

Electronic Supplementary Information for:

## Facile Synthesis and Optical Properties of Colloidal Silica Microspheres Encapsulating Quantum Dots-Layer

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### Experimental Preparations

**Surface Modification of ~800 nm SiO<sub>2</sub> Spheres:** The purchased SiO<sub>2</sub> solution (**S**<sup>0</sup>, 10% in water by w/v, Polyscience Co.) was centrifuged and the solid was dispersed in methanol (2.5% SiO<sub>2</sub> w/v). After adding APTMS (5 wt % for SiO<sub>2</sub>), the solution was refluxed overnight. After centrifugation, the solid was washed twice with methanol and then, with ethanol and finally, dispersed in ethanol to yield the amine-terminated SiO<sub>2</sub> stock solution (5% w/v).

**Synthesis and Surface Modification of CdSe/CdS core/shell QDs:** CdSe/CdS(2.5 monolayers) core/shell QDs protected by ODA were synthesized according to the published method.<sup>6</sup> For the ligand substitution by MPA, QD-ODA was dispersed in CHCl<sub>3</sub> and MPA solution (1000 eq., 0.05 M in MeOH) containing NaOH (0.06 M) was added and stirred, yielding flocculation. Instantaneous sonication (~1 s) helped homogeneous reaction during replacement. The water-soluble QDs were extracted by adding distilled water and separated by centrifugation after adding ethyl acetate/methanol (4/1, v/v) mixture and then, redispersed in distilled water to give the carboxy-terminated QD solution. This solution was freshly prepared before use.

**Synthesis of SQS (~800 nm):** The amine-terminated SiO<sub>2</sub> and the carboxy-terminated QD solutions were adjusted to pH ~4 and pH ~10 by adding diluted HCl and NaOH, respectively. The amine-terminated SiO<sub>2</sub> solution **S** was dropwise slowly into the carboxy-terminated QD solution **Q** ( $1 \times 10^{-6}$  M, 10 mL) with gentle shaking for a self-assembly of **Qs** on **S**. Pale haziness had appeared with the last drop when ~1 mL of **S** solution was added. We repeated the reaction several times. When we finished addition of **S** at the solution pH 7.6~7.8, the reaction gave the best result (homogeneous QD layer). When the addition of **S** solution continued to a lower pH, the aggregated **Qs** and departed **Qs** from **S** were observed. The solution was centrifuged and the solid **SQ** was redispersed in ethanol (40 mL) for SiO<sub>2</sub> encapsulation. NH<sub>4</sub>OH (0.6 mL), distilled water (1.2 mL), and then, TEOS (0.2 mL) was added and the solution was stirred for 3 h. The solid **SQS** was separated and washed with ethanol three times using centrifugation and then, finally dispersed in 10 mL ethanol. The respective concentration of the involved **S**<sup>0</sup> and **Q** in the final **SQS** solution is 0.5% and  $1 \times 10^{-6}$  M according to the following assumption and reasoning.

To compare their absorbance and PL intensity according to the current process, we assumed that the yield after each step is 100%. There was little or a negligible amount of **Q**, **S**, **SQ**, and **SQS** remained in the supernatant after centrifugation to collect the products **S**, **SQ** and **SQS** from the suspensions. The absorbance and PL data were collected from the diluted (20×) **Q**, (5×) **SQ**, and (20×) **SQS** solutions, which involve the same concentration of **Q** ( $5 \times 10^{-8}$  M) and **S**<sup>0</sup> (0.025% w/v) in ethanol, though their involved structures are different.

**Self-Assembly of SQS (~800 nm):** For 2D self-assembly of **SQS** microspheres, a Si wafer was treated with piranha solution, rinsed with distilled water, and then dried with nitrogen gun. The **SQS** solution (**SQS**:ethylene glycol:ethanol = 3:4:3 by v/v) were self-assembled on the surface-treated Si wafer by spin-coating with 800 rpm for 20 min.

