Supplementary Information for

Size-dependent ligand exchange of colloidal CdSe nanocrystals with S^{2-} Ions

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Table of Contents

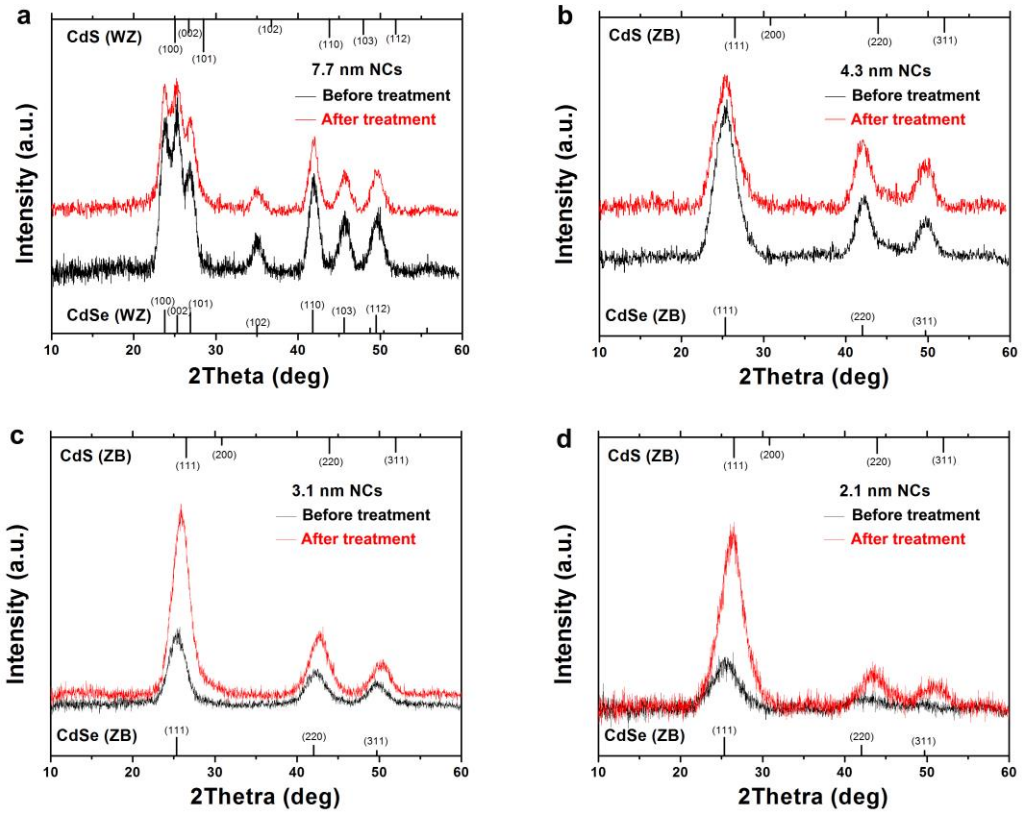

Fig. S1 XRD patterns of individual CdSe NC samples before (black curves) and after (red curves) $(NH_4)_2S$ treatment: (a) 7.7 nm, (b) 4.3 nm, (c) 3.1 nm, (d) 2.1 nm. The XRD stick patterns of bulk CdSe and CdS phases are provided for comparison.

