Photoluminescence investigations of sulfur quantum dots synthesized by a bubbling-assisted strategy

Shuo Liu,^{+[a]} Henggang Wang,^{+[a]} Anrui Feng,^[a] Jianyu Chang,^[a] Chuanchuan Zhang,^[a] Yu-e Shi,^{*[a]} Yongqing Zhai,^[a] Vasudevanpillai Biju^{*[b]} and Zhenguang Wang,^{*[a]}

a. Key Laboratory of Chemical Biology of Hebei Province, Key Laboratory of Medicinal Chemistry and Molecular Diagnosis, Ministry of Education, College of Chemistry & Environmental Science, Hebei University, Baoding 071002, China

b. Graduate School of Environmental Science, Hokkaido University, N10 W5, Sapporo, Hokkaido 060-0810, Japan.

† Those authors contribute equally.

Experimental Section

Materials. Sublimed sulfur (99.95%) and NaOH were purchased from Aladdin. Polyethylene glycol 400 (PEG-400) was obtained from Tianjin GuangFu Fine Chemical Research Institute (Tianjin, China).

Characterization. Spectrometer of UV-3600 (Shimadzu Japan) and F-7000 (Hitachi, Japan) were used to record the PL and UVabsorption spectra of S-dots. A FLS980 spectrometer (Edinburgh Instruments) equipped with an integrating sphere was employed to measure the time-resolved PL decay curves and absolute PL QY of S-dots. TEM images were acquired on a transmission electron microscopy (TEM; FEI Tecnai G2 F20 S-TWIN, FEI, USA). XPS spectra were collected on a photoelectron spectrometer (ESCALAB-MKII 250, Thermo, USA). Fourier transformed infrared (FTIR) spectra were recorded by a Nicolet IS10 FTIR spectrometer (Thermo, USA). Raman spectra were collected on a Horiba Jobin Yvon HR800, equipped with a 532 nm laser.

Synthesis of S-dots. Sublimated sulfur (1.4 g), water (50 mL), PEG-400 (3.0 mL), and 4.0 g NaOH were mixed in a flask. The mixture was allowed to react for a period of time (5 h~96 h) heated at 70 °C, equipped with an air pump to keep the ventilation of the reaction system. Intense emission appeared under the radiation of UV-light, suggesting the formation of S-dots. The products were dialyzed against distilled water through a dialysis membrane with a molecular weight cut off of 14000 for 48 h, and stored at 4 °C for further use.



Figure S1. XPS survey spectrum of S-dots.



Figure S2. PL spectra of S-dots synthesized by different reaction time, as indicated on the frame, excited at 365 nm.



Figure S3. (a-c) TEM images and (d) PL spectra of S-dots synthesized by different reaction time, as indicated on the frame. All the spectra were collected under excitation of 365 nm.



Figure S4. PL spectra of S-dots taken under different excitation wavelengths as indicated on the frame.



Figure S5. PLQY of S-dots as the function of excitation wavelength.



Figure S6. PL spectra of PEG (a), PEG/NaOH (c), under different excitation wavelengths. PLE spectra of PEG (b), PEG/NaOH (d), detected under different emission wavelength.



Figure S7. Deconvoluted PLE spectra of S-dots synthesised under different temperature, as indicated on the frame, detected at 450 nm.



Figure S8. Deconvoluted PLE spectra of S-dots synthesised by different reaction time, as indicated on the frame, detected at 450 nm.



Figure S9. Deconvoluted PLE spectra of S-dots synthesised by using different amount of NaOH, as indicated on the frame, detected at 450 nm.



Figure S10. Time-resolved PL decay curve of S-dots synthesised by different reaction time (a), and recorded at different emission wavelength (b), the excitation

Reaction Time	Detection Wavelength (nm)	τ_1 (ns)	τ_2 (ns)	$ au_{3}(ns)$	τ _{average} (ns)
5 h	440	0.97 (44.3%)	2.66 (42.2%)	8.42 (13.5%)	2.67
	460	1.09 (34.3%)	3.04 (49.4%)	8.56 (16.3%)	3.27
	480	0.79 (18.7%)	2.64 (61.2%)	7.05 (20.1%)	3.18
	520	0.84 (21.6%)	2.88 (67.3%)	8.27 (11.1%)	3.03
12 h	440	1.00 (52.0%)	2.69 (44.5%)	11.73 (3.5%)	2.21
	460	0.72 (33.2%)	2.51 (55.7%)	6.55 (11.1%)	2.36
	480	0.70 (24.9%)	2.71 (64.6%)	7.15 (10.5%)	2.68
	520	0.74 (20.4%)	2.81 (71.0%)	7.96 (8.6%)	2.83
24 h	440	0.56 (32.9%)	1.86 (54.1%)	4.08 (12.9%)	1.72
	460	0.57 (28.2%)	2.28 (62.4%)	5.11 (9.4%)	2.06
	480	0.60 (20.4%)	2.42 (68.1%)	5.00 (11.5%)	2.34
	520	0.70 (16.7%)	2.72 (78.2%)	7.21 (5.1%)	2.61
48 h	440	0.49 (27.7%)	1.60 (43.1%)	3.24 (29.2%)	1.77
	460	0.47 (20.8%)	1.69 (40.7%)	3.28 (38.5%)	2.05
	480	0.35 (10.8%)	1.37 (28.1%)	3.03 (61.1%)	2.27
	520	0.61 (13.1%)	2.68 (83.7%)	8.28 (3.2%)	2.59
96 h	440	0.49 (34.4%)	1.73 (45.8%)	3.49 (19.8%)	1.65
	460	0.40 (21.0%)	1.32 (32.1%)	3.01 (46.9%)	1.92
	480	0.57 (22.3%)	2.36 (65.7%)	4.41 (12.0%)	2.21
	520	0.71 (16.3%)	2.67 (80.7%)	8.22 (3.0%)	2.52

Table S1. PL lifetimes ($\tau_{1,2,3}$ ns) and the fraction of the emission intensity ($f_{1,2,3}$ %) obtained from fittings of experimental PL decays detected at different wavelengths for S-dots obtained by different reaction time.