Electronic supplementary information

A highly reactive chalcogenide precursor for the synthesis of metal chalcogenide quantum dots

Peng Jiang,[a] Dong-Liang Zhu,[a] Chun-Nan Zhu,[a] Zhi-Ling Zhang,[a] Guo-Jun Zhang,[b] Dai-Wen Pang*[a]

[a] Key Laboratory of Analytical Chemistry for Biology and Medicine (Ministry of Education), College of Chemistry and Molecular Sciences, State Key Laboratory of Virology, the Institute for Advanced Studies, and Wuhan Institute of Biotechnology, Wuhan University, Wuhan 430072, China.

[b] Hubei University of Chinese Medicine, School of Lab Medicine, 1 Huangjia Lake West Road, Wuhan 430065, P. R. China.

* E-mail: dwpang@whu.edu.cn

Characterizations. Transmission electron microscopy (TEM) imaging was performed by using JEM2010FEF (UHR) microscope with an acceleration voltage of 200 kV. Copper grids coated with amorphous carbon film were used as substrates for preparing the TEM samples. JEM 2010 FEF (UHR) microscope equipped with EDX spectrometry (EDAX Inc.) was used for the energy-dispersive X-ray (EDX) analysis (using Genesis software). Quantitative elemental analyses were carried out with Genesis software. The fourier transform infrared (FT-IR) spectra were measured by using Thermo Scientific Nicolet iS10 spectrometer. Bruka D8 Advanced X-Ray diffractometer (Bruker axs), with Cu K-alpha radiation wavelength of 1.5406 Å, was used to collect the X-ray powder diffraction (XRD) patterns, in which the scan rate was set as 0.5 degree/min. UV-2550 spectrophotometer (SHIMADZU) was used to record absorption spectra. Fluorolog-3 fluorescence spectrophotometer (HORIBA JOVIN YVON INC.) equipped with photomultiplier tube (PMT) (290-850 nm) and liquid nitrogen cooled InGaAs detector (800-1600 nm) was used for photoluminescence (PL) measurements.

Table S1. The reactant amounts, product weights and atomic ratios of metal (Ag, Pb or Cd) to chalcogenide (S or Se) of the metal chalcogenide NCs

NCs sample	Reactant amount (Ag, Pb, Cd)/ mmol	Reactant amount (S, Se)/ mmol	Product weight/ mg	Metal/chalcogenide atomic ratio
Ag_2S	0.1	0.05	11.4	1.6/1
PbS	0.1	0.1	15.7	0.6/1
Ag_2Se	0.05	0.025	9.4	1.3/1
PbSe	0.1	0.1	20.1	0.6/1
CdSe	0.1	0.1	15	0.4/1

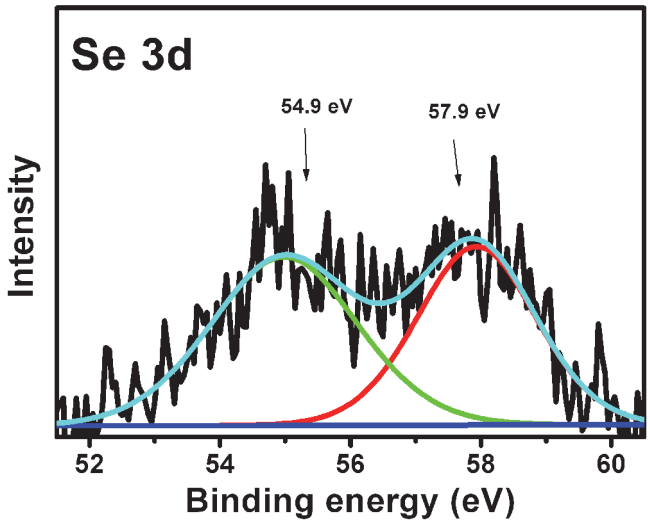

Fig. S1 High-resolution X-ray photoelectron spectroscopy (XPS) spectrum of Se (3d) for the DDAB-Se^{2-}.

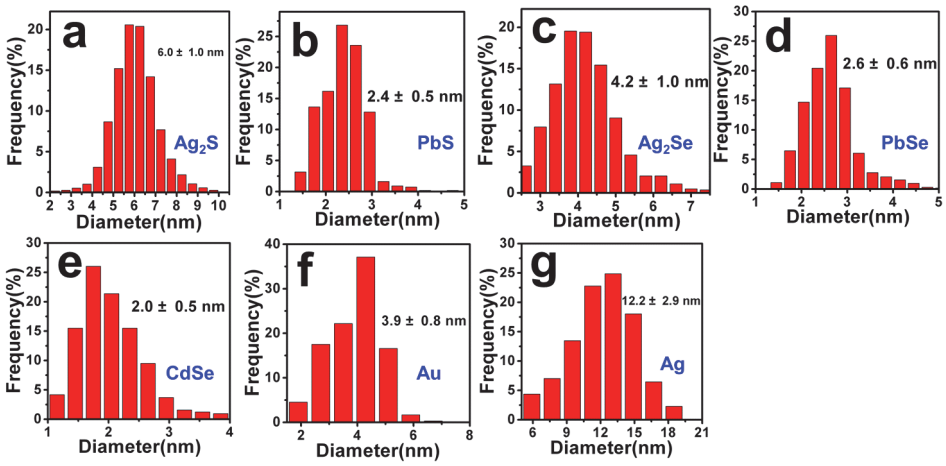

Fig. S2 The size distribution histograms of the as-prepared (a) Ag_2S, (b) PbS, (c) Ag_2Se, (d) PbSe, (e) CdSe, (f) Au and (g) Ag nanocrystals.

