Supporting Information :

Controlled synthesis of dual-emission hierarchical quantum dots hybrid nanostructure as robust ratiometric fluorescent sensor

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Experimental detail

Reagents

Tetraethyl orthosilicate (TEOS, 99%), 3-mercaptopropionic acid (MPA, 99%), sodium borohydride (NaBH₄, 98%) sodium tellerite (Na₂TeO₃, 99.9%), mercaptosuccinic acid (MSA, 98%), 3-mercaptopropyl-trimethoxysilane (MPS, 95%), 3-aminopropyltriethoxysilane (APTES, 99%), poly(diallyldimethylammonium chloride) (PDDA, Mw 100000-200000) and HAuCl₄·3H₂O were purchased from Aladdin Regent Co., Ltd. Poly-ethylene glycol tertoctylphenyl ether (Triton X-100) was obtained from Sigma-Aldrich (Shanghai) Trading co., Ltd. Ammonium hydroxide (NH₃·H₂O, 25%), cadmium chloride (CdCl₂·2.5H₂O), trisodium citrate and other common solvents and salts were obtained from Sinopharm Chemical Reagent Co., Ltd. All chemicals concerned were of analytical grade and all solutions were prepared with ultrapure water obtained from a Millipore water purification system (\geq 18 M Ω , Milli-Q, Millipore).

Instrumentation

The optical absorption spectra were acquired on a SHIMADZU UV-2550 UV-Vis spectrometer coupled with a 1.00 cm quartz cell. Fluorescence spectra were performed on a Horiba JY FluoroLog-3 spectrometer with an integrating-sphere attachment under excitation of 380 nm. X-ray photoelectron spectroscopy (XPS) data were measured using X-ray photoelectron spectroscopy (XPS, Kratos AXIS Ultra DLD). High-resolution transmission electron microscopy (HRTEM) images were acquired using a FEI Tecnai G2 F30 (300 kV) TEM at an acceleration voltage of 200 kV. The fluorescence quantum yields (QYs) of red-emitting CdTe QDs in QS-SH NPs and green-emitting MSA-capped CdTe QDs in QSQS NPs were determined according to the reported method¹.

Synthesis of CdTe QDs stabilized by 3-mercaptopropionic acid (MPA)

Water soluble CdTe QDs were synthesized according to the reported methods with minor modification.² Typically, CdCl₂·2.5H₂O (0.2284 g) was dissolved in 500 mL deionized water

in a three-necked flask, MPA (100 μ L) was added and the pH of the mixture was adjusted to 11.0 with 1.0 M NaOH under stirring. Then trisodium citrate dihydrate (0.5380 g), Na₂TeO₃ (0.0444 g) and NaBH₄ (0.1000 g) were successively added into the mixture. The final molar ratio of Cd²⁺, TeO₃²⁻ and MPA is 5: 1: 6. When the color of solution changed to pale green, the mixture was refluxed at 100 °C. All reactions were carried out under ambient atmospheric conditions. Green and red fluorescent CdTe QDs were obtained after refluxing for 0.5 and 6 h, respectively. The crude CdTe QDs solution was purified by centrifugation after adding the same volume of ethanol. The purified CdTe QDs were finally redispersed in deionized water and stocked at 4 °C for further use.

Synthesis of dual-emission CdTe@SiO2@CdTe NPs

CdTe@SiO₂@CdTe (QSQ) NPs were synthesized in two different ways. One is similar to the synthesis of QSQ-MPS. Typically, the as-prepared QS-SH solution (40 mL) (originated from 0.5 mL TEOS), cadmium chloride (0.04 M, 4 mL) and trisodium citrate dihydrate (400 mg) was added into a three-necked flask and stirred for 1 h at room temperature. After that, Na₂TeO₃ (0.01 M, 4 mL), MSA (50 mg) and NaBH₄ (50 mg) were added under vigorous stirring. Then the mixture was refluxed at 100 °C under N₂ flow for 1 h. The obtained CdTe@SiO₂@CdTe NPs (**termed as QSQ1**) were centrifuged and washed with deionized water for three times. In the other way, the green-emitting QDs with carboxylic groups were chemically bonded to the amino-modified silica nanoparticles by a covalent coupling scheme.³ In a typical process, 2 mL of green-emitting CdTe QD (λ_{em} =520 nm) solution was mixed with 0.5 mL of amino-functionalized CdTe@SiO₂@CdTe NPs (**termed as QSQ2**) were collected by centrifugation and washed with deionized water for three times.

Preparation of AuNPs

AuNPs were synthesized according to the as-reported method.⁴ Briefly, 500 μ L of 2% HAuCl₄ was diluted in 100 mL of deionized water and brought to reflux while stirring and then 1.3 mL of 1% trisodium citrate solution was added quickly, which resulted in a color

change of the solution from pale yellow to deep red. After the color changed, the solution was refluxed for an additional 15 min.



Fig. S1. TEM images (left) and size distribution histograms (right) of QS (A), QSQ-MPS (B), and QSQS NPs with TEOS feeding amount of 12.5 (C) and 50 μL (D), respectively.



Fig. S2. Fluorescence emission spectrum of the QS-SH (a) and QS-SH (b), QS-SH+CdCl₂(c), QS-SH+MSA (d), and QS-SH+CdCl₂+MSA (e) refluxed at 100 °C for 30 min, respectively.



Fig. S3. Fluorescence spectra of QSQ-MPS NPs with the CdTe precursors (a), and QSQ-MPS NPs with half concentration of the same precursors (b) refluxed at 100 °C for 25 min. Inset: corresponding fluorescence photographs were taken under a 365 nm UV lamp.



Fig. S4. TEM images of AuNPs.

Fig. S5. TEM images of the hybrid QSQS-AuNPs assemblies. The concentration of AuNPs is 0.32 (A) and 1.92 nM (B), respectively.

Fig. S6. UV–Vis absorption spectrum (a) of AuNPs, fluorescence emission spectrum (b) of QSQS NPs ($\lambda_{ex} = 380$ nm).

Fig. S7 Fluorescence decay curves ($\lambda ex = 380$ nm, measured at the maximum of the fluorescence, A: 520 nm, B: 640 nm) of QSQS-NH₂ NPs in the absence and presence of AuNPs.

Peak	mass of QSQ-MPS conc (%)	mass of QSQS conc (%)
C 1s	22.84	20.43
O 1s	27.86	34.67
Si 2p	19.75	24.41
S 2p	7.13	4.38
Te 3d	3.96	3.41
Cd 3d	18.47	12.71

Table S1. Elemental composition of QSQ-MPS and QSQS NPs obtained from XPS

Reference

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