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Fabrication of Fluorescent Nitrogen-Rich Graphene Quantum Dots by Tin(Iv) Catalytic Carbonization of Ethanolamine

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CONTENTS

Experimental Section

Reagents and Materials. High-purity 18.2 $M\Omega^{-1}$cm deionized water (DIW) was obtained from a water purification system (Chengdu ULTRAPURE Technology Co. Ltd., Chengdu, China). $SnCl_4.5H_2O$ and ethanol were purchased from Kelong Chemical Reagent Company (Chengdu, China). Ethanolamine was obtained from Chengdu United Institute of Chemical & Reagent. Folic acid was purchased from Aladdin Chemistry Co. Ltd. A phosphate buffer solution (PBS) of 0.01M was prepared by dissolving Na_3PO_4 and $NaH_2PO_4.2H_2O$ respectively and adjusted to the required pH value with each other. All chemicals were at least of analytical grade.

Quantum yield determination of N-rich GQDs.

The quantum yield of the synthesized N-rich GQDs was determined by point method [1] by the reference of quinine sulfate (0.1M H_2SO_4 as solvent; QY=0.577). The value of quantum yield in water was calculated using the equation below.

$$Q_x=Q_{st}(I_x/I_{st})(A_{st}/A_x)(\eta_x^2/\eta_{st}^2)$$

Where Q is the quantum yied (QY). I is the measured integrated fluorescence emission intensity peaked 425 nm. A represents the UV-Vis absorbance at the excitation wavelength. In order to minimize reabsorption effects, absorption intensity was controlled under 0.05 and made sure that the refractive index of the solvent remained constant. The subscript "x" refers to the sample and "st" for standard with known QY, respectively. The QYs were equal to the average of three tests.I

Table S1. QY of the as–prepared N-rich GQDs.

Sample (1)	Integrated emission Intensity (I)	Abs at 350 nm Wavelength (A)	Refractive index of solvent(n)	Quantum Yield (%)
Quinine sulfate	4584	0.033	1.33	57.7
N-rich GQDs@2h	468.1	0.018	1.33	10.80
N-rich GQDs@8h	650.3	0.023	1.33	11.74
N-rich GQDs@15h	878.5	0.024	1.33	15.20

Sample (2)	Integrated emission Intensity (I)	Abs at 350 nm Wavelength (A)	Refractive index of solvent(n)	Quantum Yield (%)

Quinine sulfate	4340	0.030	1.33	57.7
N-rich GQDs@2h	550.6	0.022	1.33	9.98
N-rich GQDs@8h	647.4	0.021	1.33	12.30
N-rich GQDs@15h	756.1	0.019	1.33	15.87

Sample (3)	Integrated emission Intensity (I)	Abs at 350 nm Wavelength (A)	Refractive index of solvent(n)	Quantum Yield (%)
Quinine sulfate	3426	24	1.33	57.7
N-rich GQDs@2h	682.4	0.025	1.33	11.03
N-rich GQDs@8h	409.9	0.012	1.33	13.81
N-rich GQDs@15h	775.2	0.020	1.33	15.67

Figure S1. The solubility of N-rich GQDs in various solvents.

