Electronic Supplementary Material (ESI) for ChemComm.

Electronic Supplementary Information

Dielectric barrier discharge-accelerated one-pot synthesis of sulfur quantum dots for fluorescent sensing of lead ions and L-cysteine

Manlin Yang[a], Chenghui Li[b], Yunfei Tian[b], Lan Wu[b], Jing Hu*[b] and Xiandeng Hou*[a,b]

a. Ms Manlin Yang and Prof. Dr. Xiandeng Hou, Key Laboratory of Green Chemistry & Technology (MOE), College of Chemistry, Sichuan University, Chengdu, 610064, China. E-mail: houxd@scu.edu.cn.
b. Dr. Chenghui Li, Dr. Yunfei Tian, Dr. Lan Wu, Dr. Jing Hu and Dr. Xiandeng Hou, Analytical & Testing Centre, Sichuan University, Chengdu, 610064, China. E-mail: hujing2019@scu.edu.cn.

Reagents and materials

Ultrapure water (18.2 MΩ cm) was prepared from a water purification system (PCWJ-10, Sichuan Ultrapure Technology Co., Ltd., Chengdu, China) and used throughout this work. Unless otherwise specified, chemicals used in this work were at least of analytical grade. Sublimed sulfur (99.95%) and various chlorides of magnesium, manganese, aluminum, copper, barium, lead, cadmium, bismuth, zirconium, sodium, yttrium, strontium, cerium, potassium, iron, tin, lithium, cobalt and chromium were purchased from Aladdin Reagent Corporation (Shanghai, China). The metal chlorides were used to prepare stock solutions of 500 μM of corresponding metal ions. Aspartic acid (Asp), methionine (Met), arginine (Arg), glutamic acid (Glu), proline (Pro), phenylalanine (Phe), tyrosine (Tyr), leucine (Leu), citrulline (Cit), histidine (His), serine (Ser), alanine (Ala), valine (Val), glycine (Gly), tryptophan (Try), glutathione (GSH) and L-Cysteine (L-cys) were also obtained from Aladdin Reagent Corporation (Shanghai, China). Sodium sulfide nonahydrate ($Na_2S·9H_2O$), polyethylene glycol-400 (PEG-400) and hydrogen peroxide (H_2O_2, 30%) were acquired from Chron Chemicals (Chengdu, China). Phosphate buffer (pH 3.6, 0.2 mol L^{-1}) was prepared using $Na_2HPO_4·2H_2O$ and citric acid. 5,5-Dimethyl-1-pyrroline *N*-oxide (DMPO, 99%) acquired from Dojindo Laboratories (Shanghai, China) was used as a trapping agent for free radicals.

Instrumentation and characterization

The DBD reactor was composed of a concentric quartz cylinder tube, with a tungsten rod inserted into the inner cylinder as an internal electrode, and a copper wire wrapped outside the tube as an external electrode. Both electrodes were connected to an electrical power supply. The Xenon lamp used in this work was purchased from Perfect Light Technology Co., Ltd (Beijing, China). Microwave and ultrasonic reactors were acquired from Sineo Microwave Chemistry Technology Co., Ltd (Shanghai, China) and Xinyi Ultrasonic Equipment Co., Ltd (Ningbo, China), respectively. Transmission electron microscope (TEM) characterization was accomplished with a Tecnai G^2 F20 S-TWIN 20 transmission electron microscope at an accelerating voltage of 200 kV. Photoluminescence and UV-Vis absorption spectra were measured using an F-7000 fluorescence spectrophotometer (Hitachi, Japan) and a UH5300 UV-Vis spectrophotometer (Hitachi, Japan), respectively. Photoluminescence quantum yield (PLQY) and lifetime measurements were conducted on a Fluorolog-3 spectrofluorometer (Horiba Jobin Yvon, USA). For the measurement of PLQY, the SQDs solution was placed in an integrating sphere (IS80, Labsphere) for collection of the integrated absorption and emission, a 450 W Xenon lamp and a CCD (SYNAPSE) were used as the excitation source and detector, respectively. An X-ray diffraction spectrometer (EMPYREAN, Netherlands) with Cu Kα radiation (λ = 1.5406 Å) was used to figure out the crystal structure of synthesized SQDs. Fourier-transform infrared (FTIR) analysis was carried out using an INVENIO R FT-IR spectrometer (Bruker, Germany). X-ray photoelectron spectroscopy (XPS) spectra were recorded with an AXIS Ultra DLD spectrometer (Kratos, UK). Electron paramagnetic resonance X-band

spectra were collected on an EMX plus spectrometer (Bruker, Germany). A LabRAM HR Raman system (Horiba, France) was employed for acquiring Raman spectra. The zeta-potentials of SQDs were measured with a Zetasizer Nano ZS analyzer (Malvern, UK). The pH was measured by a Seven Compact pH meter (Mettler Toledo, Switzerland).

