Supporting Information

A green solid-phase method for preparation of carbon nitride quantum dots and their applications in chemiluminescent dopamine sensing

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Reagents and materials.

Deionized water with conductivity of 18.2 MΩ cm^{-1} from a water purification system (ULUPURE, Chengdu, China) was used throughout. Melamine, potassium ferricyanide ($K_3[Fe(CN)_6]$) and ethylenediamine tetraacetic acid disodium salt (EDTA) were purchased from Chengdu chemical regent Co. Ltd. Dopamine (DA) was purchased from Adamas regent Co. (Shanghai, China). All the other reagents were at least of analytical grade and used as received. The phosphate buffer solution (PBS) of 0.1 M was prepared by adjusting different volume of Na_2HPO_4 and NaH_2PO_4 to required pH, the higher pH from 10 to 13 were prepared by adding NaOH.

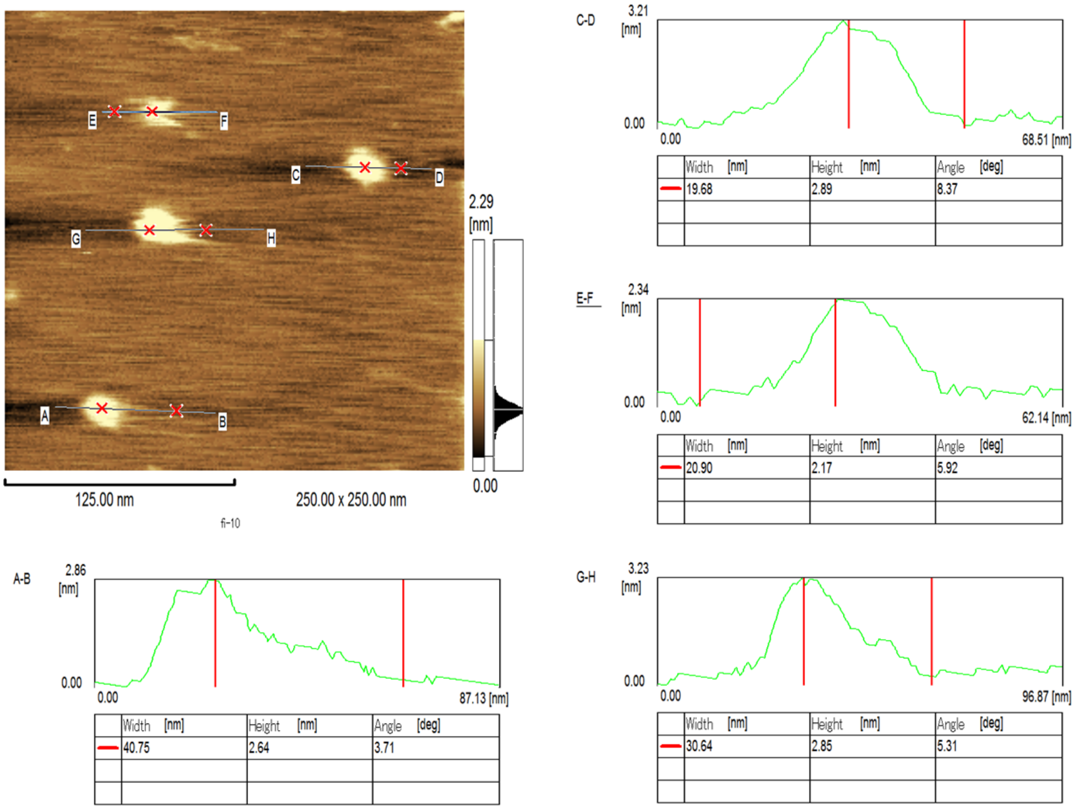
Apparatus.

