Supplementary Information

Organosilane micellization for direct encapsulation of hydrophobic quantum dots into silica beads with highly preserved fluorescence

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Experimental section

Reagents

Trioctylphosphine oxide (TOPO, 90%), hexadecylamine (HDA, 90%), trioctylphosphine (TOP, 90%), dioctylamine (DOA, 90%), 1-octadecene (ODE, 90%), stearic acid (SA, 95%), cadmium oxide (CdO, 99.99%), selenium powder (99.99%), zinc diethyldithiocarbamate (ZDC, 98%), sodium silicate solution (27 wt % SiO_2), tetraethyl orthosilicate (TEOS, 99%) and mercaptopropionic acid (MPA, 99%) were purchased from Aldrich. N-octyl triethoxy silane (OTES, 98%) was purchased from TCI. Chloroform, methanol, ethanol, and aqueous ammonia solution (28%) were supplied by Sinopharm Chemical Reagent Co., Ltd. Ultrapure water with a conductivity of 18.25 MΩ.cm was used throughout the experiments.

Preparation of CdSe/ZnS QDs

HDA and TOPO capped CdSe QDs were synthesized according to previous method[1] with slight modification. Typically, the cadmium precursor was prepared by heating a mixture of 0.1 mmol CdO and 0.4 mmol SA at 150 ºC in a three-neck flask under Ar flow until a colorless clear solution was obtained. The flask was cooled to room temperature and 1.94 g of both HDA and

TOPO were added. The mixture was then heated to 320 °C under Ar flow and the selenium

precursor (1 mmol selenium powder dissolved in 1 mL TOP and 2 mL DOA in glove box) was

swiftly injected into the flask. The solution was kept at 260 °C for the nanocrystal growth until

reached the required emission. The growth of ZnS shell was achieved by the reported single

precursor route.[2] In this case, 74 mg of ZDC was dissolved in 1 mL TOP and 2.6 mL ODE. When

the QDs solution was cooled to 160 °C under Ar flow, 0.9 mL of ZDC precursor was added with a

syringe and the solution was kept at this temperature for 30 min. 1.2 mL and 1.5 mL of ZDC

precursor were injected for the second and third round of shell growth with the same reaction

parameters. The QDs were washed with chloroform/methanol (1:1) mixture for three times and

finally dispersed in 10 mL chloroform as the stock solution. Water solubilization of CdSe/ZnS

QDs by MPA coating was performed using the previous method.[3]

Preparation of silica beads embeding CdSe/ZnS QDs

The procedure to prepare the typical 25 nm silica beads with CdSe/ZnS QDs is as follows: 750 μL

of QD stock solution (2.1×10^{-5} mol L^{-1}) was mixed with equal volume of methanol to precipitate

the QDs. The QDs were collected by centrifugation, dried under air flow and dissolved by 40 μL

OTES to obtain an optically clear solution. The organosilane was transferred to the bottom of a

glass vessel and then 40 mL water and 60 μL aqueous ammonia solution (28%) was added. The

mixture was processed by a tapered microtip sonicator (VCX800 Ultrasonic processor, Sonics)

with 6 mm diameter probe and 30% amplitude. The working circle consisted of 5 s sonicating and

3 s pausing over a period of one hour. The temperature of the solution would rise upto 65 °C

during the processing. The resulting solution was passed through a 0.22 μm pore size filter to

remove any existing cloudiness. Then 1.6 mL of sodium silicate solution (0.54 wt %) was added

to the transparent filtrate which was subsequently stirred for 72 h. To prepare the 16 nm and 38

nm silica beads, 400 µL and 1.2 mL of QD stock solution were used, respectively.

Extensive silica growth on the nanobeads

The crude solution of silica beads (25 nm) were concentrated by ultrafiltration using a 30

kDa-MWCO filter to reach an optical density of 0.1 at 566 nm (exciton absorption peak of QDs).

Then 3 mL of above solution was added to a mixture of 9 mL ethanol, 0.2 mL ammonia and 12

µL TEOS. The mixture was gently stirred for 6 h at room temperature to deposit a 15 nm silica

shell on the nanobeads.

