Supplementary Information

One-pot green synthesis of optically pH-sensitive carbon dots with upconversion luminescence

Xiaofang Jia,[a,b] *Jing Li*[a] *and Erkang Wang**[,a]

[a]State Key Laboratory of Electroanalytical Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun, Jilin 130022, P. R.China

[b]Graduate School of the Chinese Academy of Sciences, Beijing, 100039, P. R. China

*Corresponding author: Prof. Erkang Wang, Fax: +86-431-85689711, Tel: +86-431-85262003, Email: ekwang@ciac.jl.cn

Experimental section

Chemicals and materials: L-ascorbic acid (AA) was purchased from Sigma-Aldrich (St. Louis, MO, USA). $Cu(Ac)_2 \cdot H_2O$, NaCl and other used metal salts were obtained from Beijing Chemical Works (Beijing, China). Water used throughout all experiments was purified with the Millipore system.

Apparatus and characterization: UV-visible absorption spectra were recorded using a Cary 50 Scan UV-visible spectrophotometer (Varian, USA). Fluorescence spectra were collected on a Fluoromax-4 spectrofluorometer (Horiba Jobin Yvon Inc. France) using 3 nm/ 3 nm slit widths of excitation and emission. A drop of the CDs in aqueous solution was carefully placed on the copper grid and dried at ambient condition for transmission electron microscopy (TEM) characterization. TEM and High-resolution transmission electron microscopy (HRTEM) measurements were made on a JEM-2100F high-resolution transmission electron microscope （Netherlands）operated at 200 kV. The X-ray photoelectron spectroscopy (XPS) measurements were performed on an ESCALAB-MKII 250 photoelectron spectrometer (VG Co.) with $Al_{K\alpha}$ X-ray radiation as the X-ray source for excitation. Infrared spectra were collected on a VERTEX Fourier transform infrared (FTIR) spectrometer (Bruker). The ^{13}C nuclear magnetic resonance (NMR) spectra of the CDs dissolved in D_2O were recorded on a Bruker 600 M spectrometer. The luminescence decay curve was measured on a FLS920 spectrofluorometer (Edinburgh Instruments, UK) equipped with EPL375 pulsed laser diode. Differential pulse voltammetry was performed with a model CH Instrument 832B electrochemical workstation (Shanghai Chenhua Equipments, China) in 0.1 M sodium phosphate buffer.

Preparation of CDs: In a typical experiment, ascorbic acid (0.1761 g) was dissolved in water (19 mL) to form a clear solution, followed by adding a $Cu(Ac)_2$ solution (1 mL, 0.1 M). The mixture was placed in 50 mL conical flask with stirring for 10 min at room temperature. Then the resulting product was maintained at 90 °C water bath under stirring for 5 h. The reaction mixture was cooled to room temperature, and then centrifuged at 8000 rpm to retain the supernatant.

Without the addition of $Cu(Ac)_2$ solution, luminescent CDs were also obtained with a longer reaction time. Furthermore, CDs with different emission wavelengths can be readily prepared through fine adjustment of the experimental conditions (e.g., reaction time, temperature and concentration of the starting materials).

Fig. S1 The digital photograph of CDs solution (one-pot synthesis) after centrifugation at 8000 rpm. The upper volume of the beaker is 1000 mL. For large-scale preparation of CDs in one pot, 7.0448 g ascorbic acid was dissolved in water (760 mL) to form a clear solution, followed by adding a $Cu(Ac)_2$ solution (40 mL, 0.1 M). After centrifugation at 8000 rpm, the solvent of suspension was removed with the aid of a rotary evaporator. Then the final sample was obtained by vacuum drying at 60 °C. The CDs with measured weight up to 6.2 g was obtained in one pot.