The batch experiment was performed with a BPCL ultra-weak CL analyzer (Institute of Biophysics, Chinese Academy of Science, Beijing, China) with high-energy cutoff filters of various wavelengths from 400 to 625 nm. The solution was pumped with a constant flow pumps (Model BT100-2, Baoding, China) into the spiral flow CL cell, which was installed in front of the photomultiplier tube (PMT). Transmission electron microscopy (TEM) image was carried out on a Tecnai G2 F20 S-TWIN transmission electron microscope (FEI Co., America) operating at 200 kV. The samples for TEM measurements were prepared by the deposition of one drop of aqueous dispersion on a copper grid coated with thin films of carbon, and the solvent was removed by evaporation in air. The atomic force microscopy (AFM) images were obtained a tapping mode of Agilent 5500 Atomic Force Microscope. XRD patterns of the samples were measured using X’ Pert Pro X-ray diffractometer (Philips) with Cu Kα radiation (λ= 1.54178 Å). X-ray photoelectron spectroscopy (XPS) was recorded a XSAM 800 electron spectrometer (Kratos) using Al Kα as the excitation source (1486.6 eV) and binding energy calibration was based on C1s at 284.8 eV. Fourier Transform Infrared (FTIR) spectra from 4000 to 400 cm^{-1} were recorded in KBr discs on a Nicolet IS10 FTIR spectrometer (Thermo Inc., America). The particle sizes and ζ-potential values of the products were analyzed using a dynamic lights cattering Zetasizer Nano ZS (Malvern Co., UK). The UV absorption and emission spectra were recorded by a U-2910 UV-Vis spectrophotometer and an F-7000 fluorescence spectrophotometer (Hitachi Co., Tokyo, Japan). Electron paramagnetic resonance (EPR) spectra were obtained using a JES FA200 X-band electron paramagnetic resonance spectrometer (JEOL, Japan).

Quantum Yield Measurements for g-CNQDs. Quantum yield was measured according to the established procedure.[38] The optical densities were measured on a UV–Vis spectrophotometer. Quinine sulfate in 0.1 M H_2SO_4 (literature quantum yield of 0.54 at 360 nm) was used as the standard. Absolute values were calculated using the standard reference sample that has a fixed and known fluorescence quantum yield value according to the following equation:

$$\phi_x=\phi_s (A_s / A_x)(I_x / I_s)(\eta^2_x / \eta^2_s) \qquad (1)$$

Where ϕ is the quantum yield, I is the measured integrated emission intensity, A is the optical density, and η is the refractive index. In order to minimize re-absorption effects absorbencies in the 10 mm fluorescence cuvette were kept under 0.1 at the excitation wavelength (360 nm). Excitation and emission slit widths were set at 5.0.



C-D

	Width [nm]	Height [nm]	Angle [deg]
—	19.68	2.89	8.37

E-F

	Width [nm]	Height [nm]	Angle [deg]
—	20.90	2.17	5.92

A-B

	Width [nm]	Height [nm]	Angle [deg]
—	40.75	2.64	3.71

G-H

	Width [nm]	Height [nm]	Angle [deg]
—	30.64	2.85	5.31

Figure S1. AFM image of as-prepared g-CNQDs deposited on a mica substrate; (d) the corresponding height image of four dots.

