Supplementary Material (ESI) for Nanoscale

A novel one-pot route for large-scale preparation of highly photoluminescent carbon quantum dots powders

Juan Hou,[a] Jin Yan,[a] Qi Zhao,[a] Yi Li,[b] Hong Ding,[b] Lan Ding*[a]

[a] College of Chemistry, Jilin University, 2699 Qianjin Street, Changchun 130012, P. R .China.
Fax: +86-431-85112355; Tel: +86-431-85168399; E-mail: dinglan@jlu.edu.cn
[b] State Key Laboratory of Inorganic Synthesis and Preparative Chemistry, College of Chemistry, Jilin University, Changchun 130012, P.R. China

Experimental section

Briefly, a certain proportion of carbon precursor and phosphate dispersed in a certain amount of volume of distilled water into a 250 mL beaker and sonicated for 3 min. The mixture was heated 2—3 min in an ordinary household microwave oven at 750 W, until the water was completely volatilized and brownish-yellow solid powders were obtained. The powders were dissolved in 15 mL × 3 (15.0 mL each time and dissolved three times) ethonal-water (V:V, 80:20), sonicated for 5—10 min and centrifuged at a high speed to remove the insoluble impurities. Anion and cation ion exchange resins were added into the supernatant above and the CDs solution was purified further. Finally, the purified solid samples could be obtained by evaporating the solvents. The CDs, which had excellent solubility in water and some organic solvents, were dissolved in water at a concentration of 1mg mL-1 for advanced analysis.

Interestingly, unlike other synthetic methods reported in previous literatures, CDs powders with high product yield could be obtained directly in one step. The effects of experimental conditions on the photoluminescence (PL) of the CDs were also investigated. The amount of water should be proper. Too little water added, the reaction developed too quickly to control. While too much water added led to time consumption. Generally, 10 mL-15 mL was appropriate. With the increase of microwave irradiation time, the water was evaporated and the nucleis were formed. And then the nucleis grew up. Apparently, the color of solid powders became darker gradually. Long time continuous microwave heating, the powders started becoming black and had no fluorescence which indicated excessive carbonation. In fact, due to the ionic conduction effect, the introduction of phosphates elevated the temperature of the system by the oscillation of the ion through the media, and dramatically shorten the reaction time. Moreover, the phosphates began polycondensation and the generated water molecules volatilized quickly to form lots of holes. During the procedure, the phosphates acted as foaming agents and decentralized the reactants to prevent over-polymerization and non-uniform nucleation growth, so that the CDs obtained had a narrow size distribution. Although the CDs could also be obtained without phosphates added, due to the uneven distribution of the center carbon nuclear, the degree of aggregation was different as well, which led to excessive carbonation and uneven distribution of the CDs.

The initial CDs prepared were solid and the yield was high, so aqueous ethanol could be utilized for preliminarily purifying the sample. The entire purification process was simple without complex equipment requirement and processes referred in most literature, such as centrifugation, dialysis, electrophoresis or other separation technique. Hereon base, the method proposed simplified the preparation process and realized the large-scale production.

This method is not limited to the carbon source mentioned in this communication, other small molecular organic compounds with hydroxyl groups are also applicable. Experimental conditions for some other carbon sources are listed in Table S1.

Compared with the CDs prepared from citric acid (CDs-CA), the CDs prepared from triammonium citrate (CDs-ACA) increased the absorbance in the range of 200 to 500 nm (see Fig. 4) and greatly enhanced the PL intensity (Fig. S2). The quantum yield is also greatly improved (Table S2). Interestingly, their maximum emission wavelength was very similar. Therefore, the amino groups of the ACA might act the role of self-passivation agent and small molecular organic compounds with amino groups were probably superior for the PL characters.

Characterization.

