Supplementary material (ESI) for Green Chemistry
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Electronic Supporting Information

for

A large-scale synthesis of photoluminescent carbon quantum dots: a self-exothermic reaction driving the formation of the nanocrystalline core at room temperature †

Bin Bin Chen,[a] Ze Xi Liu,[b] Wen Chan Deng,[b] Lei Zhan,[b] Meng Li Liu[a] and Cheng Zhi Huang[b*]

[a] *Key Laboratory of Luminescent and Real-Time Analytical Chemistry (Southwest University), Ministry of Education, College of Chemistry and Chemical Engineering, Southwest University, Chongqing 400715, China.*

[b] *Chongqing Key Laboratory of Biomedical Analysis (Southwest University), Chongqing Science & Technology Commission, College of Pharmaceutical Science, Southwest University, Chongqing 400716, China. Tel: +86-23-68254659. Fax: +86-23-68866796. E-mail: chengzhi@swu.edu.cn. (C. Z. Huang).*

Materials and methods

Materials. Hydroquinone was commercially available from Aladdin Reagent Co., Ltd. (Shanghai, China). *p*-Benzoquinone was from Huaxia Chemical Reagent Co., Ltd. (Chengdu, China). H_2O_2 and EDA were both purchased from Kelong Chemical Group Co., Ltd. (Chengdu, China). All vitamins including vitamin A (VA), vitamin B1 (VB1), vitamin C (VC), vitamin D3 (VD3), vitamin E (VE), vitamin H (VH) and VB12 were purchased from Aladdin Reagent Co., Ltd. (Shanghai, China).

Synthesis and purification process of the as-prepared CQDs. Hydroquinone (100 mg) was dissolved in 1.75 ml water, and then 2.5 ml H_2O_2 (20%) was added into the solution. Dark brown CQDs solution was observed within 15 min after the addition of 0.75 ml EDA at room temperature. Residual amounts of hydroquinone and EDA were removed through a cellulose ester dialysis membrane (100-500 MWCO) over 24 h. The resulting material was dried by lyophilization to obtain CQDs powder, which were dispersed in water for further characterization and use.

Characterization. The absorption spectral feature of CQDs was measured with a Shmadzu UV 3600 spectrophotometer (Tokyo, Japan). The elemental composition of CQDs was measured with an ESCALAB 250 X-ray photoelectron spectroscopy. The FT-IR spectrum of CQDs was collected on a Hitachi FTIR-8400S Fourier Transform Infrared spectrometer (Tokyo, Japan). The TEM and HRTEM data of CQDs were performed on a Tecnai G2 F20 field emission transmission electron microscope (FEI, USA). The fluorescence spectra of CQDs were recorded with a Hitachi F-2500 fluorescence spectrophotometer (Tokyo, Japan). The Raman spectrum of CQDs on the AgNPs solution was scanned through a LabRAM HR800 laser confocal Raman spectrometer. The fluorescence lifetime of CQDs was measured with a FL-TCSPC fluorescence spectrophotometer (Horiba Jobin Yvon, France).

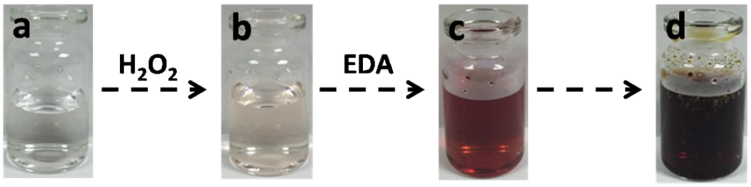

Fig. S1 Scheme of the green synthesis routine of the CQDs. (a) The hydroquinone solution; (b) the reaction solution after adding H_2O_2; (c) the resulting solution after adding EDA; (d) the final CQDs solution.