**Microscopy and Spectroscopy:** The SEM images were taken with FEI XL30-ESEM (15 kV). The TEM/STEM/HRTEM images were taken with FEI Tecnai G2 F20 (200 kV). The FIB SEM (FEI Helios 600) was applied to slice the epoxy resin embedded with **SQS** microspheres. FT-IR (Mattson IR 300), UV-Vis (Perkin Elmer Lambda 25), and Fluorescence spectrometer (Hitachi F-4500) were used for spectroscopic

analysis. For the absorbance and PL data, the QD concentration was fixed to  $5 \times 10^{-8}$  M in all the traces. All the PL data were recorded with 485 nm excitation.

### **Control Experiment for a Comparison of the Absorbance and PL of Various Solutions in Relation to ~300 nm SQS**

The purchased SiO<sub>2</sub> solution (S<sup>o</sup>, 5 mL, 10% in water by w/v, Polyscience Co.) was centrifuged and the solid was dispersed in 20 mL of methanol (2.5% SiO<sub>2</sub> by w/v). After adding APTMS (10 wt % for SiO<sub>2</sub>), the solution was refluxed overnight. After centrifugation, the solid was washed twice with methanol and then, with ethanol and finally, dispersed in 10 mL of ethanol. Its respective pH and concentration was adjusted to ~4 and 5% (w/v) to yield S solution.

The carboxy-terminated QD solution was newly prepared from a different batch of QDs using the same procedure applied in ~800 nm SQS synthesis and adjusted to pH ~10 and to  $1 \times 10^{-6}$  M to yield Q solution.

The S solution involving 5% S<sup>o</sup> was dropwised slowly into Q solution ( $1 \times 10^{-6}$  M, 10 mL) with gentle shaking for a self-assembly of Qs on S. When the solution pH reached 7.6, the addition was finished. The added volume of S solution was 1.0 mL. The solution was centrifuged and the solid SQ was redispersed in 40 mL of ethanol for SiO<sub>2</sub> encapsulation. Here, 1 mL of SQ solution was saved for the analysis. NH<sub>4</sub>OH (0.6 mL), distilled water (1.2 mL), and then, TEOS (0.2 mL) was added and the solution was stirred for 3 h. The solid SQS was separated and washed with ethanol three times using centrifugation and finally dispersed in 9.75 mL ethanol.

To compare their absorbance and PL intensity according to the current process, we assumed that the yield after each step is 100%. There was little or a negligible amount of Q, S, SQ, and SQS remained in the supernatant after centrifugation to collect the products S, SQ and SQS from the suspensions. The absorbance and PL data were collected from the diluted (20×) Q, (5×) SQ, and (20×) SQS solutions, which involve the same concentration of Q ( $5 \times 10^{-8}$  M) and S<sup>o</sup> (0.025% w/v) in ethanol, though the involved structures are different. It means that the colloidal silica number concentration as well as the QD number concentration is the same throughout the whole solutions for optical data whenever the solution involves them though the involved structures are different.

A mixture solution (S<sup>o</sup> + Q) composed of Q ( $5 \times 10^{-8}$  M) and initial silica microsphere with hydroxyl groups (S<sup>o</sup>, 0.025% w/v) was prepared. S<sup>o</sup> was chosen to minimize the adsorption of Qs on silica surface. The concentration of S<sup>o</sup> was calculated from the added volume (1.0 mL) of S solution (5% w/v) when we prepared SQ according to the current synthesis.

The absorbance and PL spectra were recorded from various solutions involving the same concentration of S<sup>o</sup> (0.025% w/v) and/or Q ( $5 \times 10^{-8}$  M) though their involved structures are different, and displayed in Figure S3 and S4.

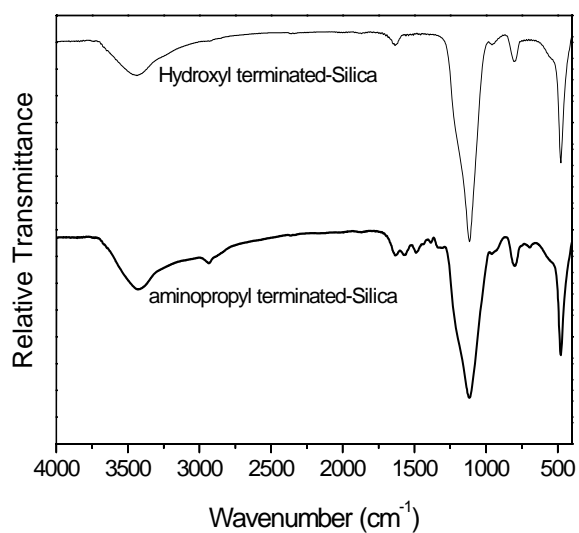


Figure S1. FT-IR spectrum of ~80 nm SiO<sub>2</sub> spheres with different surface molecules.