The morphology and dimension of the sample was revealed with a JEOL JEM-2100 transmission electron microscope (TEM) operating at 200 kV. Fluorescence spectroscopy was performed with a Shimadzu RF-5301 PC spectrophotometer equipped with a xenon lamp using right-angle geometry. UV-vis absorption spectra were recorded using a Shimadzu UV-2550 spectrophotometer. In the experiments, a 1 cm path-length quartz cuvette was used. IR spectra were taken on a Nicolet AVATAR 360 FT-IR spectrophotometer. The X-ray diffraction (XRD) was investigated by a Shimadzu XRD-6000 spectrometer.

Quantum Yield Measurements.

The quantum yields of the CDs obtained were measured by following equation:

$$Q = Q_R \frac{I}{I_R} \frac{OD_R}{OD} \frac{n}{n_R^2}^2$$

Where Q is the quantum yield, I represents the measured integrated emission intensity (Emission wavelength: 345nm), n is the refractive index, and OD is the optical density measured on a UV-Vis spectrophotometer which is limited less than 0.05. The subscript R refers to the reference fluorophore of known quantum yield. Herein, we chose quinine sulfate dissolved in 0.1 M H_2SO_4 as a reference

whose quantum yield was 0.546 (Q_R=0.546) and the CDs were dissolved in distilled water. The datas of the as-prepared CDs were shown in Table S2.

General procedure for detection of tetracycline hydrochloride (Tc).

The amount of 40.0 μL CDs-ACA solution (50 μg mL^{-1}), 40.0 μL Tris-HCl buffer solution (pH=7.8) and different concentrations of Tc were diluted with deionized water to the total volume of 2.0 mL in a 4.0-mL centrifuge tube. Subsequently, the mixture was vortex-mixed and placed for 3 min before measurements.

The fluorescence spectra were recorded at the spectrophotometer by fitting the excitation wavelength at 350.0 nm, during which the spectral bandwidths were kept at 10.0 nm. Fluorescence intensity was measured at 440.0 nm.

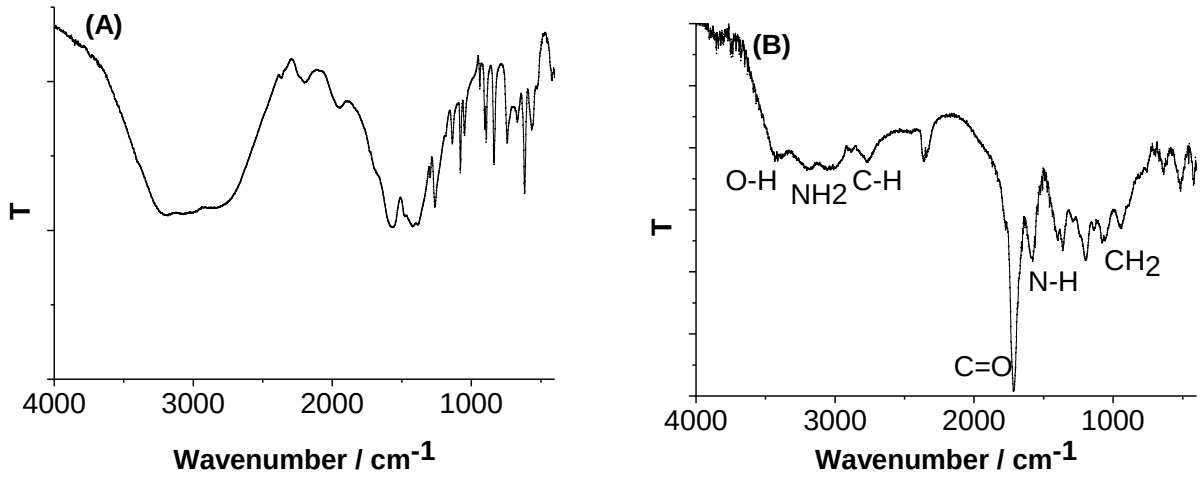

Fig.S1 FTIR spectra of (A) ACA and (B) CDs-ACA.