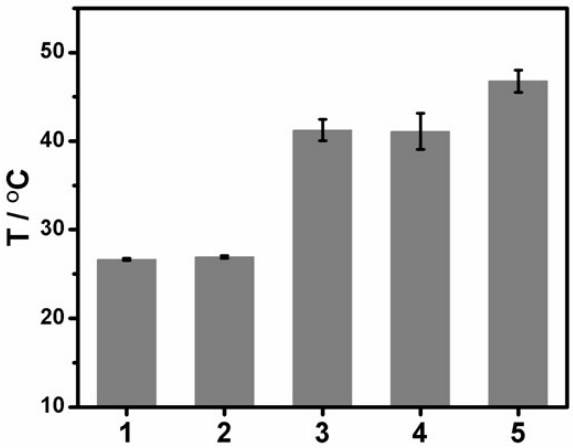

Fig. S2 Increased temperature of exothermic system. 1, Control (water); 2, Hydroquinone + 10% H_2O_2; 3, 15% EDA; 4, Hydroquinone + 15% EDA; 5, *p*-Benzoquinone + 15% EDA. Hydroquinone: 100 mg; *p*-Benzoquinone: 100 mg.

Fig. S3 The digital photographs of CQDs solution (one-pot synthesis) after 15min.

Table S1 Comparison of the characterization of CQDs obtained in our experiment with CQDs prepared by different chemical oxidation methods at room temperature in the literatures.

CQDs	Oxidizing agent	Absolute QY	Relative QY (quinine sulfate as reference)	Reference
C1	HNO_3	12.6%	/	1
C2	HNO_3	2%	/	2
C3	H_2SO_4	13%	/	3
C4	HNO_3	0.43%	/	4
C5	NaOH	/	2.2%	5
C6	HNO_3	1.6%	/	6
C7	H_2SO_4	/	1.95%	7
C8	H_2O_2	24.6%	/	This work

Table S2 The absolute quantum yield (QY) of CQDs prepared by hydrothermal route in oil bath. Hydroquinone: 100 mg; The volume fractions of H_2O_2 and EDA is 10% and 15%; Reaction time: 15 min.

T/°C	Absolute QY/% (n=3)
100	20.4 ± 0.9
125	21.2 ± 1.3
150	22.1 ± 1.6
175	17 ± 1.2
200	15.7 ± 2.0

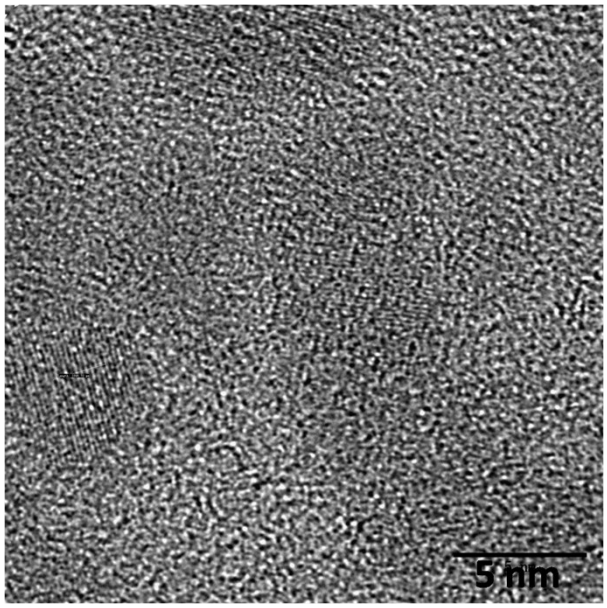

Fig. S4 The HRTEM image of the as-prepared CQDs.