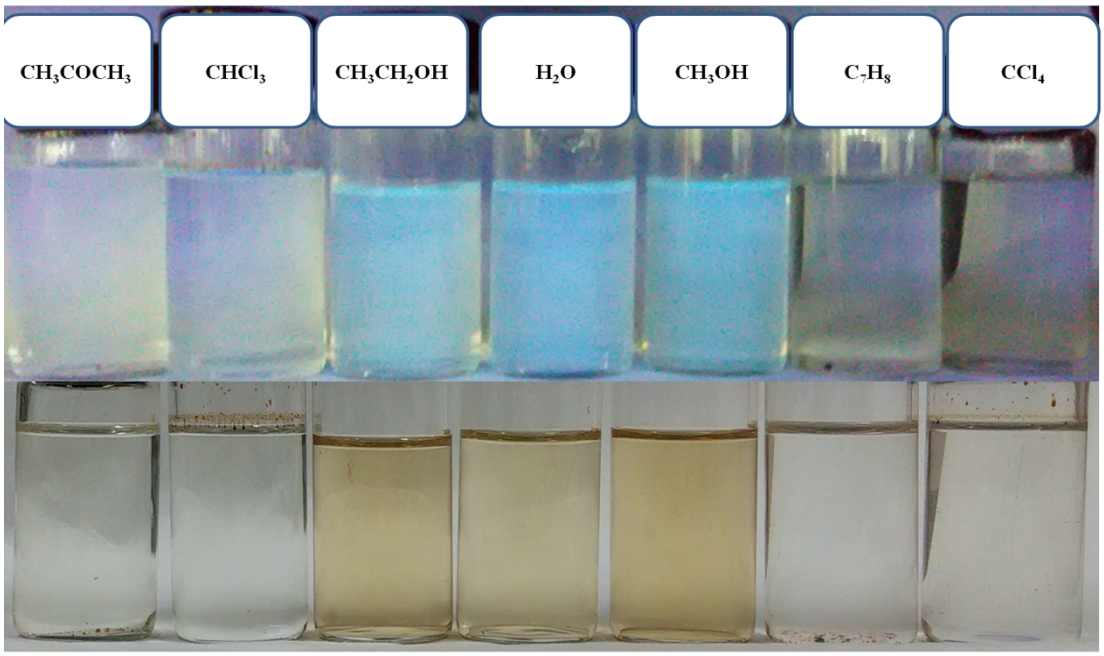

Figure S2. XRD of N-rich GQDs.

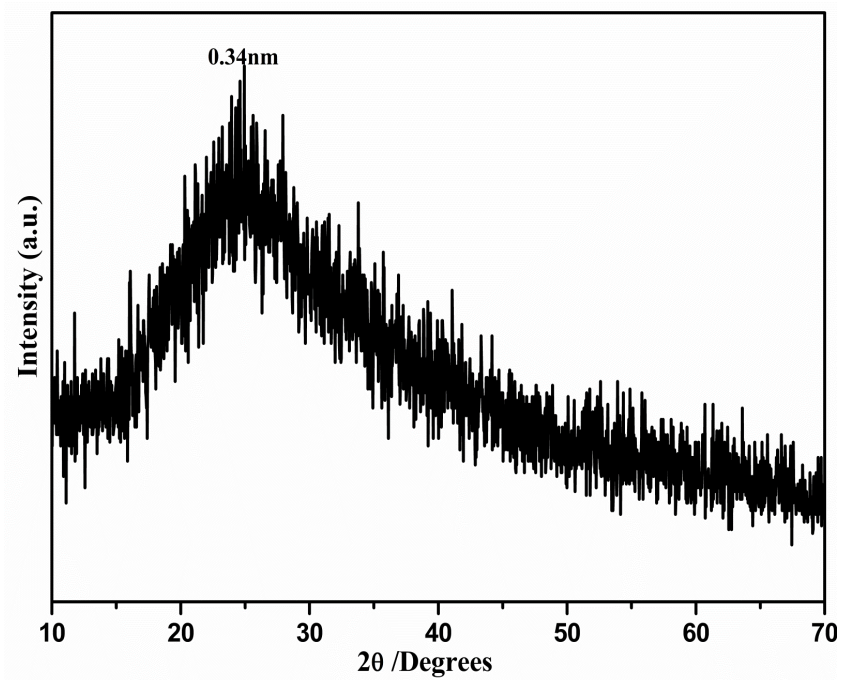

Figure S3. AFM of N-rich GQDs.

