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Supporting Information (ESI) for

Facile synthesis of carbon dots in immiscible system with excitation-independent emission and thermally activated delayed fluorescence

Juan Hou, Long Wang, Ping Zhang, Yuan Xu and Lan Ding[*]

College of Chemistry, Jilin University, 2699 Qianjin Street, Changchun 130012, PR China

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[*] Corresponding author.
Phone: +86-431-85168399.
Fax: +86-431-85112355.
E-mail: dinglan@ jlu.edu.cn

Experimental section

Materials

All the reagents were of analytical grade and used as received without further purification. Octadecenoic acid (Oct) and acetic acid were obtained from Beijing Chemical Corp (Beijing, China). High purity water with a resistivity of 18.2 MΩ cm was obtained from the United States Milli-Q purification system.

Preparation of CDs

Firstly, 13 mL of acetic acid, 2 mL of distilled water and 10 mL of Oct were mixed in a 100 mL beaker. Stirring or ultrasonic treatment were not required. Subsequently, the mixture was heated in a common household microwave oven at 375 W for 10 min. In this open system, the reaction temperature was measured by a thermocouple. After natural cooling to room temperature, the CDs products were extracted from the system with 20 ml of water. The CDs powders (about 0.102 g) could be obtained by evaporating the water.

The preparation mechanism is schematically shown in Scheme 1. In this work, microwave irradiation provides continuous, homogeneous and efficient heating. The preparation procedure involved three raw materials, and each of these three reactants (acetic acid, water and Oct) played a vital role.

Choosing the carbon precursors

Acetic acid is chosen as the carbon precursor. Firstly, acetic acid has rich oxygen-containing groups (-COOH), which endows the CDs with reasonable hydrophilic properties. CDs with excellent water-solubility have potential applications in bio-sensor and cellular imaging. Secondly, acetic acid has simple structure and chemical component, which contributes to the formation of CDs with homogeneous surface defects. Meanwhile, one acetic acid molecule may react with another to produce acetic anhydride. Acetic anhydride possesses good dehydrating ability, thus accelerating the carbonization reaction. After the reaction, excess acetic acid can be removed from the system easily by evaporation. No further purification process is required including centrifugation, dialysis and filtration, *etc*. Other common liquid- or solid-state precursors (ethylene glycol, milk, citric acid, *etc*.) cannot achieve the above goals. Solid-state precursors (such as citric acid, glucose and amino acids) require to be dissolved in more water. The carbon precursors will precipitate with the water evaporation, thus decreasing the product yield. Other liquid-state precursors (such as ethylene glycol, milk and polyvinyl alcohol) cannot be carbonized well at low temperature. Additionally, the relatively complex chemical components will introduce a large number of by-products and impurities, increasing the difficulty in purification.

Effect of the initial amount of water

The carbonization reaction requires a suitable temperature. The carbonization reaction cannot be promoted at low temperature, whereas a high degree of carbonization will occur at high temperature. Fig. S1 illustrates the change of temperature during the preparation process. Herein, water servers as a strong microwave absorption medium. Initially, the temperature of the open system can be elevated rapidly during the microwave treatment. Afterwards, the vaporization of water molecules can remove the excessive heat and the temperature is controlled at the boiling point of water (100 ^{o}C). During the carbonization reaction, water can be refilled into the system. Therefore, the carbonization reaction starts and continues at a relatively constant temperature. The nanobubbles generated from water vapor can mix the reactants well and prevent over-polymerization and non-uniform nucleation growth, thereby leading to a uniform size distribution of CDs.

As shown in Table S3, if too much water is added to the system, acetic acid will be diluted. Drastic boiling water vapor will prevent the nucleation, and the size of CDs is smaller (Fig. S14A). Drastic boiling nanobubbles will also take acetic acid vapor away, leading to a significant decrease in the product yield. If we decrease the initial amount of water to 1 mL, the reaction time is prolonged. With the loss of water vapor, the reaction temperature cannot be controlled well. The CDs show inhomogeneous distribution (Fig. S14B).

