# **Supplementary Information**

# **Facile synthesis of N-doped graphene quantum dots as fluorescent sensor for Cr(VI) and folic acid detection**

Chu-Sen Ni, :\* Wen-Jie Zhang, :\* Wen-Zhu Bi, \*\*,b Ming-Xia Wu, \*\*,b Su-Xiang Feng, \*b.c.d Xiao-Lan Chene **and Ling-Bo Qu<sup>e</sup>**

<sup>a</sup> School of Pharmacy, Henan University of Chinese Medicine, Zhengzhou, 450046, China. E-mail: mxwu711@163.com.

<sup>b</sup> Henan Engineering Research Center of Modern Chinese Medicine Research, Development and Application, Zhengzhou, 450046, China.

<sup>c</sup> Academy of Chinese Medical Sciences, Henan University of Chinese Medicine, Zhengzhou, 450046, China. Email: fengsx221@163.com.

<sup>d</sup> Collaborative Innovation Center for Chinese Medicine and Respiratory Diseases co-constructed by Henan province & Education Ministry of P. R. China, Zhengzhou, 450046, China.

<sup>e</sup> College of Chemistry, Zhengzhou University, Zhengzhou, 450001, China.

‡ These authors contributed equally to this work and should be considered as co-first authors.

Corresponding E-mail: biwenzhu2018@hactcm.edu.cn

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## **1. Table S1 Comparison of carbon dots-based fluorescence probes for Cr(VI) detection**





# **2. Table S2 Comparison of carbon dots-based fluorescence probes for FA detection**





#### **3. Materials and instruments**

All reagents used in this work showed below were purchased from commercial suppliers without further purification. Soluble starch  $(C_{12}H_{22}O_{11}$ , CAS: 9005-84-9), L-arginine (L-Arg,  $C_6H_{14}N_4O_2$ , CAS: 74-79-3), glucose  $(C_6H_{12}O_6, \text{CAS: } 50-99-7), \text{ starch } ((C_6H_{10}O_5)n, \text{CAS: } 9005-25-8), \text{ glutathione (GSH, } C_{10}H_{17}N_3O_6S), \text{ serine (Ser, } C_{10}N_3O_6S)$  $C_3H_7NO_3$ ), glycine (Gly,  $C_2H_5NO_2$ ), alanine (Ala,  $C_3H_7NO_2$ ), L-threonine (L-Thr,  $C_4H_9NO_3$ ), L-cysteine (L-Cys,  $C_3H_7NO_2S$ ), L-lysine (L-Lys,  $C_6H_{14}N_2O_2$ ), L-glutamic acid (L-Glu,  $C_5H_9NO_4$ ), L-histidine (L-His,  $C_6H_9N_3O_2$ ), folic acid (FA,  $C_{19}H_{19}N_7O_6$ ), ascorbic acid (AA,  $C_6H_8O_6$ ), vitamin B6 (VB6,  $C_8H_{11}NO_3$ •HCl), nicotinamide  $(C_6H_6N_2O)$ , citric acid (CA,  $C_6H_8O_7$ ), urea (CH<sub>4</sub>N<sub>2</sub>O), silver nitrate (AgNO<sub>3</sub>), aluminum chloride (AlCl<sub>3</sub>) barium chloride dihydrate (BaCl<sub>2</sub>•2H<sub>2</sub>O), calcium chloride (CaCl<sub>2</sub>), cadmium sulfate 8/3-hydrate (3CdSO<sub>4</sub>•8H<sub>2</sub>O), cobalt sulfate heptahydrate (CoSO<sub>4</sub>•7H<sub>2</sub>O), chromium (III) trichloride hexahydrate (CrCl<sub>3</sub>•6H<sub>2</sub>O), dichromate potassium dichromate  $(K_2Cr_2O_7)$ , cupric sulfate (CuSO<sub>4</sub>), ferric chloride hexahydrate (FeCl<sub>3</sub>•6H<sub>2</sub>O), mercury(II) thiocyanate (Hg(SCN)<sub>2</sub>), potassium bromide (KBr), potassium chloride (KCl), potassium carbonate (K<sub>2</sub>CO<sub>3</sub>), potassium iodide (KI), potassium phosphate (K<sub>3</sub>PO<sub>4</sub>), manganese (II) chloride tetrahydrate (MnCl<sub>2</sub>•4H<sub>2</sub>O), sodium perchlorate,(NaClO4), sodium fluoride (NaF), sodium sulfate (Na2SO4), ammonium chloride (NH4Cl), nickel(II) chloride (NiCl<sub>2</sub>), lead(II) nitrate (Pb(NO<sub>3</sub>)<sub>2</sub>), stannous chloride dihydrate (SnCl<sub>2</sub>•2H<sub>2</sub>O), zinc sulfate heptahydrate (ZnSO<sub>4</sub>•7H<sub>2</sub>O). Sucrose (C<sub>12</sub>H<sub>22</sub>O<sub>11</sub>) was obtained from the local supermarket.

