Supporting information

Two-step synthesis of high-quality water-soluble near-infrared emitting quantum dots via amphiphilic polymers

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Experimental

Synthesis of PbS QDs: PbS QDs were synthesized by using OLA as ligands.[S1] Typically, $PbCl_2$ (3.6 mmol) in OLA (2.4 mL) and sulfur (0.36 mmol) in OLA (0.24 mL) were purged, respectively, by N_2 at room temperature for 30 min. The $PbCl_2$-OLA suspension was heated to 160 °C and kept at this temperature for at least 1 h. The homogeneous $PbCl_2$-OLA suspension was cooled to 120 °C, under vacuum for 15 min. The flask was then reopened and the N_2 flux was restored. Sulfur in OLA at room temperature was quickly injected into the $PbCl_2$-OLA suspension under vigorous stirring. The reaction cell was quenched with cold water after the growth reaction was conducted at 100 °C for 1−10 min to obtain PbS QDs of different sizes. Alcohol was added (QDs solution: alcohol = 1:5 in volume), and then the suspension was centrifuged and supernatant was removed. The QDs were re-dispersed in hexane. This process was repeated for two times. The QDs were re-dissolved in toluene finally.

Synthesis of PbS/CdS QDs: PbS/CdS QDs were synthesized via a cation exchange method.[S2] Typically, CdO (2.3 mmol), oleic acid (OA, 2 mL) and phenyl ether (10 mL) were heated to 255 °C under N_2 for 20 min. The clear solution was cooled to 155 °C under vacuum

for 15 min. The flask was then reopened and the N_2 flux was restored. PbS QDs suspension in toluene (1 mL, Absorbance = 3 at 1460 nm) was diluted in 10 mL toluene, bubbled for 30 min and then heated to 100 °C immediately. The Cd/OA mixture was injected. The reaction cell was quenched with cold water after the growth reaction was conducted at 100 °C for different time. Alcohol was added, and then the suspension was centrifuged and supernatant was removed. QDs were re-dispersed in hexane. This process was repeated for two times. The final QDs were re-dispersed in chloroform.

Synthesis of amphiphilic polymer (PMAO–PEG): Amphiphilic polymers were synthesized according to a published method.[S3] A typical reaction is as follows: 1 g of PMAO and 1.5 g of PEG-OH were mixed with 50 μL of concentrated H_2SO_4 and refluxed in chloroform (10 mL) at 61 °C for 12 h. The mixture was neutralized by 1 M NaOH and then centrifuged to remove Na_2SO_4 and water.

Transfer of the PbS QDs or PbS/CdS QDs into water via PMAO–PEG: Water-soluble PbS QDs were achieved by performing following procedures: monodispersed PbS QDs (1 mL, absorbance = 1 at 1460 nm) were mixed with PMAO–PEG (1.6 mL, 30 mM) in chloroform and stirred for 6 h, after that, N_2 bubbled water (2.6 mL) was added to the chloroform solution. Chloroform was then gradually removed by evaporation. The water-soluble PbS QDs were further centrifuged at 8000 rpm for 30 min.

Characterizations: PbS and PbS/CdS QDs were characterized by transmission electron microscopy (TEM, JEOL 2100F) equipped with an energy dispersive X-ray spectrometer (EDX). The Pb/Cd ratio was measured at the University of Toronto by using inductively coupled plasma optical emission spectrometry (ICP-OES, Perkin Elmer Model Optima 7300 DV ICP-OES). X-ray photoelectron spectrometry (XPS, VG Escalab 220i-XL, Al Kα source) was employed for qualitative composition analyses.

Dynamic light scattering technique (Malvern, Zetasizer Nano S90) was used to determine the hydrodynamic radius of QDs. Absorption spectra were acquired with a Cary 5000 ultraviolet (UV)-visible (Vis)-NIR spectrophotometer (Varian) with a scan speed of 600 nm/min. Fluorescence spectra were taken with a Fluorolog®-3 system (Horiba Jobin Yvon) using an excitation wavelength of 674 nm.

Quantum yield measurement was performed at HORIBA Jobin Yvon, NJ, USA. The dye IR-125 dissoved in dimethyl sulfoxide was used as a reference. Lifetimes of PbS or PbS/CdS QDs in different solvents were measured using a pulsed laser diode of 636 nm and the fast multichannel scaler mode in the Fluorolog®-3 system. The decay signals were found to be best fitted to a single-exponential function, $I(t) = I_0 \exp(-t/\tau)$, where τ is lifetime, I is photoluminescence, t is time and I_0 is the initial photoluminescence at $t = 0$. The photostability of PbS/CdS QDs dispersed in PBS buffer were tested using a 4 W UV lamp (115 V, 60 HZ, Model 22-UV, Optical Engineering, UV light Inc.).

