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## Rapid and Scalable Synthesis of Sulfur Quantum Dots through Ozone Etching: Photoluminescence and FRET mediated Co<sup>2+</sup> Sensing

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Table S1. Comparison of different methods for the synthesis of luminescent SQDs from elemental

Synthetic method	Reaction time (h)	Reaction temperature (°C)	PLQY (%)	Reference
Assembly-fission synthesis	125	70	3.8	1
Assembly-fission followed by $H_2O_2$ etching	125	70	23	2
Hydrothermal fission-aggregation mechanism	4	170	4.02	3
Oxygen acceleration	10	90	21.5	4
Ultrasonication-promoted synthesis	12	-	2.1	5
Copper-Ion-Assisted Precipitation Etching Method	74	70	32.8	6
Microwave-assisted synthesis	55	70	49.25	7
Bubbling-assisted strategy	96	70	8	8
Ultrasound-microwave-assisted etching with hydrogen peroxide	2	70	58.6	9
Solvothermal Synthesis	42	220	10.30	10
Dielectric barrier discharge-accelerated one-pot synthesis	20	-	2.0	11
Mechanical grinding assisted approach	1	-	21	12
Ethylenediamine-assisted solvothermal treatment	5	170	87.8	13
Ethylenediamine-assisted acceleration strategy	6	70	14.22	14
Ethanol assisted solvothermal treatment	36	220	7.04	15
solvent-type passivation strategy	4	160	8.7	16
Ozone assisted top- down approach	4	90	9.26	Present work

sulfur.



**Fig. S1**. PL spectra (excited at 410 nm) of S dots with different durations of ozone treatment as indicated on the frame.



**Fig. S2**. (a) PL spectra of NPEG at different excitation wavelengths. (b) PL spectra (excited at 410 nm) of NPEG and Oz-SQDs.



Fig. S3. Excitation-independent PL spectra of S dots.



**Fig. S4.** PL (solid red line, excited at 490 nm), PLE (dash red line, detected at 575 nm) of S dots and PL (solid green line, excited at 410 nm), PLE (dash green line, detected at 496 nm) of Oz-SQDs.



**Fig. S5**. The three-dimensional excitation and emission matrix (3D-EEM) fluorescence spectrum of Oz-SQDs.



Fig. S6. PL peak energy and FWHM as a function of the temperature.



Fig. S7. XRD patterns of S dots and Oz- SQDs.



Fig. S8. SAED pattern of S dots.



Fig. S9. UV-Visible absorption spectra of the sample with 2h ozone treatment after diluting (a) 2000



times with water (b) 100 times with water.

Fig. S10. (a) XPS survey spectra of (a) S dots (b) Sample with 2 h ozone treatment.



Fig. S11. S2p XPS spectrum of the sample with 2 h ozone treatment.



Fig. S12. Variation in the amount of different sulfur species with ozone treatment duration.

Table S2.	Comparison	of different	methods f	for the c	determination	of Co <sup>2+</sup> .
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Methods	Sensing material	Linear range (µM)	Detection limit (µM)	Reference
Fluorometric	Carbon dots	0 - 40	0.45	17
Fluorometric	Nitrogen and sulfur co-doped graphene quantum dots	0 - 40	1.25	18
Potentiometric	p-(4-n-butylphenylazo) calix[4]arene	9.2- 10000	4.00	19
Colorimetric	Biofunctionalized silver nanoparticles	5 - 100	7.00	20
Fluorometric	Sulfur quantum dots	0 - 90	0.02	21
Fluorometric	Sulfur quantum dots	0-25	1.57	22
Fluorometric	Cysteine-decorated sulfur dots	0 - 40	0.16	23
Fluorometric	Sulfur quantum dots	19.6 – 56.6	2.44	Present work



Fig. S13.  $F_0$  /F value of the Oz-SQDs against different concentrations of Pb<sup>2+</sup>.



**Fig. S14.** Color of the Oz-SQDs aqueous solution after adding different concentrations of (a)  $Co^{2+}$  (b)  $Pb^{2+}$ 

[ (1). 0  $\mu$ M, (2). 19.6  $\mu$ M, (3). 22.8  $\mu$ M, (4) 29.1  $\mu$ M, (5) 32.2  $\mu$ M, (6). 38.5  $\mu$ M, (7). 44.6  $\mu$ M (8) 56.6  $\mu$ M, (9) 62.5  $\mu$ M, (10). 90.9  $\mu$ M, (11). 117.6  $\mu$ M, (12). 142.8  $\mu$ M, (13). 166.6  $\mu$ M, (14). 210.5  $\mu$ M, (15). 249.9  $\mu$ M ]



**Fig. S15.** Relative PL intensity of Oz-SQDs in the presence of different organic solvents (3 M); 1-Methyl-2-pyrrolidone (NMP), tert-Butanol (Butanol), Ethylene glycol (EG), Methanol, Ethanol (EtOH), Isopropyl alcohol (IPA).



**Fig. S16.** UV-Visible absorption spectra of Oz-SQDs in the presence of different concentrations of  $Co^{2+}$ .

Table S3. PL lifetime components and corresponding amplitude fractions of Oz-SQDs and Oz-SQDs/  $Co^{2+}$  system.

