Supporting information

One-step facile synthesis of novel β-amino alcohol functionalized carbon dots for the fabrication of selective copper ions sensing interface based on the biuret reaction

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Quantum yield (QY) measurements: The QY was measured according to a previous report.[1] Briefly, quinine sulfate in a 0.1 mol L^{-1} H_2SO_4 aqueous solution (QY is 0.546) was selected as a reference for CDs. The QYs were determined by comparing the integrated fluorescence intensity (excited at 360 nm for quinine sulfate and CDs) and the absorbance value (less than 0.05 at the excitation wavelength) of samples with that of the references. The slope method was used to calculate the QYs of CDs using the equation:

$$QY_x = QY_{std}\,(m_x/m_{std})(n_x/n_{std})^2$$

Where QY is the quantum yield, m is the slope determined by the curves in Fig S1, n is the refractive index (1.33 for water and 0.1 mol L^{-1} H_2SO_4 aqueous solution). The subscript "std" refers to the quinine sulfate and "x" refers to the CDs.

Table S1 The detailed information of the QY of quinine sulfate and CDs hydrothermal reacted for different time.

		Calibration equation	R^2	QY (%)
Quinine sulfate		IF[a] = 651856A + 2826.1	0.9988	54.6
CDs	4 h	IF = 56543A + 599.71	0.7516	4.7
	6 h	IF = 70712A + 37.69	0.9739	5.9
	8 h	IF = 91892A - 389.34	0.9211	7.7
	10 h	IF = 98055A - 176.34	0.9682	8.2
	12 h	IF = 79728A + 20.358	0.9792	6.7
	14 h	IF = 69964A + 279.62	0.9679	5.9

[a]IF: the integrated FL intensity.

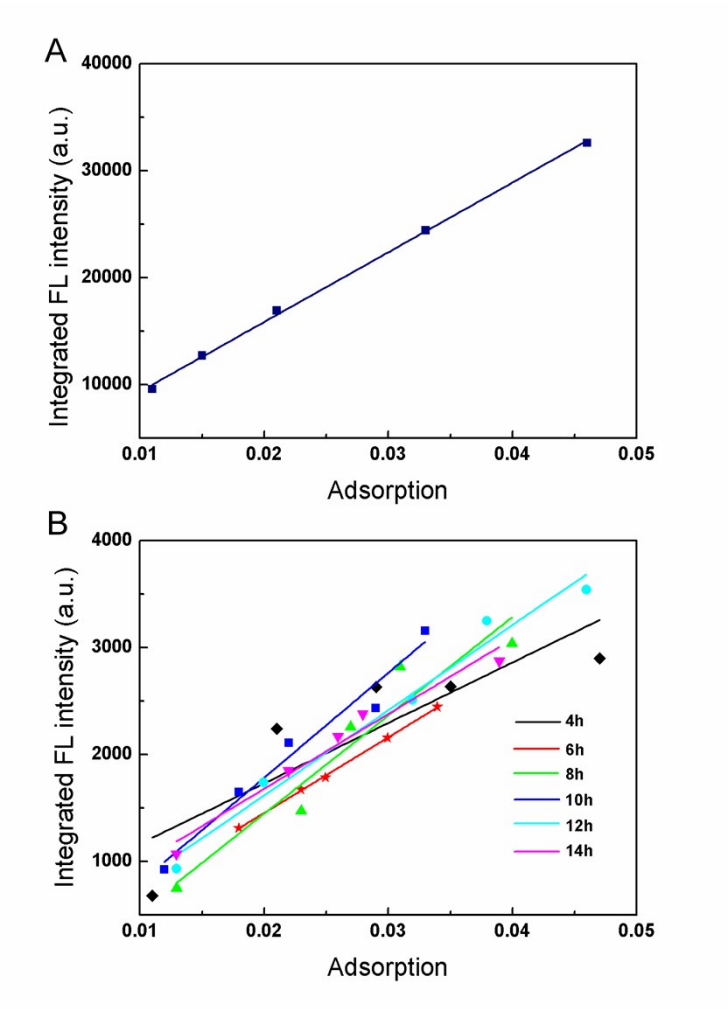

Fig. S1 (A) Fluorescence and absorbance of quinine sulfate and (B) CDs hydrothermal treatment for different time.

