

Supplementary Information

Brilliant sandwich type fluorescent nanostructure incorporating compact quantum dots layer and versatile silica substrates

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Experimental section

Reagents

Cadmium oxide (CdO, 99.99%), stearic acid (SA, 95%), selenium powder (99.99%), trioctylphosphine (TOP, 90%), dioctylamine (DOA, 90%), hexadecylamine (HDA, 90%), trioctylphosphine oxide (TOPO, 90%), zinc diethyldithiocarbamate (ZDC, 98%), 1-octadecene (ODE, 90%), sodium silicate solution (27 wt % SiO₂), tetraethyl orthosilicate (TEOS, 99%), Triton X-100 and (3-Mercaptopropyl)trimethoxysilane (MPS, 95%) were purchased from Aldrich. N-octyltrimethoxysilane (OTMS, 97%) was purchased from Alfa Aesar. Ammonia aqueous solution (28 wt %), methanol, ethanol, acetone, butanol, iso-propanol, chloroform and toluene, were supplied by Sinopharm Chemical Reagent Co., Ltd. Ultrapure water with a conductivity of 18.25 MΩ.cm was used throughout the experiments.

Synthesis of CdSe/ZnS QDs

CdSe QDs were synthesized using HDA and TOPO as capping ligands. Typically, 0.1 mmol of CdO and 0.4 mmol of SA were heated at 150 °C in a three-neck flask until a colorless clear solution was obtained. The flask was cooled and 1.94 g of both HDA and TOPO were added. The

flask was degassed, filled with argon and then heated to 320 °C when a selenium precursor solution (by dissolving 1 mmol of selenium powder in 1 mL TOP and 2 mL DOA) was swiftly injected. The CdSe QDs was kept at 260 °C for growth until the required emission was reached. For preparing CdSe/ZnS QDs, the CdSe QDs solution was cooled to 160 °C and 0.9 mL of zinc and sulfur precursor (by dissolving 74 mg of ZDC in 1 ml TOP and 2.6 ml ODE) was added dropwise. The solution was kept at 160 °C for 30 min for the growth of ZnS shell. The procedure was repeated for the second and third injection of zinc and sulfur precursor solution of 1.2 mL and 1.5 mL, respectively. The final product was washed with chloroform/methanol (1:1) mixture for three times and finally dispersed in 10 mL toluene.

Preparation of SiO₂ substrates and their surface modification

SiO₂ spheres with a diameter of 56 nm were prepared via reverse microemulsion approach. Typically, 15 ml of cyclohexane, 3.6 ml of hexanol and 3.54 ml of Triton X-100 were mixed and stirred for 15 min. Then, 680 µl of H₂O and 130 µl of ammonia were introduced and the mixture were stirred for another 15 min. The microemulsion was subsequently added with 200 µl of TEOS and stirred for 24 h. The solution was added with 10 ml of acetone, shaken and centrifuged at 10000 rpm for 10 min and the precipitate was washed sequentially with butanol, iso-propanol, ethanol and water. To prepare large SiO₂ spheres with 90 nm and 200 nm diameters, a seeded growth *via* Stöber method was adopted as described in previous literatures.¹⁻² The gold nanorod (AuNR) incorporated silica substrates were prepared by silica coating on AuNRs first in aqueous solution and then the Stöber system.³ Notably, the initially formed mesoporous silica (mSiO₂) shell should be eliminated by washing the AuNR@mSiO₂ particles thoroughly followed by growth *via* Stöber method to reach desired shell thickness. For surface modification with thiol

groups, the purified SiO₂ substrates dispersed in 15 ml of ethanol was added with 150 µl of MPS and 375 µl of ammonia and stirred for 12 h. The product was collected by centrifugation and washed with ethanol three times.

Preparation of SiO₂@QDs@SiO₂ nanocomposites

For assembling with QDs, a wet precipitate of thiolated SiO₂ spheres (56 nm) from ethanol solution (corresponding to 12 mg of dry powder) was mixed with 1.2 ml of CdSe/ZnS QDs toluene solution and sonicated for 10 min to obtain a clear solution. The SiO₂@QDs assemblies were recovered by centrifugation at 10000 rpm for 5 min and washed with toluene to remove excess QDs. The precipitate (red and optically clear) was properly dried under air flow and dissolved by 60 µl of OTMS with the aid of ultrasonication. The fluid was subsequently mixed by 4.5 ml of methanol and 112 µl of ammonia. The phase transfer of SiO₂@QDs assemblies were realized by sonicating the above mixture for 30 min and the assemblies were collected by centrifugation at 10000 rpm and washed with methanol to remove excess OTMS. The silanized SiO₂@QDs assemblies were dispersed in a solution of 9.6 ml of water and 0.4 ml of sodium silicate solution (0.54 wt %) and stirred for at least 12 h to deposit a thin silica layer which would favor their dispersing in Stöber system. To grow silica shell by Stöber method, the above solution (10 ml) was mixed with 40 ml of ethanol and 1.25 ml of ammonia, each 50 µl of TEOS was injected and stirred for 3 h until the desired shell thickness was reached.