Supporting figures

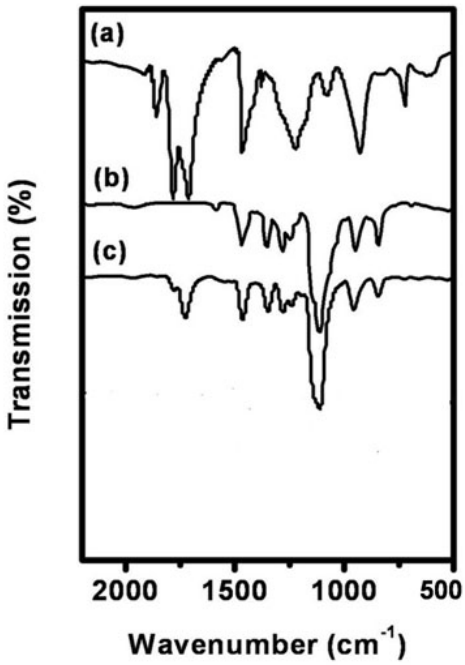

Figure S1 FT-IR characterizations of (a) PMAO, (b) PEG–OH and (c) PMAO–PEG.

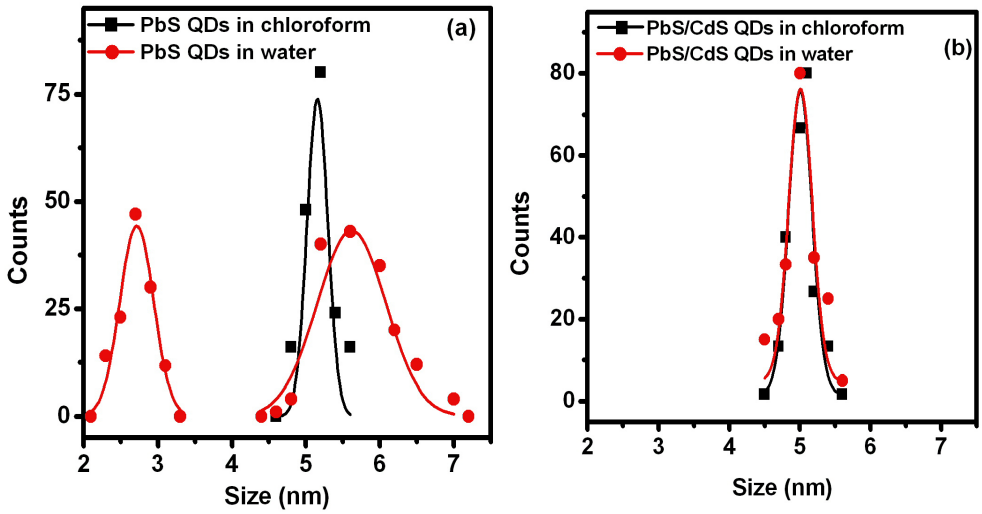

Figure S2 (a) Size distribution of PbS QDs in chloroform (5.2 ± 0.2 nm) and in water (5.6 ± 0.9 nm and 2.7 ± 0.4 nm). (b) Size distribution of PbS/CdS QDs in chloroform (5.0 ± 0.3 nm) and in water (5.0 ± 0.3 nm).

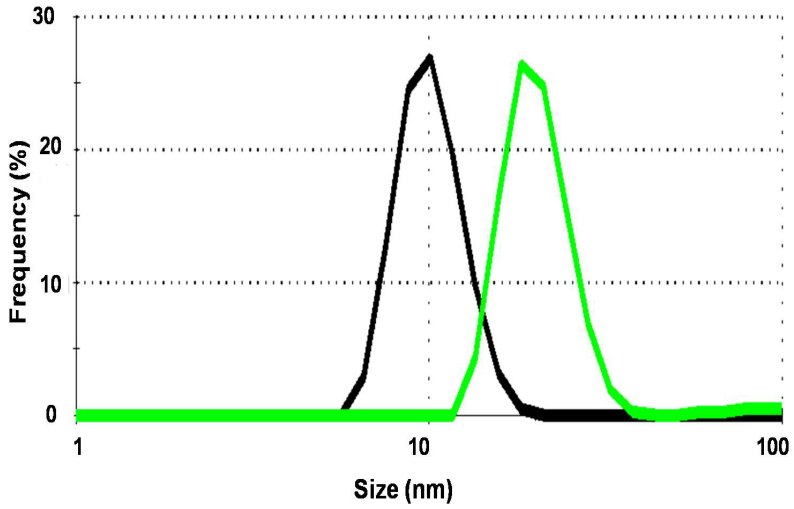

Figure S3 Dynamic light scattering measurements of the hydrodynamic diameter of PbS/CdS QDs in chloroform (~10 nm) and after transfer into water (~22 nm).