Fluorescent sensing of Pb^{2+} ions and L-cysteine

Purified SQDs solutions (0.5 mL) were added with 0.5 mL of different concentrations of Pb^{2+}. After incubation for 2 min at room temperature, the fluorescence spectra were recorded. For the detection of L-cys, PBS buffer (0.2 M, pH=3.6, 0.4 mL), Pb^{2+} (100 μM, 0.5 mL) and SQDs (0.5 mL) were mixed first, then, 0.4 mL of different concentrations of L-cys were added into the mixture. The fluorescence spectra were collected after one minute.

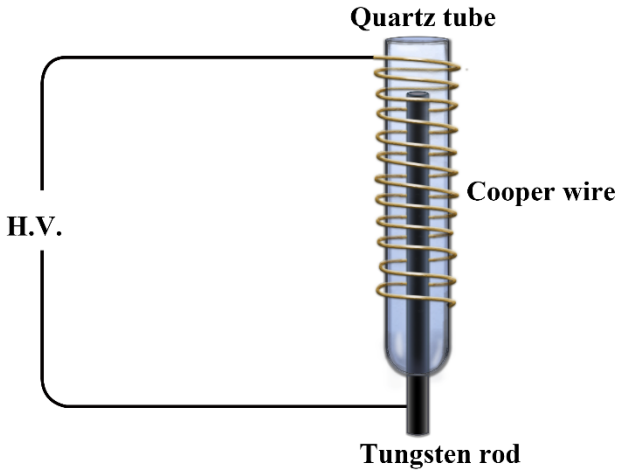

Fig. S1. The structure of the dielectric barrier discharge (DBD) device.

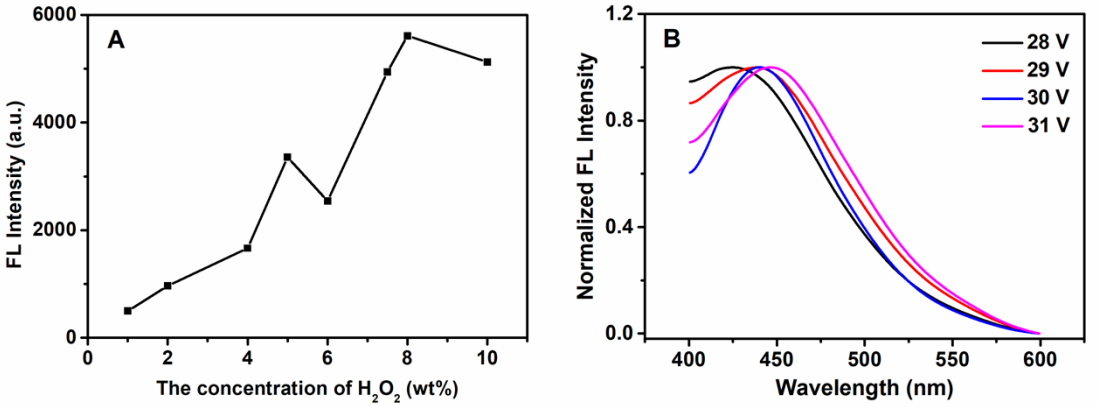

Fig. S2. Effect of (A) the concentration of H_2O_2 and (B) DBD discharge voltage on the emission intensity and FL spectra of SQDs recorded at an excitation wavelength of 340 nm.

Table S1. Comparison of the PLQY of SQDs reported in previous studies and this work.

Preparation method	Reaction time	PLQY (%)	Ref
Acid etching	36 h	0.55	1
Alkali etching	125 h	3.8	2
H_2O_2 assisted etching	5-125 h	23	3
O_2 assisted etching	10 h	21.5	4
Ultrasonication	12 h	2.1	5
Ultrasound microwave radiation	2 h	58.6	6
Mechanochemical synthesis	1 h 15 min	4.8	7
DBD assisted etching	20 min	2.0	This work