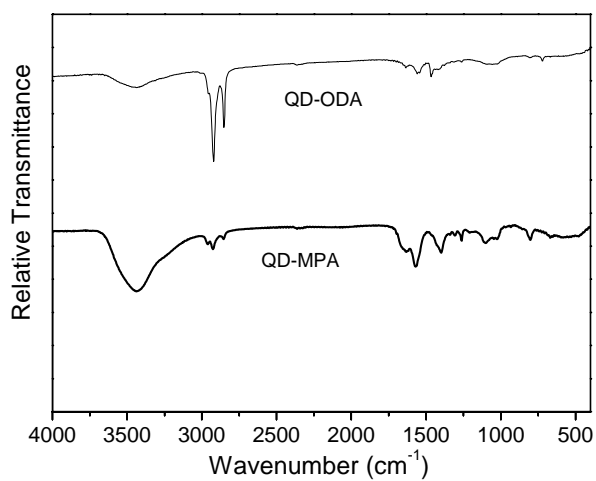


Figure S2. FT-IR spectrum of QDs with different surface ligands.

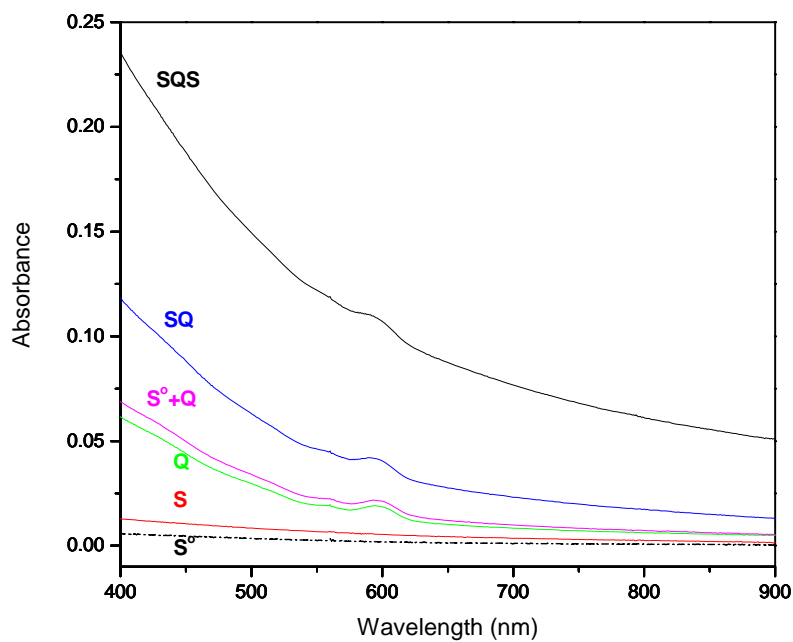


Figure S3. The absorbance spectra of various solutions involving  $S^{\circ}$  (0.025%) and/or  $Q$  ( $5 \times 10^{-8}$  M) into a different structure.

