Supplementary Information for

Surfactant encapsulating N-doped carbon dots with enhanced optical properties as selective sensor for Cr(VI) detection

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Chemicals

All chemicals are analytical grade and can be used without further purification. Ammonium citrate, urea, cetyltrimethylammonium bromide (CTAB), cetyltrimethylammonium chloride (CTAC), sodium dodecyl benzene sulfonate (SDBS), sodium dodecyl sulfate (SDS), polyvinylpyrrolidone (PVP), Tween-80, and potassium dichromate ($K_2Cr_2O_7$) were purchased from Sigma-Aldrich Trading Ltd. The $K_2Cr_2O_7$ was used to prepare standard Cr(VI) solution, and the metal ion solutions were made of their nitrates, sulfates or chlorides. All solutions were prepared with ultrapure water.

Instruments and characterization

Fluorescence measurements were performed on a FLS-1000 steady-state/transient fluorescence spectrometer (Edinburgh, UK). The transmission electron microscopy (TEM) images were carried out on a JEM-2100F field emission transmission electron microscope (JEOL, Japan). The UV-vis absorption spectra were measured by USB-2000 UV-Vis Spectrometer (Ocean Optics, USA). X-ray photoelectron spectroscopy (XPS) was performed on a Thermo Scientific K-Alpha (Thermo Fisher Scientific, USA). The functional groups of the samples were characterized by Fourier transform infrared (FT-IR) spectroscopy (Perkin-Lamer, USA).

Synthesis of N-CDs

The N-CDs was prepared via a solid-state reaction strategy according to previous literature.[1] Briefly, ammonium citrate (0.2 g) and urea (0.2 g) were ground uniformly. Subsequently, the mixture was hated to 200 ℃ for 1.5 h in an oil bath. After that, the N-CDs was purified with ultrapure water, and collected by centrifugation. Then, the obtained N-CDs solution was filtered with 0.22 μm filter membrane for further use.

Synthesis of N-CDs-CTAC

For synthesis of N-CDs-CTAC, 2 mL of the prepared N-CDs solution was mixed with 4 mL of 20 mg mL^{-1} CTAC solution. Then the mixture solution was ultrasound for 30 min to obtain N-CDs-CTAC, which was stored at 4 °C for further experiments.

In order to obtain the optimal optical properties of N-CDs-CTAC, the preparation conditions were optimized, including the molar ratio of ammonium citrate to urea (1:4~1:8), reaction time (20~120 min), reaction temperature (140~220 °C), concentration of CTAC (0~20 mM), and the type of surfactants.

Fluorescence detection of Cr(VI)

The fluorescence characteristics of N-CDs-CTAC were studied under different excitation wavelengths, and the excitation and emission slits were set to 0.6 nm and 0.6 nm, respectively. Under the optimal conditions, 200 μL of different concentrations of Cr(VI) solution were mixed with 600 μL of N-CDs-CTAC solution, then 700 μL of BR buffer solution (pH=4) was added to above mixture, and start timing immediately. After reaction for 10 min, the fluorescence was tested at 405 nm excitation wavelength. All of the experiments were repeated three times.

Detection of Cr(VI) in real water samples

The real water samples were collected from a lake at Southwest Jiaotong University and a tap at laboratory to estimate the viability of the proposed sensor. The environmental waters were first centrifuged for 10 minutes, then treated with a 0.45 μm filter membrane treatment for further use.

Fluorescence method: The detection process was the same as the fluorescence detection of Cr(VI) mentioned above except that the Cr solution was prepared with actual water.

Standard 1,5 dtphenylcarbohydrazide spectrophotometric method: First, the 500 μM Cr(VI) stock solution was prepared with ultrapure water. Then the different volumes of Cr(VI) stock solution were added into the cuvette and diluted to 5 ml with ultrapure water. After that, 0.05 mL of 1+1 H_2SO_4 and 0.05 mL of 1+1 H_3PO_4 were added

into above solution. Finally 0.2 mL of 1,5 dtphenylcarbohydrazide solution was further added for chromogenic reaction, and the absorbance at 540 nm was measured after reaction for 10 minutes. For assaying Cr(VI) in real samples, the detection process was the same as the standard 1,5 dtphenylcarbohydrazide spectrophotometric method except that the Cr solution was prepared with actual water.