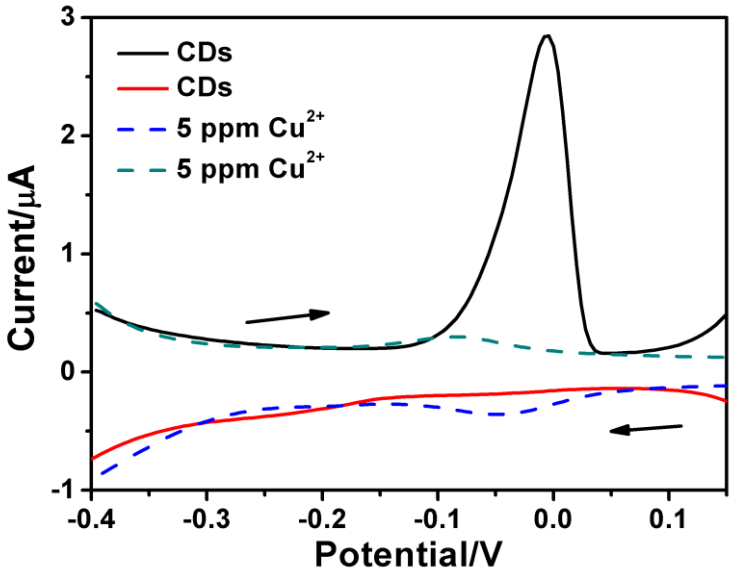

Fig. S2 Differential pulse voltammetry of CDs (solid line) and 5 ppm Cu^{2+} (dashed line) in 0.1 M sodium phosphate buffer (pH=7.0). The DPV was firstly scanned from 0.4 V to -0.4 V and subsequently from -0.4 V to 0.4 V., with a pulse amplitude 50 mV, pulse width 0.2 s, and pulse period 0.5 s. 5 ppm Cu^{2+} was served as a control by substituting the CDs in the procedure above. Compared with Cu^{2+} ions, the stronger oxidative peak without reductive peak revealed the reduction of Cu^{2+} ions with ascorbic acid resulting in the formation of metallic Cu^0 structures.

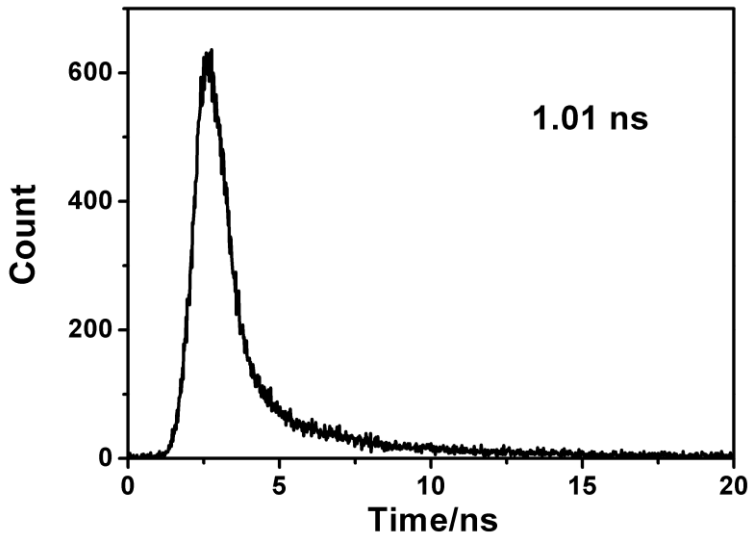

Fig. S3 Fluorescence decay profile (λ_{ex} = 375 nm, λ_{em} = 450 nm) of CDs.

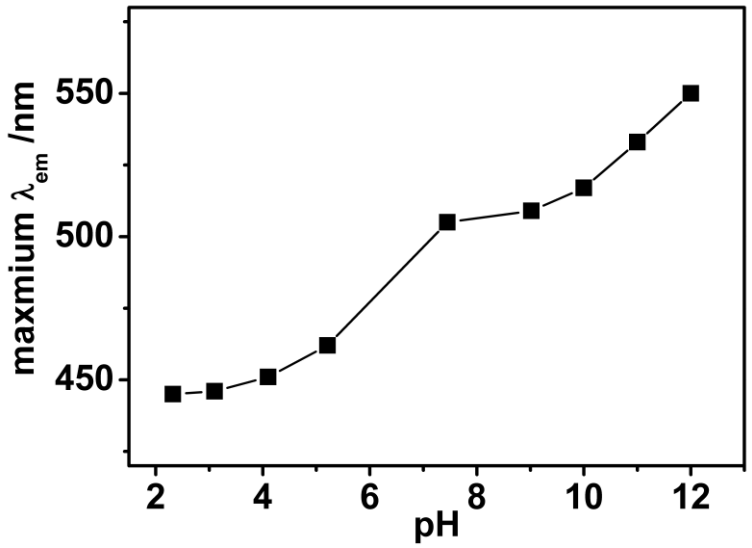

Fig. S4 Dependence of maximum emission wavelength of CDs aqueous solution on the pH value.