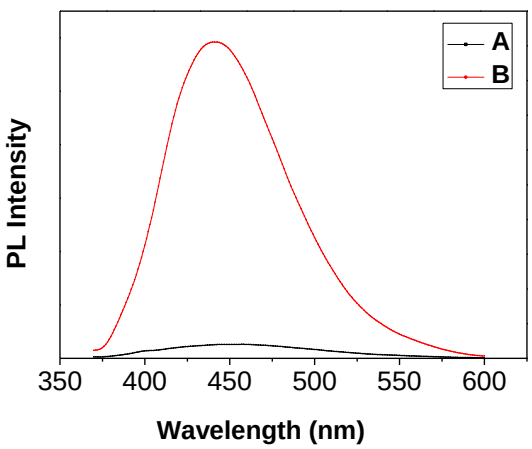

Fig. S2 PL emission spectra of the CDs-ACA (A: red line) and the CDs-CA (B: black line).

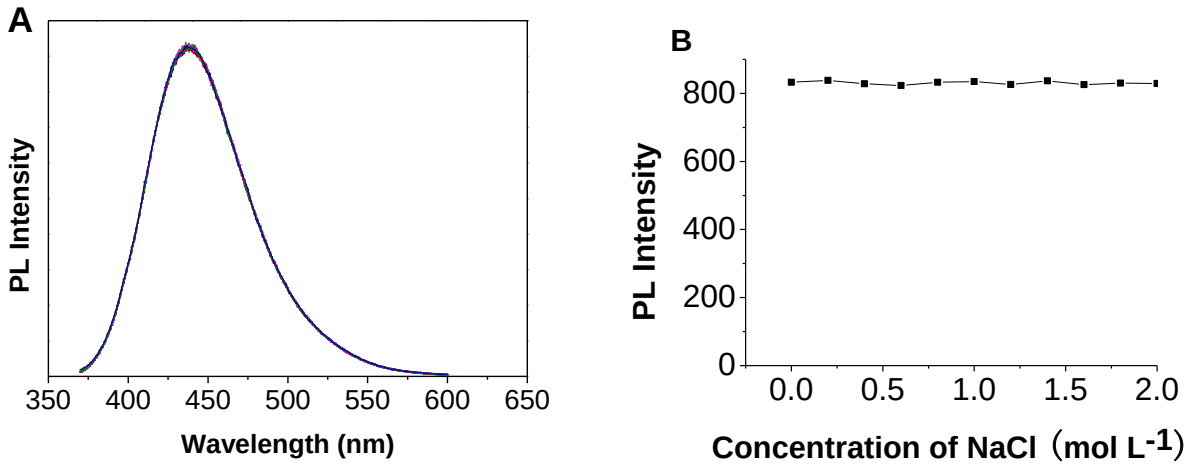

Fig. S3 Effect of the concentration of NaCl from 0 to 2 M and increase with 0.2 M increments on the PL intensity of the CDs-ACA. Excitation wavelength: 350nm; Emission wavenlength: 440nm.

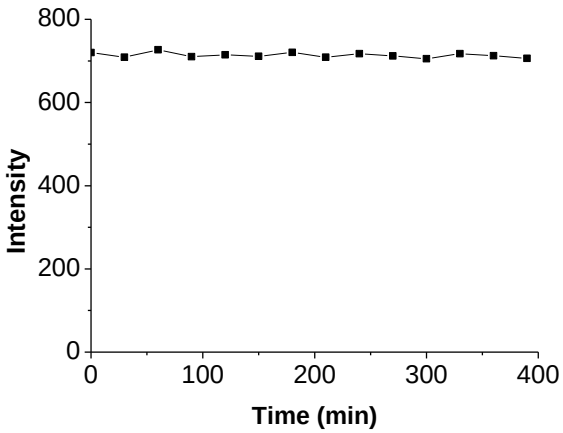

Fig. S4 PL intensity of the CDs-ACA during continuous excitation at 365nm with a UV beam. Irradiation time start from 0 min to 420 min and increase with 30 min increments. Excitation wavelength: 350 nm; Emission wavenlength: 440 nm.