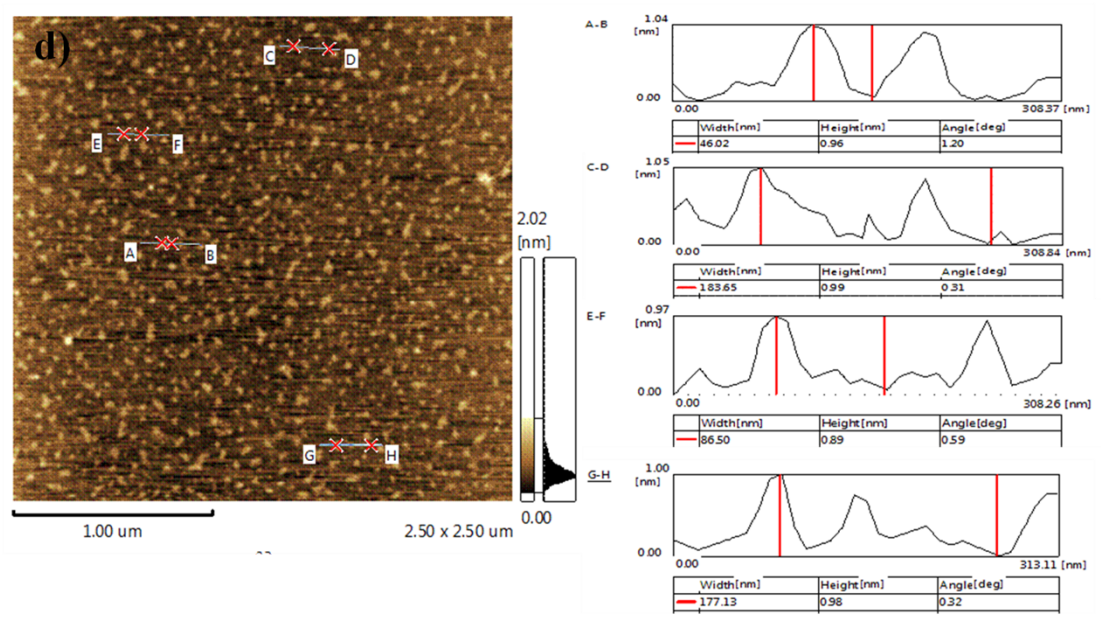

Figure S4. Raman spectra of N-rich GQDs.

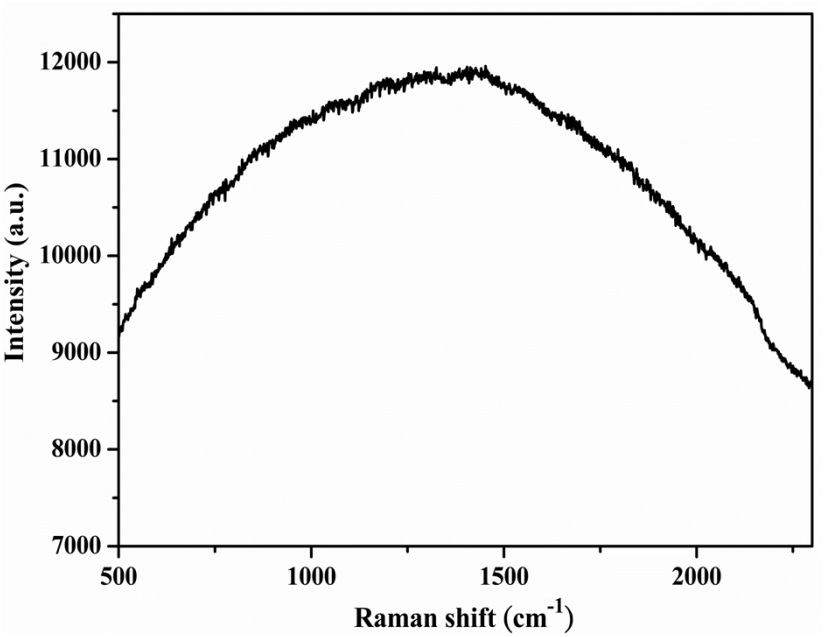

Figure S5. FTIR of N-rich GQDs.

