Supplementary Information

Synthesis of Mo,N-doped carbon dots for fluorescence detection of $Cr_2O_7^{2-}$ and luteolin and application in anti-counterfeiting

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No.	Carbon Dots	Linear range	Limit of detection	Fluorescence quantum yield	Response time	Reference	
1	EDTA/DMF derived CDs	0-0.1 M	10 µM	/	5 min	Front. Chem. 2020, 8, 595628	
2	MR-CDs	0.2-50 μM	20 nM	18%	10 min	Nanomaterials 2020, 10, 1924	
3	N,P-CDs	0.05-3 μM	26 nM	1.8%	10 min	Microchem. J. 2021 , 166, 106219	
4	N,S-CDs	0-120 μΜ	1.04 µM	4.37%	5 min	RSC Adv. 2021 11, 35946	
5	af-CDs	0.8-80.0 µM	242 nM	2.3%	1 min	J. Photochem. Photobiol. A Chem. 2021, 417, 113359	
6	NH ₂ - mSiO ₂ @CDs	0.5-9 μΜ	5 nM	/	1 min	J. Hazard. Mater. 2021, 415, 125699	
7	S,N-CDs	0.03-50 μM	21.14 nM	17%	3 min	Microchem. J. 2021 , 167, 106284	
8	Cs-CDs	1-130 μM	0.91 µM	58%	/	Nano 2021, 16, 2150103	
9	PGP-CDs	0.1-100 μM	4 nM	15%	1 min	J. Mol. Liq. 2022, 346, 117088	
10	O-phenylenediamine/ DL-Thioctic acid derived CDs	0-60 μΜ	0.64 μΜ	21.82%	/	Colloids Surf. A Physicochem. Eng. Aspects 2022, 638. 128164	
11	Poria cocos polysaccharide/ethylene diamine derived CDs	1-100 μM	0.25 μΜ	4.82%	25 min	J. Pharm. Anal. 2022, 12, 104	
12	R-CDs	0.3-50 μM/0.03-3 μM	80 nM/9.1 nM	22.96%	10 min	Biosensors 2022, 12, 432	
13	N,S-CDs	0-0.588 ppm	0.038 ppm	/	5 min	Chem. Pap. 2022, 76, 7793	
14	N,P-CDs	0.68-87.38 μΜ	0.18 μΜ	11.3%	10 min	J. Anal. Test. 2022, 6, 335	
15	SNCDs	5 nM-25 μM	5 nM	17.67%	/	J. Lumin., 2022 244, 118767	
16	N,S-doped CDs	3.8-38.9 µM	47.2 nM	16%	/	Anal. Bioanal. Chem. 2022, 414, 7253	

1. Table S1 Comparison of carbon dots-based sensors for Cr₂O₇²⁻ detection.

17	N-CQDs	0-15 μΜ	300 nM	18%	4 min	Diam. Relat. Mater. 2022, 126, 109138		
18	FW-CDs	0.1-60 μM	0.07 μΜ	14.8%	30 min	Molecules 2022 , 27, 1258		
19	Citric acid/glutamic acid derived CDSs	0.5-400 μΜ	0.1 µM	48.41%	1 min	J. Fluoresc. 2022, 32, 2343		
20	Arg-L-CQDs	0-400 μM	0.8625 μM	/	/	Macromol. Chem. Phys. 2023, 224, 2200380		
21	N,Cl-doped-CQDs	5-350 μM/250-600 μM/300-850 μM	0.28 μM/0.87 μM/0.90 μM	3.58%	5 min	Colloids Surf. A Physicochem. Eng. Aspects 2023, 669, 131471		
22	N-CQDs	0-40 µM	0.16 μΜ	/	/	J. Fluoresc. 2023 , 139, 1573		
23	BCD1	0-220 μΜ	0.242 μM	8.9%	15 min	ACS Omega 2023 , 8, 6550		
24	N-CQDs	20-200 μM	1.4 µM	5.6%	/	Packag. Technol. Sci. 2023 , 36, 465		
25	N,Zn-doped CDs	0.005-0.135 μM	0.47 nM	13.6%	/	Sensors 2023, 23, 1632		
26	N-CDs-CTAC	0.5-1000 μΜ	40 nM	44.6%	10 min	Analyst 2023, 148, 2818		
27	ILCDs	1-750 μΜ	0.5 μΜ	16.34%	35 min	Ind. Eng. Chem. Res. 2023, 62, 10849		
28	N-GQDs	5-100 μM	0.70 μΜ	/	/	J. Environ. Chem. Eng. 2024, 12, 112391		
29	CQDs	20-90 μM	3.86 µM	/	30 min	Water Air Soil Pollut. 2024, 235, 449		
30	N-GQDs	0-50 μΜ	0.80 µM	10.9%	10 sec	RSC Adv. 2024, 14, 26667		
31	D-CDs	0.5-400 μΜ	0.08 µM	4.02%	1 min	Diam. Relat. Mater. 2024, 148, 111382		
32	N,S-CQDs	0-33 μΜ	0.11 μM	33.4 %	/	ChemistrySelect 2024 , 9, e202403924		
33	Mo,N-CDs	0-50 μΜ	0.96 µM	41.5%	< 10 sec	This work		