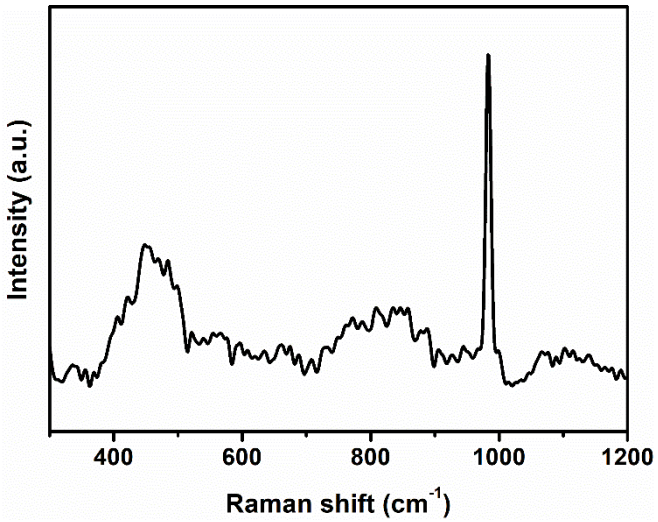

Fig. S3. Raman spectrum of the as-synthesized SQDs.

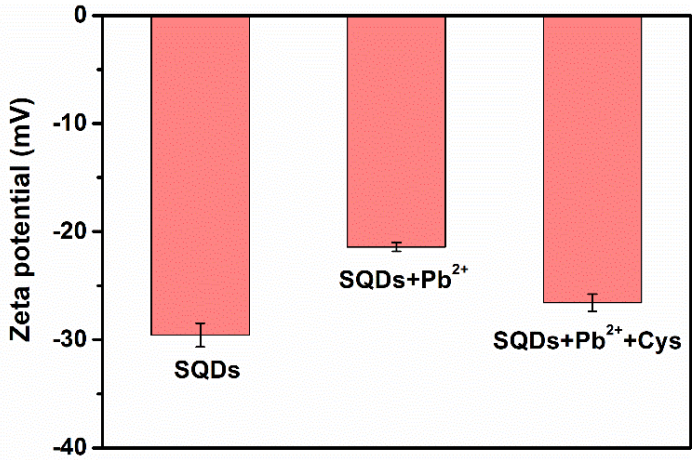

Fig. S4. Zeta potentials of the as-synthesized SQDs, SQDs after addition of Pb^{2+}, as well as SQDs after addition of Pb^{2+} and Cys.

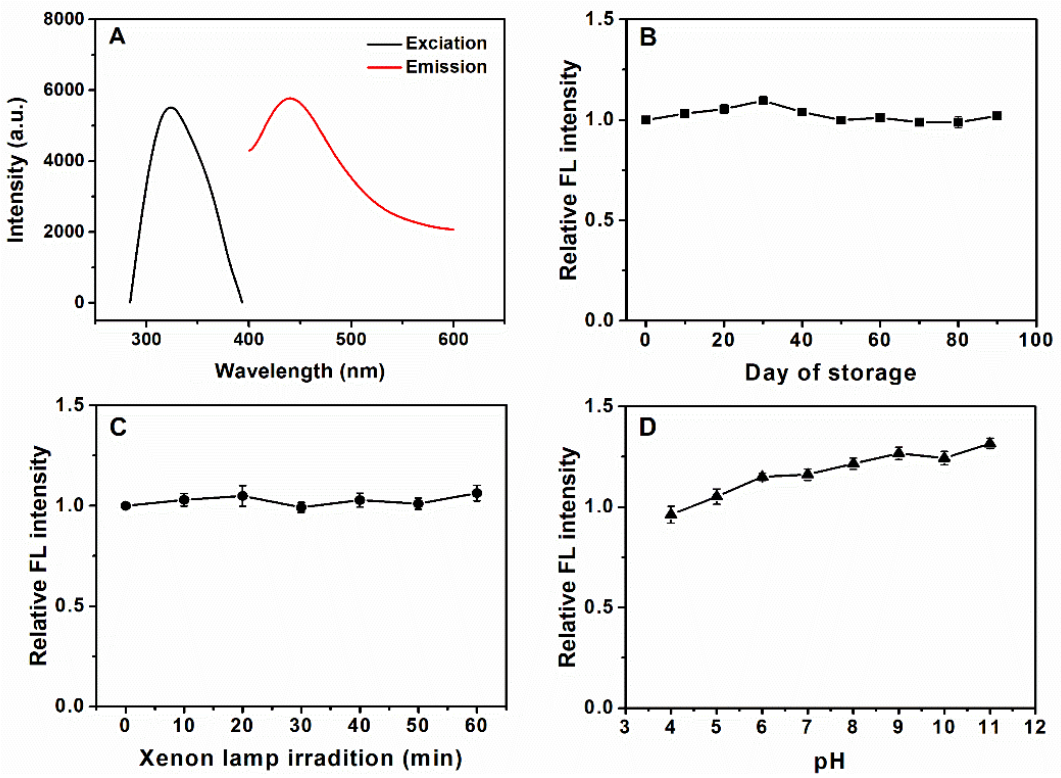

Fig. S5. (A) the excitation and emission spectra of SQDs; (B) stability of the as-prepared SQDs stored over time; (C) variations in the FL intensity of SQDs exposed to Xenon lamp irradiation (300 W); and (D) effect of pH on the relative FL intensity of SQDs.