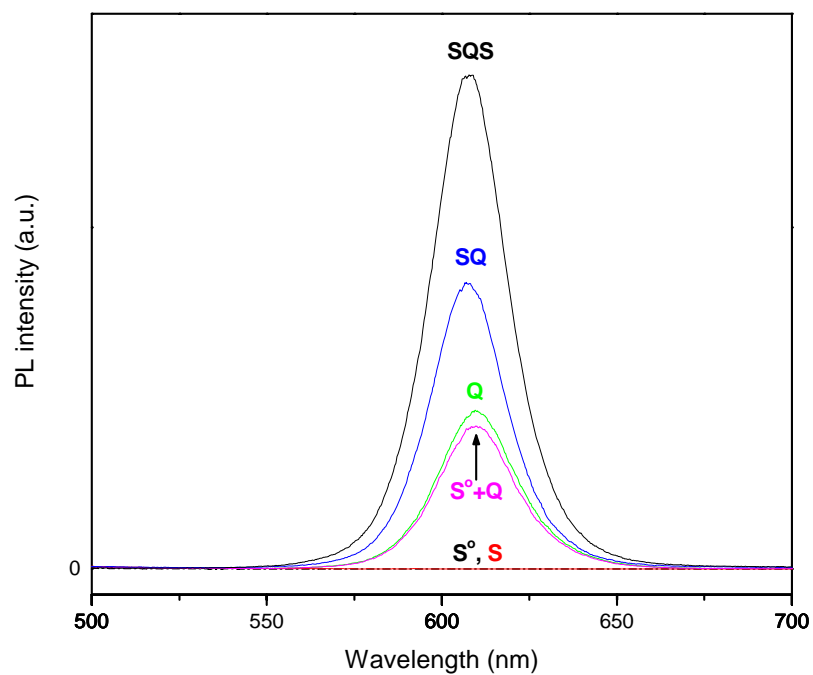


Figure S4. The photoluminescence spectra of various solutions involving  $S^{\circ}$  (0.025%) and/or  $Q$  ( $5 \times 10^{-8}$  M) into a different structure.

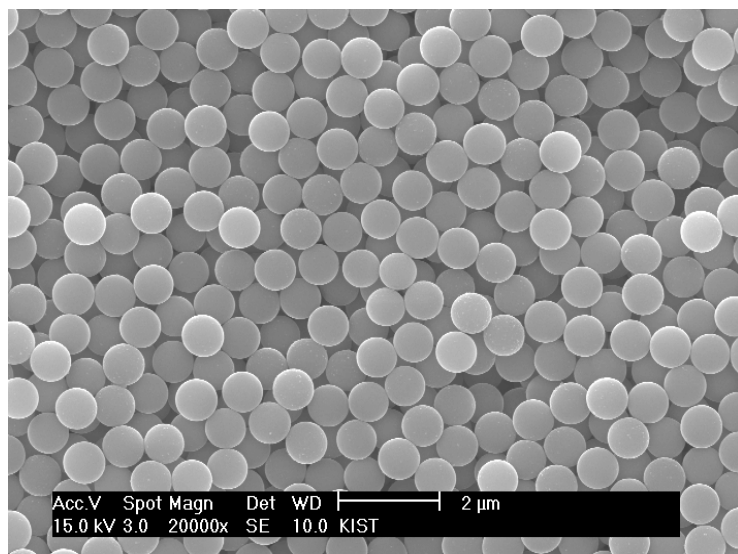


Figure S5. The SEM image of **S**: average diameter  $\pm$  standard deviation =  $826 \pm 21$  nm over 100 spheres.

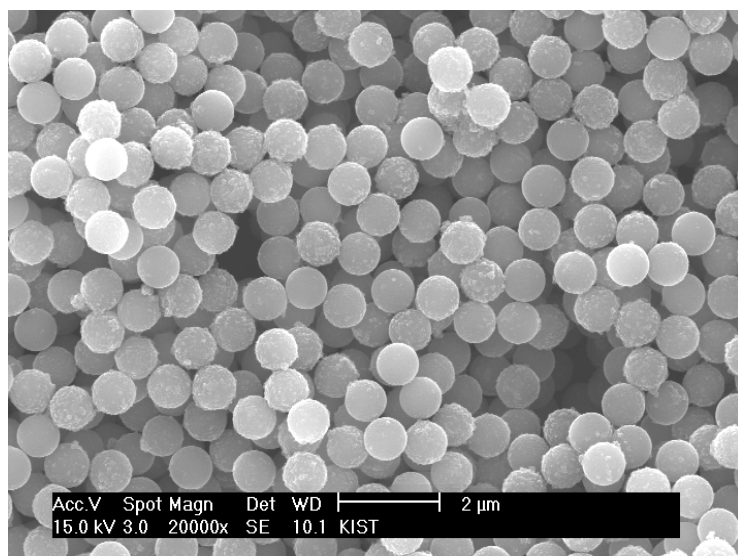


Figure S6. The SEM image of **SQS**: average diameter  $\pm$  standard deviation =  $865 \pm 25$  nm over 100 spheres.