2. Materials and instruments.

All reagents used in this work showed below were purchased from commercial suppliers without further purification. L-arginine (L-Arg, $C_6H_{14}N_4O_2$, CAS: 74-79-3), ammonium molybdate ((NH₄)₂MoO₄, CAS: 13106-76-8), 1-pyrenecarboxaldehyde (C₁₇H₁₀O, CAS: 3029-19-4), glutathione (GSH, C₁₀H₁₇N₃O₆S), glucose (C₆H₁₂O₆), L-cysteine (L-Cys, C₃H₇NO₂S), L-glutamic acid (L-Glu, C₅H₉NO₄), luteolin (C₁₅H₁₀O₆) nicotinamide (C₆H₆N₂O), ascorbic acid (AA, C₆H₈O₆), citric acid (CA, C₆H₈O₇), urea (CH₄N₂O), silver nitrate (AgNO₃), aluminum chloride (AlCl₃), barium chloride dihydrate (BaCl₂•2H₂O), calcium chloride (CaCl₂), cadmium sulfate 8/3-hydrate (3CdSO₄•8H₂O), chromium (III) trichloride hexahydrate (CrCl₃•6H₂O), cupric sulfate (CuSO₄), mercury(II) thiocyanate (Hg(SCN)₂), magnesium sulfate (MgSO₄), potassium bromide (KBr), potassium chloride (KCl), sodium perchlorate (NaClO₄), potassium carbonate (K₂CO₃), dichromate potassium dichromate (K₂Cr₂O₇), sodium fluoride (NaF), potassium iodide (KI), potassium phosphate (K₃PO₄), sodium sulfate (Na₂SO₄), ammonium chloride (NH₄Cl), nickel(II) chloride (NiCl₂), stannous chloride dihydrate (SnCl₂•2H₂O), zinc sulfate heptahydrate (ZnSO₄•7H₂O).

Fluorescence spectra were measured by Hitachi F7000 with the slit width of 5/5 nm. Other instruments employed in this work are UV-Visible spectrophotometer (Thermo Evolution 260 Bio), pH Meter (Five Easy Plus FE28), Transmission electron microscope (TF20), X-ray powder diffractometer (Bruker D8 Advance), X-ray photoelectron spectrometer (Thermo ESCALAB 250), Fourier transform infrared spectrometer (Perkin Elmer Frontier), Steady-state/transient fluorescence spectrometer, Zeta potential analyzer and Thermo Scientific DXR 3Xi Raman Spectrometer.

3. Optimization of the hydrothermal reaction conditions for the synthesis of Mo,N-CDs.

L-arginine (0.1-0.5 g), ammonium molybdate (0.2-0.4 g) and 1-pyrenecarboxaldehyde (0-0.03 g) were firstly mixed in pure water (12.5 mL) and ultrasonic treatment for 5 minutes. Then, the mixtures were sealed into 25 mL stainless autoclaves lined with Teflon and heated at 180-200 °C for 3-5 h. After that, the mixtures were naturally cooled to room temperature and the Mo,N-CDs aqueous solutions were obtained by centrifugation at 15,000 rpm for 15 minutes. The obtained Mo,N-CDs aqueous solutions were stored as stock solution at room temperature for further use. Fluorescence intensities of the synthesized Mo,N-CDs were obtained with diluted stock solutions (500 μ L to 5.0 mL in pure water).



Figure S1 Fluorescence spectrum of Mo,N-CDs under different conditions in Table S2: (a) entry 1-4; (b) entry 2, 5-6; (c) entry 2, 7-8; (d) entry 2, 9-10; (e) entry 2, 11-12; (f) entry 2, 13-14.