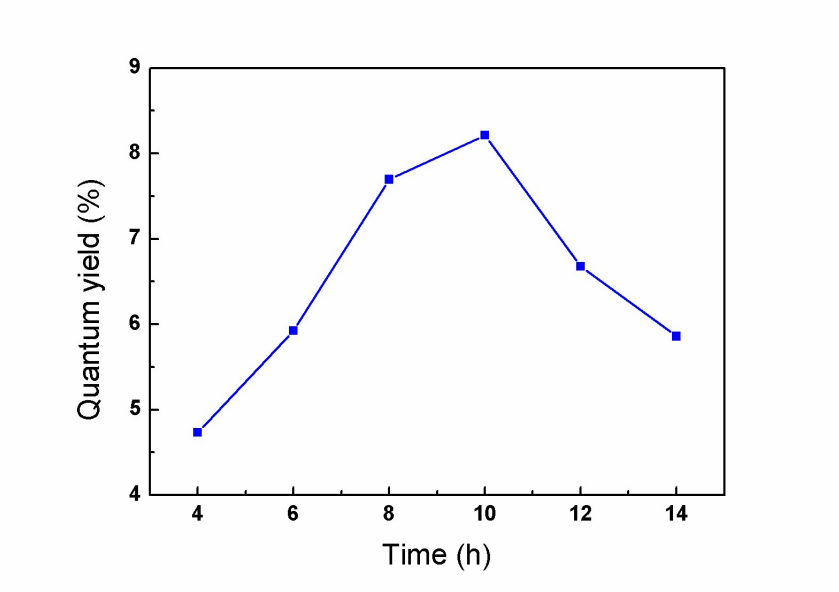

Fig. S2 The quantum yields of the CDs with different hydrothermal reaction time.

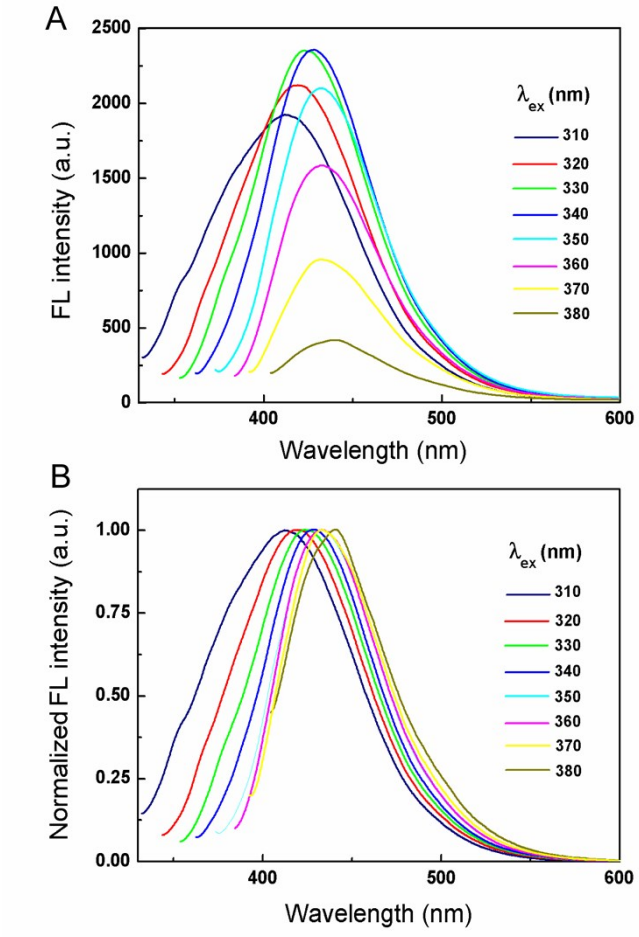

Fig. S3 (A) Fluorescence emission spectra of CDs (with progressively longer excitation wavelengths from 310 nm to 380 nm in 10 nm increment). (B) The

normalized fluorescence emission spectra.