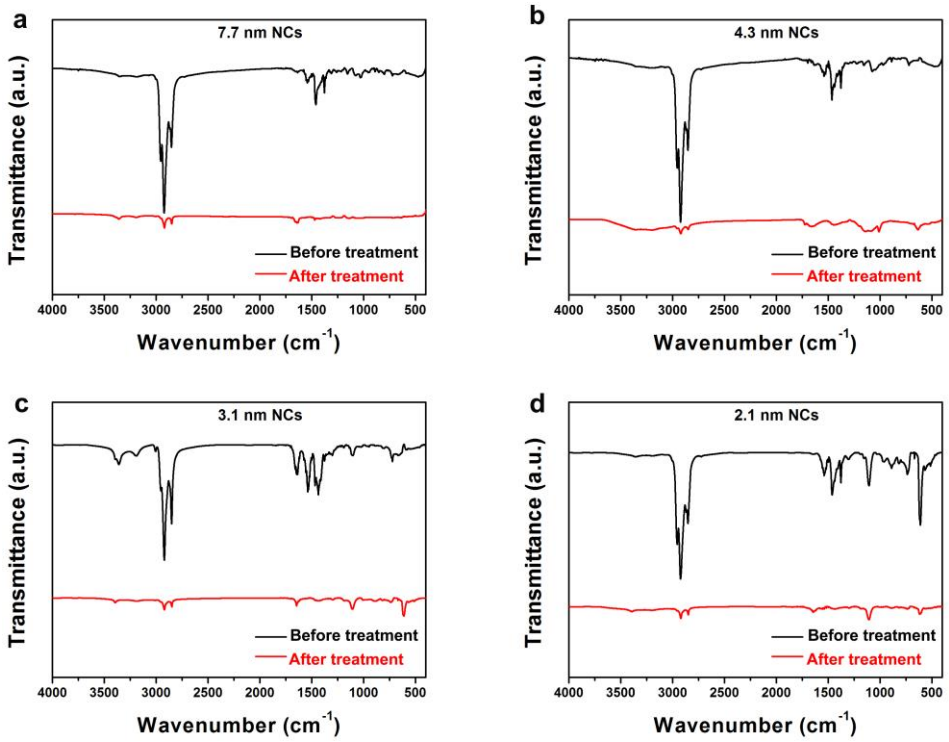

Fig. S2 FTIR spectra of different-sized CdSe NCs before (black curves) and after (red curves) $(NH_4)_2S$ treatment: (a) 7.7 nm, (b) 4.3 nm, (c) 3.1 nm, (d) 2.1 nm.