 Table S2 Optimization of the hydrothermal reaction conditions.

Entry	L-arginine (g)	ammonium molybdate (g)	1-pyrene- carboxalde hyde(g)	Temper- ature (°C)	Time (h)	λ_{max}^{ex} (nm)	λ_{max}^{em} (nm)	Fluorescence intensity (a.u.)
1	0.3	0.3	/	190	4	340	411	530
2	0.3	0.3	0.02	190	4	365	494	5820
3	0.3	0.3ª	0.02	190	4	363	401/490	895/818
4	0.3	0.3 ^b	0.02	190	4	369	401/498	201/1739
5	0.1	0.3	0.02	190	4	341	493	4353
6	0.5	0.3	0.02	190	4	343	492	3757
7	0.3	0.2	0.02	190	4	364	495	3874
8	0.3	0.4	0.02	190	4	365	492	4470
9	0.3	0.3	0.01	190	4	365	494	4754
10	0.3	0.3	0.03	190	4	366	494	1718
11	0.3	0.3	0.02	180	4	365	497	4388
12	0.3	0.3	0.02	200	4	370	493	3829
13	0.3	0.3	0.02	190	3	364	493	4872
14	0.3	0.3	0.02	190	5	369	497	3335

^a molybdic acid was used as the molybdenum source. ^b sodium molybdate was used as the molybdenum source.

4. Raman spectrum of the as-synthesized Mo,N-CDs.



Figure S2 Raman spectrum of the as-synthesized Mo,N-CDs.

5. EDX spectrum of the as-synthesized Mo,N-CDs.



Figure S3 EDX spectrum the as-synthesized Mo,N-CDs.

6. Calculation of fluorescence quantum yield of Mo,N-CDs.

The fluorescence quantum yield (QY) of Mo,N-CDs was determined by a common method according to previous reports using quinine sulfate in pure water as a reference (QY = 55%). The fluorescence QY value of Mo,N-CDs was calculated as follows:

$$QYt = QYr \times (It/Ir) \times (Ar/At) \times (\eta t/\eta r)^2$$

The subscript "t" and "r" refer to the Mo,N-CDs and quinine sulfate. A is the optical density, I is the integrated emission intensity, and η is the refractive index of the solvent. To get more reliable results, the absorption of the two solutions were adjusted to less than 0.1 to prevent the reabsorption effect.



Figure S4 Plots of integrated intensity of Quinine sulfate and Mo,N-CDs.

7. General experimental procedure.

Procedures for photobleaching resistance

Mo,N-CDs stock solution (500 μ L) was diluted by pure water to 5.0 mL. Then the fluorescence intensity of the solution at 494 nm were measured at continuous excitation wavelength of 365 nm for 90 min.

Procedures for pH stability

Mo,N-CDs stock solution (500 μ L) was diluted by PBS solution (pH 3-12, 10 mM) to 5.0 mL. Then the fluorescence intensity of the solution at 494 nm were measured at the excitation wavelength of 365 nm and repeated for 3 times.

Procedures for salt tolerance

Mo,N-CDs stock solution (500 μ L) was diluted by NaCl solution (0-100 mM) to 5.0 mL. Then the fluorescence intensity of the solution at 494 nm were measured at the excitation wavelength of 365 nm and repeated for 3 times.

Procedures for thermostability

Mo,N-CDs stock solution (500 μ L) was diluted by pure water to 5.0 mL. The solutions were incubated at different temperatures (5-85 °C) for 30 min. Then the fluorescence intensity of the solution at 494 nm were measured at the excitation wavelength of 365 nm and repeated for 3 times.

Detection of Cr₂O₇²⁻

Mo,N-CDs stock solution (500 µL) was firstly diluted by pure water (3.0 mL) and different amount of

 $Cr_2O_7^{2-}$ were added. Then the solutions were further diluted by pure water to 5.0 mL. The concentrations of $Cr_2O_7^{2-}$ in the solutions were 0-200 μ M. Then the fluorescence intensities of the mixed solutions were measured and repeated for 3 times. Other cations (Ag⁺, Al³⁺, Ba²⁺, Ca²⁺, Cd²⁺, Cr³⁺, Cu²⁺, Hg²⁺, K⁺, Mg²⁺, Na⁺, NH₄⁺, Ni²⁺, Sn²⁺ and Zn²⁺ (10 mM, 50 μ L)) and common anions (Br⁻, Cl⁻, ClO₄⁻, CO₃²⁻, Cr₂O₇²⁻, F⁻, I⁻, NO₃⁻, PO₄³⁻ and SO₄²⁻ (10 mM, 50 μ L)) were added under the same conditions.