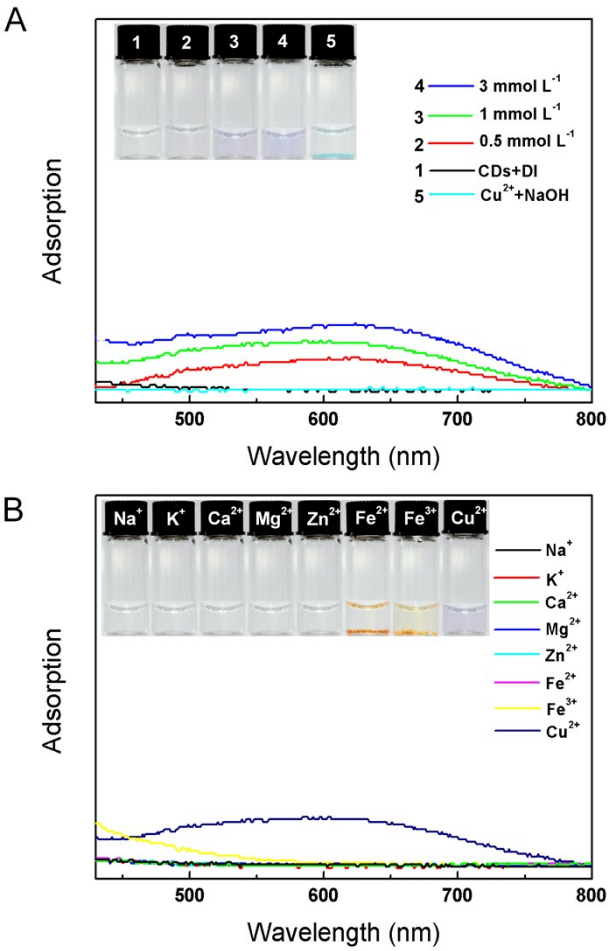

Fig. S4 (A) The UV-Vis spectra of NaOH (0.1 mol L^{-1}) at the presence and absence of Cu^{2+} and CDs. The inset images show the corresponding color change under daylight. (B) The UV-Vis spectra of the supernatants of the CDs and NaOH (0.1 mol L^{-1}) with other metal ions and Cu^{2+} (1 mmol L^{-1}). The inset images show the corresponding color change under daylight.

UV-Vis sensing procedure: CDs and NaOH (0.1 mol L^{-1}) were mixed according to the mass concentration ratio of 1.5:1 (CDs: NaOH). Then, different amounts of Cu^{2+} were added to form a series of concentrations. The formation of violet complex

during the biuret reaction was observed under daylight after 500 s. The solutions were centrifuged at 10000 rpm for 10 min and the supernatants were measured by UV-visible spectrophotometer. The mass concentration ratio of CDs and NaOH was optimized among 2:1-1:2 to improve the sensitivity of visual observation, when the ratio was 1.5: 1 (CDs: NaOH), the violet complex was capable to be observed by naked eyes at the LOD of 1 mmol L^{-1}.

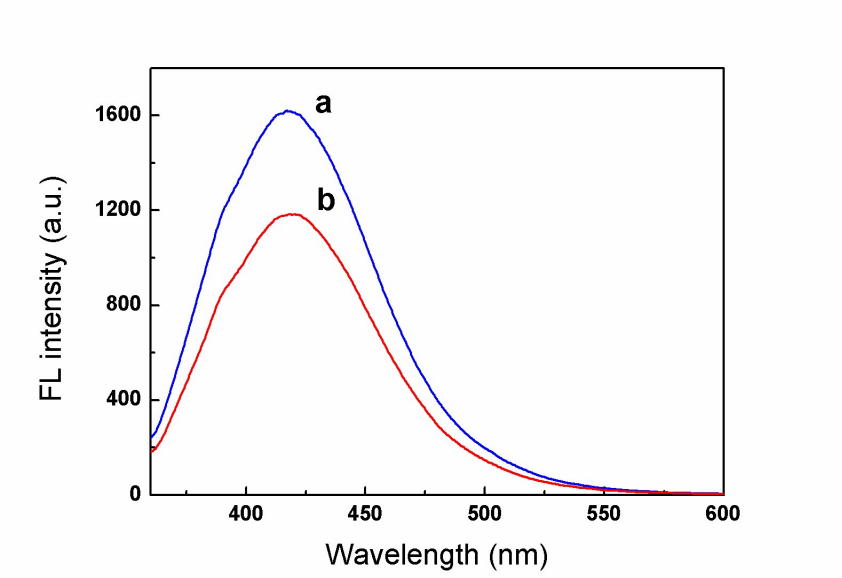

Fig. S5 The fluorescent emission spectra of CDs before (a) and after (b) the addition of 20 μmol L^{-1} Cu^{2+}.