Quantum yield calculation

The relative quantum yields (QY) of N-CDs and N-CDs-CTAC were determined in reference to fluorophore fluorescein (η=1.33, QY=95%) in 0.10 M NaOH solution.[2] The slit width and excitation wavelength (λ_{ex}=405 nm) were kept consistent during QY measurements, and the calculation formula of QY is as follows:

$$QY = QY_{ref}\frac{\eta^2\ I A_{ref}}{\eta_{ref}^2 A I_{ref}}$$

In the formula, QY_{ref} is the quantum yield of the reference compound, η is refractive index of the solvent, I represents the integrated fluorescence intensity at λ_{ex}=405 nm, A is absorbance at 405 nm. To minimize the reabsorption effect, the absorbance value at 405 nm is below 0.05.[3]

Table S1 Fluorescence lifetimes of N-CDs, N-CDs-CTAC, and N-CDs-CTAC in the presence of Cr(VI).

Samples	Average τ (ns)
N-CDs	5.39
N-CDs-CTAC	10.23
N-CDs-CTAC+ Cr(VI)	7.77

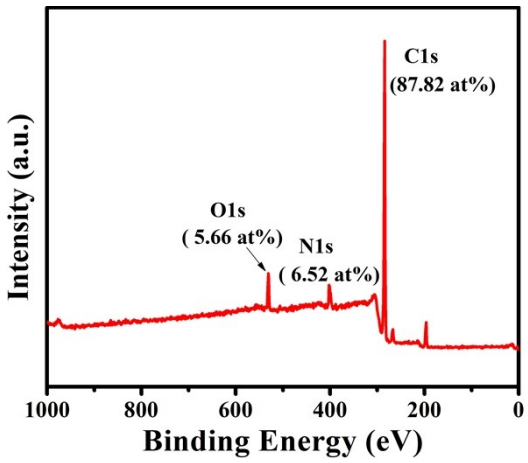
Table S2 Comparison of materials preparation conditions and Cr(VI) detection with other reported CD-based fluorescent sensors.

Materials	**Synthesis condition**	**Quantum yield (%)**	**Linear range (μM)**	**LOD (μM)**	**Ref.**
N-CQDs	Hydrothermal 220 ℃, 6 h	22.14	0-500	2.1	4
CCDa	Hydrothermal 180 ℃, 4 h	6.2	5-125	1.17	5
MCDb	Hydrothermal 190 ℃, 12 h	/	0-35	4	6
CD	Hydrothermal 250 ℃, 4 h	39	10-50	0.73	7
ACDsc	Hydrothermal 200 ℃, 5 h	8.47	0.5-100	0.034	8
N, SCDs	Hydrothermal 200 ℃, 12 h	18.7	1-40	0.52	9
Pn N-CDs	Hydrothermal 180 ℃, 12 h	18.41	0-6	0.185	10
N-CDs-CTAC	Solid-state reaction 200 ℃, 1.5 h	44.6	0.5-1000	0.04	This work

a = Cobalt(II)-doped carbon dots

b = CD loaded in the porous structure of microcline

c = Aqueous soluble CDs



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78 **Fig. S1** XPS survey spectrum of N-CDs-CTAC.

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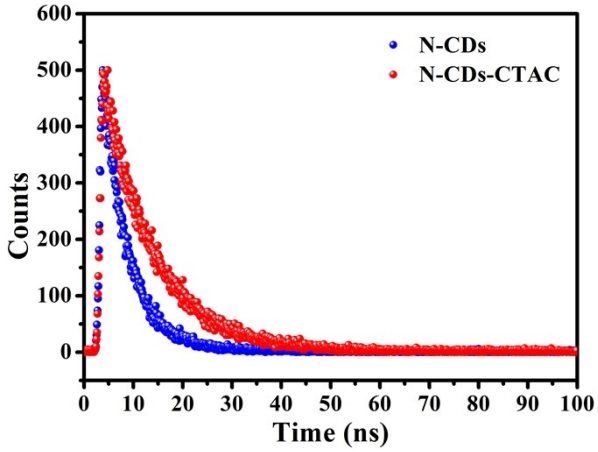

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81 **Fig. S2** The fluorescence decay curves of N-CDs and N-CDs-CTAC.