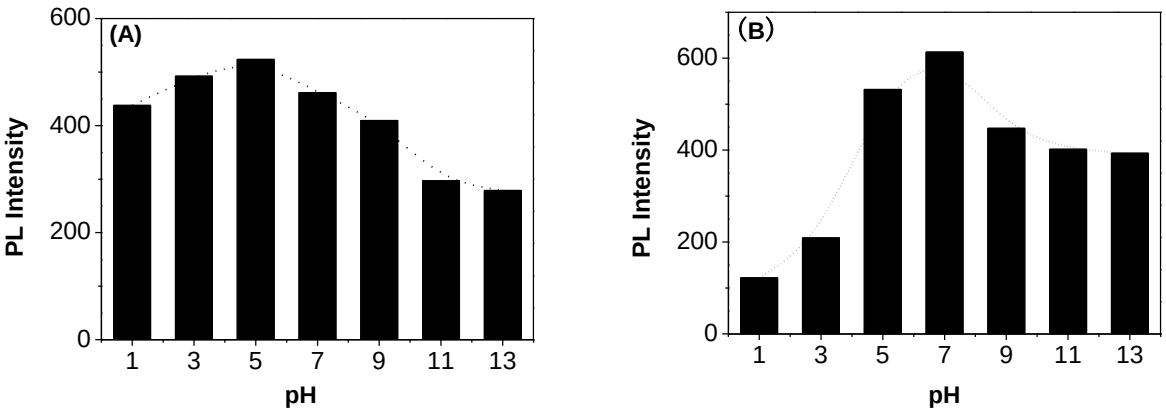

Fig. S5 Effect of solution pH on the PL intensity of (A) CDs-ACA; (B) CDs-CA. Excitation wavelength: 350nm; Emission wavenlength: 440 nm.

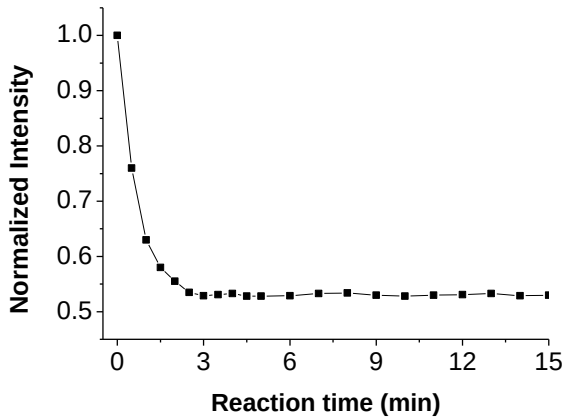

Fig. S6 Effect of 0.05 mmol L^{-1} Tc on the PL intensity of original CDs-ACA at different reaction times.

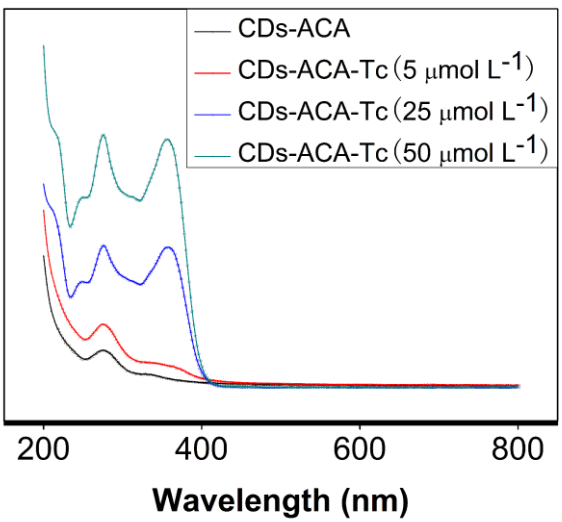

Fig. S7 Change in the absorbance spectra of CDs-ACA with adding different concentrations of Tc (pH=7).

