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N-doped carbon dot for fluorescence and colorimetry dual-mode detection of curcumin

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Experimental

Reagents

Ethylenediamine was purchased from Sigma-Aldrich Trading Reagent Factory and different common antibiotics and drugs (Cefradine (CED) Cefotaxime (CTX) Oleanolic (Ole) Lincomycin (Lin) Amoxicillin (AMX) Ursolic(Urs) Thiamphenicol (Thi) Kanamycin (KAN) Vancomycin (Van) Azithromycin (AZM) Trimethoprim (Tri) Penicillin (PEN) Tetracycline (TCY) and Cur, dopamine, potassium chloride (KCl), acetic acid, boric acid, and acetic acid were all purchased from Aladdin Reagent Factory.

Preparation of N-CDs

The N-CDs were synthesized by a one-step hydrothermal method. 0.1000 g of dopamine, 2.0 mL of ethylenediamine and 20 mL of distilled water were dissolved ultrasonically and mixed evenly in a 50 mL beaker. The reactant was moved to theteflon autoclave as well as heated up to 200°C for 10 h. The large impurities were get rid ofthrough centrifugation (8000 rpm, 15 min) after the mixture was cooled down, subsequently it was dialyzed with a dialysis membrane (500-1000 Da) for 8 h. Finally, the N-CDs powders were gathered.

Detection of Cur

Typically, 50 μL of N-CDs solution (2 mg/mL) was injected into quartz cuvette with a pipette. Then the concentration of N-CDs was diluted to 49 μg/mL with ultrapure water. Next, different concentrations of Cur were separately introduced to the N-CDs solution. To assess the selectivity of N-CDs, a series of common antibiotics (0.01 mol/L) and drugs (0.01 mol/L) were added instead of Cur with the same detection condition as mentioned above. In order to evaluate the anti-interference ability of the established method, the fluorescence intensity of 2 mL ultrapure water with 50 μL N-CDs (2mg/mL) in 1×1 cm cuvette was measured. Then 100 μL interference compounds (0.01 mol/L) were added into the system and the fluorescence intensity was measured again. Finally, 10 μL Cur (0.01 mol/L) was added and the fluorescence intensity was recorded. The anti-interference ability was evaluated by comparing the fluorescence intensity changes of the three measurements.

Characterization

The characterization and the involved sample preparation of prepared N-CDs refer to our previous articles [1-6].

Sample pretreatment

All real samples were purchased from a local supermarket in Taiyuan, China. 0.1 g red pepper powder and ginger powder were mixed with 2.0 mL ethanol. The mixture was centrifuged at 8000 rpm for 25 min. Hereafter, the supernatant was collected and filtered it through a microporous membrane (0.25 μm). The ginger juice was gained through juicer and the ginger juice was dissolved with ultrapure water to obtain 0.1 g/mL solution. Afterwards, the filtered extracts of red pepper powder, refined ginger powder and ginger juice were diluted to an appropriate concentration. 50 μL (2 mg/mL) of the above-mentioned N-CDs solution and 2 mL of ultrapure water were added in the quartz cuvette, and the fluorescence intensities were measured. Then different concentrations ofextracts were complemented and the fluorescence intensities measured again at 405 nm excitation wavelength [7].

Table S1 Elemental analysis of the prepared N-CDs: (A) elemental content and (B) relative number of atoms in a N-CDs.

(A)

Elemental content (weight %)				
Sample name	C	H	N	O
N-CDS	38.67	6.84	20.87	28.6

(B)

Relative number of atoms					
Sample name	C	H	N	O	Empirical
N-CDs	16	34	7	9	$C_{16}H_{34}N_7O_9$

Quantum yield (Φ) measurements

The fluorescence quantum yield was determined with reference to quinine sulfate (ψ = 0.54) in 0.10 mol/L H_2SO_4. Different concentrations of N-CDs solution and quinine sulfate solution were prepared respectively, and the absorbance of each solution at 405 nm was measured by using Lambda 950 absorption spectrophotometer. A Varian Cary Eclipse fluorometer was used to record the PL spectral area when the excitation wavelength was 405 nm. (In this experiment, the area under the PL curve in the wavelength range of 410-700 nm is the fluorescence integration area.) Then plot the curve between the fluorescence integration area and the absorbance. According to the method

reported in the literature, the calculation formula is as follows:

$$\Phi_x=\Phi_{st}(K_x/K_{st})\ (\eta_x/\eta_{st})^2$$

K ---------- The slope of the curve drawn by the fluorescence integral area and absorbance

η---------refractive index.