Characterization

Transmission electron microscopy (TEM) image and energy- dispersive X-ray spectroscopy (EDX)

were acquired on JEM-2010FEF transmission electron microscope with an EDAX attachment

operating at an accelerating voltage of 200 kV. Dynamic light scattering was measured on Malvern

Zetasizer Nanoseries using 633 nm laser at 25 °C. Aliquots of the reaction mixture were run over a

0.22 µm pore size filter before any size measurement. Ultraviolet-Visible (UV-Vis) absorption

spectra were recorded on Nicolet Evolution 300 Ultraviolet-Visible spectrometer.

Photoluminescence (PL) spectra and PL decay curves were measured on Edinburgh FLS920

spectrometer (λ_{ex}=390 nm, λ_{em}=580 nm). PL stability was tested on Perkin Elmer LS-55

spectrometer in time drive mode (λ_{ex}=390 nm, λ_{em}=580 nm). The photoluminescence quantum

yield (PL QY) of CdSe/ZnS QDs before and after silica coating were calculated with the described

procedure[1], using Rhodamine 6G in ethanol as a standard (PL QY = 95%).

References

1   L. H. Qu and X. G. Peng, *J. Am. Chem. Soc.*, 2002, **124**, 2049.

2   W. J. Zhang, G. J. Chen, J. Wang, B. C. Ye and X. H. Zhong, *Inorg. Chem.*, 2009, **48**, 9723.

3   J. H. Gao, K. Chen, R. G. Xie, J. Xie, S. Lee, Z. Cheng, X. G. Peng, and X. Y. Chen, *Small.*,
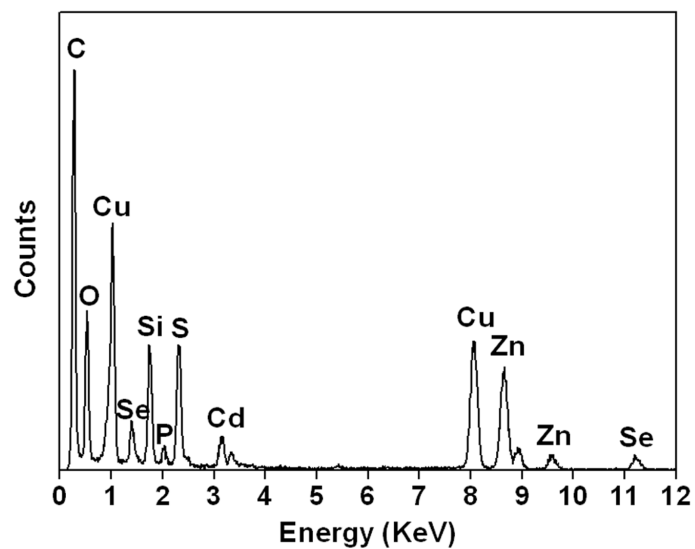
    2010, **6**, 256.

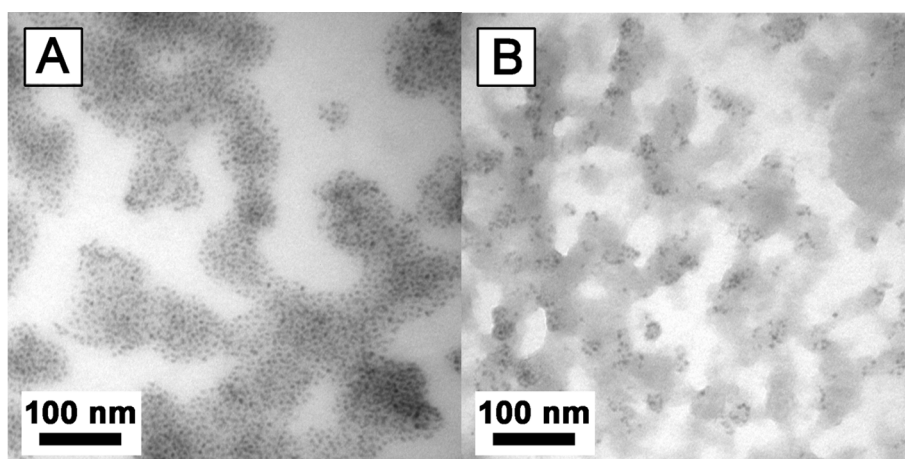**Fig. S1** EDX analysis of CdSe/ZnS QDs incorporated silica beads.

