Sample	Paths	Bond length R (ang)	Coordi Number	Debye Waller (DWF) (\AA^2)	Energy Shift ΔE (eV)
UV sample	Au-S	2.23 ± 0.02	0.9 ± 0.1	0.005	2.4 ± 1.4
	Au-Au	2.87 ± 0.02	7.8 ± 0.1	0.008	
No-UV sample	Au-S	2.24 ± 0.02	1.7 ± 0.1	0.005	3.5 ± 3.7
	Au-Au	3.02 ± 0.02	1.5 ± 1.1	0.008	
Au salt	Au-low Z	1.96 ± 0.02	2.4 ± 0.1	0.005	6.3 ± 2.2
	Au-Au	3.02 ± 0.02	1.2 ± 0.1	0.008	

Table S2: List of paths generated with FEFF6 and used for fitting the data:

Path	Bond Length (\AA)	Coordination Number
Au-Au	2.88	12
Au-S	2.30	4
Au -low Z element	2.00	6

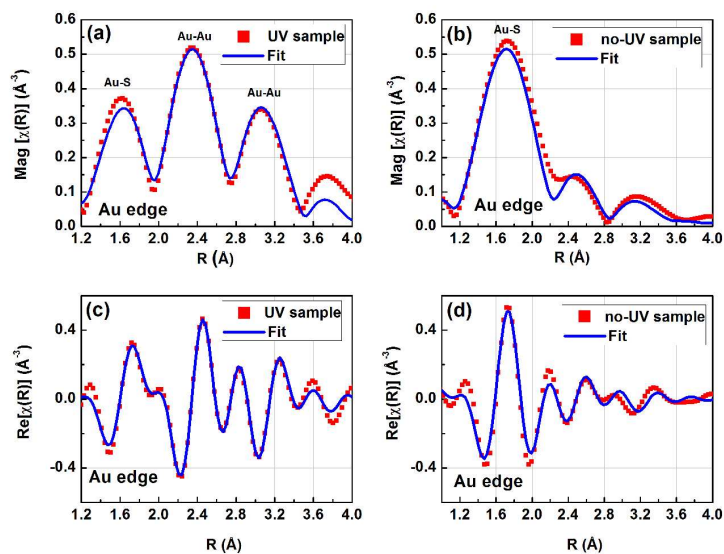


Figure S13. – Magnitude and real space Fourier transformed data and fit results for Au edge of CdSe/CdS core-shell NPs. The UV and no-UV samples have very different local structure around the Au atoms according to EXAFS spectra.

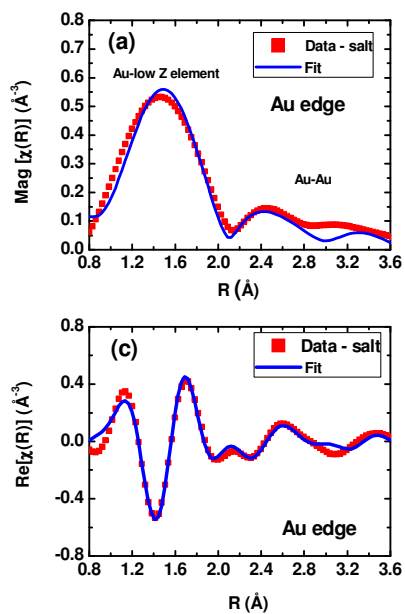


Figure S14. Magnitude and real space Fourier transformed data and fit results for Au precursors.