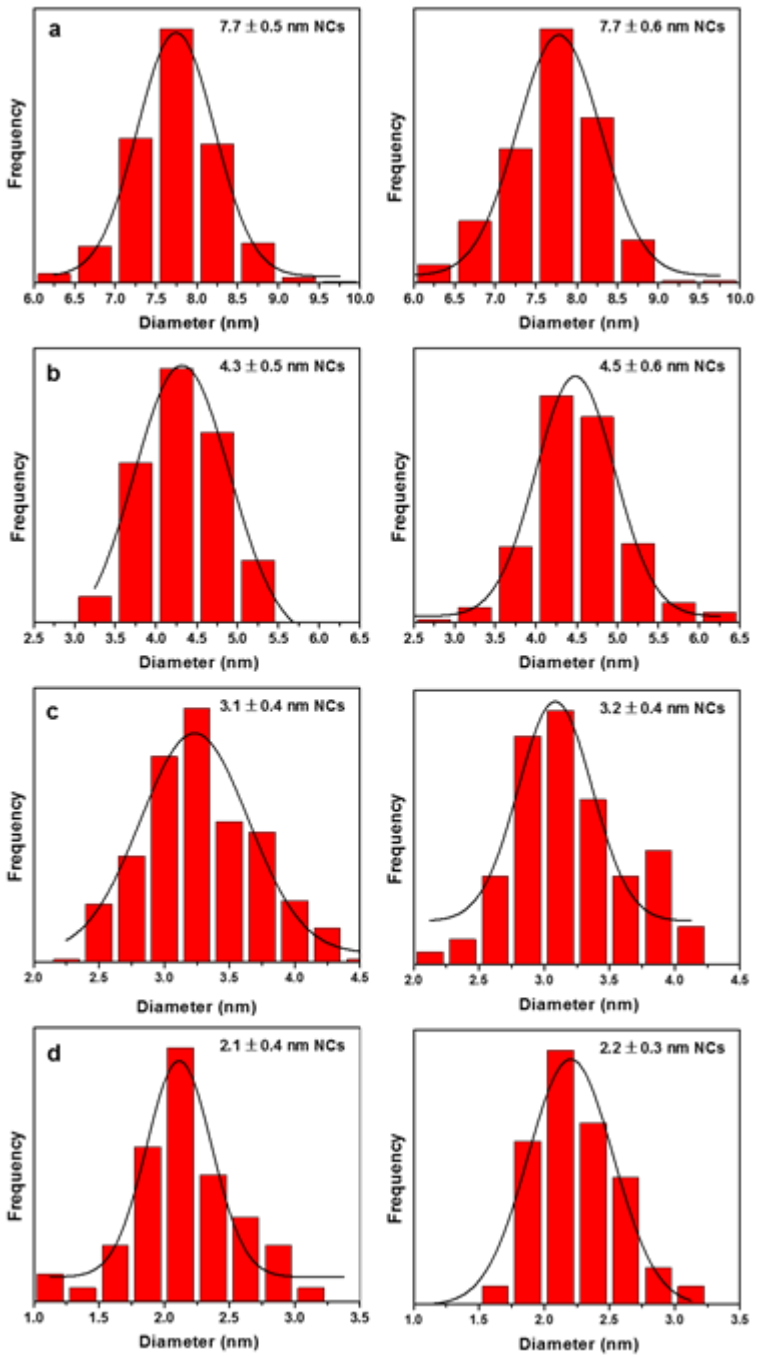

Fig. S3 Size distribution histograms of different-sized CdSe NCs before (left column) and after (right column) ligand exchange with $(NH_4)_2S$: (a) 7.7 nm, (b) 4.3 nm, (c) 3.1 nm, (d) 2.1 nm.