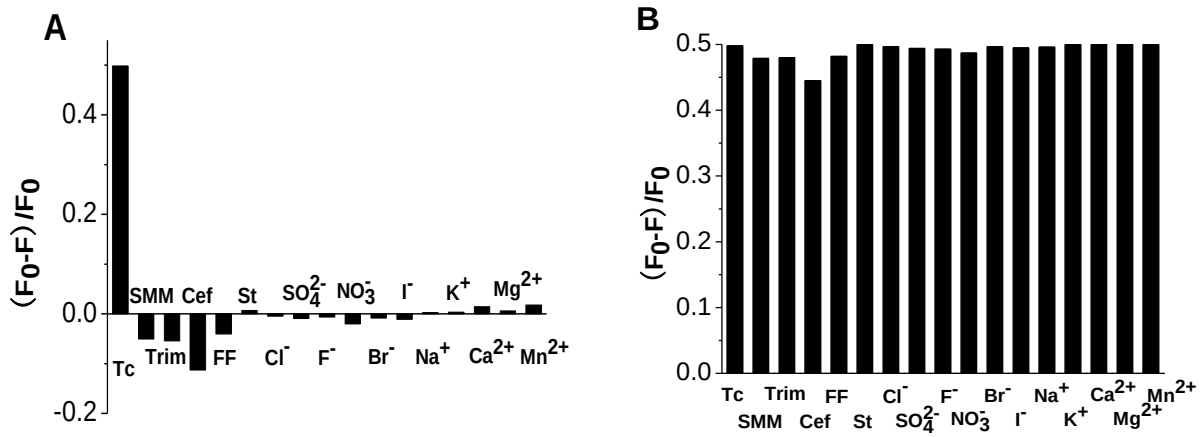

Fig. S8 Effect of a serious of pollutants on the PL intensity of CDs-ACA alone (A) and CDs-ACA-Tc (0.05 mM) system (B). Concentrations: Tc, SMM, Trim, Cef, FF, St, Ca^{2+}, Mg^{2+}, Mn^{2+}, 0.05 mM; Cl^-, SO_4^{2-}, F^-, NO_3^-, Br-, I^-, Na^+, K^+, 0.5 mM. Concentration of CDs-ACA (1 μg mL^{-1}); Excitation wavelength: 350 nm; Emission wavenlength: 440 nm.

Table S1 The detail parameters and experimental results of different precursors (carbon source) to form the CDs.

Carbon source	The amount of carbon source (g)	The amount of phosphates (g)	solvent	Microwave power	Microwave irradiation time	The amount of CDs obtained (after purification) (g)
glucose	3	1	10ml water	750w	2min10s	0.5859
sucrose	5	1	15ml water	750w	2min20s	1.0045
citric acid (CA)	5	1	10ml water	750w	2min10s	1.2264
ammonium citrate (ACA)	5	1	10ml water	750w	2min20s	1.3528
glycine	4	1.5	10ml water	750w	2min	0.6741
tyrosine	4	1.2	6ml water and 4ml formic acid	750w	2min30s	0.6213

Table S2 The quantum yield (QY) of the CDs from different carbon sourse.

carbon source	I	OD	n	n_R	QY
glucose	3955.493	0.041	1.33	1.33	6.9%
sucrose	3498.600	0.031	1.33	1.33	7.2%
citric acid (CA)	2140.663	0.021	1.33	1.33	5.6%
ammonium citrate (ACA)	11453.275	0.044	1.33	1.33	14.3%
glycine	7614.280	0.047	1.33	1.33	8.9%
tyrosine	7463.1976	0.050	1.33	1.33	8.2%

OD_R=0.017, I_R=16895.945; Emission wavelength: 345 nm, the range of detection wavelength: 370 nm—580 nm.