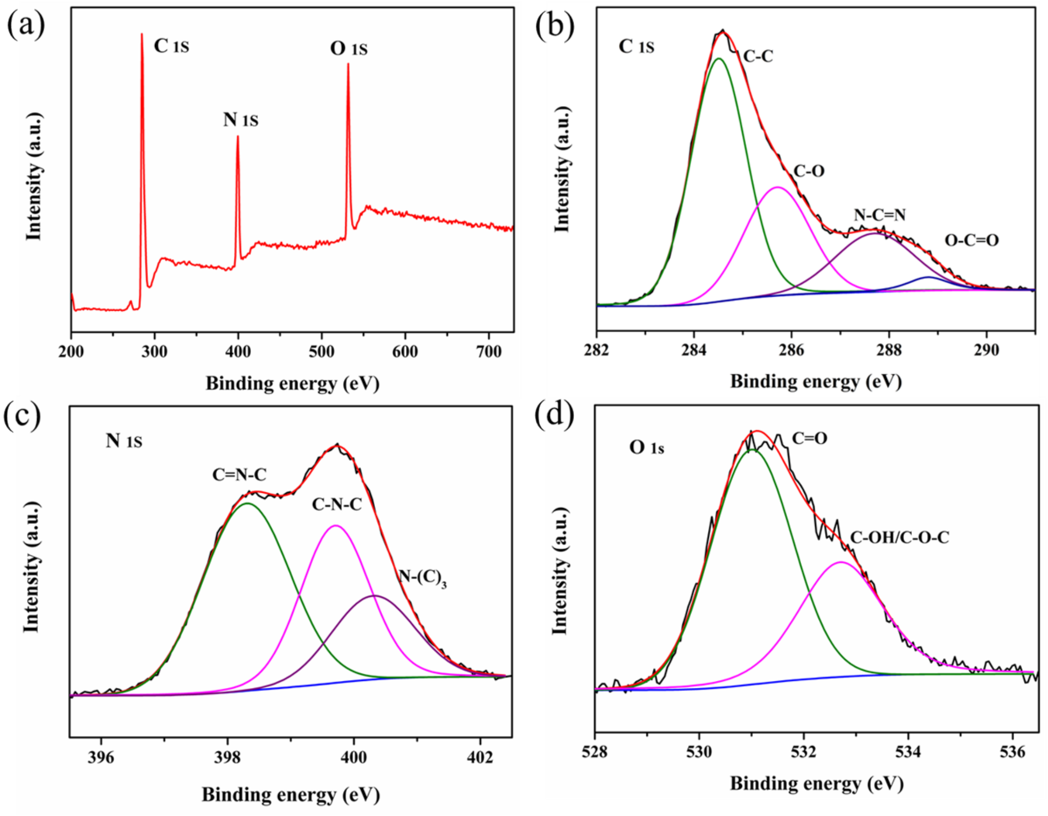


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Figure S2. (a) The XPS spectra of the obtained g-CNQDs; (b), (c) and (d) the corresponding C_{1S} spectrum ,N_{1S} spectrum and O_{1S} spectrum of g-CNQDs.

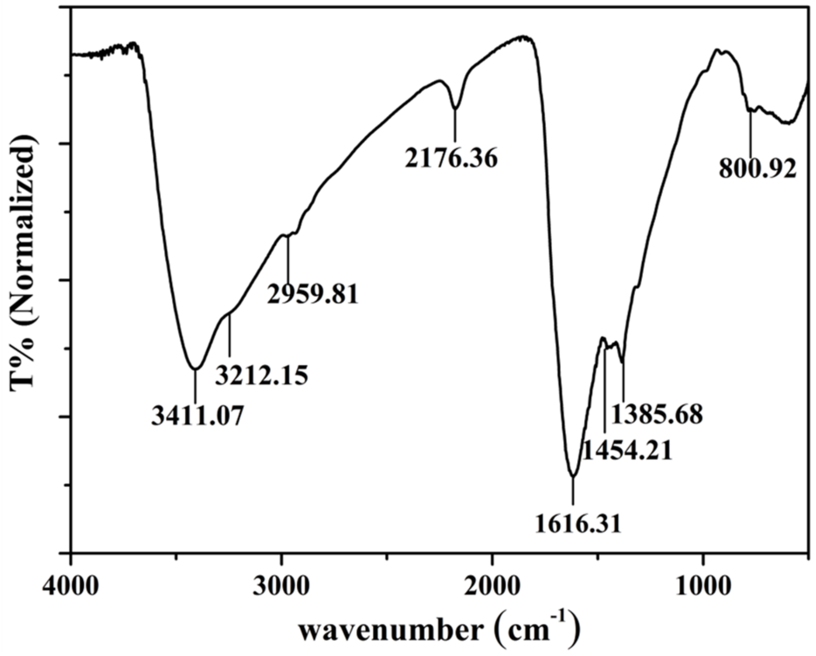

Figure S3. The IR spectra of the obtained g-CNQDs.