The subscripts "st" and "x" refer to the reference and sample, respectively.For these aqueous solutions, $\eta_x/\eta_{st}=1$. In order to minimize the self-absorption effect, the absorbance must be kept below 0.10 at the excitation wavelength.

Table S2 Integrated fluorescence intensity against absorbance of quinine sulfate and N-CDs.

N-CDs		quinine sulfate	
A	F	A	F
0.016	921.35	0.012	17151
0.031	1160.8	0.036	26889
0.042	1281.6	0.054	31788
0.074	1561.1	0.076	39201
0.092	1772.8	0.082	40713

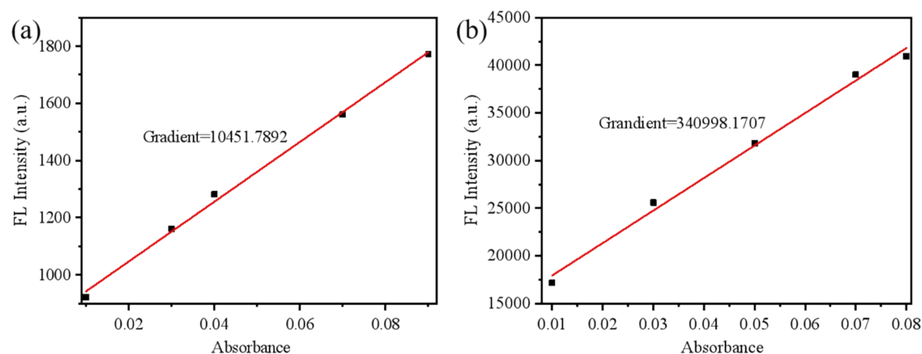

Fig.S1 Plots of integrated fluorescence intensity against absorbance of (**a**) N-CDs at excitation and absorption wavelengths of 405 nm and (**b**) quinine sulfate

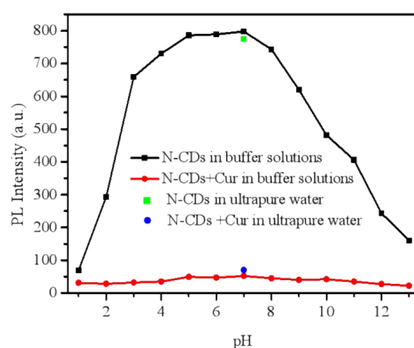

Fig. S2 Effect of pH on fluorescence intensity of N-CDs in the presence and absence of Cur