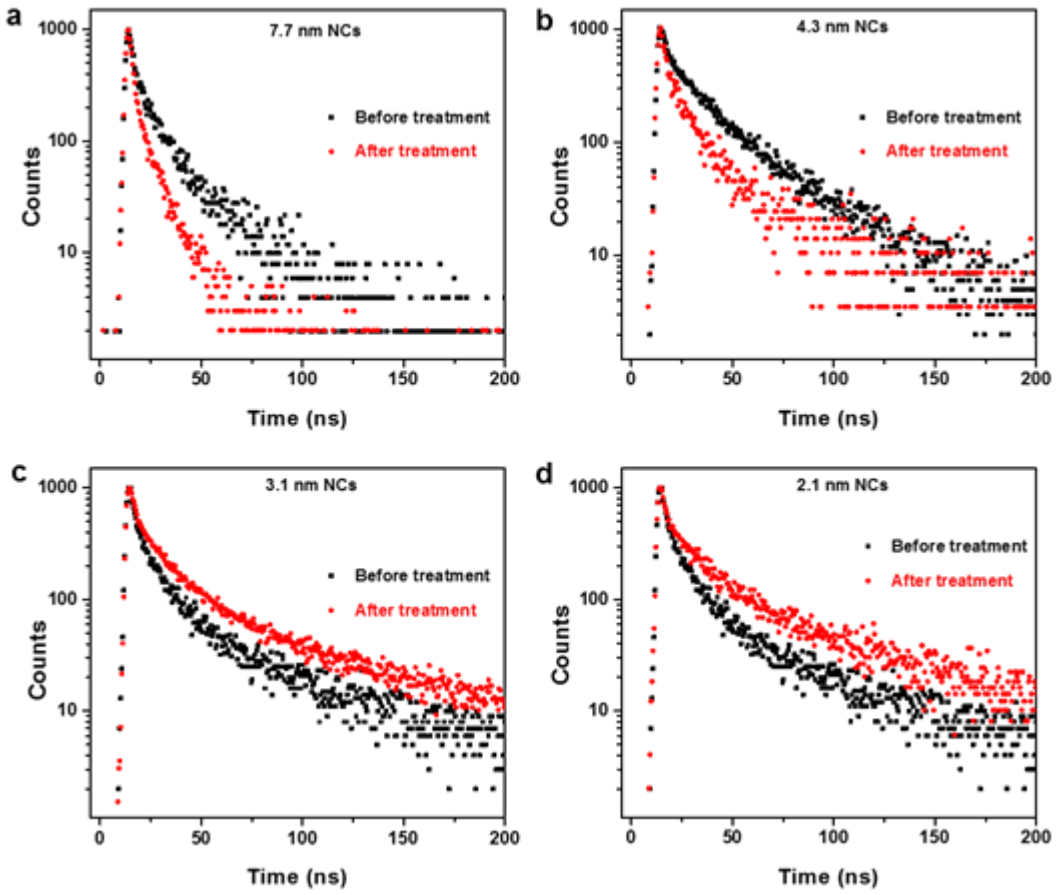

Fig. S4 PL decay dynamics of different-sized CdSe NCs before (black curves) and after (red curves) ligand exchange with $(NH_4)_2S$: (a) 7.7 nm, (b) 4.3 nm, (c) 3.1 nm, (d) 2.1 nm. The untreated CdSe NCs are dispersed in hexane, while the S^{2-}-treated NCs are dispersed in FA for measurements.

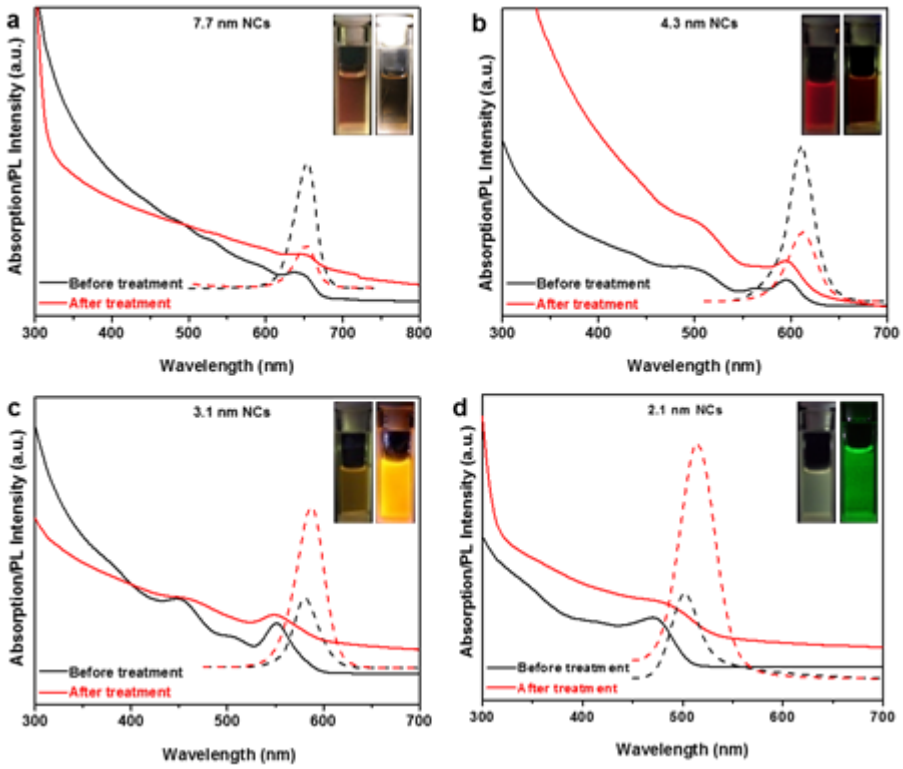

Fig. S5 UV-Vis absorption spectra (solid curves) and PL spectra (dashed curves) of different-sized CdSe NCs before (black curves) and after (red curves) K_2S treatment: (a) 7.7 nm, (b) 4.3 nm, (c) 3.1 nm, (d) 2.1 nm. The insets show the corresponding luminescent photographs of NC dispersions before (left) and after (right) K_2S treatment upon illumination with a UV lamp. The untreated NCs are dispersed in hexane, while the S^{2-}-treated NCs are dispersed in FA with the same concentration.