Fig. S2 TEM images of silane-QDs micelles with starting QD concentrations (in OTES) of 1.1×10^{-3} mol L^{-1} (A) and 4×10^{-5} mol L^{-1} (B).
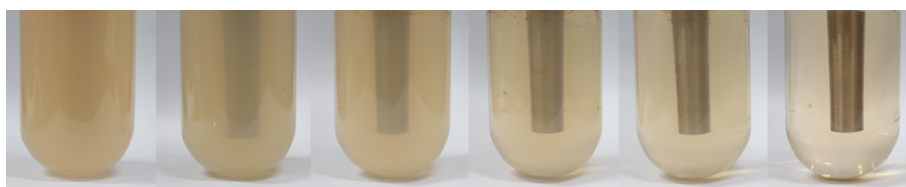

Fig. S3 Appearance of the oil in water microemulsion (left to right) with ultrasonication time of 5 min, 10 min, 20 min, 30 min, 40 min and after filtration.
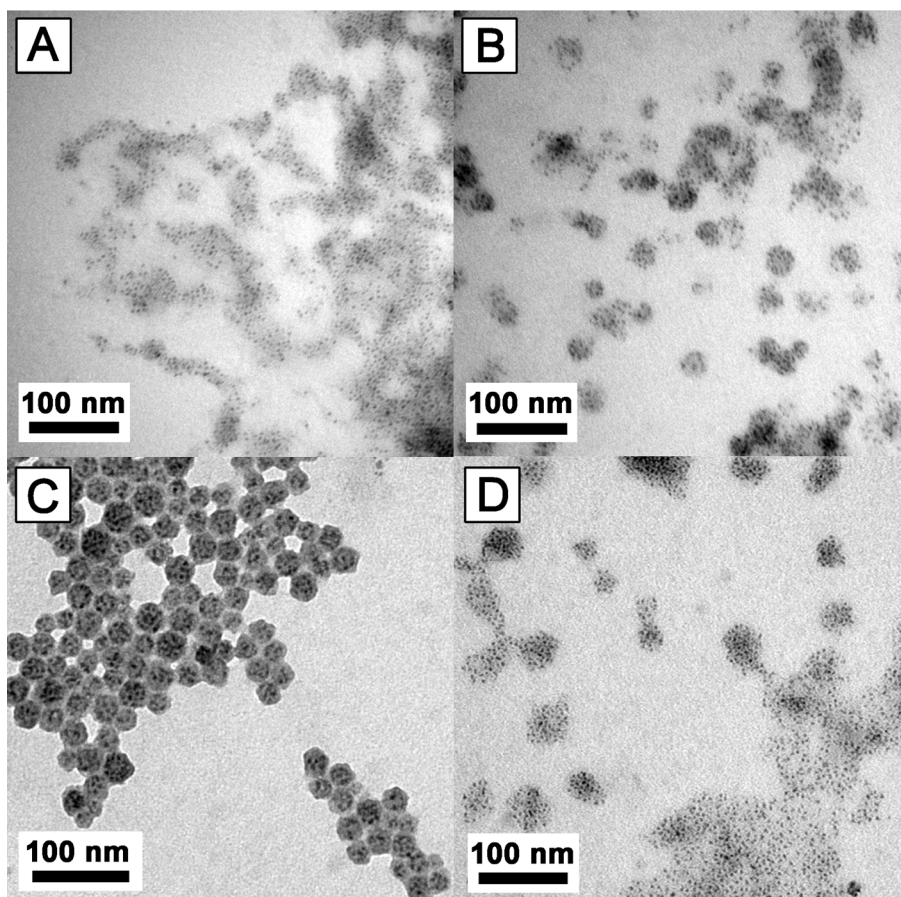
Fig. S4 TEM images of silane-QDs micelles after silicate deposition for 0 h (A), 24h (B), 72h (C)