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 (FiveEasy Plus FE28), Transmission electron microscope (TF20), Atomic force microscopy (Bruker Dimension Icon), 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.

#### **4. Optimization of the hydrothermal reaction conditions for the synthesis of N-GQDs**

Carbon sources (glucose, sucrose, soluble starch and starch) (0.15 g) and L-arginine (L-arg, 0.3-1.2 g) were firstly mixed in pure water (12.5 mL) and stirred at 60 °C for 15 min. Then, the mixture was sealed into a 25 mL stainless autoclave lined with Teflon and heated at 180-200 °C for 3-5 h. After that, the mixture was naturally cooled to room temperature and the N-GQDs were obtained by centrifugation at 15,000 rpm for 15 min. The obtained N-GQDs were stored as stock solution at room temperature for further use.

Entry	<b>Carbon source</b>	Nitrogen source	Temperature $({}^{\circ}C)$	Time (h)	$_{\rm ent}$ 'max (nm)	<b>Fluorescence</b> intensity (a.u.)
1	glucose, $0.15$ g	L-arg, $0.9 g$	190	$\overline{4}$	442	935
$\overline{2}$	sucrose, $0.15$ g	L-arg, $0.9 g$	190	$\overline{4}$	439	637
3	soluble starch, $0.15$ g	L-arg, $0.9 g$	190	$\overline{4}$	445	1380
$\overline{4}$	starch, $0.15$ g	L-arg, $0.9 g$	190	$\overline{4}$	423	1181
5	soluble starch, $0.15$ g	L-arg, $0.3$ g	190	$\overline{4}$	446	432
6	soluble starch, $0.15$ g	L-arg, $0.6$ g	190	$\overline{4}$	443	816
7	soluble starch, $0.15$ g	L-arg, $1.2 g$	190	4	439	1245
8	soluble starch, $0.15$ g	L-arg, $0.9 \text{ g}$	180	$\overline{4}$	425	1043
9	soluble starch, $0.15$ g	L-arg, $0.9 g$	200	$\overline{4}$	444	819
10	soluble starch, $0.15$ g	L-arg, $0.9 g$	190	3	436	935
11	soluble starch, 0.15 g	L-arg, $0.9 g$	190	5	440	1006

**Table S3** Optimization of the hydrothermal reaction conditions.



**Fig. S1** Fluorescence spectra of the as-synthesized N-GQDs under different conditions in Table S3: (a) entry 1-4; (b) entry 3, 5-7; (c) entry 3, 8-9; (d) entry 3, 10-11.

### **5. FTIR spectrum of N-GQDs**



**Fig. S2** FTIR spectrum of N-GQDs.

### **6. Calculation of fluorescence quantum yield of N-GQDs**

The fluorescence quantum yield (QY) of N-GQDs 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 N-GQDs 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 N-GQDs and quinine sulfate. A is the optical density, I is the integrated emission intensity, and ŋ 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.



- 1				Quinine sulfate			<b>N-GQDS</b>					
	Absorban ce	0.022	0.038	0.061	0.082	0.102	0.022	0.041	0.059	0.080	0.100	
	Integrated Intensity	18296.11	48906.1	81227.1	122660	165966.2	5032.859	11132.78	20046.67	27565.03	32218.84	
	<b>Excitation</b> (nm)	380					380					
	Slope			1828241.6			362356.1					
	QY (%)			55			10.9					

**Fig. S3** Plots of integrated intensity of Quinine sulfate and N-GQDs.

#### **7. Thermostability, photostability and reproducibility of N-GQDs**



**Fig. S4** (a) Fluorescence spectra of N-GQDs under different incubation temperatures; (b-d) fluorescence intensities of N-GQDs at 445 nm: (b) under different incubation temperatures  $(n = 3)$ ; (c) at continuous excitation wavelength of 370 nm; (d) between 8 different batches of N-GQDs.