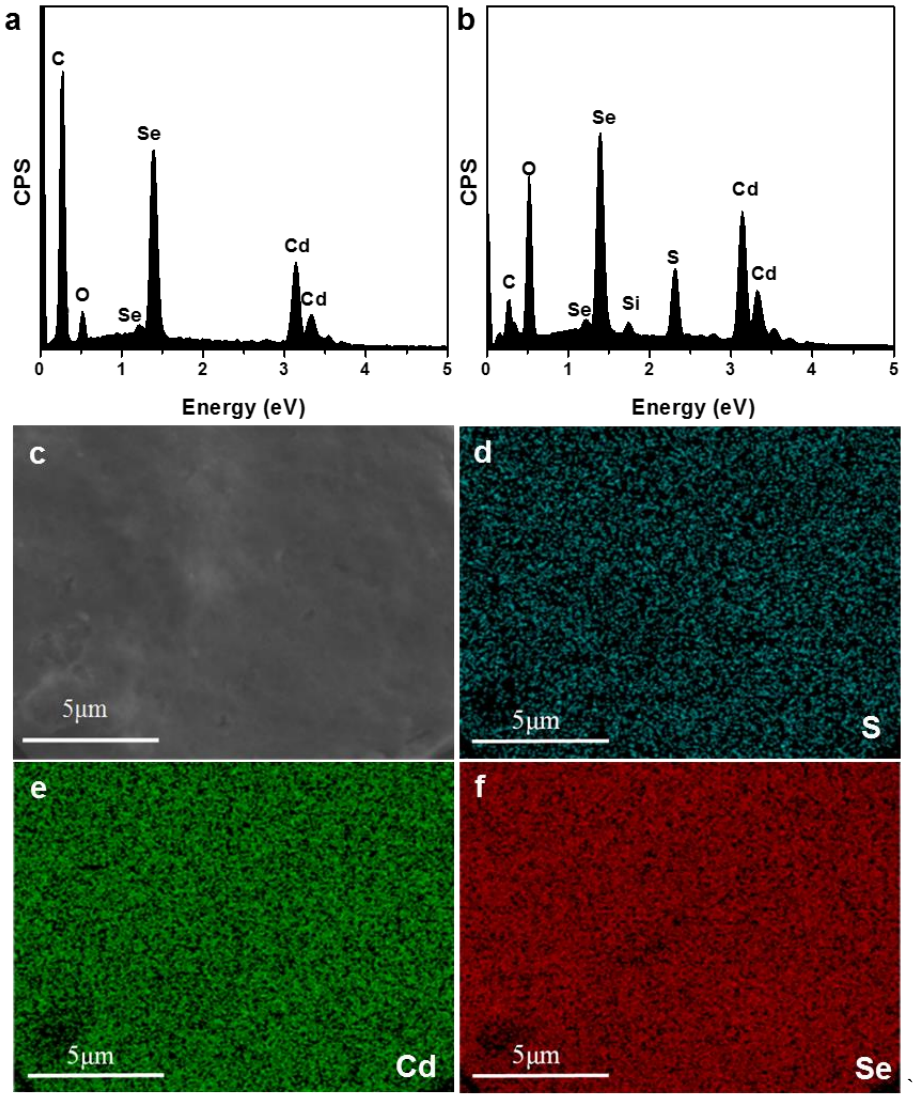

Fig. S6 Representative EDS spectra of 3.1 nm CdSe NCs before (a) and after (b) $(NH_4)_2S$ treatment, respectively. The Si signal in (b) is due to the use of the Si wafer substrate. (c) Representative SEM image and the corresponding elemental mappings (d-f) of S^{2-}-treated CdSe NCs, showing the uniform distribution of S upon ligand exchange.