As a control, carbon dots can also be prepared in the same manner without the addition of water (designated as CDs-2). In this case, the reaction temperature is controlled by the vaporization of acetic acid (~117 ^{o}C). As shown in Fig. S14C, the size of CDs-2 presents an average value of about 3.1 nm. The CDs-2 show bright fluorescence emission under the UV beam, however, no afterglow can be observed when we turn off the UV beam. XPS survey of CDs-2 demonstrates that the atomic contents of C and O are 73.6% and 26.4%, respectively (Fig. S15). The oxygen content of CDs-2 is lower than that of CDs prepared by the proposed method. It is speculated that the increase of carbonization reaction temperature will benefit the formation of C=C core component. According to previous reports,[S1,S2] the aromatic carbonyl groups are considered as the origin of the triplet state emission. Both the surface states and oxygenous defects of the CDs-2 are different from the CDs obtained by the proposed method. Thus, delayed fluorescence cannot be observed from CDs-2. In spite of this, the effect of specific surface structure on the emission has not been answered yet and is worth further study.

Effect of the amount of Oct

Oct has weak microwave absorption capability, high boiling point and viscosity, which can effectively capture hot acetic acid vapor. Thus the loss of the carbon precursors can be suppressed effectively. As evidence in Table S4, the product yield of CDs decreases sharply when the amount of Oct is less than 10 mL. If 15 mL of Oct is added to the system, too long reaction time will also lead to the volatilization of acetic acid and reduce the product yield. So, 10 mL of Oct is appropriate. Furthermore, Oct serves as the water-immiscible solvent. After the preparation, Oct can be separated from the system and recycled.

Briefly speaking, the starting materials for the CDs preparation are simple, inexpensive and easily accessible. The synthetic process can be controlled by relatively mild conditions at a steady temperature. With the aid of boiling of water, extra stirring and ultrasound treatment are not required. Meanwhile, pure water-soluble CDs can be directly obtained without complicated purification process. The proposed synthetic method is facile, safe and cost effective.

Characterization

The morphology and dimension of CDs were revealed with a JEOL JEM-2100 transmission electron microscope (TEM) operating at an accelerating voltage of 200 kV. Prior to the TEM analysis, the samples was dropped on a Cu grid coated with a thin carbon film and then dried under ambient condition. X-ray diffraction (XRD) measurement was performed on a Shimadzu XRD-6100 spectrometer. Fourier transform infrared spectra (FT-IR) spectrum was accomplished by a Nicolet AVATAR 360 FT-IR spectrophotometer using KBr powder as the sample matrix. X-ray photoelectron spectroscopy (XPS) analysis was recorded by an ESCA Lab 220i-XL electron spectrometer. Raman spectrum was obtained on a Renishaw-1000 Raman spectrometer with 532 nm wavelength incident laser light. UV-vis absorption spectrum was achieved by a Shimadzu UV-2550 spectrophotometer. Fluorescence spectra were recorded on a Shimadzu RF-5301 PC spectrophotometer equipped with a xenon lamp using right-angle geometry. In the experiment, a 1 cm path-length quartz cuvette was used. The fluorescence lifetime was recorded by using the Edinburgh Instrument (FLS 920).

Quantum Yield Measurements

The quantum yield (QY) of the CDs in water was calculated by following equation:

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

Where QY is the quantum yield, I represents the measured integrated emission intensity (Emission wavelength: 360 nm), 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. QY of CDs was calculated to be about 40.1% at the excitation of 360 nm. (Table S1)

Applications of the CDs

CDs as invisible fluorescent ink for patterning

The CDs solution was used as an invisible fluorescent ink for painting various patterns. The CDs solution was filled into a pen and drawing patterns at room temperature. These patterns were invisible under daylight but visible under 365 nm excitation (Fig. S6).

CDs as fluorescent sensors for pH

As illustrated in Fig. S11, the fluorescence of the CDs is sensitive in a broad pH range of 3-11, and significant decrease of FL intensity can be observed with increasing pH value. The FL switching experiments can be repeated for at least 7 consecutive cycles with excellent reversibility during the two-way switching process between pH=3 and pH=11. Good fitted linearity curve with pH variation (5.0-9.0) can be obtained, which demonstrates the CDs can be served as potential pH biosensors in biological or environmental systems. Such pH-dependent FL behavior may be attributed to change of the electronic effect on the surface of CDs due to protonation-deprotonation, which eventually lead to the change of FL intensities.[13]

To estimate the selectivity of the pH sensor in complex system, the stability of the CDs was investigated by the interference of some other common ions and compounds (0.01 M), which may coexist in environmental or biological system (Fig. S12). The relative FL intensity was determined by calculating the ratio of the FL intensities of the CDs solutions in the presence and absence of the interference ions. Little effects were observed on the FL intensity ratio of the CDs, which reveals the sensors possess high selectivity and good anti-interference capability.