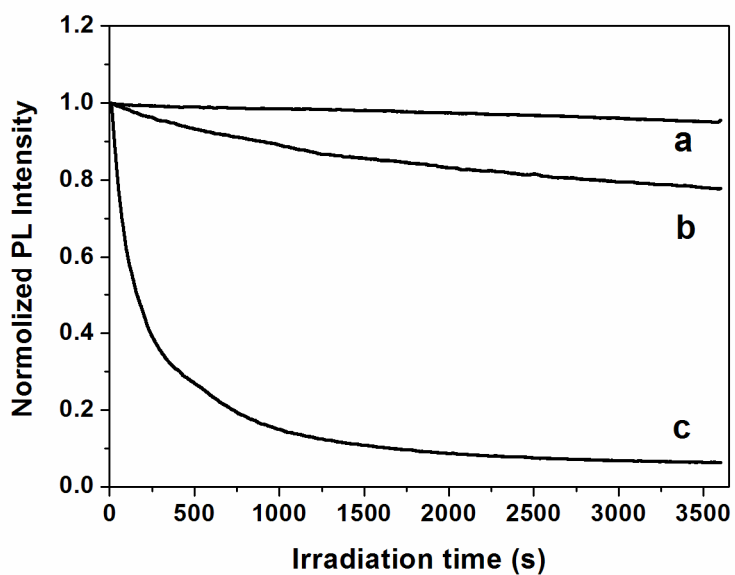and controlled micelles after 72 h stirring without silicate deposition (D).

Fig. S5 PL intensity changes of QDs incorporated silica beads (a), silane micelles (b) and MPA

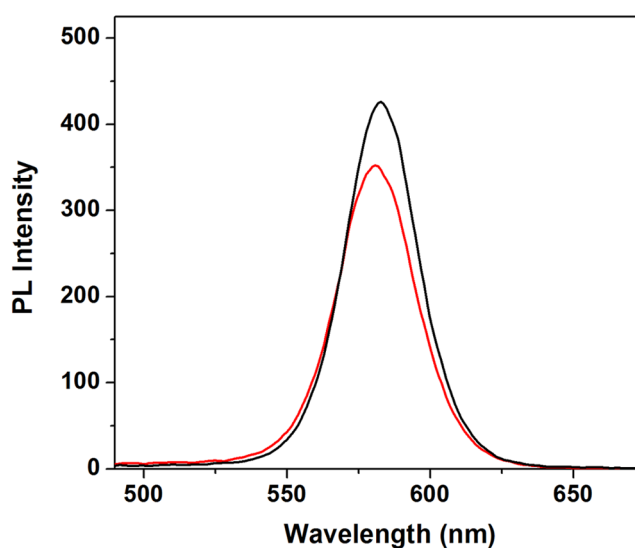coated QDs (c) within 3600 s excitation.

Fig. S6 PL spectra of QDs/SiO$_2$ nanobeads before (black) and after (red) extensive silica coating for 6 h in ethanol/water mixture.

Table S1 Decay times, amplitudes of the components and mean lifetimes from CdSe/ZnS QDs at different synthetic stages

Sample	τ_1 (ns)	B_1 (%)	τ_2 (ns)	B_2 (%)	τ (ns)
1	5.52	59.43	21.12	40.57	16.80
2	6.56	55.01	22.46	44.99	18.28
3	8.16	50.10	27.15	49.90	22.75
4	10.78	49.17	27.93	50.83	23.27
5	12.00	39.52	23.67	60.48	20.77

Sample 1-5 represent the CdSe/ZnS QDs when ultrasonicated for 40 min, deposited with silicate for 24 h, 48 h, 72 h and before encapsulation (in chloroform), respectively. The biexponential fitting of PL decay curve can be described by: $F(t) = A + B_1 \exp(-t/\tau_1) + B_2 \exp(-t/\tau_2)$, where τ_1 and τ_2 represent the decay times and B_1 and B_2 stand for amplitudes of the fast and slow components, respectively. The mean lifetime (τ) can be calculated by: $\tau = (B_1\tau_1^2 + B_2\tau_2^2)/(B_1\tau_1 + B_2\tau_2)$.