

**Quantification of Humic Substances in Natural Water Using Nitrogen-Doped
Carbon Dots**

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This SI contains 14-page document, including 2-page descriptions about the quantum yield calculations, the preparation of the portable HA test paper and the microwave-assisted preparation of N-doped C-dots, 1 table, 8 figures, reference page and this cover page.

Quantum Yield Calculations. The quantum yield was obtained based on the method described in “A Guide to Recording Fluorescence Quantum Yields” offered by Jobin Yvon Horiba Co. at <http://www.jobinyvon.co.uk/ukdivisions/Fluorescence/plqy.htm>¹. Briefly, quinine sulfate was dissolved into H₂SO₄ while the N-doped C-dots were dissolved into water. The absorbance and fluorescence intensity of the above prepared aqueous solutions were recorded separately. The quantum yield was calculated according to eq. 1.

$$\Phi_x = \Phi_{ST} (m_x/m_{ST}) (\eta^2_x/\eta^2_{ST}), \quad (1)$$

where Φ is the quantum yield of N-doped C-dots, m denotes the slope of the integrated photoluminescence intensity versus absorbance, η is the refraction index of the solvent, ST is the standard (quinine sulfate), and X is the sample (N-doped C-dots). Based on the report by Zhou et al.¹, 1.33 of refraction index (η) of 0.1 M H₂SO₄ and water solution is adopted in this work. The quantum yield (Φ) of quinine sulfate is 0.54.

Preparation of the Portable HA Test Paper. The portable HA test paper was prepared on a piece of filtration paper by a commercial inject printer (HP DeskJet 1110 Printer series, HP, USA).² Briefly, carbon dots solution was injected into a vacant cartridge sprayed onto the test paper. Then, the prepared test paper was immersed into HA solution and the fluorescence was observed at 302 nm UV lamp and recorded by the excitation emission matrix after drying.

Preparation of N-Doped C-Dots by Microwave-Assisted Method. Microwave-assisted synthesis method was adopted to additionally prepare the

N-doped C-dots according to a previous report with minor modification.³ Briefly, 1 g of citrate sodium was dissolved into 10-mL DI, and 200 μ L ethylenediamine was then added under vigorous stirring. The transparent solution was transferred into a microwave oven and heated at 600 W for 10 min. The N-doped C-dots were obtained after cooling to room temperature.

Table S1 Comparison between This work and the Reported Methods for HS Quantification						
standards used	detection method	detection limit	linear range	ion strength	pH	reference
HA (Janssen Chemica:12.086.58)	fluorescence	/	< 5	/	/	4
HS(International Humic Substances Society)	fluorescence	/	5-100	0-1 M KCl	Increase with pH	5
HA(International Humic Substances Society)	cathodic stripping voltammetry	0.005	0.06-0.6	/	8.0	6
HA(International Humic Substances Society)	alkaline extraction	4.62	14.7-2000	/	1.0	7
HA(Aldrich)	HPLC	5.46 mg C/L	Not given	/	8.2	8
HA (RCNC Co., China)	UV-vis	0.8	0-40	/	7.0	9
HA (Aldrich and Acros)	chemiluminescence	0.01	0.03-10	/	/	10
HA (Shanghai Jufeng Co., China)	flow injection chemiluminescence	0.0005	0.001-1	/	/	11
			1-10			
HA (Aldrich)		0.2	0-100	10⁻⁷-1	3.0-12.0	this work

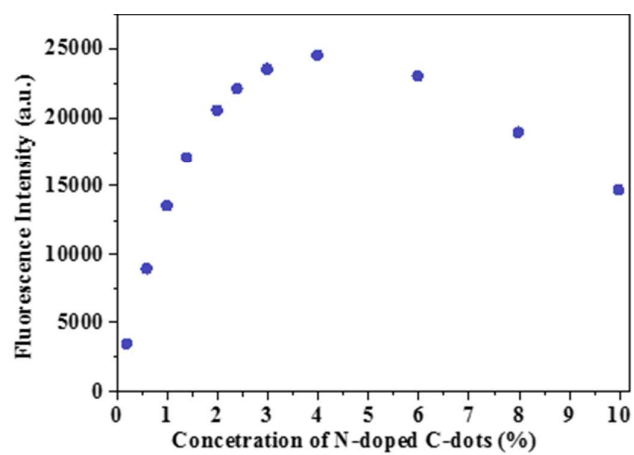


Figure S1. Fluorescence intensity variations of the N-doped C-dots at different concentrations.