pH detection for environmental water samples and human urine samples

The pH-sensitive properties of the CDs could be applied to the pH detection of environmental water and human urine samples. Three types of water samples (lake water, rain water and tap water) were collected and passed through a microfiltration membrane. Human urine samples were collected from 3 healthy volunteers. After the sample collection, the fluorescence analysis was conducted immediately. As shown in Table S2, the results from our proposed method are consistent with those from a 510 pH meter, which demonstrates that the CDs can be utilized as a fluorescent pH indicator for real water samples and human urine samples.

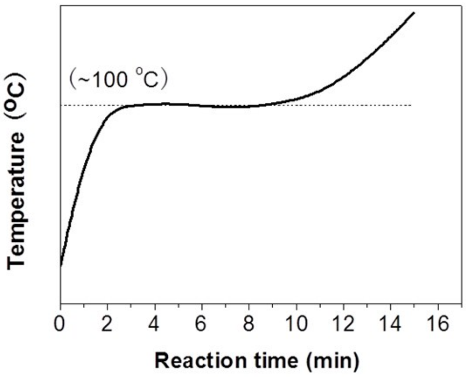

Fig. S1 The change of temperature during the preparation process

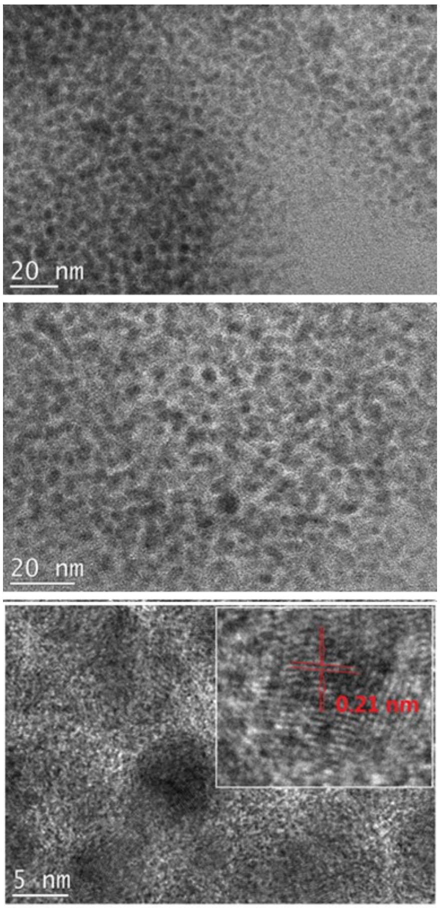

Fig. S2 Additional TEM images of the as-prepared CDs

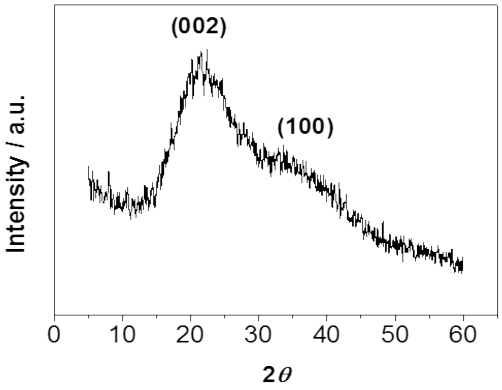

Fig. S3 XRD pattern of CDs

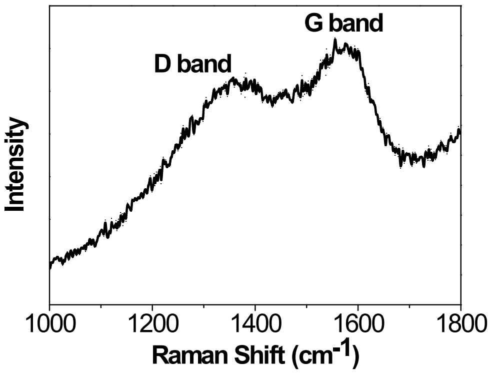

Fig. S4 Raman spectrum of CDs

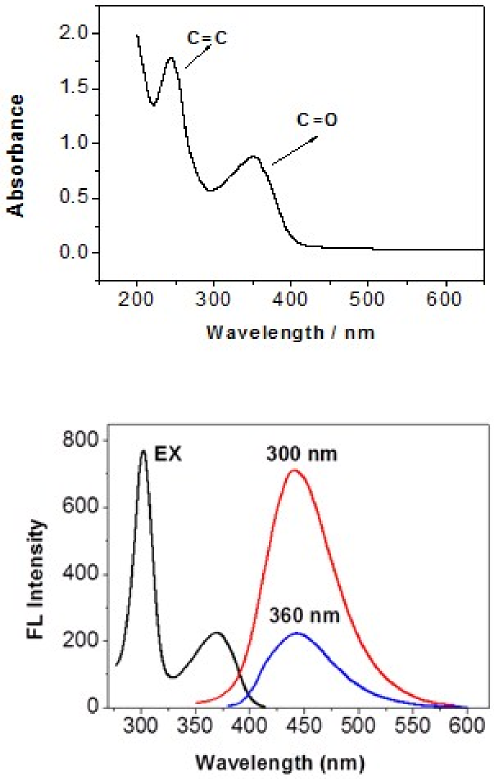

Fig. S5 Absorption spectrum, FL excitation and emission spectra of CDs

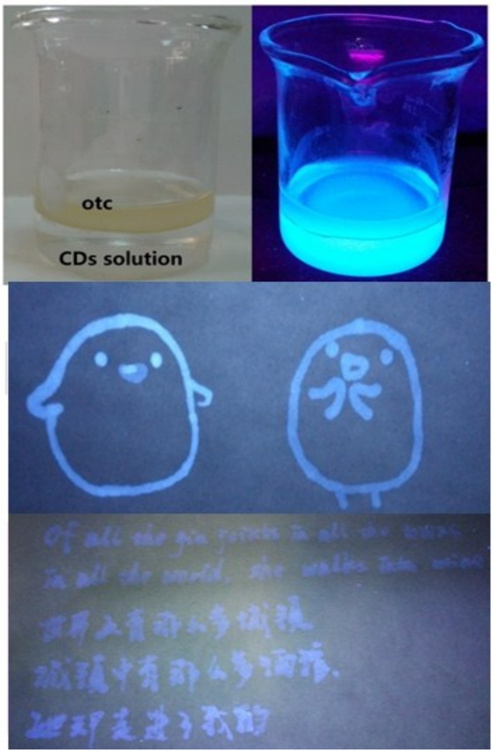

Fig. S6 The image of CDs and fluorescence patterns under visible light and a UV beam of 365 nm

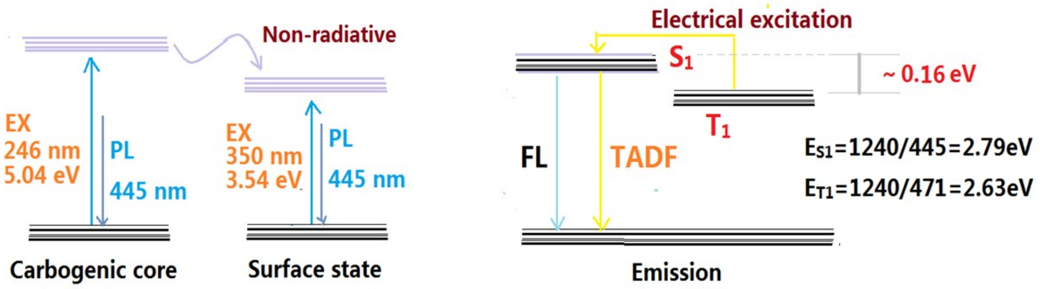

Fig. S7 The proposed luminescence mechanism for the as-prepared CDs.

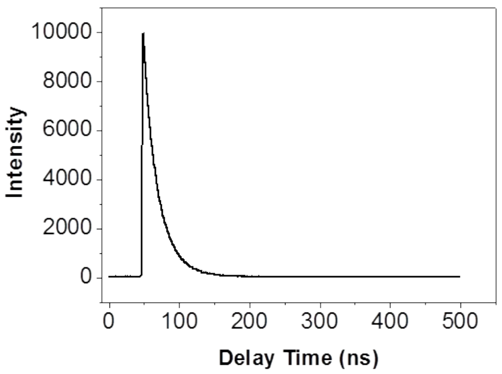

Fig. S8 Fluorescence decay curve for the CDs at 300 K in air.