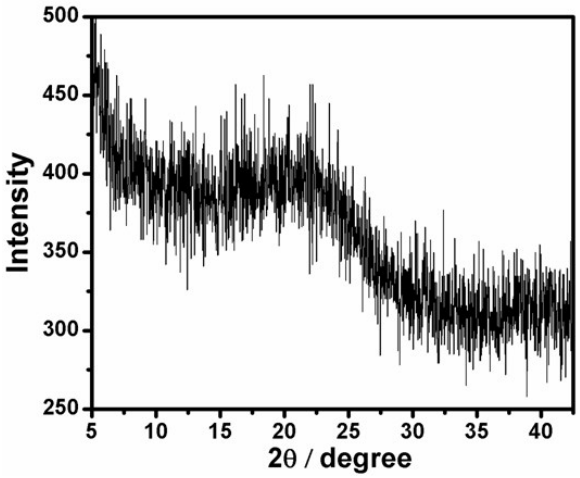

Fig. S5 XRD pattern of the as-prepared CQDs.

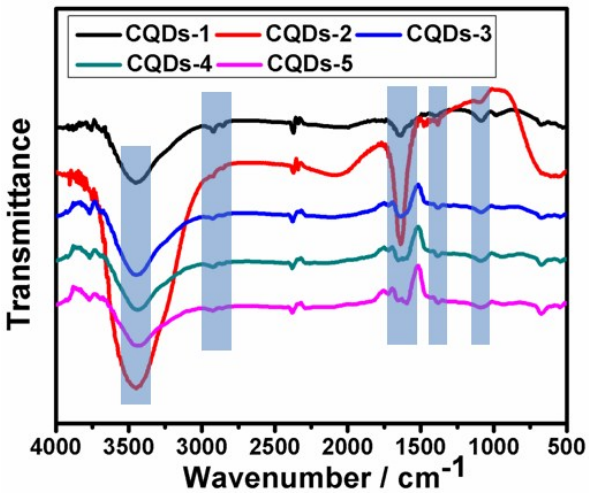

Fig. S6 The FT-IR spectra of CQDs (five randomly chosen components) obtained by silica gel column separation at different time. Mobile-phase, CH_2Cl_2:CH_3OH=20:1; Solid-phase, 300-400 mesh silica gel.

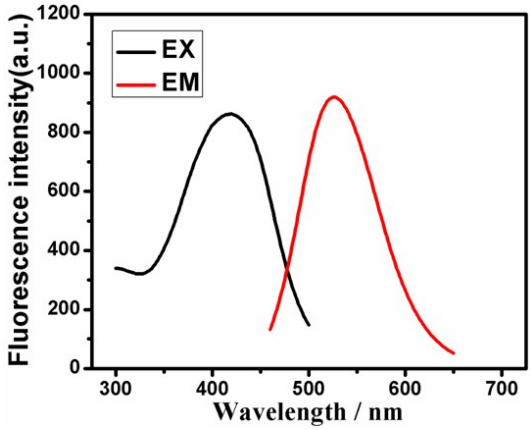

Fig. S7 Excitation (λ_{em} = 525 nm) and emission (λ_{ex} = 370 nm) spectra of CQDs.

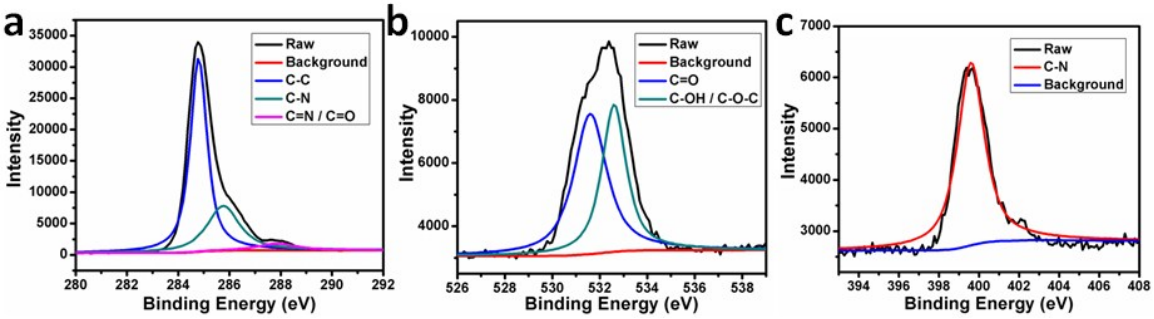

Fig. S8 The surface structure analysis of the as-prepared CQDs. (a) C1s, (b) O1s and (c) N1s spectra of the CQDs.