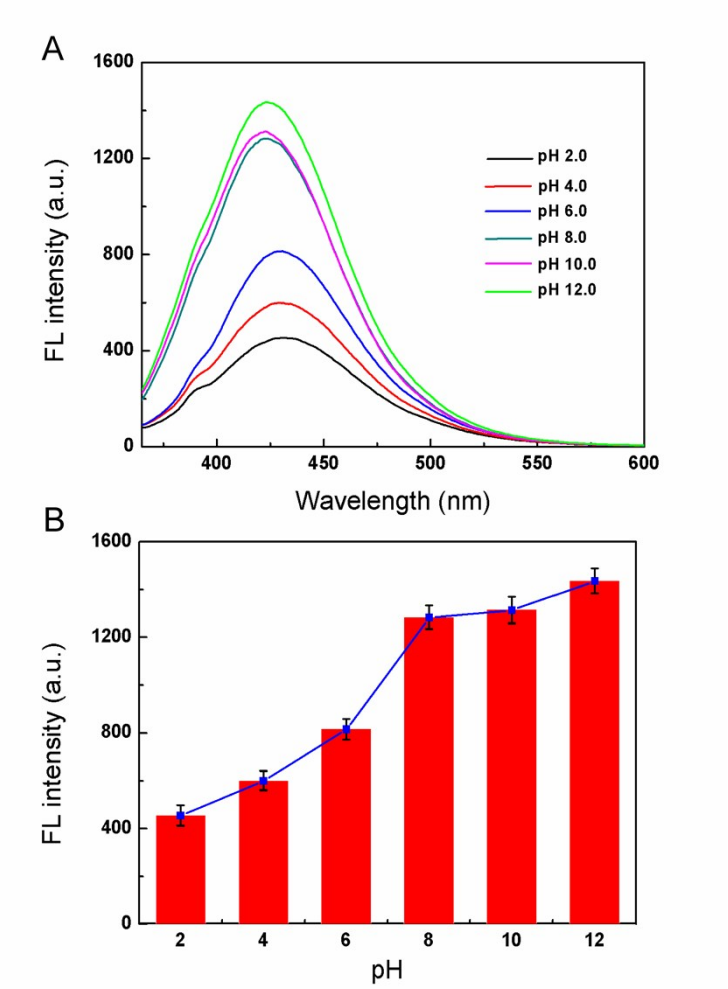

Fig. S6 (A) The fluorescence spectra of the CDs in PBS with different pH values (0.01 mol L^{-1}, pH 2.0-12.0). (B) Changes of the fluorescence intensity of the CDs upon different pH values of PBS (0.01 mol L^{-1}, pH 2.0-12.0).