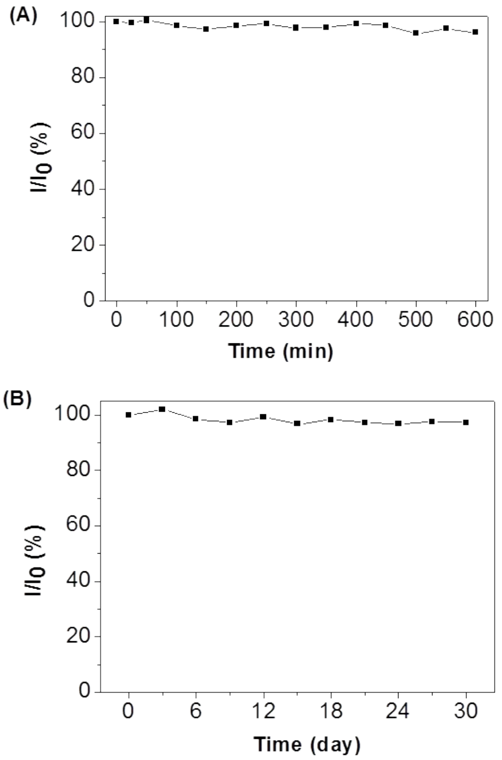

Fig. S9 (A) FL intensity of the as-prepared CDs during continuous excitation at 365nm with a UV beam (Excitation wavelength: 300 nm); (B) FL stability of the as-prepared CDs for 1 month at room temperature in air-tight closed tubes.

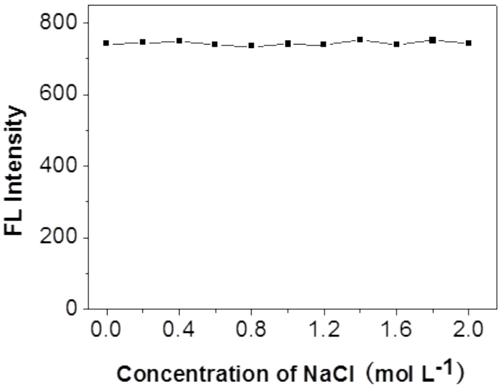

Fig. S10 Effect of the concentration of NaCl from 0 to 2 M and increase with 0.2 M increments on the FL intensities of CDs.