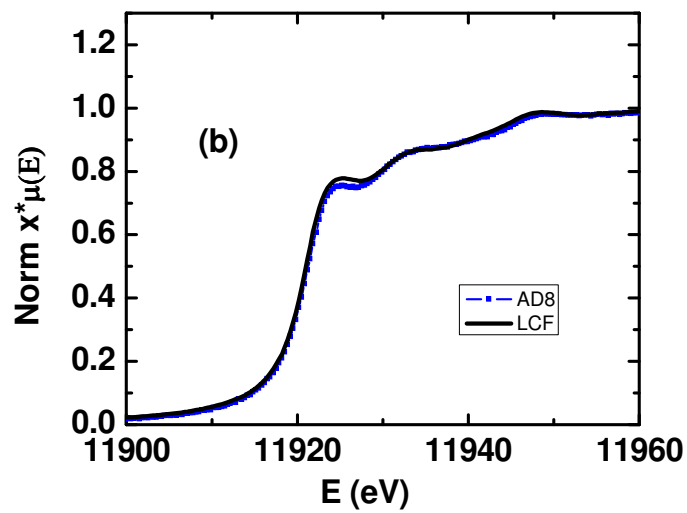
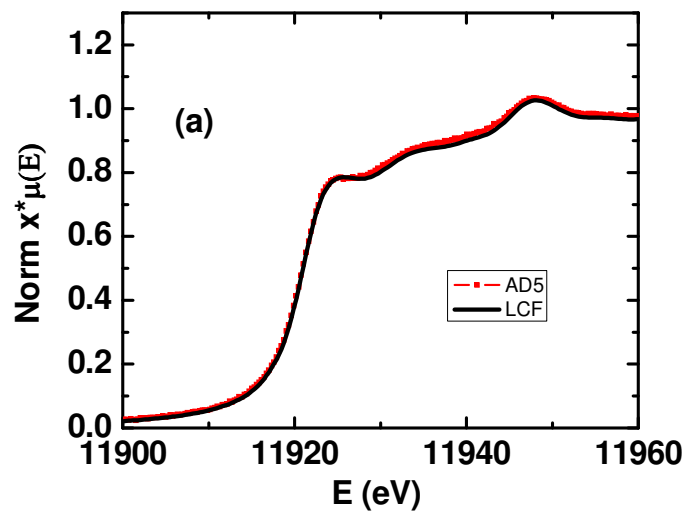


Figure S15. Normalized absorption Au L3-edge data along with linear combination fit (LCF) for samples UV and no-UV samples. Fit range : -20 eV below Au edge (11919 eV) to +30 eV above Au edge.

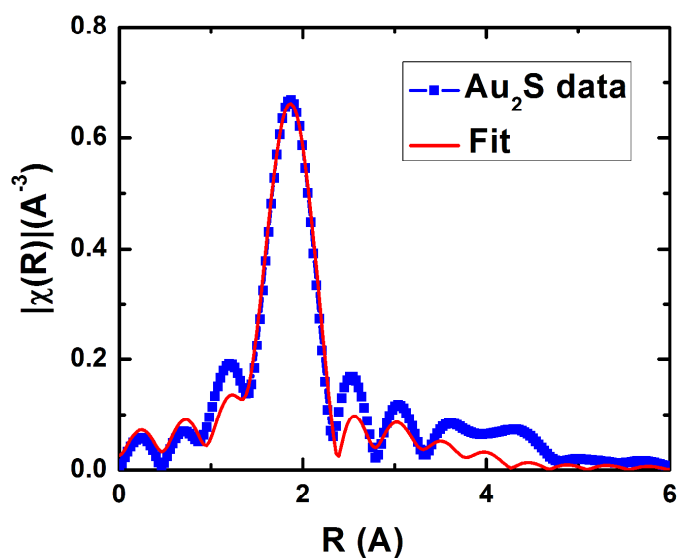


Figure S16. Radial structure distribution function obtained by Fourier transform of the k^3 -weighted EXAFS function and fit from Au_2S standard compound. The data range is from 2 - 10 \AA^{-1} and the fit range is from 1.2 - 3.5 \AA . The Au-S and Au-Au correlations needed for this fit was generated using FEFF6 from the Au_2S compound. The fit has 10 independent points and 6 variables. R-factor for the fit is 0.026. The data assume that Au in Au_2S sees 2 S atoms at $R=2.17 \text{ \AA}$ and 8 Au atoms at $R=3.55 \text{ \AA}$.

References:

1. Dworak, L.; Matylitsky, V. V.; Breus, V. V.; Braun, M.; Basché, T.; Wachtveitl, J., *J. Phys. Chem. C* **2011**, *115* (10), 3949-3955.