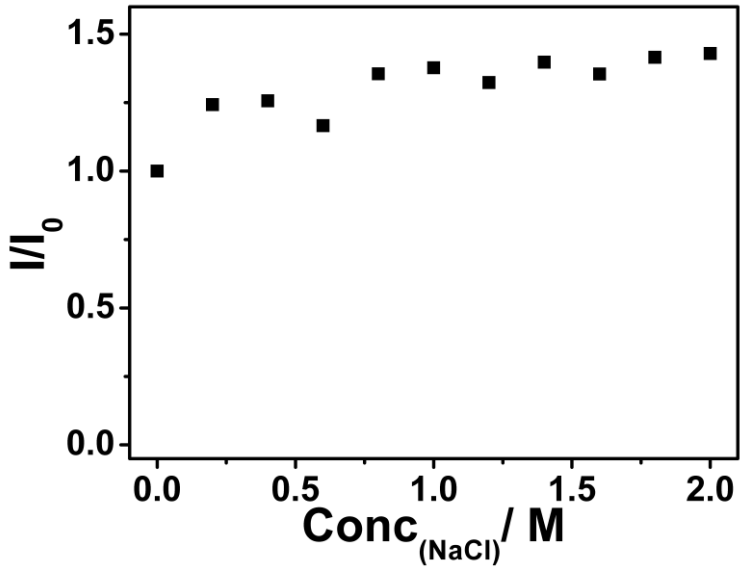

Fig. S5 Effect of ion strength on the PL intensity ratio. I and I_0 denote the PL intensity of CDs after and before adding different concentration of NaCl, respectively.

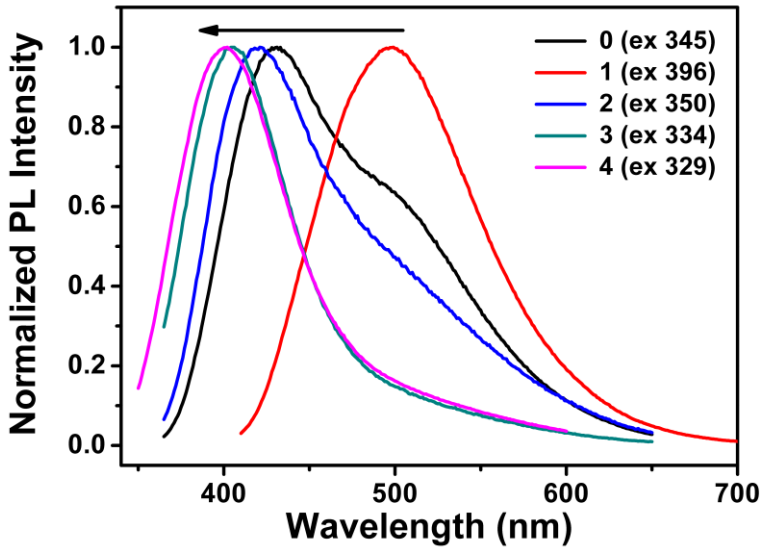

Fig. S6 Normalized PL intenstiy spectra (excitation at maximum emission) of different fraction. Aqueous solution of the as-prepared CDs was purified by column chromatography on silica gel using water as eluent. Colored fractions were collected for PL characterization. 0 denotes untreated as-prepared CDs sample; 1 and 4 represent the first and the last fraction, respectively.

Table R1. Measured average zeta potential of the CDs at various pH values.

pH	2.56	7.10	10.65
zeta potential (mV)	15.2	-3.57	-15.5