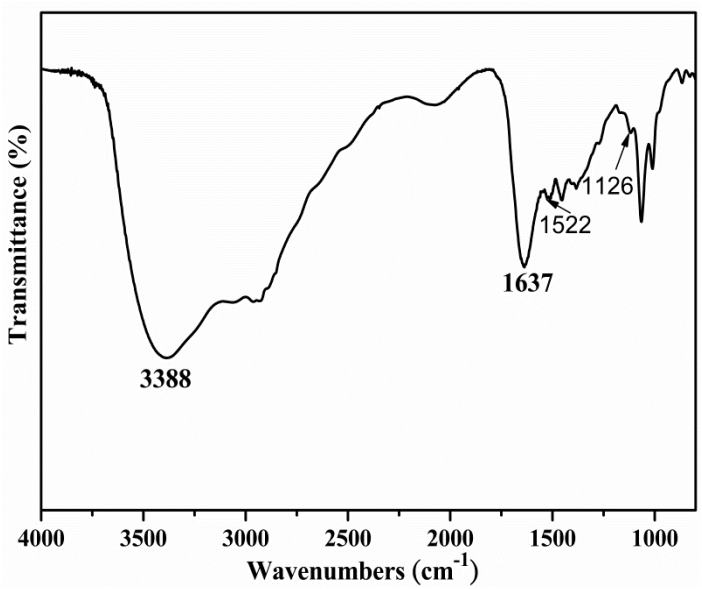

Figure S6. Investigate the factors influencing N-rich GQDs formation. The ratio of $SnCl_4.5H_2O$ and $HO(CH_2)_2NH_2$ （a）, reation time（b） and catalytic effencity of $SnCl_4.5H_2O$ at 100℃（c）。

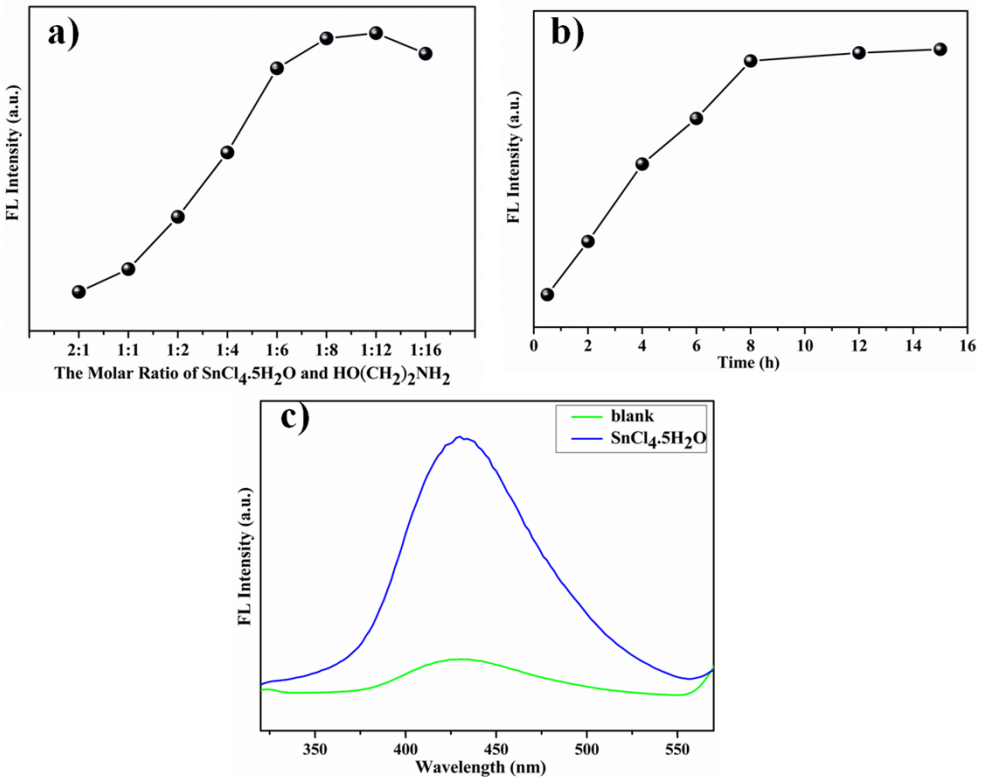

Figure S7. SEM (a), EDS (b), XRD (c) of SnO_2..