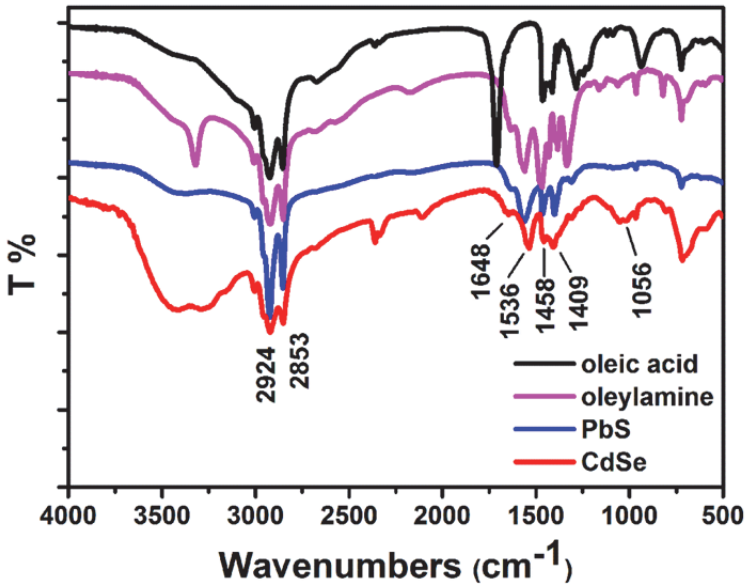

Fig. S3 Fourier transform infrared (FT-IR) spectra of PbS and CdSe NCs.The peaks located at 2924 cm^{-1} and 2853 cm^{-1} were assignable to C-H symmetric and asymmetric stretching vibrations of oleylamine (OAm) and oleic acid (OAc).[1] The peak related to the bending vibration of CH_2 was at 1458 cm^{-1}. The sharp and strong peak situated at 1536 cm^{-1} and 1409 cm^{-1} could be assigned to the asymmetric and symmetric stretching mode of COO^-,[2] implying that the OAc ligand existed on the surface of PbS nanocrystal. The NH_2 scissoring mode and C-N stretching mode were observed at 1648 cm^{-1} and 1056 cm^{-1},[3] respectively, implying the existence of OAm ligand. These results indicated that the obtained nanocrystal capped with OAc and OAm ligand.

Table S2. The quantum yield of the obtained metal chalcogenide NCs

NCs sample	QY of the NCs	Reference dye	QY of the dye
PbS	64%	ICG	13%
PbSe	26%	ICG	13%
Ag_2S	8%	ICG	13%
CdSe	8%	fluorescein	91%

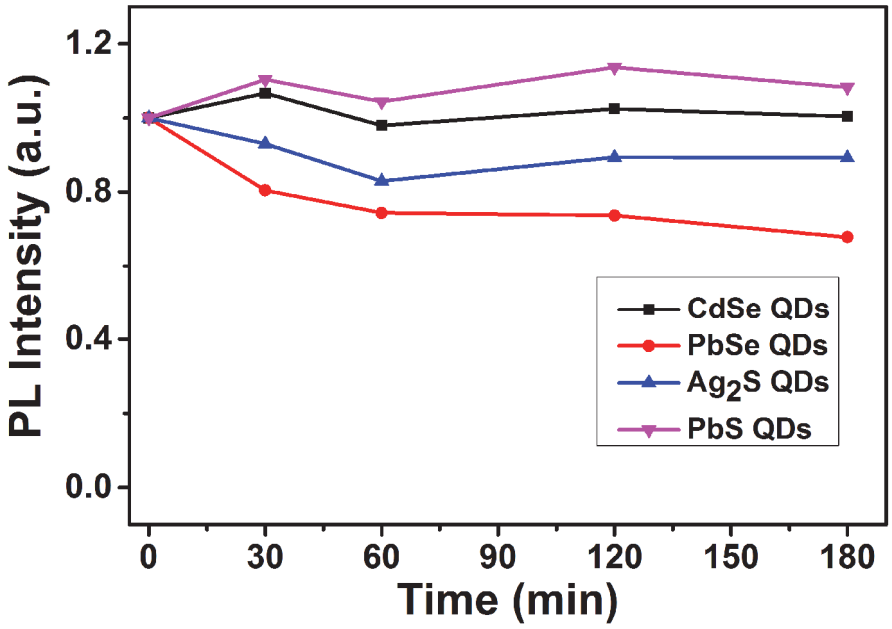

Fig. S4 PL intensities of the CdSe, PbSe, Ag_2S and PbS QDs after continuous illumination with mercury lamp.