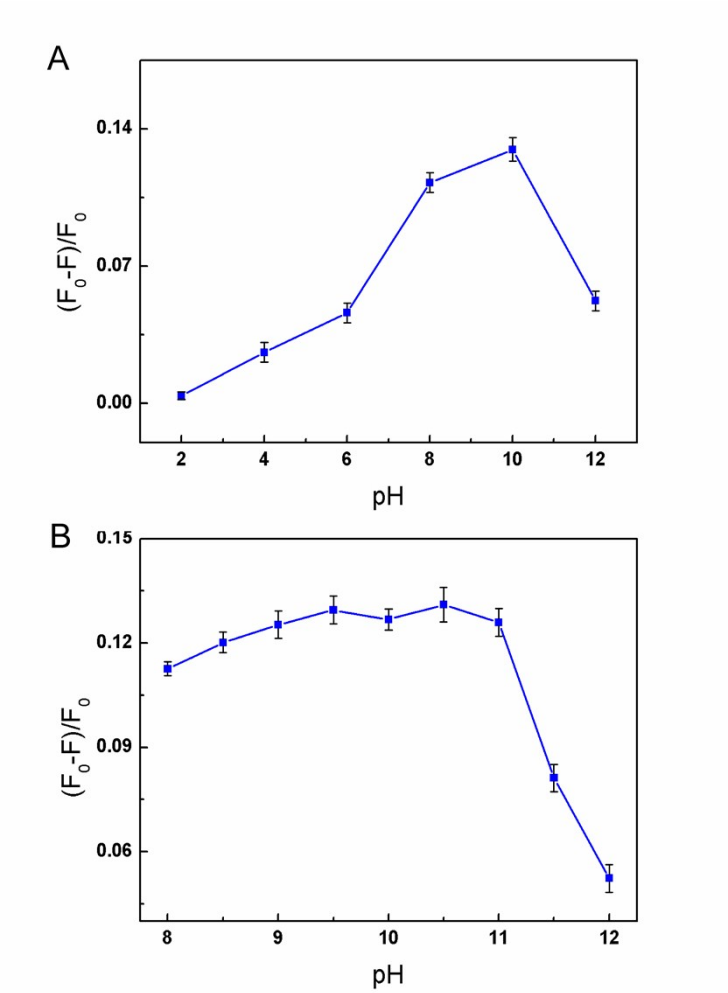

Fig. S7 (A) Plot of fluorescence quenching efficiency of the CDs as a function of pH values (2.0-12.0) with the addition of 20 μmol L^{-1} Cu^{2+}. (B) Plot of fluorescence quenching efficiency of the CDs as a function of pH values (8.0-12.0) with the addition of 20 μmol L^{-1} Cu^{2+}.

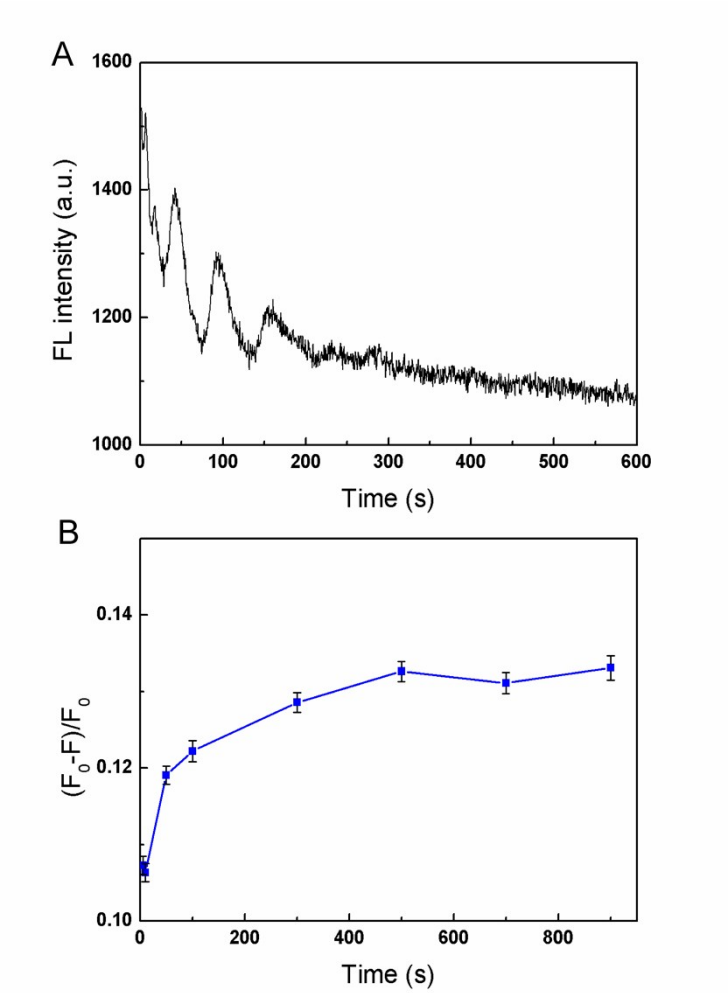

Fig. S8 (A) Time dependence of fluorescence intensity variation upon the addition of 20 μmol L^{-1} Cu^{2+} in PBS (0.01 mol L^{-1}, pH 10.5) at room temperature. (B) Plot of fluorescence quenching efficiency of the CDs as the function of reaction time with the addition of 20 μmol L^{-1} Cu^{2+}.