Sample	τ <sub>1</sub> (ns)	a <sub>1</sub> (%)	$\tau_2$ (ns)	a₂ (%)	τ <sub>avg</sub> (ns)
Oz-SQDs	1.23	90.78	3.22	9.22	1.65
Oz-SQDs/ Co <sup>2+</sup>	0.75	97.51	3.29	2.49	1.01



**Fig. S17.** Relative PL intensity of Oz-SQDs/ Co<sup>2+</sup> system in the presence of various reducing agents; Norfloxacin (Nor), Sodium borohydride (Sbh), Ascorbic acid (Aa), Glucose (Glu), Oxalic acid (Oa) and Urea (Ur).

## **REFERENCES**

- 1 L. Shen, H. Wang, S. Liu, Z. Bai, S. Zhang, X. Zhang and C. Zhang, J. Am. Chem. Soc., 2018, **140**, 7878–7884.
- 2 H. Wang, Z. Wang, Y. Xiong, S. V. Kershaw, T. Li, Y. Wang, Y. Zhai and A. L. Rogach, *Angew. Chemie Int. Ed.*, 2019, **58**, 7040–7044.
- 3 L. Xiao, Q. Du, Y. Huang, L. Wang, S. Cheng, Z. Wang, T. N. Wong, E. K. L. Yeow and H. Sun, *ACS Appl. Nano Mater.*, 2019, **2**, 6622–6628.
- 4 Y. Song, J. Tan, G. Wang, P. Gao, J. Lei and L. Zhou, *Chem. Sci.*, 2020, **11**, 772–777.
- 5 C. Zhang, P. Zhang, X. Ji, H. Wang, H. Kuang, W. Cao, M. Pan, Y. E. Shi and Z. Wang, *Chem. Commun.*, 2019, **55**, 13004–13007.
- 6 Q. Le Li, L. X. Shi, K. Du, Y. Qin, S. J. Qu, D. Q. Xia, Z. Zhou, Z. G. Huang and S. N. Ding, *ACS Omega*, 2020, **5**, 5407–5411.
- 7 Z. Hu, H. Dai, X. Wei, D. Su, C. Wei, Y. Chen, F. Xie, W. Zhang, R. Guo and S. Qu, *RSC Adv.*, 2020, **10**, 17266–17269.
- 8 S. Liu, H. Wang, A. Feng, J. Chang, C. Zhang, Y. Shi, Y. Zhai, V. Biju and Z. Wang, *Nanoscale Adv.*, 2021, **3**, 4271–4275.
- 9 Y. Sheng, Z. Huang, Q. Zhong, H. Deng, M. Lai, Y. Yang, W. Chen, X. Xia and H. Peng, *Nanoscale*, 2021, **13**, 2519–2526.

- 10 C. Wang, Z. Wei, C. Pan, Z. Pan, X. Wang, J. Liu, H. Wang, G. Huang, M. Wang and L. Mao, Sensors Actuators, B Chem., 2021, **344**, 130326.
- 11 M. Yang, C. Li, Y. Tian, L. Wu, J. Hu and X. Hou, *Chem. Commun.*, 2022, **58**, 8614–8617.
- 12 K. S. Sunil, K. Bramhaiah, S. Mandal, S. Kar, N. S. John and S. Bhattacharyya, *Mater. Adv.*, 2022, **3**, 2037–2046.
- 13 P. Gao, Z. Huang, J. Tan, G. Lv and L. Zhou, ACS Sustainable. Chem. Eng., 2022, **10**, 4634–4641.
- 14 F. Yan, M. Xu, J. Xu, Y. Wang, C. Yi, Y. Dong, X. Wang and J. Xu, *Sensors Actuators B Chem.*, 2022, **370**, 132393.
- 15 Z. Wei, W. Lu, C. Pan, J. Ni, H. Zhao, G. Huang and C. Wang, *Dalt. Trans.*, 2022, **51**, 10290– 10297.
- 16 C. Wu, S. Zhang, Y. Zheng, A. Wang, Q. Zhao, W. Sun, W. Liu, C. Long and Q. Wang, *Inorg. Chem.*, 2022, **61**, 21157–21168.
- 17 D. Kong, F. Yan, Z. Han, J. Xu, X. Guo and L. Chen, *RSC Adv.*, 2016, **6**, 67481–67487.
- 18 W. Boonta, C. Talodthaisong, S. Sattayaporn, C. Chaicham, A. Chaicham, S. Sahasithiwat, L. Kangkaew and S. Kulchat, *Mater. Chem. Front.*, 2020, **4**, 507–516.
- 19 P. Kumar and Y. B. Shim, *Talanta*, 2009, **77**, 1057–1062.
- 20 Y. Yao, D. Tian and H. Li, ACS Appl. Mater. Interfaces, 2010, 2, 684–690.
- 21 S. Wang, X. Bao, B. Gao and M. Li, *Dalt. Trans.*, 2019, **48**, 8288–8296.
- 22 F. Arshad and M. P. Sk, ACS Appl. Nano Mater., 2020, **3**, 3044–3049.
- 23 L. Li, C. Yang, Y. Li, Y. Nie and X. Tian, J. Mater. Sci., 2021, 56, 4782–4796.