Characterization

Transmission electron microscopy (TEM) image was acquired on JEM-2010FEF transmission electron microscope operating at an accelerating voltage of 200 kV. Ultraviolet-Visible (UV-Vis) absorption spectra were measured by Nicolet Evolution 300 Ultraviolet-Visible spectrometer.

Photoluminescence (PL) spectra and PL decay curves were recorded by Edinburgh FLS920 spectrometer. The quantum yield (PL) of CdSe/ZnS QDs and SiO₂@QDs@SiO₂ nanocomposites were calculated according to reported procedure,⁴ using Rhodamine 6G in ethanol as a standard (QY = 95%). To eliminate the scattering effect of silica on QD optical characterization, the nanocomposites were precipitated and redispersed in ethanol-toluene (1:4) mixture before the measurements.

References

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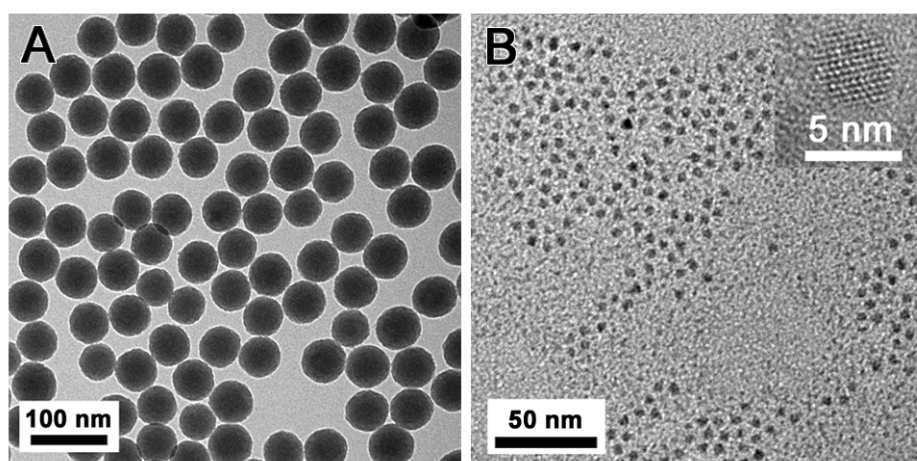


Fig. S1 TEM images of thiolated SiO₂ spheres (A) and oil soluble CdSe/ZnS QDs (B). Inset is the magnification image of single QD.

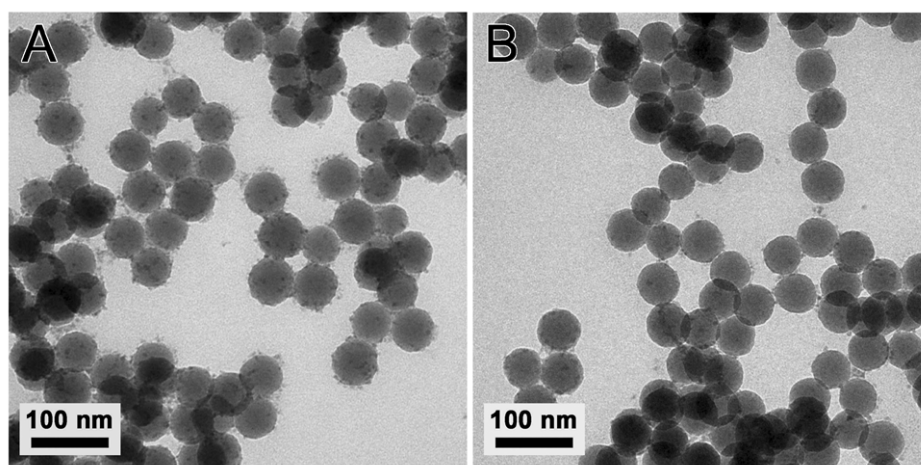


Fig. S2 TEM images of SiO₂@QDs assemblies with small amount (A) and excess (B) of DDT addition in organic phase before assembling.