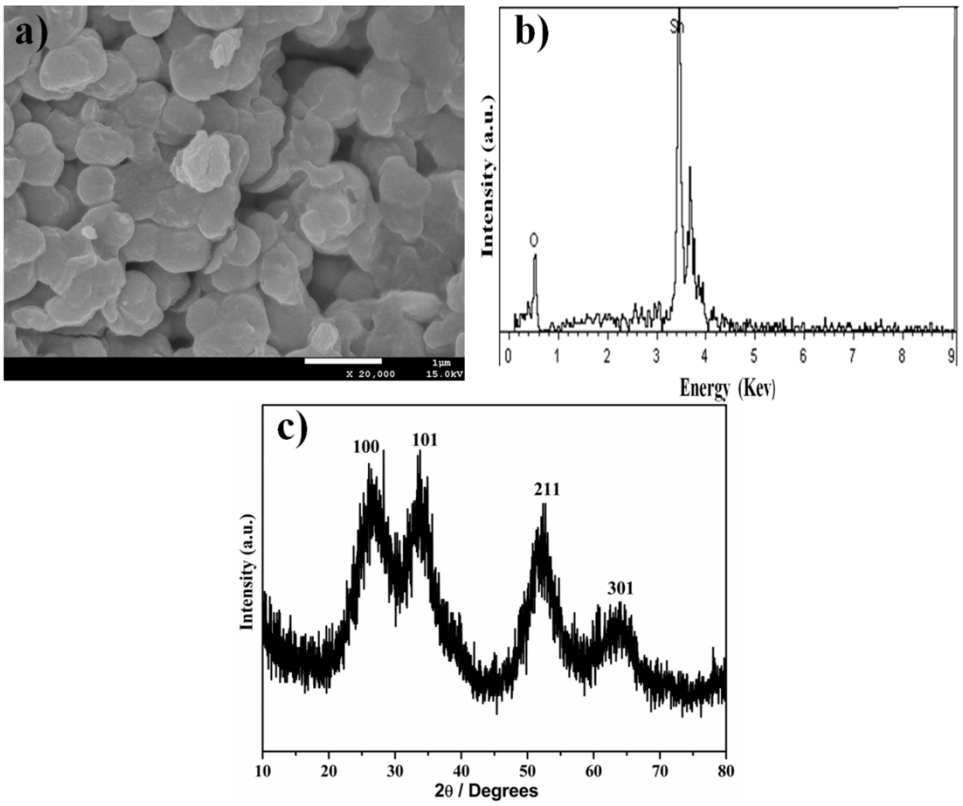

Figure S8. XPS full scan spectrum of N-rich GQDs@2h (a) and N-rich GQDs@6h (b).

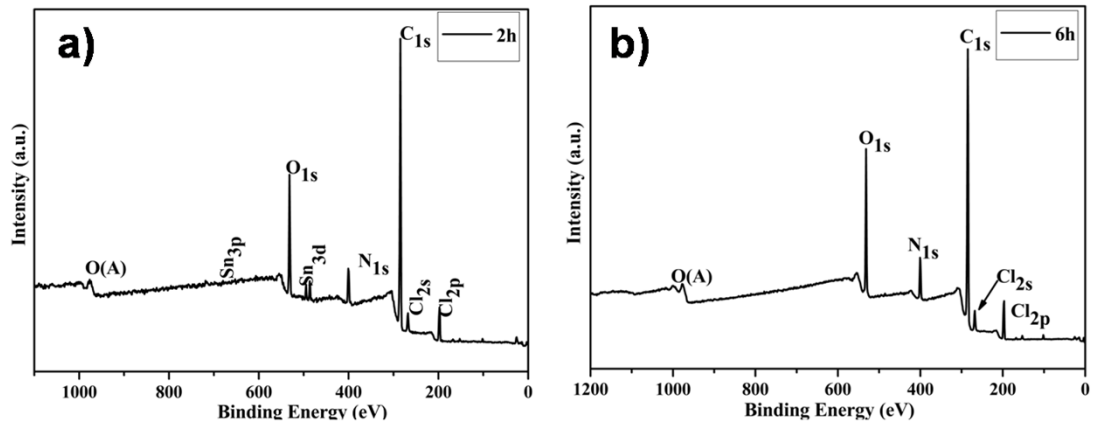

Figure S9. FL (a) and UV-Vis (b) spectra of N-rich GQDs at different stages.