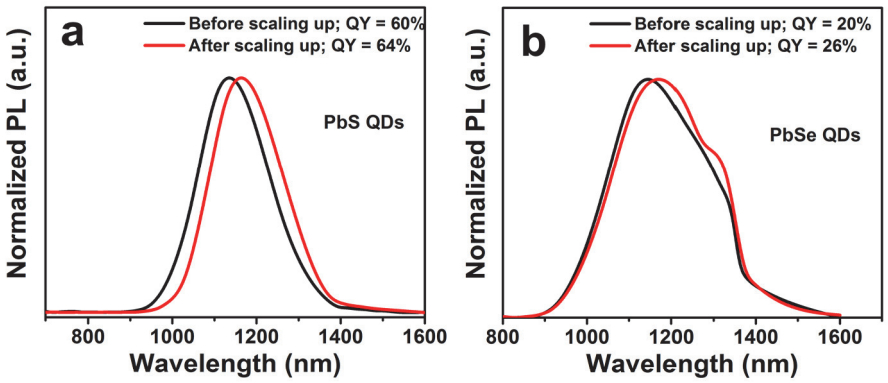

Fig. S5 The normalized PL spectra and quantum yield (QY) of the (a) PbS and (b) PbSe QDs synthesized before and after scaling-up. In the original synthesis, the amount of reactants (Pb, S and Se precursors) were 0.1 mmol, while the amount of the reactants increased to 1 mmol in the scaled-up synthesis.

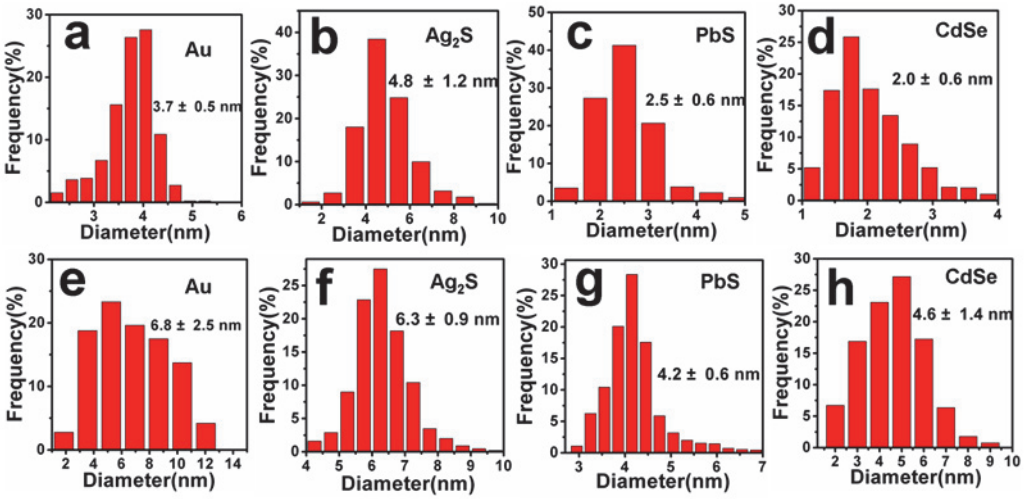

Fig. S6 The size distribution histograms of (a, e) Au, (b, f) Ag_2S, (c, g) PbS and (d, h) CdSe nanocrystals synthesized before (a-d) and after (e-h) the seed-mediated growth step.

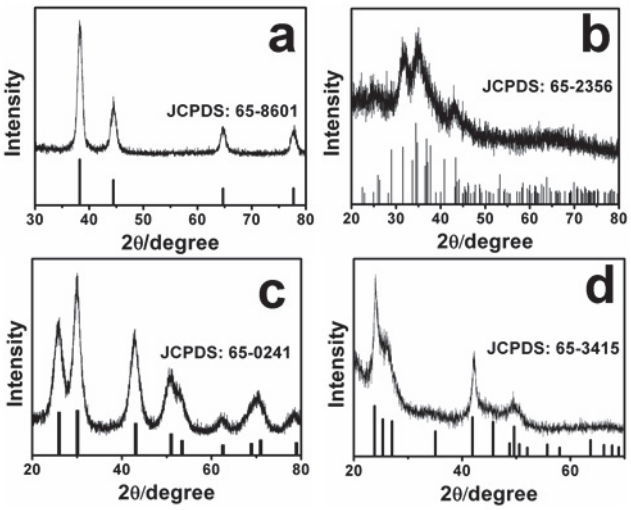

Fig. S7 XRD patterns of (a) Au, (b) Ag_2S, (c) PbS and (d) CdSe nanocrystals synthesized after the seed-mediated growth step.

Reference

1. X. Zhao, Y. Cai, T. Wang, Y. Shi and G. Jiang, *Anal. Chem.* , 2008, **80**, 9091-9096.
2. W. W. Yu, Y. A. Wang and X. G. Peng, *Chem. Mater.*, 2003, **15**, 4300-4308.
3. J. K. Cooper, A. M. Franco, S. Gul, C. Corrado and J. Z. Zhang, *Langmuir*, 2011, **27**, 8486-8493.