Detection of luteolin

Mo-CDs stock solution (500 μ L) was firstly diluted by pure water (3.0 mL) and different amount of luteolin were added. Then the solutions were further diluted to 5.0 mL. The concentrations of luteolin in the solutions were 0-100 μ M. Then the fluorescence intensities of the mixed solutions were measured and repeated for 3 times. Other interfering compounds (GSH, glucose, L-Arg, L-Cys, L-Glu, niacinamide, AA, CA and Urea (10 mM, 25 μ L)) were added under the same conditions.

Detection of Cr₂O₇²⁻ in actual water samples:

The actual samples selected for the determination of $Cr_2O_7^{2-}$ were tap water, lake water and C'estbon bottled drinking water. Tap water was collected from laboratory water piping, C'estbon bottled drinking water was purchased from the local supermarket and the lake water was collected from Longzi Lake. The practical water samples were centrifuged at 8000 rpm for 20 min and filtered through a 0.22 μ m microporous membrane. Then, different amount of $Cr_2O_7^{2-}$ were added into the above water samples to calculate the recovery rate and relative standard deviation (RSD). All measurements were repeated for 3 times.

Detection of luteolin in Du Yi Wei capsule

Du Yi Wei capsule were purchased at a local drugstore. The average weight of 10 capsules powder was calculated after removing the capsule shell. The mass of 1/10 Du Yi Wei powder was accurately weighed and dissolved in 20 mL pure water with ultrasonic assistance. The solution was centrifuged at 8000 rpm for 20 min and filtered through a 0.22 μ M microporous membrane. The working solution was prepared by diluting the sample solution with pure water to maintain the concentration of the working solution within the linear range. Then, different amount of luteolin were added into the above working solution to calculate the recovery rate and relative standard deviation (RSD). All measurements were repeated for 3 times.

Detection of luteolin in Du Yi Wei tablet

Du Yi Wei tablets (5 mg/tablet) were purchased at a local drugstore. The average weight of 10 tablets was calculated after thorough pulverization into fine powder. An amount of Du Yi Wei powder equal to the mass of one Du Yi Wei tablet was accurately weighed and dissolved in 20 mL pure water with ultrasonic assistance. The solution was centrifuged for 20 min at 8000 rpm and filtered through 0.22 µm membrane syringe filters. The working solution was prepared by diluting the sample solution with pure water to maintain the concentration of the working solution within the linear range. Then, different amount of luteolin were added into the above working solution to calculate the recovery rate and relative standard deviation (RSD). All measurements were repeated for 3 times.

8. Response time of Mo,N-CDs to Cr₂O₇²⁻.



Figure S5 Fluorescence intensity of Mo,N-CDs ($\lambda ex = 365 \text{ nm}$, $\lambda em = 494 \text{ nm}$) in the absence/presence of $Cr_2O_7^{2-}$ (100 μ M).

No.	Fluorescence Intensity (a.u.)	F/F_0
1	5636	0.9999
2	5651	1.0026
3	5618	0.9967
4	5657	1.0036
5	5643	1.0011
6	5623	0.9976
7	5620	0.9971
8	5658	1.0038
9	5639	1.0004
10	5620	0.9971
σ	0.0028	

9. Table S3 Fluorescence intensity and standard deviation.

10. The response time of Mo-CDs to luteolin.



Figure S6 Fluorescence intensity of Mo-CDs ($\lambda ex = 365 \text{ nm}$, $\lambda em = 494 \text{ nm}$) in the absence/presence of luteolin (50 μ M).



11. The geometry of quartz cuvette.

Figure S7 Geometry of a quartz cuvette, where d, g and s are 1.00, 0.25 and 0.50 cm.

12. Relationship between $F_{cor,\theta}/F_{cor}$ and $Cr_2O_7^{2-}$.



Figure S8 The ratio of corrected fluorescence emission intensities without/with $Cr_2O_7^{2-}$ ($F_{cor.o}/F_{cor}$) versus the concentration of $Cr_2O_7^{2-}$.

13. Relationship between $F_{cor,0}/F_{cor}$ and luteolin.



Figure S9 The ratio of corrected fluorescence emission intensities without/with luteolin ($F_{cor.o}/F_{cor}$) versus the concentration of luteolin.