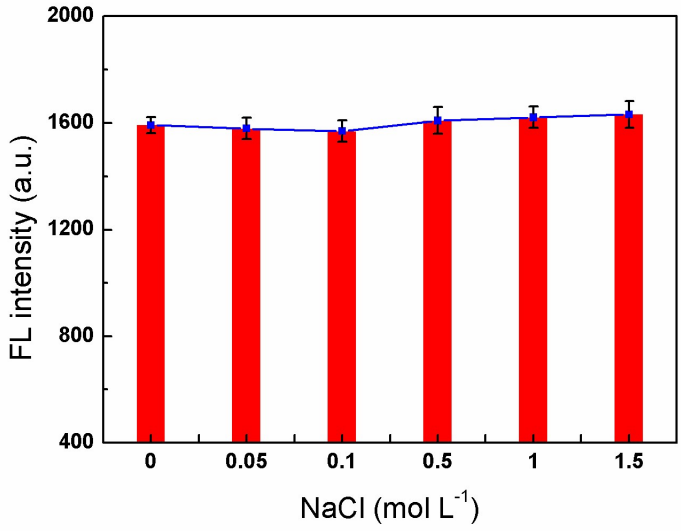

Fig. S9 Salt effect of the NaCl concentration on the fluorescence intensity.

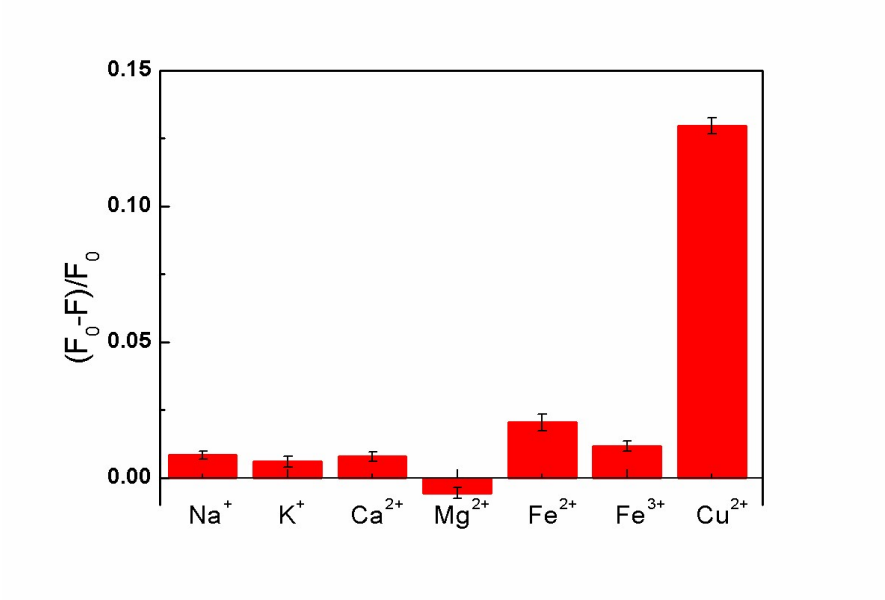

Fig. S10 Selectivity of the CDs for Cu^{2+} (20 μmol L^{-1}) with Na^{+}, K^{+}, Ca^{2+}, Mg^{2+} (100 μmol L^{-1}, respectively), and Fe^{2+}, Fe^{3+} (20 μmol L^{-1}, respectively).