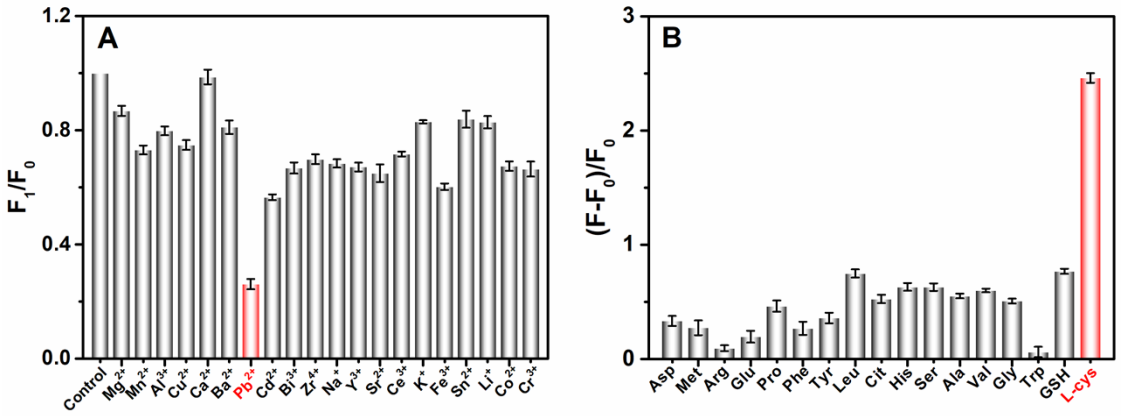

Fig. S6. (A) Effect of different metal ions on the FL intensities of SQDs; and (B) effect of various amino acids on the FL intensity of the SQDs-Pb^{2+} system. The concentration of all metal ions and amino acids involved were 100 μM.