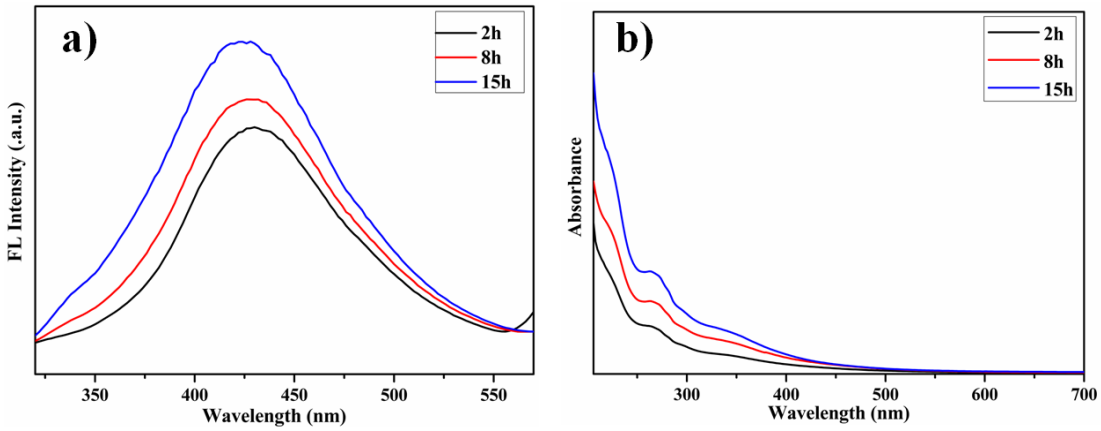

Figure S10. N-rich GQDs prepared in different condition

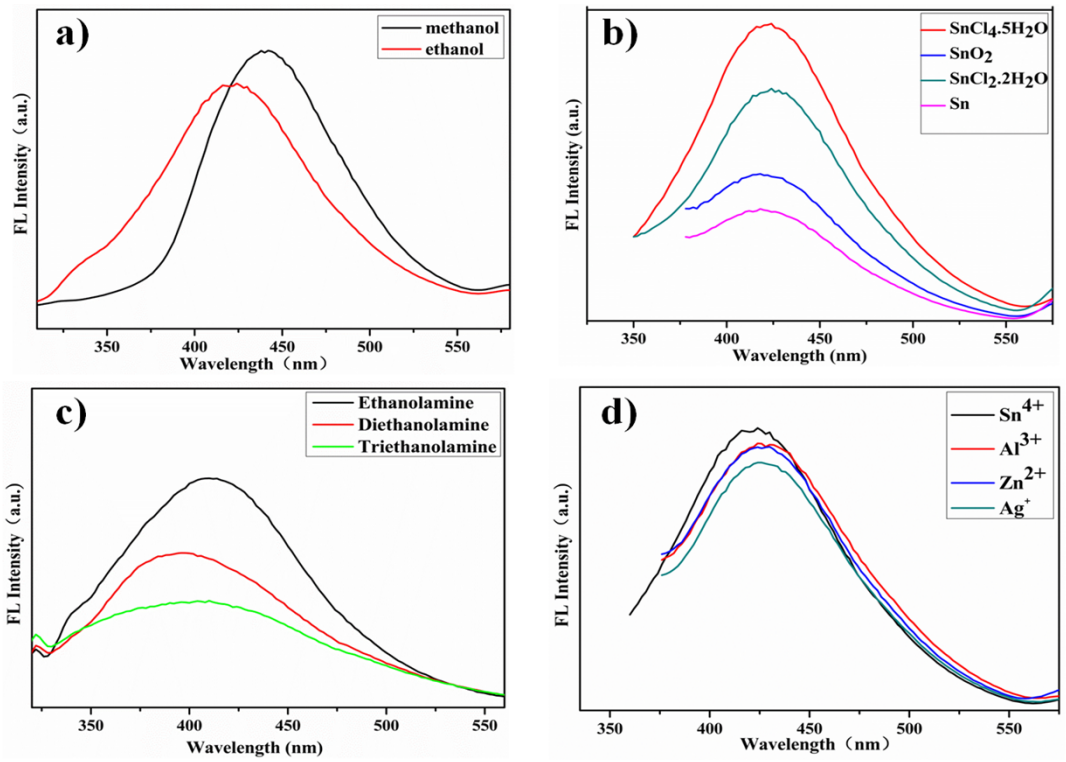

Figure S11. UV-Vis spectra of N-rich GQDs, folic acid and N-rich GQDs & folic acid.

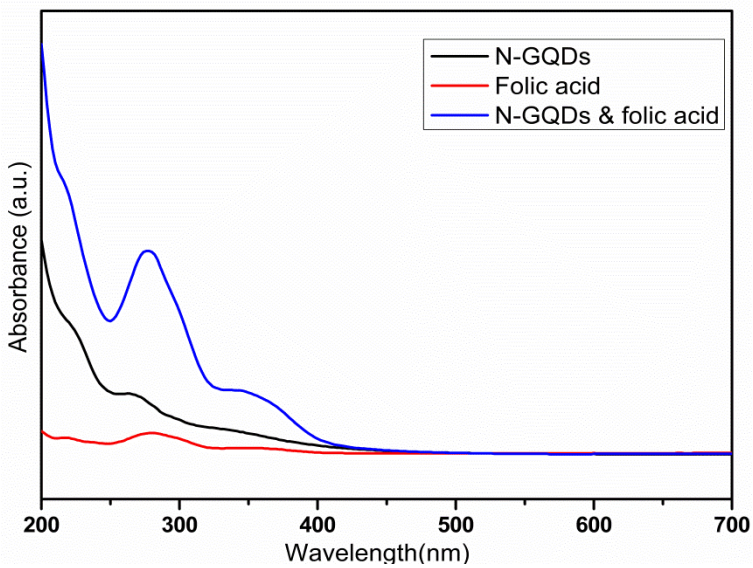

Table S2. Element analysis of N-rich GQDs at different stage.

Sample	C(wt%)	H(wt%)	N(wt%)
N-GQDs@2h	64.65	12.95	22.4
N-GQDs@8h	64.44	13.64	21.92
N-GQDs@15h	67.29	13.92	18.79

Table S3. The relative contents of O atoms in different chemical environment of the N-rich GQDs at different reaction time analyzed by XPS.

Binding energy	Integrated Area		
(eV)	N-rich GQDs@2h	N-rich GQDs@8h	N-rich GQDs@15h
C=O	45120.52	29405.00	28309.52
C-O	3424.86	14149.40	16208.98

Table S4. Fluorescence lifetimes of N-rich GQDs in the presence and absence of folic acid. The lifetimes were obtained by three-exponential fitting and <τ> stands for the average lifetime calculated using formula 1 (t is the time, τ is the lifetime, and A is the pre-exponential factor)

Sample	τ1/ns(A1%)	τ2/ns(A2%)	τ3/ns(A3%)	<τ>/ns
N-rich GQDs	1.08(9.67)	5.45(40.90)	13.53(49.43)	11.38
N-rich GQDs@Folic Acid	0.97(8.80)	5.28(42.59)	13.24(48.61)	11.08

$1\langle\tau\rangle=(A1\tau1^2+A2\tau2^2+A3\tau3^2)/(A1\tau1+A2\tau2+A3\tau3)$

[1] L. L. Li, G. H. Wu, T. Hong, Z. Y. Yin, D. Sun, E. S. A-H, J-J Zhu, *ACS Appl. Mater. Interfaces* **2014**, *6*, 2858−2864.

Figure S12. Selectivity of FL probe based on the nitrogen-rich graphene quantum dots (the concentration of folic acid: 20 μM; the concentration of others: 200 μM).