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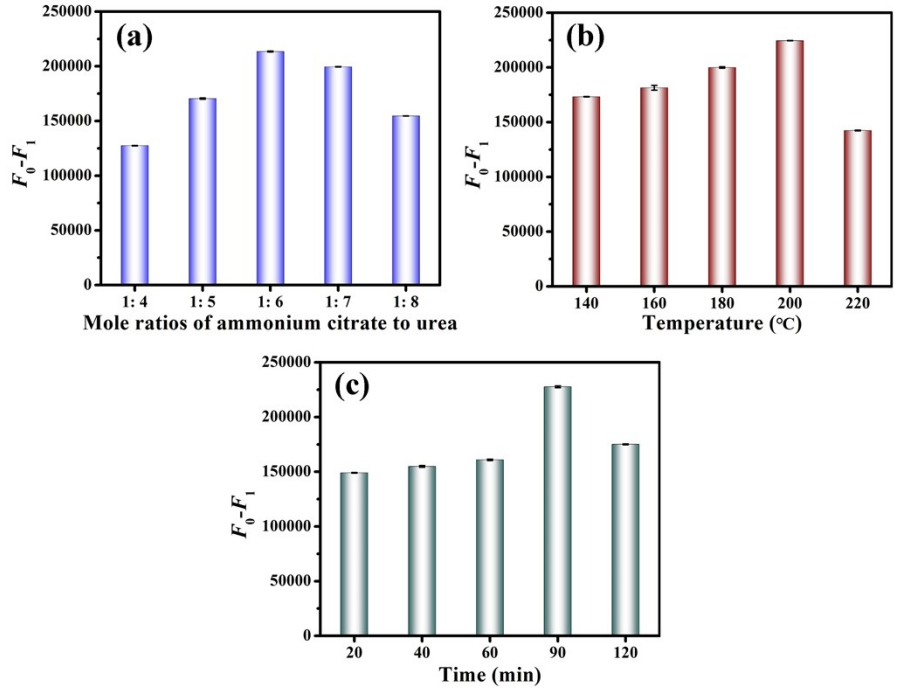


Fig. S3 Optimization of preparation conditions for N-CDs. (a) Molar ratio of ammonium citrate to urea, (b) reaction temperature and (c) reaction time.

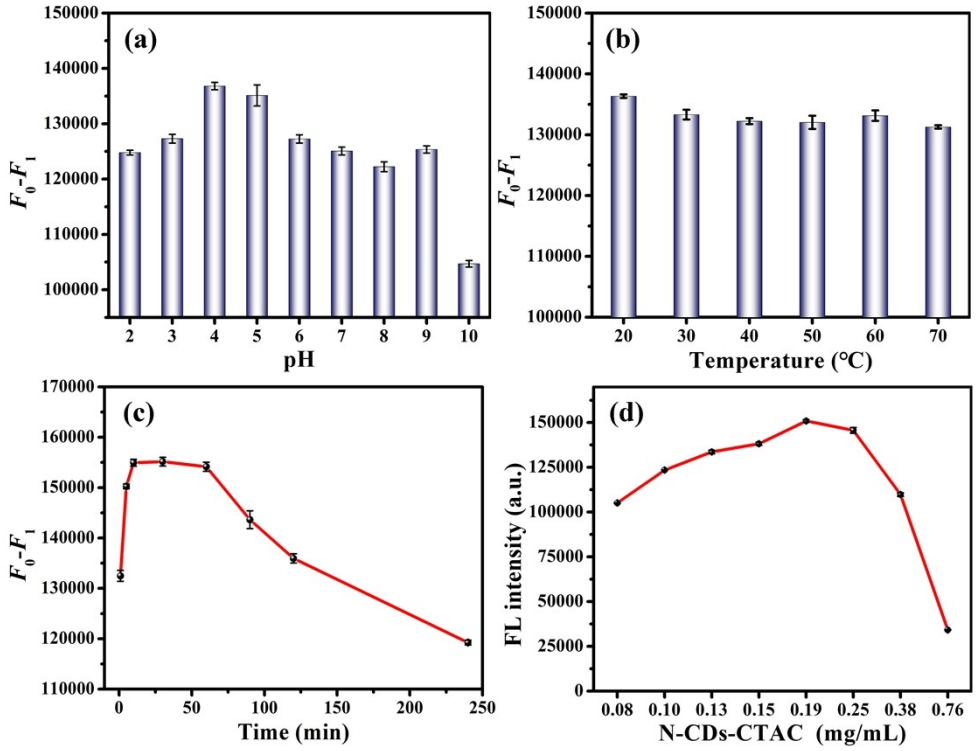
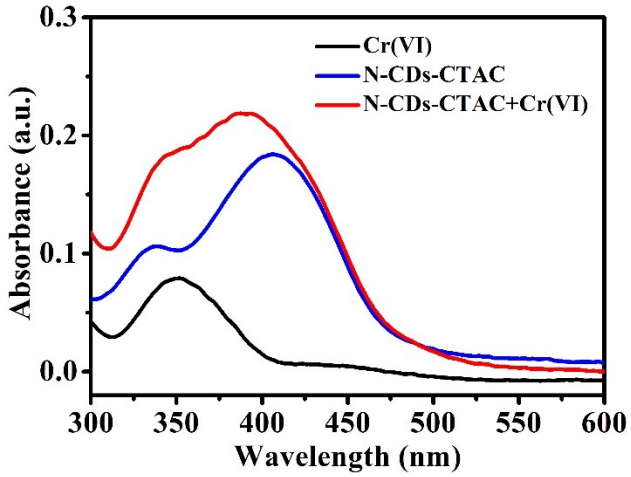