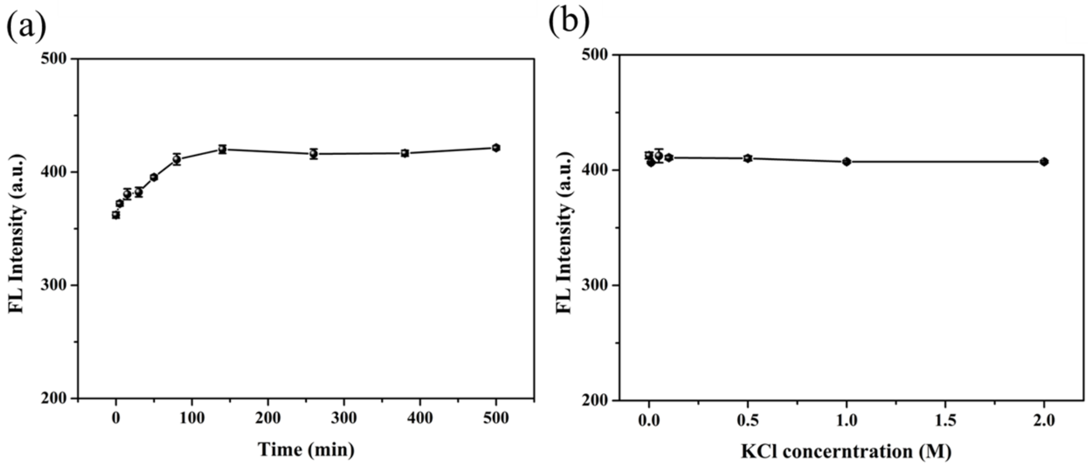

Figure S4. (a) The effect of the time under UV light; (b) the effect of ion strength at different concentration of KCl solution on the fluorescence of g-CNQDs.

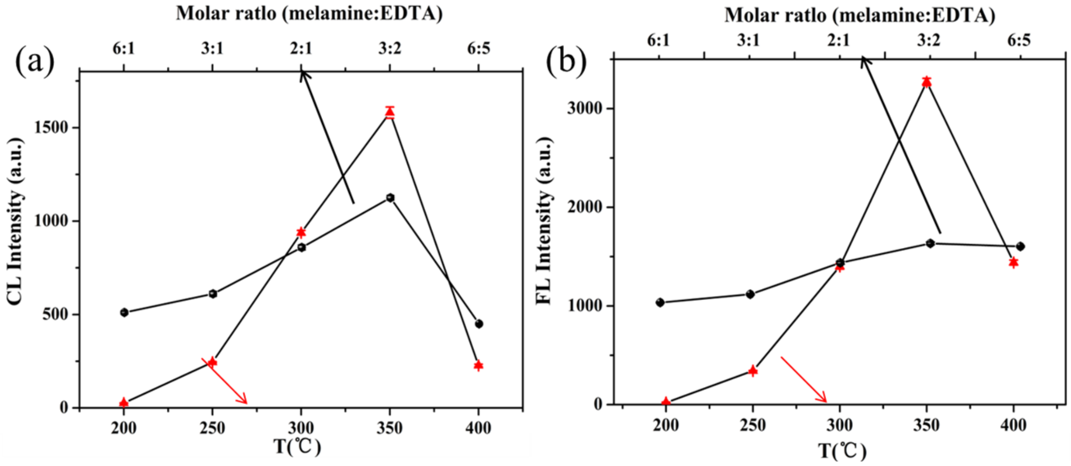

Figure S5. (a) The effect of temperature and molar ratio of melamine to EDTA on the CL intensity of the g-CNQDs; (b) the effect of temperature and molar ratio of melamine to EDTA the FL intensity (excited at 360nm) of the g-CNQDs.