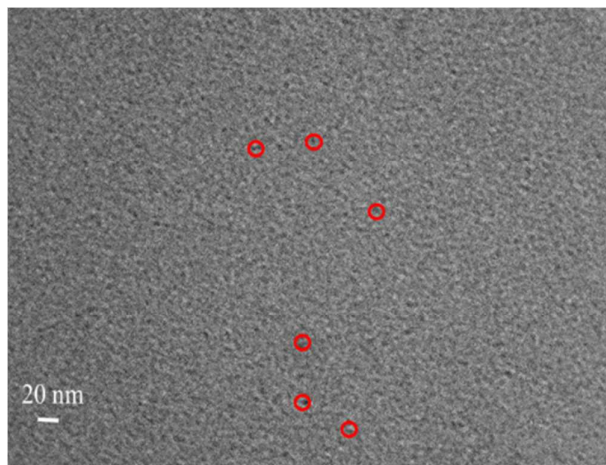


Figure S2. Transmission electron microscopy (TEM) images of the N-doped C-dots

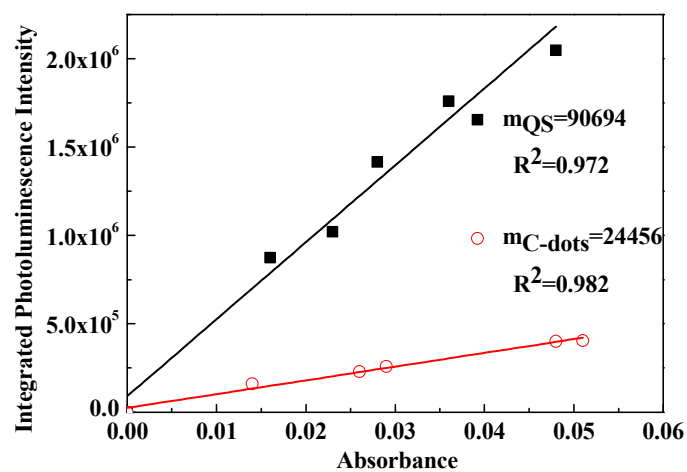


Figure S3. Photoluminescence and absorbance of the quinine sulfate and N-doped C-dots

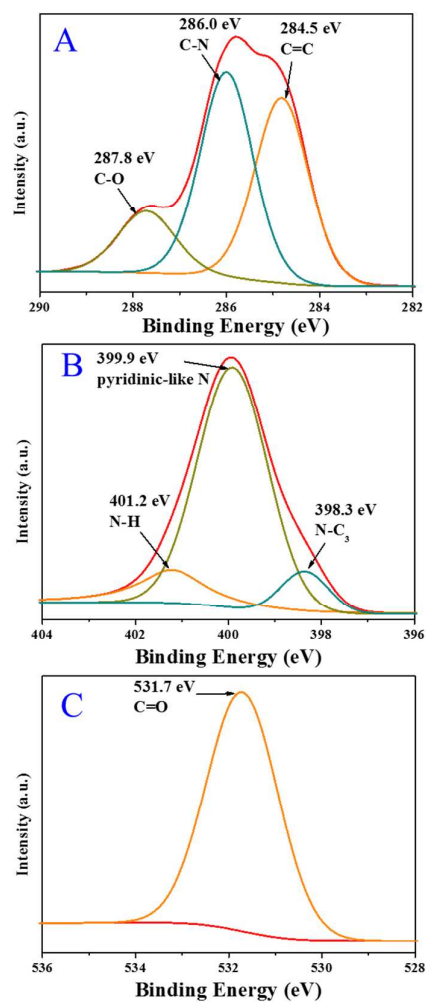


Figure S4. (A) C 1s, (B) N 1s and (C) O 1s of the N-doped C-dots

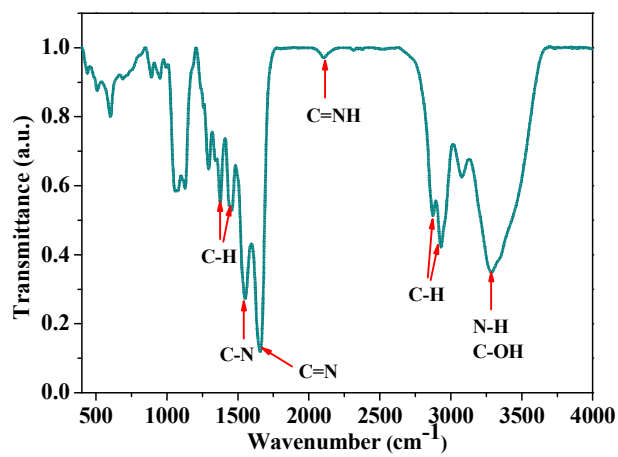


Figure S5. Fourier transform infrared spectroscopy (FTIR) spectra of the N-doped C-dots