### **8. General experimental procedure**

#### **Detection of Cr(VI)**

N-GQDs stock solution (500 μL) was firstly diluted by pure water (3.0 mL) and different amount of Cr(VI) were added. Then the solutions were further diluted by pure water to 5.0 mL. The concentrations of Cr(VI) in the solutions were 0-175 μM. Then the fluorescence intensities of the mixed solutions were measured and repeated for 3 times. Other cations  $(Ag^+, A^{13+, Ba^{2+}, Ca^{2+}, Ca^{2+}, Co^{2+}, Cr^{3+}, Cu^{2+}, Fe^{3+}, Hg^{2+}, K^+, Mn^{2+}, Na^+, NH_4^+, Ni^{2+}, Pb^{2+}, Ca^{2+}, Ca^{2+}, Ca^{2+}, Co^{2+}, Cr_4^-, H_4^+, Na^{2+}, Na^{2+}, N^-, M^+, N^+, M^+, N^+$  $\text{Sn}^{2+}$  and  $\text{Zn}^{2+}$  (10 mM, 87.5 µL)) and common anions (Br, Cl-, ClO<sub>4</sub>-, CO<sub>3</sub><sup>2</sup>-, F-, I-, NO<sub>3</sub>-, PO<sub>4</sub><sup>3-</sup>, SCN<sup>-</sup> and SO<sub>4</sub><sup>2-</sup>  $(10 \text{ mM}, 87.5 \mu L)$ ) were added under the same conditions.

#### **Detection of FA**

N-GQDs stock solution (500 μL) was firstly diluted by pure water (3.0 mL) and different amount of FA were added. Then the solutions were further diluted to 5.0 mL. The concentrations of FA in the solutions were 0-200 μM. Then the fluorescence intensities of the mixed solutions were measured and repeated for 3 times. Other interfering compounds (GSH, Glucose, Ser, Gly, Ala, L-Arg, L-Thr, L-Cys, L-Lys, L-Glu, L-His, AA, VB6, niacinamide, CA and Urea (10 mM, 50 μL)) were added under the same conditions.

### **Detection of Cr(VI) in actual water samples:**

The actual samples selected for the determination of Cr(VI) were tap water, C′eastbon bottled drinking water and lake 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 Tianyi Lake in Henan University of Chinese Medicine. The practical water samples were centrifuged at 8000 rpm for 20 min and filtered through a 0.22 μm microporous membrane. Then, different amount of Cr(VI) 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 FA in FA tablet**:

FA 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 FA powder equal to the mass of one FA 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 FA 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 FA in orange juice**:

The orange juice samples were centrifuged at 8000 rpm for 20 min and filtered through a 0.22 μM 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 FA were added into the above working solution to calculate the recovery rate and relative standard deviation (RSD). All measurements were repeated for 3 times.

#### **9. Fluorescence detection of Cr(VI)**



**Fig. S5** Fluorescence spectra (a,c)/intensities (b,d) of N-GQDs (λex = 370 nm, λem = 445 nm) with different cations or anions (175 μM) (n = 3).

## **10. Response time of N-GQDs to Cr(VI)**



**Fig. S6** Fluorescence intensity of N-GQDs (λex = 370 nm, λem = 445 nm) in the absence/presence of Cr(VI) (175 μM).

# **11. Photographs of N-GQDs solution with Cr(VI)**



**Fig. S7** Photographs of N-GQDs solution with Cr(VI) (from left to right: 0, 20, 40, 60, 80 and 100 μM) under fluorescent lamp (above) and 365 nm UV light (below).

No.	Fluorescence Intensity (a.u.)	$F/F_0$
1	1310	1.0022
2	1312	1.0037
3	1308	1.0007
4	1309	1.0014
5	1304	0.9976
6	1307	0.9999
7	1302	0.9961
8	1302	0.9961
9	1311	1.0030
10	1306	0.9992
σ	0.0026	

**12. Table S4 Fluorescence intensity and standard deviation**

### **13. Fluorescence detection of FA**



**Fig. S8** Fluorescence spectra of N-GQDs (λex = 370 nm, λem = 445 nm) with different compounds (200 μM).

#### **14. The response time of N-GQDs to FA**



**Fig. S9** Fluorescence intensity of N-GQDs (λex = 370 nm, λem = 445 nm) in the absence/presence of FA (200 μM).

#### **15. Photographs of N-GQDs solution with FA**



**Fig. S10** Photographs of N-GQDs solution with FA (from left to right: 0, 20, 40, 60, 80 and 100 μM) under fluorescent lamp (above) and 365 nm UV light (below).

#### **16. Exploration of the quenching mechanism by calculation methods.**

 $A_{ex}$ ,  $A_{em}$  and  $F_{obsd}$  are the absorbance and fluorescence intensities of N-GQDs at optimal excitation (Ex = 370) nm) and optimal emission (Em = 445 nm).  $F_{cor}$  (corrected fluorescence emission intensities of N-GQDs at 445 nm) was calculated according to Eq. 1 (the Parker's equation). Then, *CF* (correction factor),  $E_{obsd}$  (observed fluorescence suppression efficiency), *Ecor* (corrected fluorescence suppression efficiency) and *Fcor.o*/*Fcor* (the ratio of corrected fluorescence emission intensities of N-GQDs at 445 nm without/with analytes) were calculated as shown in Table S5 and S6 (CF  $\leq$  3 to ensure the accuracy of the results). The IFE ratio was then calculated by  $(E_{obsd} - E_{cor})/E_{obsd}$  to be 79.74% for Cr(VI) and 90.11% for FA.