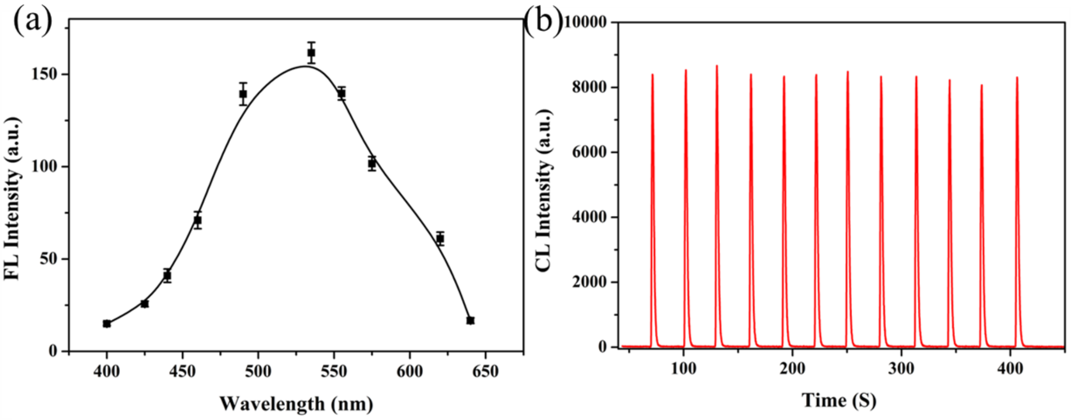

Figure S6. (a) The spectrum for the flow-injection CL system; (b) the reproducibility of the CL system.

Table S1. The synthetic methods in reported papers

Precursor	**Method**	**T/P**	**time**	**QYs**	**Ref.**
dicyanamide HNO_3	1.Heating 2.refluxed	550 120	4 h 24 h	3.0%	1
Melamine	1.heating 2.hydrothermal treatment	550 180	4 h 10 h	16.9%	2
N,N-dimethylformamide (DMF), chloro-sulfonic acid (CSA), H_2SO_4,HCl, HNO_3	acid-driven, microwave-assisted	700 W	40 s	9%	3
$CCl_4$and 1,2-ethylenediamine	reflux, or microwave, or solvothermal heating	80°C 700w 150	60min 3.5min 120min	11%	4
organic amines, H_2SO_4, chlorosulfonic acid (CSA), HNO_3,HCl	microwave heating	700w	60s	8.9%	5
$HCONH_2$	microwave mediated	180°C	30min	29%	6
urea and sodium citrate	low-temperature solid-phase method	180°C	1h	42%	7
guanidine hydrochloride and EDTA	microwave-assisted	700 W	2 min	36%	8

bulk g-C_3N_4	1.acid treatment H_2SO_4 , HNO_3 2.hydro-thermal treatment $NH_3 \cdot H_2O$ 3. ultrasound exfoliation	1.RT 2.180 °C 3.RT	1. 2 h 2. 12h 3. 6 h	–	9

T: Temperature P: Power RT: room temperature

1. L. C. Chen, D. J. Huang, S. Y. Ren, T. Q. Dong, Y. W. Chi, G. C. Chen, *Nanoscale,* 2013, **5**, 225 – 230

2. S. W. Zhang, J. X. Li, M. Y. Zeng, J. Z. Xu, X. K. Wang, W. P. Hu, *Nanoscale*, 2014, **6**,4157–4162

3. S. Liu, L. Wang, J. Q. Tian, J. F. Zhai, Y. L. Luo, W. B. Lu, X. P. Sun, *RSC Adv.* , 2011, **1**, 951–953.

4. S. Liu, J. Q. Tian, L. Wang, Y. L. Luo, J. F. Zhai, X. P.Sun, *J. Mater. Chem.* , 2011, **21**, 11726–11729.

5. S. Liu, J. Q. Tian, L. Wang, Y. L. Luo, X. P.Sun, *RSC Adv.* , 2012, **2**, 411–413.

6. S. Barman, M. Sadhukhan, *J. Mater. Chem.*, 2012, **22**, 21832–21837.

7. J. Zhou, Y. Yang, C. Y. Zhang, *Chem. Commun*., 2013, **49**, 8 605—8607.

8. Y. R. Tang, Y. Y. Su, N. Yang, L. C. Zhang, Y. Lv, *Anal. Chem.*, 2014, **86**, 4528− 4535.

9. X. D. Zhang, H. X. Wang, H. Wang, Q. Zhang, J. F. Xie, Y. P. Tian, J. Wang, Y. Xie, *Adv. Mater.*, 2014, **26**, 4438–4443.