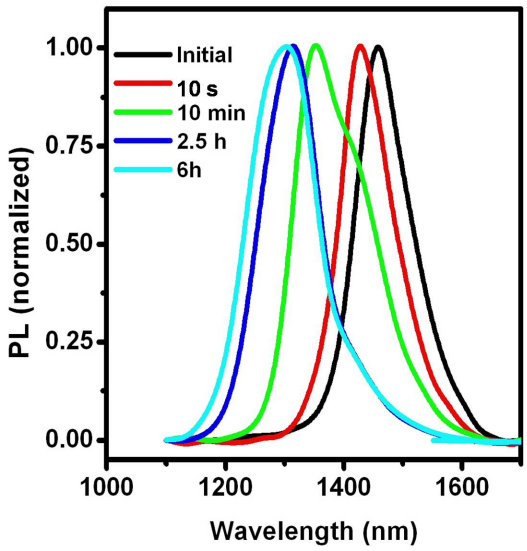

Figure S4 PL spectra of PbS QDs during the formation of the CdS shell.

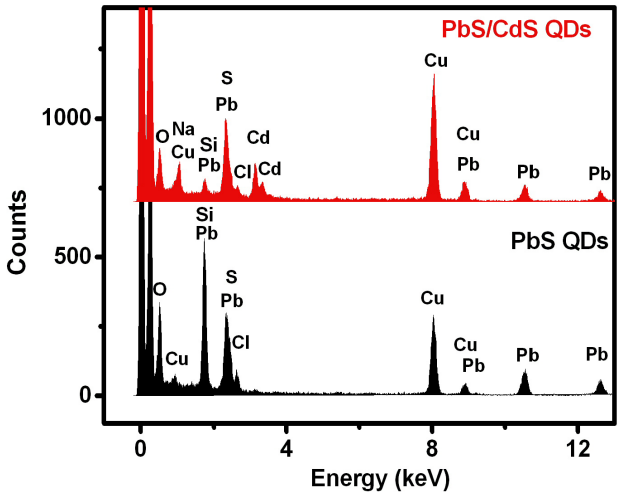

Figure S5 EDX spectra of PbS and PbS/CdS QDs, indicating the presence of Pb, S and Cd.

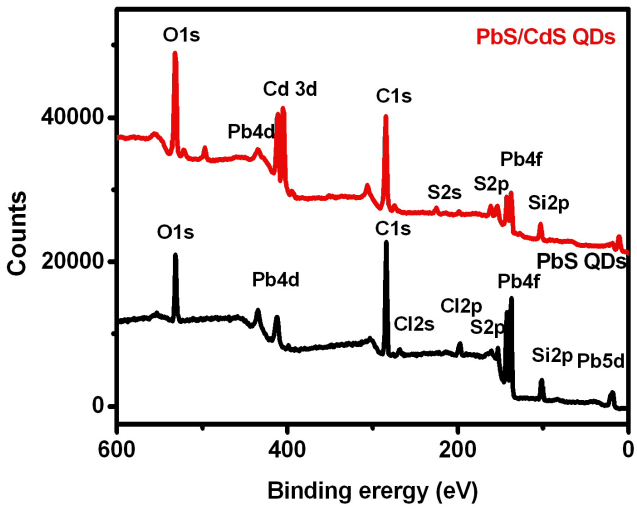

Figure S6 XPS spectra of PbS and PbS/CdS QDs, indicating the presence of Pb, S and Cd.