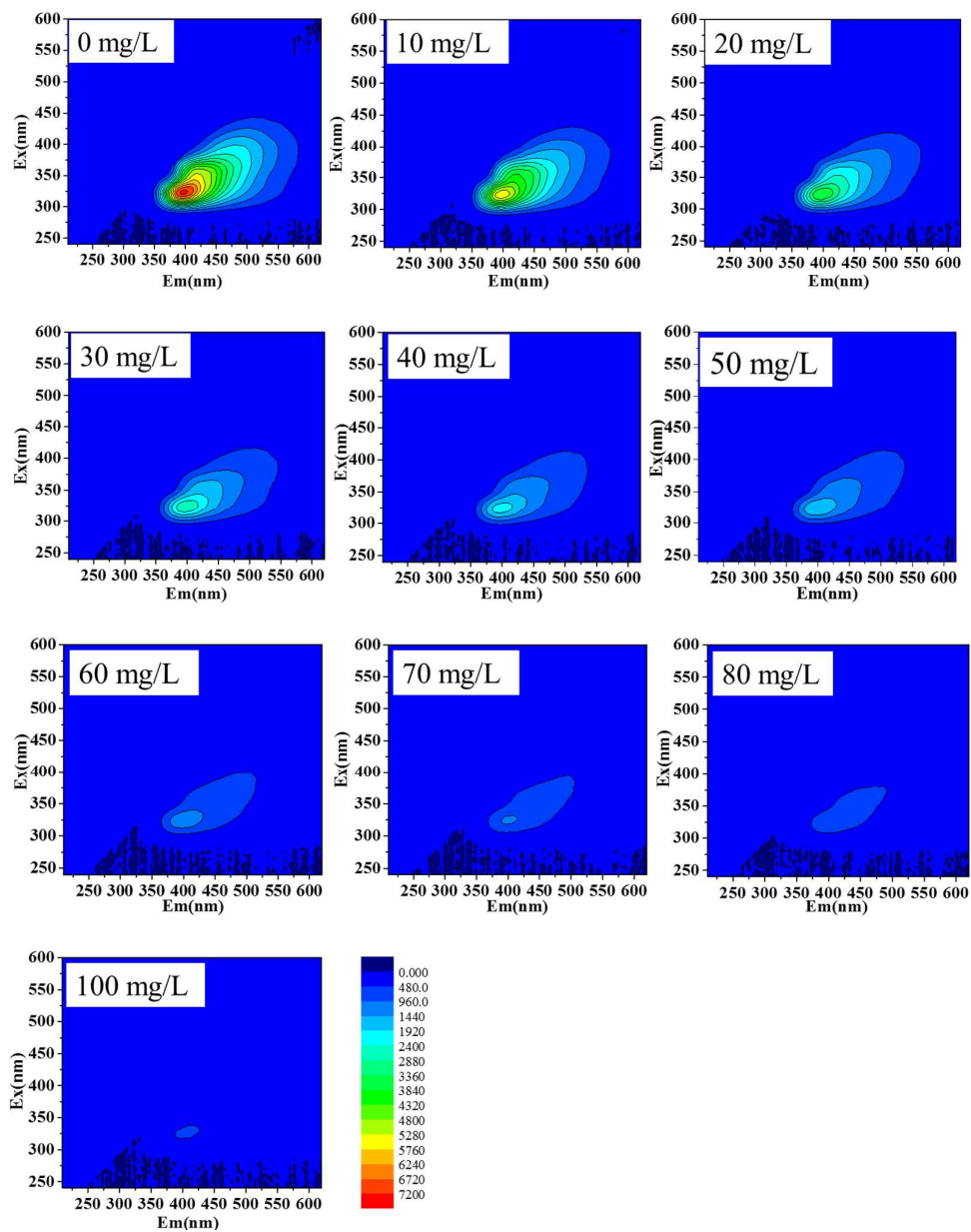


Figure S6. Three-dimensional excitation emission fluorescence spectroscopy spectra of the N-doped C-dots with the increasing HA concentration

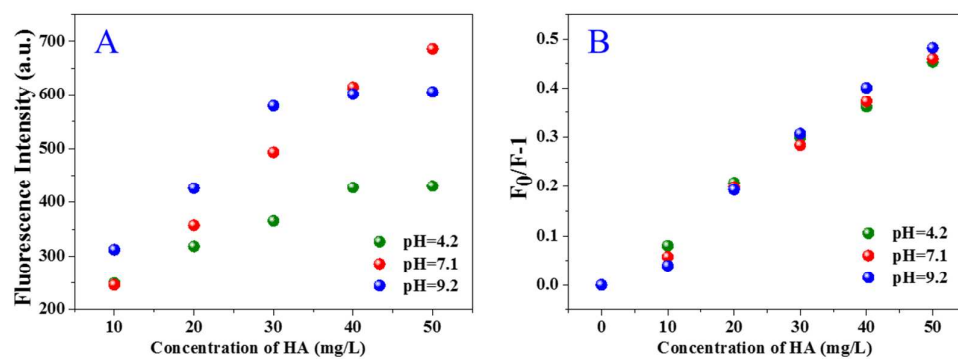


Figure S7. Influence of pH on (A) fluorescence of HA and (B) quantification of HA by the N-doped C-dots.

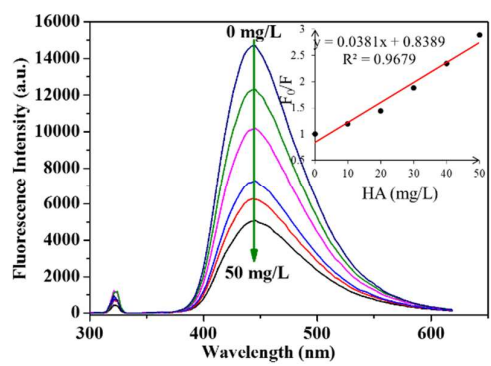


Figure S8. Quantification of HA by using the microwave-assisted synthesized N-doped C-dots.

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