The ratio of corrected fluorescence emission intensities of N-GQDs at 445 nm without/with analytes

(*Fcor.o*/*Fcor*) versus the concentration of analytes were plotted as shown in Fig S10. In the presence of  $Cr(VI)$ ,  $F_{cor.0}/F_{cor}$  has a linear relationship with the concentration of  $Cr(VI)$  (Fig. S10b), which indicates the presence of static quenching effect and dynamic quenching effect in the system according to Stern-Volmer equation (Eq. 2). While, *Fcor,0*/*Fcor* was not linearly related to FA, which indicated that the static quenching effect and dynamic quenching effect between N-GQDs and FA are negligible.



**Fig. S11** Geometry of a quartz cuvette, where d, g and s are 1.00, 0.25 and 0.50 cm.

**Table S5** Parameters used to calculate the IFE percentage of Cr(VI) to N-GQDs fluorescence

Cr(VI) $(\mu M)$	$A_{ex}$	$A_{em}$	CF	$F_{obsd}$	$F_{cor}$	$E_{obsd}$	$E_{cor}$	$F_{cor.0}/F_{cor.}$
$\theta$	0.34	0.06	1.55	1004.17	1556.46	0.00	0.00	1.00
5	0.41	0.07	1.69	902.00	1524.38	0.10	0.02	1.02
10	0.49	0.09	1.85	806.13	1491.35	0.20	0.04	1.04
15	0.54	0.09	1.94	754.17	1463.08	0.25	0.06	1.06
20	0.59	0.10	2.03	699.57	1420.12	0.30	0.09	1.10
25	0.66	0.11	2.21	622.40	1375.50	0.38	0.12	1.13

 $CF = F_{cor}/F_{obsd}$ ;  $E_{obsd} = 1 - F_{obsd} / F_{obsd,0}$ ;  $E_{cor} = 1 - F_{cor} / F_{cor,0}$ 

**Table S6** Parameters used to calculate the IFE percentage of FA to N-GQDs fluorescence

FA $(\mu M)$	$A_{ex}$	$A_{em}$	CF	$F_{obsd}$	$F_{cor}$	$E_{obsd}$	$E_{cor}$	$F_{cor.0}/F_{cor}$
$\boldsymbol{0}$	0.39	0.10	1.71	1008.30	1724.19	0.00	0.00	1.00
10	0.47	0.11	1.85	895.77	1657.19	0.11	0.04	1.04
15	0.52	0.11	1.95	854.80	1666.86	0.15	0.03	1.03
20	0.59	0.13	2.12	796.40	1688.37	0.21	0.02	1.02
25	0.64	0.13	2.22	740.33	1643.54	0.27	0.05	1.05

 $CF = F_{cor}/F_{obsd}$ ;  $E_{obsd} = 1 - F_{obsd} / F_{obsd,0}$ ;  $E_{cor} = 1 - F_{cor} / F_{cor,0}$ 

$$
\frac{F_{cor}}{F_{obsd}} = \frac{2.3dA_{ex}}{1 - 10^{-dA_{ex}}} 10^{gA_{em}} \frac{2.3sA_{em}}{1 - 10^{-sA_{em}}}
$$
\n
$$
\frac{F_{obsd}}{1 - 10^{gA_{em}}} \tag{Eq. 1}
$$

*Fcor and Fobsd* are N-GQDs corrected and measured fluorescence intensities (Em = 445 nm); *d*, *g* and *s* are the geometric parameters of the quartz cuvette (Fig. S9) 1.00, 0.25 and 0.50 cm respectively; *Aex* and *Aem* are the absorbance of N-GQDs at optimal excitation ( $Ex = 370$  nm) and optimal emission ( $Em = 445$  nm).



**Fig.** S12 Observed and corrected fluorescence intensity suppression efficiency ( $E_{obsd}$  and  $E_{cor}$ ) (a,c); Relationship between Cr(VI) (b) or FA (d) concentrations and *Fcor,0/Fcor*.

$$
F_{cor,0}/F_{cor} = 1 + K_{SV}[Q] \qquad (Eq. 2)
$$

*Fcor,0* and *Fcor* are corrected fluorescence intensities without and with the addition of Cr(VI) or FA; *Ksv* is the Stern-Volmer constant; [*Q*] is the concentration of Cr(VI) or FA.