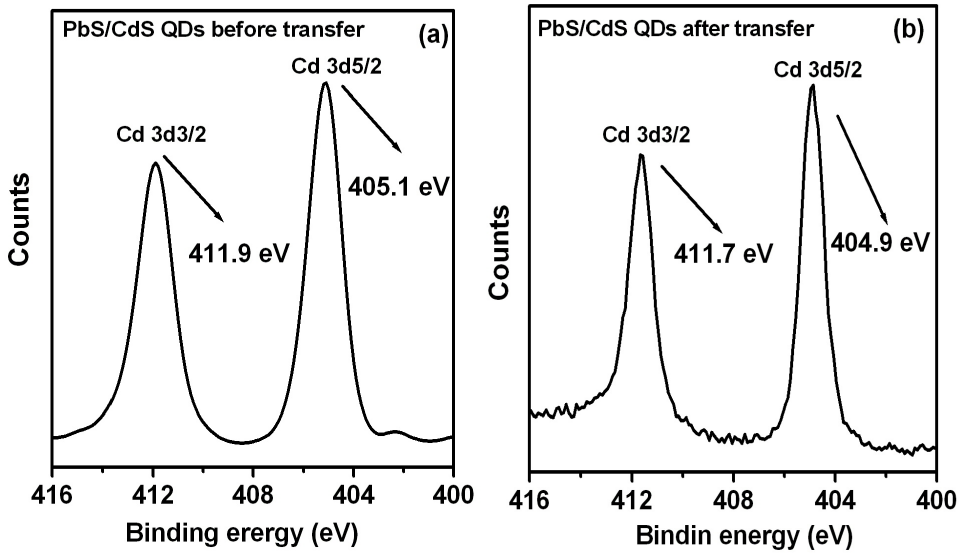

Figure S7 High resolution XPS spectra of Cd 3d of PbS/CdS QDs before and after transfer into water via PMAO–PEG, indicating the CdS shell is stable during the transfer process.

Scheme S1 Synthesis of PbS/CdS QDs by cation exchange.

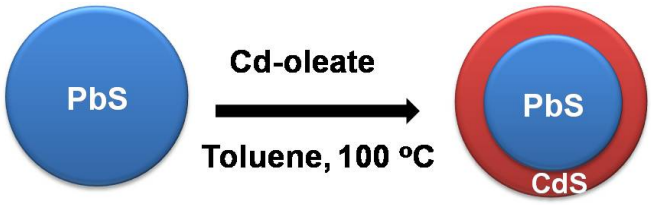

Table S1. Comparison of the measured and estimated absorption peak positions for PbS QDs, and hybrid QDs of PbS and CdS assuming core/shell and alloy structures respectively .

QDs	Absorption Peak (nm)	Molar Ratio of Pb/Cd	Size (nm)	Estimated Absorption Peak *1 (nm)
PbS	1460	1	5.2	1410
PbS/CdS Core@shell	1190	1:1.7	3.8 *2	1103
PbS-CdS Alloy *3	1190	1:1.7	5.0	610

***1**: Estimated absorption peak position based on the size of PbS according to reference S4.
***2**: The core size of PbS/CdS core/shell QDs was estimated based on the ratio of Cd/Pb measured by ICP-OES at University of Toronto**.**
***3:** The 5-nm hybrid QDs were assumed to be an alloy of $Pb_xCd_{1-x}S$, and then the bandgap energy was estimated by the following equation according to the Vegard's Law: [S5]

$$Eg = Eg_{(PbS)}x + Eg_{(CdS)}(1-x)$$

where *Eg* is the bandgap energy of alloyed QDs, *x* and *(1-x)* are the molar percentage of PbS and CdS, respectively, based on ICP-OES measurements. The bandgap energy of 2.7 eV is applied for CdS QDs, according to reference S6.

The estimated blue shift of the absorption peak positions from PbS to PbS/CdS core/shell QDs is 307 nm, which is close to the observed peak shift of 270 nm. However, this value is quite different from that estimated for the PbS-CdS alloy (800 nm). These calculations and comparisons exclude the possibility of PbS-CdS alloy formation, while further verify the formation of the PbS/CdS core/shell structure.

S1 (*a*) H. G. Zhao, M. Chaker, D. Ma, *J. Phys. Chem. C,* 2009, **113**, 6497–6504; (*b*) L. Cademartiri, J. Bertolotti, R. Sapienza, D. S. Wiersma, V. Kitaev and G. A. Ozin, *J. Phys. Chem. B,* 2006, **110**, 671–673.

S2 J. M. Pietryga, D. J. Werder, D. J. Williams, J. L. Casson, R. D. Schaller, V. I. Klimov and J. A. Hollingsworth, *J. Am. Chem. Soc.,* 2008, **130**, 4879–4888.

S3 W. W. Yu, E. Chang, J. C. Falkner, J. Zhang, A. M. Al-Somali, C. M. Sayes, J. Johns, R. Drezek and V. L. Colvin, *J. Am. Chem. Soc*., 2007, **129**, 2871–2879.

S4 L. Cademartiri, E. Montanari, G. Calestani, A. Migliori, A. Guagliardi and G. A. Ozin, *J. Am. Chem. Soc.,* 2006, **128**, 10337–10346.

S5 P. Reiss, M. Protière and L. Li, *Small*, 2009, **5**, 154–168.

S6 J. Thessing, J. H. Qian, H. Y. Chen, N. Pradhan, X. G. Peng, *J. Am. Chem. Soc.* 2007, **129**, 2736–2737.