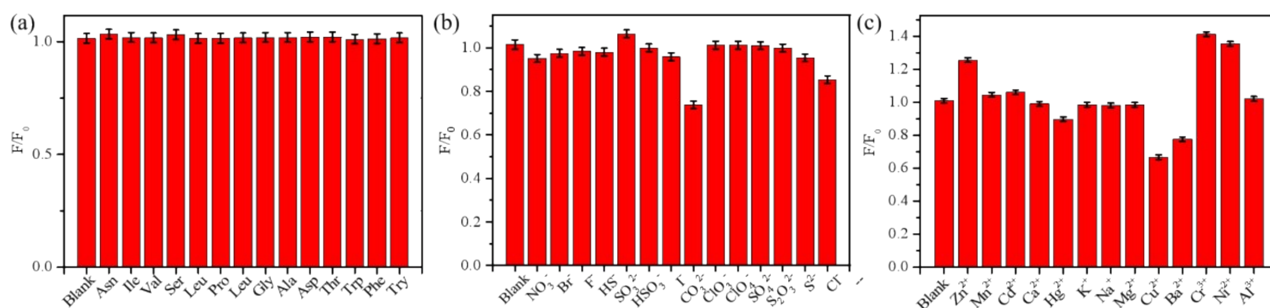

Fig. S3 The ion selectivity of N-CDs. Comparison of fluorescence intensity of 49 μg/mL N-CDs after the addition of (a) 0.01 mol/L amino acids (b) 0.1 mol/L anion and (c) 0.1 mol/L metal ions.

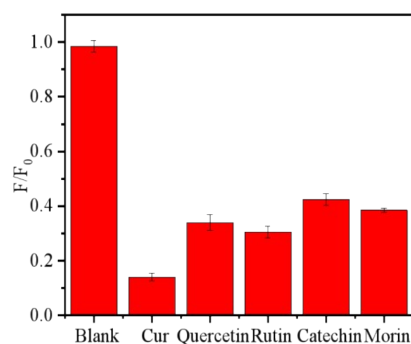

Fig. S4 The influence of 0.01mol/L other similar active ingredients.

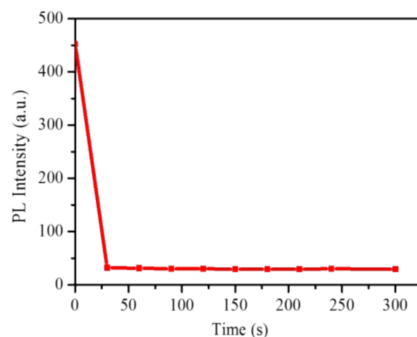

Fig. S5 The effect of time on the fluorescence intensity of N-CDs when adding 0.01mol/L Cur.

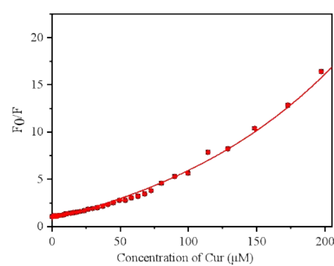

Fig. S6 F_0/F and Cur concentration in the range of 0-191 μM.

Table S3 Comparison of different analytical methods for detection of Cur.

Methods	Comments	Linear range	LOD	Reference
UHPLC-UV-Vis	Reverse phase	0.27~136 μM	67.88 nM	8
LC-MS/MS	Reverse phase	2.06~411.4 nM	2.06 nM	9
HPLC-PDA	Reverse phase	32.58~48.88 μM	3.26 nM	10
HPLC	SP, silical gel	0.14~0.82 mM	21.72 μM	11
Voltammetry	NiCl2/GCE	10~600 μM	0.109 μM	12
Fluorescence	FDM	0.062~6.79 μM	19.01 nM	13
Fluorescence	N-CDs	2.01~14.1 μM	0.12 μM	14
Fluorescence	N-CDs	0.2~10 μM	84.8 nM	15
Fluorescence	N,Cl-CDs	0.1~35 μM	38 nM	16
Fluorescence/Colorimetric	N-CDs	97.5 nM-67.9 μM	94 nM	This work

Table S4 Analytical results for Cur in real samples

Sample	Initial Cur amount(μM)	RSD（%, n=6）
red pepper powder	0.51	1.32
ginger powder	0.3	1.58

ginger juicer	0.2	2.01

Table S5 Standard recovery experiment

Sample	Spiked/(μM)	Found/(μM)	Recovery(%, n=6)	RSD(%, n=6)
red pepper powder	0.5	0.47	94.00	2.90
	10	10.11	101.10	1.40
	50	49.51	99.02	0.49
ginger powder	0.5	0.55	110.00	1.20
	10	10.24	102.40	0.68
	50	49.75	99.50	1.99
ginger juicer	0.5	0.52	104.00	0.30
	10	9.94	99.40	0.70
	50	49.88	99.76	1.10

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