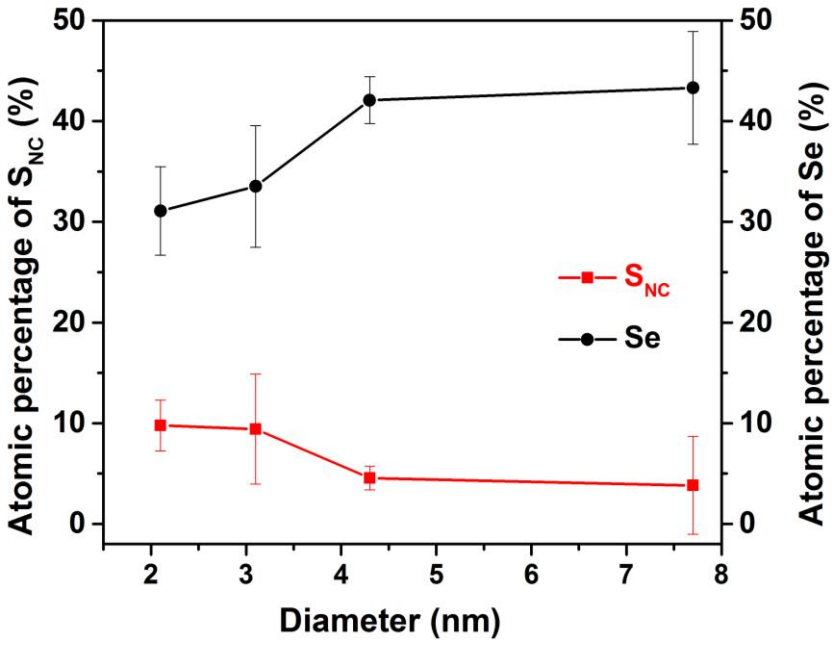

Fig. S7 Plots of atomic percentages of S_{NC} and Se as a function of NC diameters upon K_2S treatment.

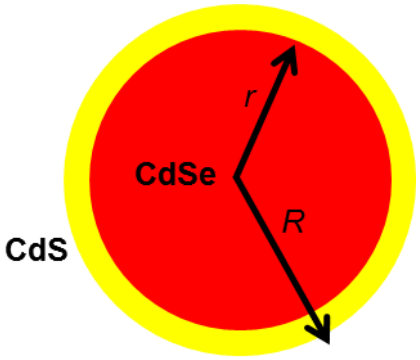

Fig. S8 Cross-sectional view of CdSe/CdS core-shell NCs.

The CdS shell thickness can be roughly calculated by comparing the volume of CdSe core (with radius *r*) to that of core-shell NCs (with radius *R*).[1] The molar ratio of Se/(Se + S_{NC}) in core-shell NCs = the volume of the CdSe core/the volume of the CdSe core and the volume of the CdS shell = r^3/R^3. Take 3.1 nm CdSe NCs as an example, the molar ratio of Se/(Se + S_{NC}) = 28.56/(28.56 + 17.24) = $r^3/1.55^3$; r = 1.32 nm. Therefore, the CdS shell thickness is determined to be R-r = 1.55 - 1.32 = 0.23 nm.

Table S1 PL QY of CdSe NCs before and after K_2S treatment

NC size (nm)	PL QY (%)	
	Before treatment	After treatment
7.7	0.7	0.2
4.3	1.2	0.7
3.1	1.9	3.3
2.1	1.6	26.1

Additional References:

1. Y. Liu, F. Wang, J. Hoy, V. L. Wayman, L. K. Steinberg, R. A. Loomis, W. E. Buhro, *J. Am. Chem. Soc.*, 2012, **134**, 18797.