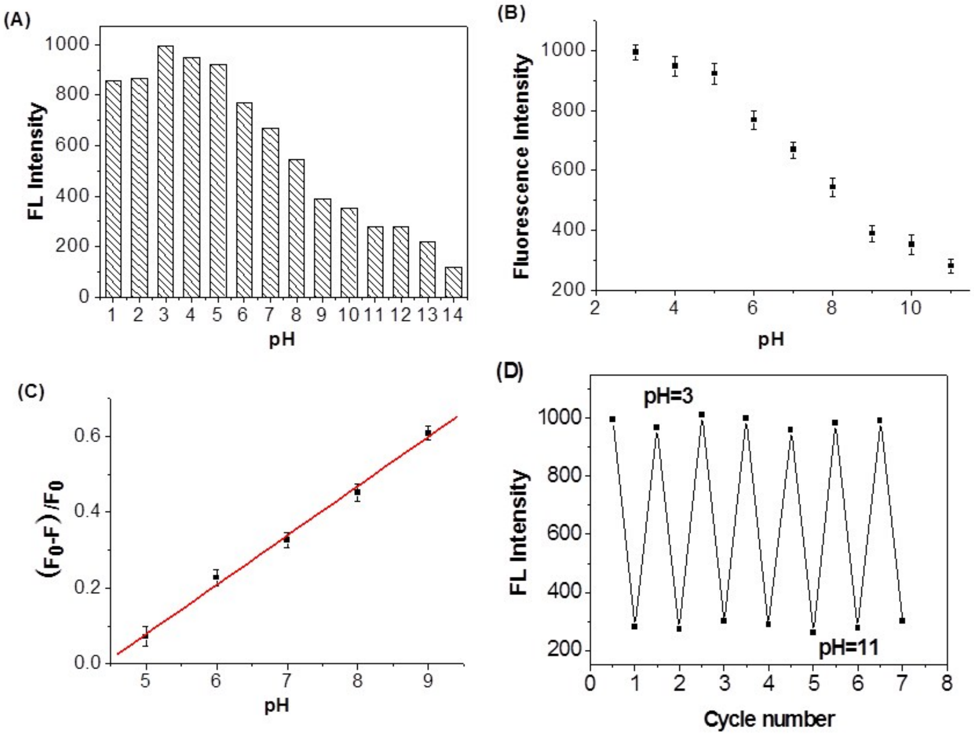

Fig. S11 (a) FL intensity of CDs at various pH values; (b) The relationship between the FL intensity and pH variation in the range of 3~11; (c) pH variation around physiological condition (5.0~9.0), and the fitted linear curve is $(F_0\text{-}F)/F_0$=0.1301pH-0.5731, R^2=0.9948 (F_0 is the FL intensity of the CDs at pH=3); (d) FL intensity upon the cyclic switching of CDs under alternating conditions of pH = 3 and pH = 11.

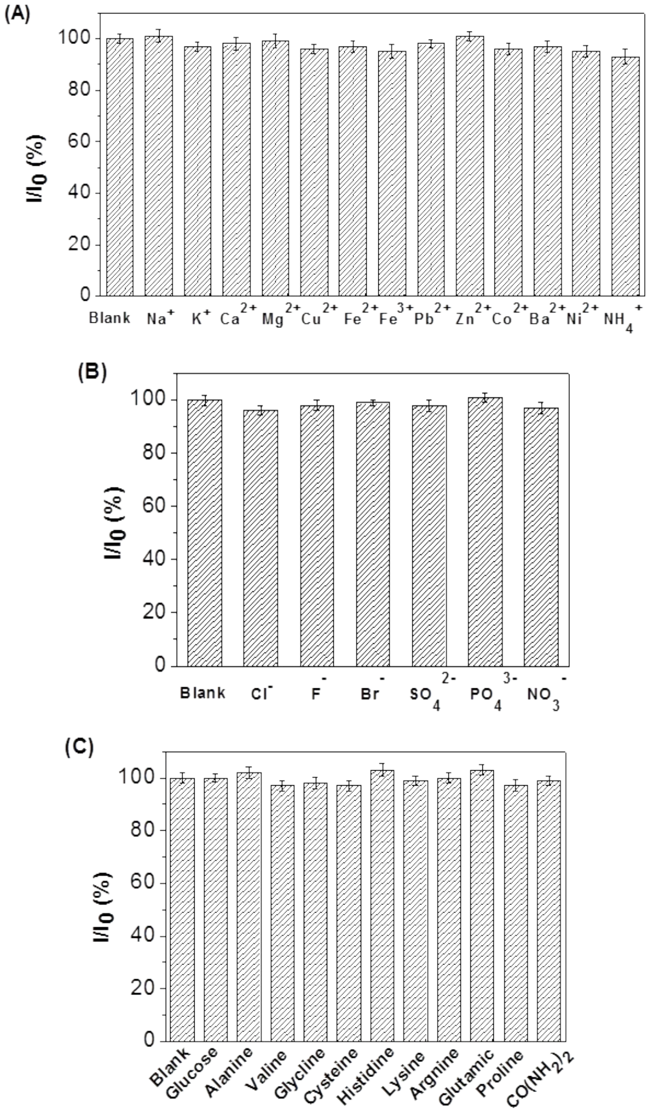

Fig. S12 Selectivity experiments of the CDs sensor towards (A) cation ions, (B) anion ions and (C) various compounds. Error bars denote standard error measurements obtained by three parallel experiments.

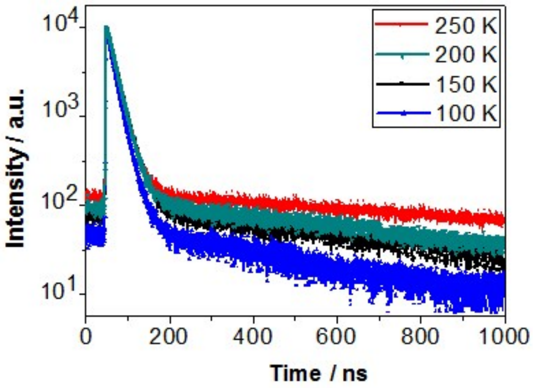

Fig. S13 FL decay profiles for the CDs measured at 100-250 K.