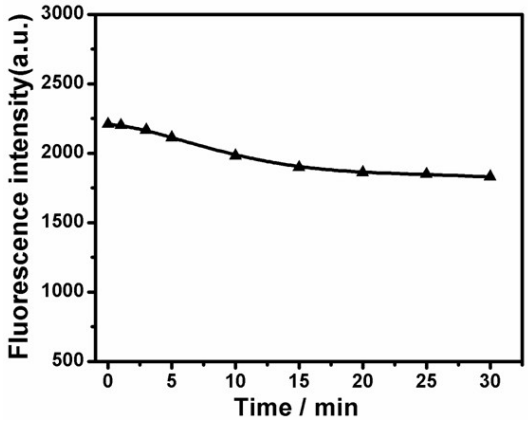

Fig. S9 Fluorescence intensity of CQDs during continuous excitation with a UV beam. Irradiation time was from 0 to 30 min. Excitation wavelength: 370 nm; Emission wavelength: 525 nm. c_{CQDs}, 10 μg/ml.

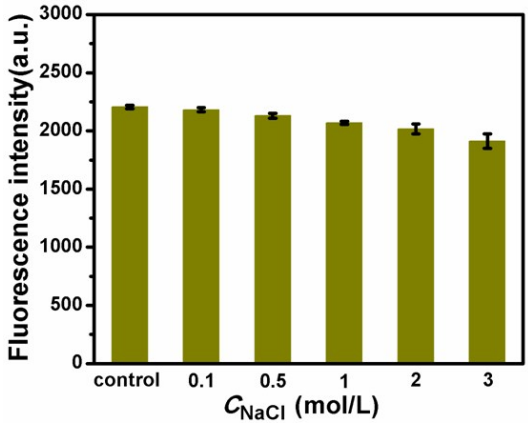

Fig. S10 The stability investigation of CQDs in a salt medium. Excitation wavelength: 370 nm; Emission wavelength: 525 nm. c_{CQDs}, 10 μg/ml.

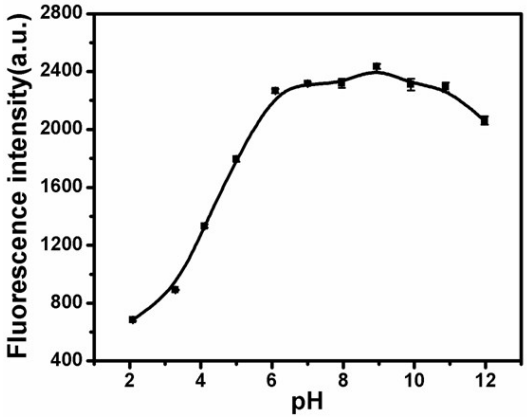

Fig. S11 The stability investigation of CQDs in different BR buffer solution. Excitation wavelength: 370 nm; Emission wavelength: 525 nm. c_{CQDs}, 10 μg/ml.

Table S3 Zeta potentials vary from different pH value. c_{CQDs}, 10 μg/ml.

pH	Zeta potential/mV (n=3)
2.21	1.23 ± 0.44
3.29	-2.67 ± 0.18
4.10	-3.05 ± 0.13
5.02	-3.59 ± 0.40
6.09	-5.24 ± 0.93
7.00	-8.81 ± 0.44
7.96	-10.00 ± 1.41
8.95	-11.40 ± 1.97
9.91	-8.67 ± 1.34
10.88	-9.41 ± 3.71
11.98	-8.76 ± 2.77

Table S4 The comparison of the determination of VB12.