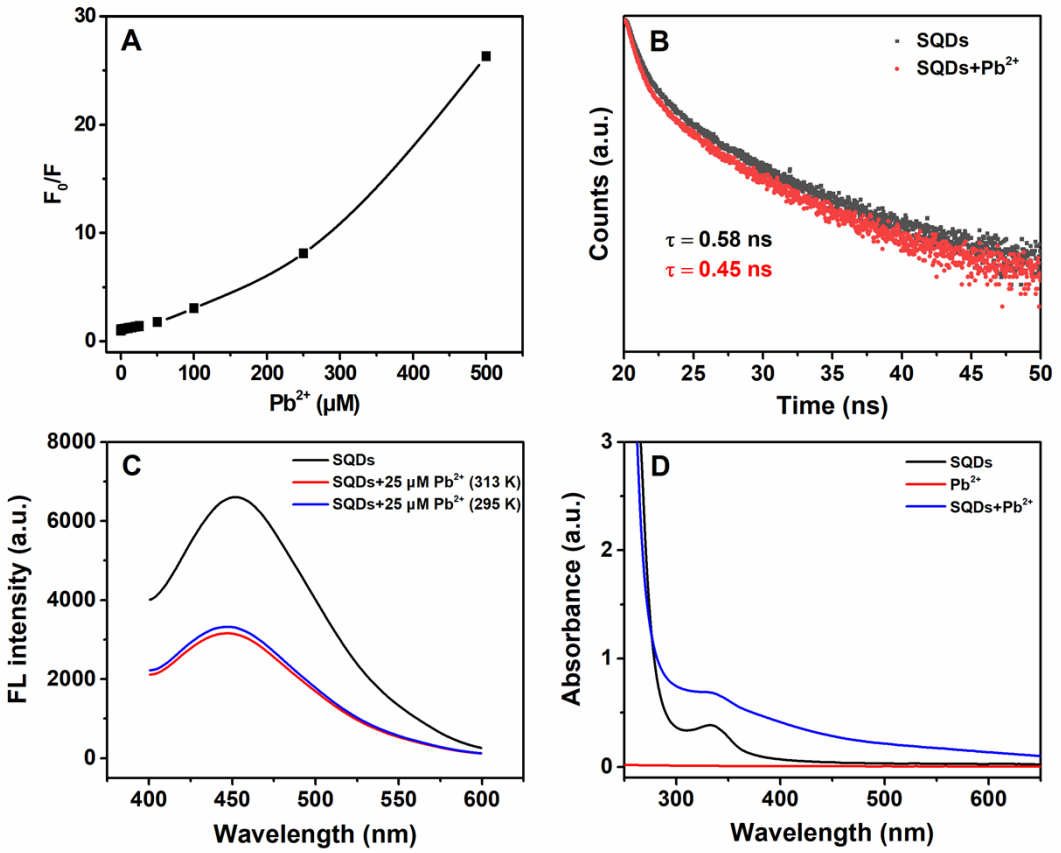

Fig. S7. (A) Stern-Volmer plot, F_0 and F were the FL intensities of SQDs in the absence and presence of Pb2+, respectively; (B) fluorescence lifetimes of SQDs in the absence and presence of Pb^{2+}; (C) fluorescence spectra of SQDs in the presence of Pb^{2+} at different temperature; and (D) UV-Vis spectra of SQDs in the absence and presence of Pb^{2+}.

Table S2. Comparison of analytical performance for sensing of L-cys and Pb^{2+} or other metal ions.

Sensing material	Analyte	Method	Linear range (μM)	LOD (μM)	Reference
Half-salamo	Pb^{2+}	Fluorescence	N.A.	0.06	8
	L-cys		N.A.	0.38	
Au(I)@Ag_2/Ag_3	Pb^{2+}	Fluorescence	0-5	0.15	9
	L-cys		0.05-10	0.05	
Graphene oxide	Ag^{+}	Fluorescence	0.1-10	0.05	10
	L-cys		0.5-6	0.10	
Carbon dots	Cr(VI)	Fluorescence	0.5-263	0.26	11
	L-cys		4-18	0.14	
Sulfur QDs	Pb^{2+}	Fluorescence	0.5-50	0.26	This work
	L-cys		2-25	0.08	

References

1. S. X. Li, D. J. Chen, F. Y. Zheng, H. F. Zhou, S. X. Jiang and Y. J. Wu, *Advanced Functional Materials*, 2014, **24**, 7133-7138.
2. L. H. Shen, H. N. Wang, S. N. Liu, Z. W. Bai, S. C. Zhang, X. R. Zhang and C. X. Zhang, *Journal of the American Chemical Society*, 2018, **140**, 7878-7884.
3. H. G. Wang, Z. G. Wang, Y. Xiong, S. V. Kershaw, T. Z. Li, Y. Wang, Y. Q. Zhai and A. L. Rogach, *Angewandte Chemie International Edition*, 2019, **58**, 7040-7044.
4. Y. H. Song, J. S. Tan, G. Wang, P. X. Gao, J. H. Lei and L. Zhou, *Chemical Science*, 2020, **11**, 772-777.
5. C. C. Zhang, P. Zhang, X. J. Ji, H. G. Wang, H. Z. Kuang, W. L. Cao, M. Y. Pan, Y. E. Shi and Z. G. Wang, *Chemical Communications*, 2019, **55**, 13004-13007.
6. Y. L. Sheng, Z. N. Huang, Q. Zhong, H. H. Deng, M. C. Lai, Y. Yang, W. Chen, X. H. Xia and H. P. Peng, *Nanoscale*, 2021, **13**, 2519-2526.
7. F. Arshad, M. P. Sk, S. K. Maurya and H. R. Siddique, *ACS Applied Nano Materials*, 2021, **4**, 3339-3344.
8. L. Wang, Y. Q. Pan, J. F. Wang, Y. Zhang and Y. J. Ding, *Journal of Photochemistry and Photobiology A: Chemistry*, 2020, **400**, 112719.
9. M. Ganguly, J. Jana, C. Mondal, A. Pal and T. Pal, *Physical Chemistry Chemical Physics*, 2014, **16**, 18185-18197.
10. X. Chen, Y. R. Chen, X. D. Zhou and J. M. Hu, *Talanta*, 2013, **107**, 277-283.
11. Y. F. Gao, Y. Jiao, W. J. Lu, Y. Liu, H. Han, X. J. Gong, M. Xian, S. M. Shuang and C. Dong, *Journal of Materials Chemistry B*, 2018, **6**, 6099-6107.