Fig. S4 The effects of (a) pH values, (b) incubation temperature, (c) response times, and (d) N-CDs-CTAC concentration on Cr(VI) detection.



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92 **Fig. S5** The UV-vis absorption spectra of Cr(VI), N-CDs-CTAC, and N-CDs-CTAC with the addition of Cr(VI).

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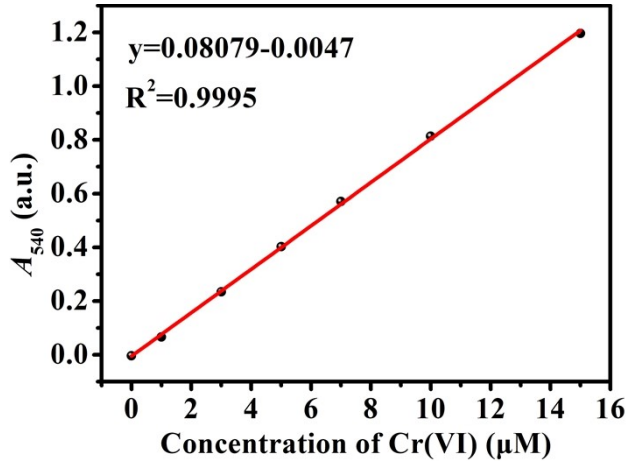

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95 **Fig. S6** The standard curve of Cr(VI) measured by 1,5 dtphenylcarbohydrazide spectrophotometric method.

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References

1 W. U. Khan, D. Wang and Y. H. Wang, *Inorg. Chem.*, 2018, **57**, 15229-15239.

2 C. Ruiz-Palomero, M. L. Soriano, S. Benítez-Martínez and M. Valcárcel, *Sens. Actuators B Chem.*, 2017, **245**, 946-953.

3 M. Zheng, Z. G. Xie, D. Qu, D. Li, P. Du, X. B. Jing and Z. C. Sun, *ACS Appl. Mater. Interfaces*, 2013, **5**, 13242-13247.

4 G. Q. Wang, S. R. Zhang, J. Z. Cui, W. S. Gao, X. Rong, Y. X. Lu and C. Z. Gao, *Anal. Chim. Acta*, 2022, **1195**, 339478.

5 H. Y. Zhang, Y. Wang, S. Xiao, H. Wang, J. H. Wang and L. Feng, *Biosens. Bioelectron.*, 2017, **87**, 46-52.

6 S. Bardhan, S. Roy, D. K. Chanda, S. Ghosh, D. Mondal, S. Das and S. Das, *Dalton Trans*., 2020, **49**, 10554-10566.

7 M. R. Pacquiao, M. D. G. de Luna, N. Thongsai, S. Kladsomboon and P. Paoprasert, *Appl. Surf. Sci.*, 2018, **453**, 192-203.

8 J. F. Li, P. X. Li, D. X. Wang and C. Dong, *Talanta*, 2019, **202**, 375-383.

9 J. Shen, S. M. Shang, X. Y. Chen, D. Wang, Y. Cai, *Sensor. Actuator. B Chem.*, 2017, **248**, 92e100.

10 X. D. Zheng, K. H. Qin, L. P. He, Y. F. Ding, Q. Luo, C. T. Zhang, X. M. Cui, Y. Tan, L. N. Li and Y. L. Wei, *Analyst*, 2021, **146**, 911-919.