Method	Linear detection range	Detection limit	Reference
Electrochemical method with carbon paste electrode	10-60 μM	5 μM	8
Chemiluminescence analysis with flow injection	2.0×10^{-10}-1.2×10^{-6} g/L (0.15 pM-0.9 nM)	5.0×10^{-11} g/L (0.0375 pM)	9

Electrochemical method with carbon nanotube	5-80 nM	2.1 nM	10
Fluorescent method with graphene oxide nanolayer	/	0.32 μM	11
High-performance liquid chromatography	2.5-12.5 μg/mL (1.84-9.22 μM)	0.92 μM	12
Fluorescent method with reduced carbon dots	1-12 μg/mL (0.7-8.9 μM)	0.1 μg/mL (0.07 μM)	13
Fluorescent method with CQDs	0.75-100 μM	0.2 μM	This work

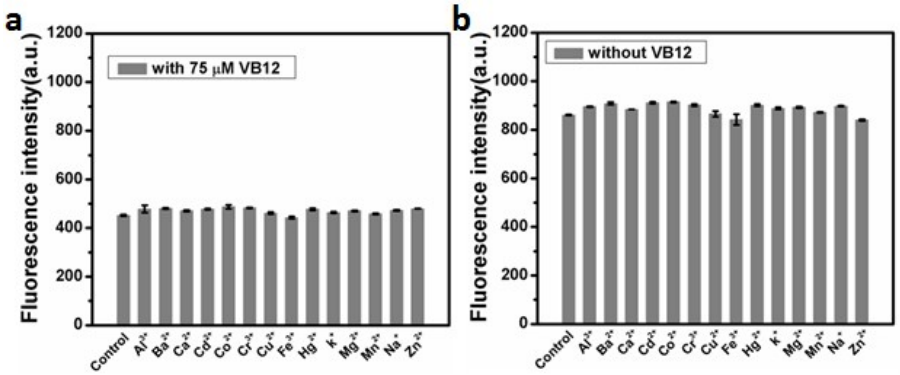

Fig. S12 Selective detection of the CQDs for VB12 in BR buffer (pH 6.09). Fluorescence responses of the CQDs in the presence (a) and absence (b) of 75 μM VB12. The concentrations of metal ions are 100 μM.

Table S5 Concentration values of VB12 in three injection samples obtained from our proposed and UV-Vis spectrophotometry (Chinese pharmacopoeia (2010 edition)), respectively. pH, 6.09; c_{CQDs}, 5 μg/ml.

Sample	UV-Vis spectrophotometry (μM)	Spiked (μM)	Proposed method (μM)	Recovery (%)
1	9.13±0.19	0	9.08±0.23	-
2	9.10±0.15	15	23.78±1.07	97.9
3	8.89±0.16	40	45.86±0.31	92.4

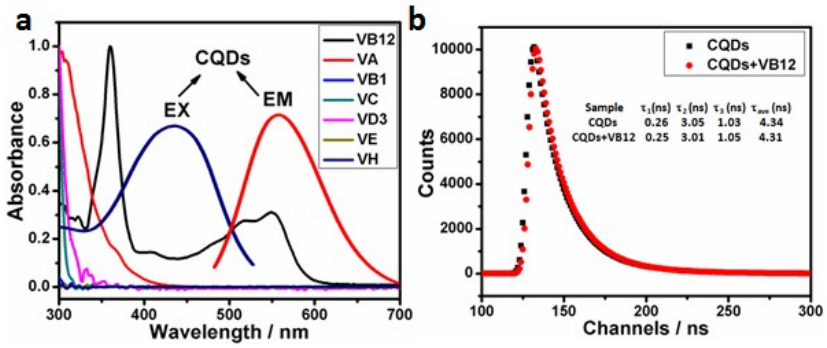

Fig. S13 Sensing principle of the CQDs-based probe for VB12. (a) The UV-Vis absorption spectra of all vitamins and the fluorescence excitation and emission spectra of CQDs; (b) Time-resolved decay of the CQDs in the presence and absence of VB12 (1 μM) in BR buffer (pH 6.09). The inset table presents the lifetime value.

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