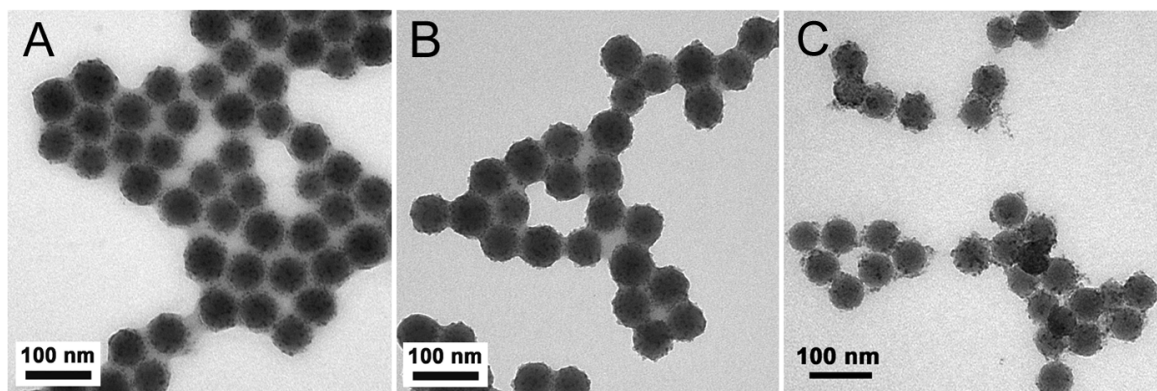


Fig. S3 (A-B) TEM images of SiO₂@QDs@OTMS composites in methanol (A) and after transferred into water (B) by ultrasonication in methanol/ammonia mixture. (C) TEM image of SiO₂@QDs@OTMS composites after ultrasonication in water/ammonia mixture.

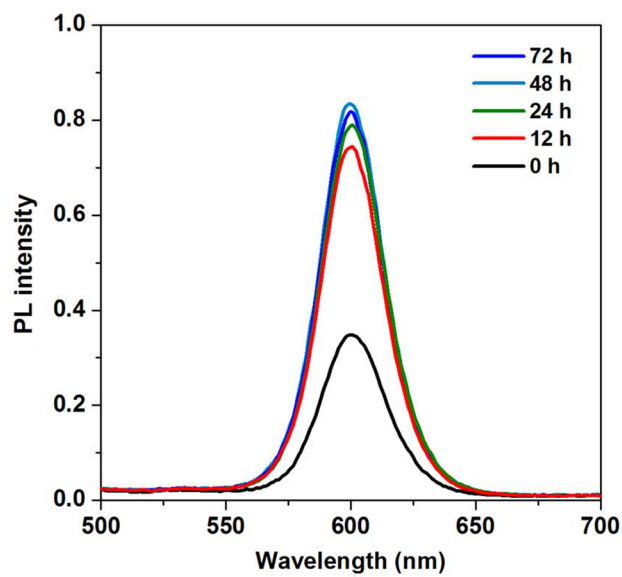


Fig. S4 PL spectra of $\text{SiO}_2@\text{QDs}@\text{SiO}_2$ fluorescent spheres with different sodium silicate deposition times in aqueous phase.