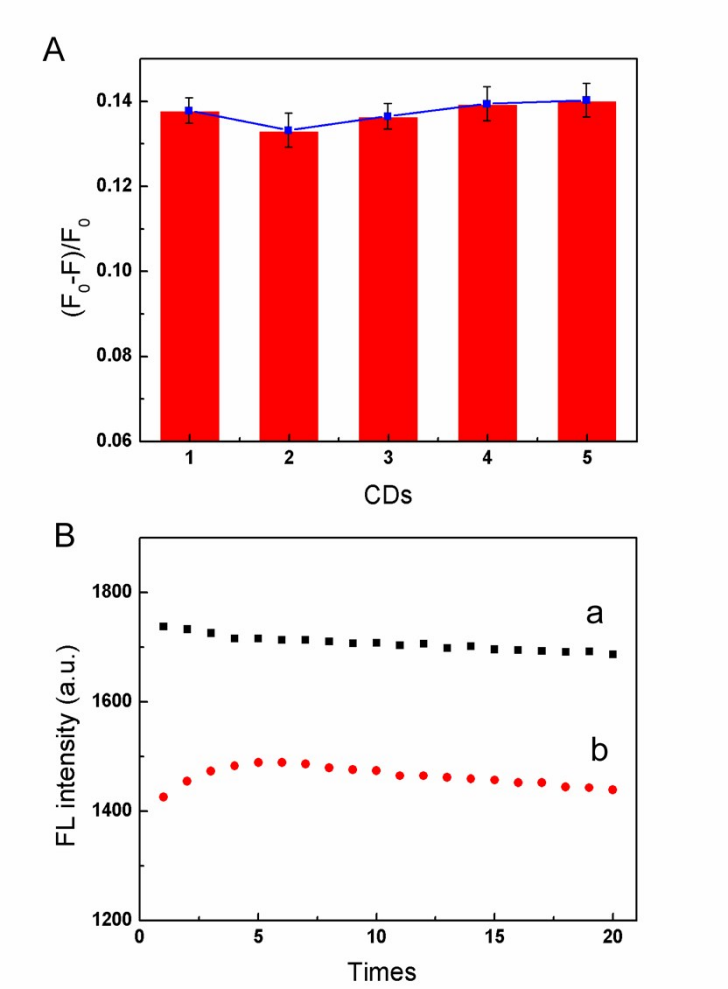

Fig. S11 (A) The fluorescence spectra of five batches CDs with Cu^{2+} (20 μmol L^{-1}). (B) The fluorescence intensities of CDs scanning for 20 times (a) before and (b) after a month.

Table S2 Calibration equations, linear range, limits of detection (S = 3σ) and coefficients of determination (R^2).

Calibration equation (μmol L^{-1})	Linear range (μmol L^{-1})	LOD (nmol L^{-1})	R^2
F = 0.067C + 0.0039	0.01-1	3.2	0.9926
F = 0.0018C + 0.0727	1-100		0.9942

Table S3 Comparing of the presented fluorescent sensing CDs with previous probes.

Probes	Real sample	LOD (nmol L^{-1})	Linear range (μmol L^{-1})	Reference
BPEI-CQDs[a]	River water	6	0.01-1.1	2
F-CNPs[b]	-	10	-	3
F-CNPs, CdSe/ZnS QDs	Cells	1000	1-100	4
F-CNPs	-	5	-	5
TPEA[c]-F-CNPs	Cells	10	1-100	6
CDs	Lake water Tap water	3.2	0.01-1, 1-100	This work

[a]BPEI-CQDs: Branched poly(ethylenimine)-functionalized carbon quantum dots.

[b]F-CNPs: Functionalized carbon nanoparticles.

[c]TPEA: N-(2-aminoethyl)-N,N,N′-tris(pyridin-2-ylmethyl) ethane-1,2-diamine.

References

[1] Z. Yang, M. H. Xu, Y. Liu, F. J. He, F. Gao, Y. J. Su, H. Wei, Y. F. Zhang, *Nanoscale*, 2014, **6**, 1890-1895.

[2] Y. Q. Dong, R. X. Wang, G. L. Li, C. Q. Chen, Y. W. Chi, G. N. Chen, *Anal. Chem*., 2012, **84**, 6220-6224.

[3] Y. F. Sha, J. Y. Lou, S. Z. Bai, D. Wu, B. Z. Liu, Y. Ling, *Mate. Res. Bull.*, 2013, **48**, 1728-1731.

[4] A. W. Zhu, Q. Qu, X. L. Shao, B. Kong, Y. Tian, *Angew. Chem., Int. Ed.*, 2012, **51**, 7185-7189.

[5] A. D. Zhao, C. Q. Zhao, M. Li, J. S. Ren, X. G. Qu, *Anal. Chim. Acta*, 2014, **809**, 128-133.

[6] Q. Qu, A. W. Zhu, X. L. Shao, G. Y. Shi, Y. Tian, *Chem. Commun.*, 2012, **48**, 5473-5475.