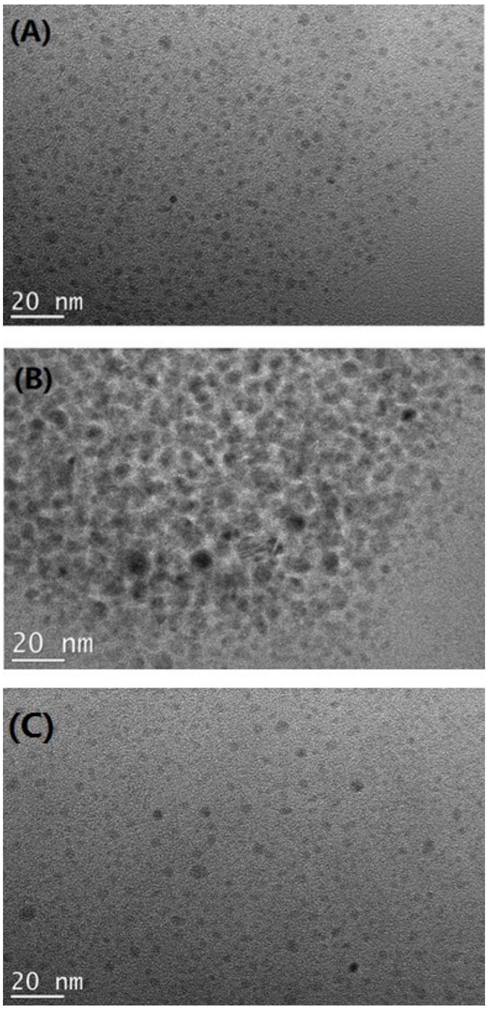

Fig. S14 TEM images of the CDs, conditions: (A) the amount of water was 5 mL; (B) the amount of water was 1 mL; (C) the amount of water was 0 mL.

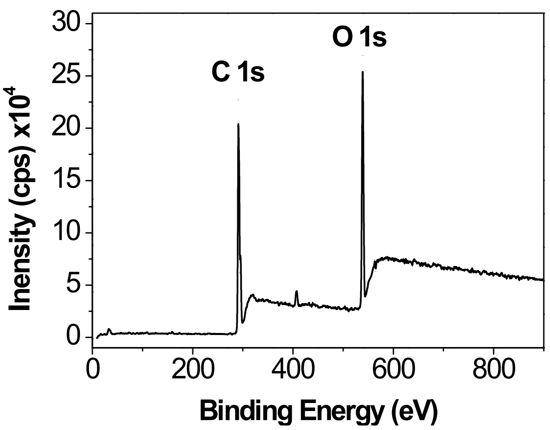

Fig. S15 XPS spectrum of the CDs-2 (conditions: Oct 10 mL, acetic acid: 13 mL, water: 0 mL)

Table S1 The quantum yield (QY) of the CDs

	I	OD	n	n_R	QY
CDs	40033	0.030	1.33	1.33	40.1%
Quinine sulfate	72643	0.041	1.33	1.33	54.6%

Excitation wavelength: 360 nm, the range of detection wavelength: 360 nm—580 nm.

Table S2 pH detection in real water samples and human urine samples

Sample	pH_1 (measured by a pH meter)	pH_2 (obtained by the proposed method)	RSD (%, n=3)
Lake water	7.56	7.70	2.4
Rain water	6.22	6.31	2.5
Tap water	7.25	7.11	2.1
Urine 1	6.45	6.58	2.6
Urine 2	6.87	6.69	1.9
Urine 3	7.25	7.41	2.3

Table S3 Effect of the amount of water

Water (mL)	Product yield (g)	Time to reach 100 ^{o}C (s)	Average size (nm)	TEM image
1	0.015	243	6.6	Fig. S13B
2	0.102	124	5.8	Fig. 1A and Fig. S2
5	0.037	32	2.9	Fig. S13A

Table S4 Effect of the amount of Oct

Oct (mL)	Product yield (g)	Reaction time (min)
15	0.094	22
10	0.102	10
5	0.022	8
0	0	2

References

S1 Y. Deng, Dongxu Zhao, X. Chen, F. Wang, H. Song and D. Shen, *Chem. Commun*., 2013, **49**, 5751–5753.

S2 X. Dong, L. Wei, Y. Su, Z. Li, H. Geng, C. Yang and Y. Zhang, *J. Mater. Chem. C,* 2015, **3**, 2798–2801.