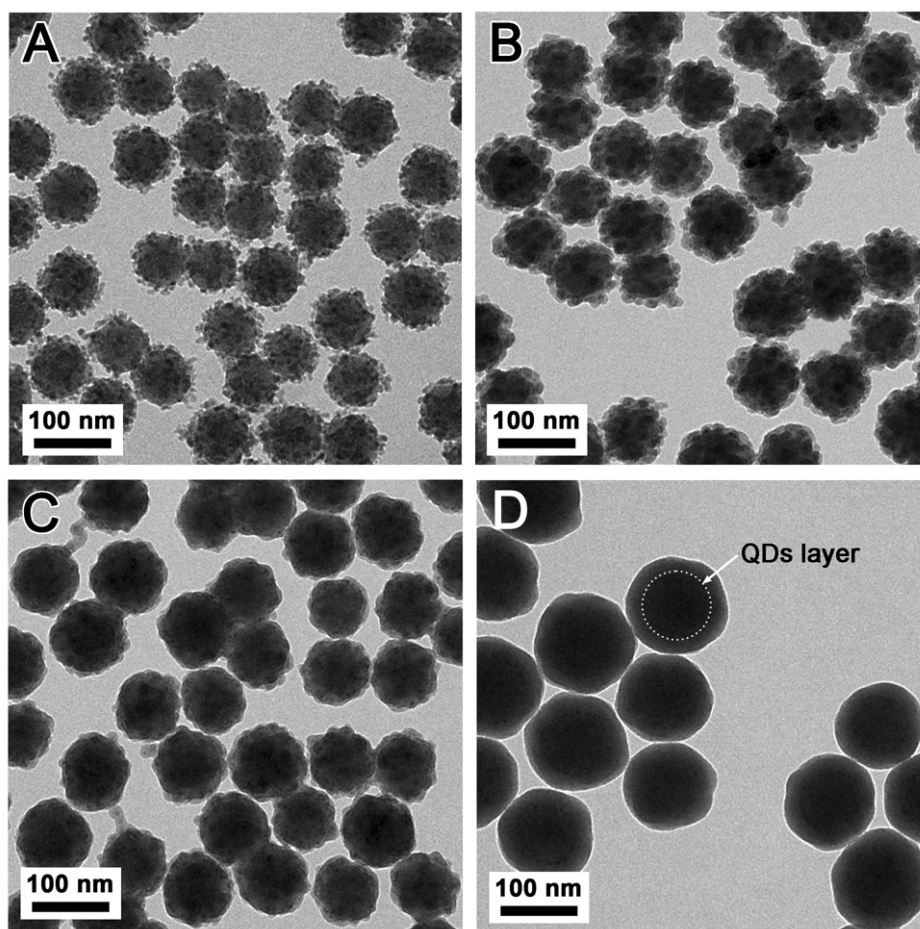


Fig. S5 TEM images of $\text{SiO}_2@\text{QDs}@\text{SiO}_2$ spheres with different silica coating times by Stöber method: (A) 20 min, (B) 1h, (C) 2h and (D) 4h.

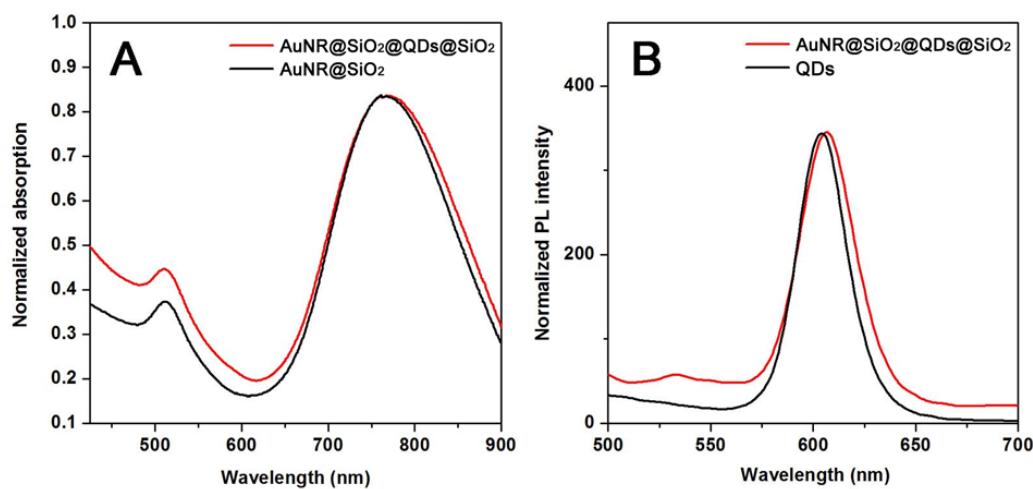


Fig. S6 (A) UV-Vis absorption spectra of AuNR@SiO₂@QDs@SiO₂ nanocomposites and AuNR@SiO₂ substrates. (B) PL spectra of AuNR@SiO₂@QDs@SiO₂ nanocomposites and hydrophobic QDs.

Table S1 Bi-exponential fitting results from fluorescent decay curves of QDs and SiO₂@QDs@SiO₂

fluorescent spheres					
Sample	τ_1 (ns)	B_1 (%)	τ_2 (ns)	B_2 (%)	τ (ns)
QDs	8.66	40.89	22.61	59.11	19.69
SiO ₂ @QDs@SiO ₂	8.56	39.80	24.32	60.20	21.34

The bi-exponential 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 component, respectively. The mean lifetime (τ) can be calculated by: $\tau = (B_1\tau_1^2 + B_2\tau_2^2)/(B_1\tau_1 + B_2\tau_2)$.