Electronic supplementary information

Green Synthesis of Carbon Dots with Down- and Up-conversion Fluorescent Properties for Sensitive Detection of Hypochlorite with Dual-Readout Assay

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Quantum yield measurements:

The QYs of down-conversion were measured according to the reference. Quinine sulfate in a 0.1 mol•L^{-1} H_2SO_4 aqueous solution (quantum yield is 0.54)of was selected as references for the C-dots aqueous solutions. The QYs were determined by comparing the integrated fluorescence intensity and the absorbance value of the C-dots samples with that of the references. Both C-dots and quinine sulfate excited at 320 nm and the absorbance (less than 0.05 at the excitation wavelength) at 280nm and 310nm for C-dots and quinine sulfate, respectively. The slope method was used to calculate the QYs of C-dots using the equation:

$$QY_u = QY_s (m_u/m_s) (n_u/n_s)$$

Where QY is the quantum yield, m is the slope determined by the curves and n is the refractive index (1.33 for water and a 0.1 mol·L^{-1} H_2SO_4 aqueous solution). The subscript "s" refers to the standards and "u" refers to the unknown samples. For these aqueous solutions, $n_u/n_s=1$, A series of concentrations for the references and the C-dots samples were measured to obtain the slopes. The QY of carbon dots in a different condition are list in table S 1. The carbon dots obtained at 180 ^oC for 5 for used as an example, as shown in Figure S2, the m values were calculated to be 16863 and 47188 for C-dots and quinine sulfate, respectively. The QY of the C-dots was 19.3%.

Table S 1. Comparison of C-dots prepared at different reaction condition

Factor	T（°C）	t（h）	$r_{pepper/water}$	QY（%）
1	160	5	1	10.2
2	180	3	1	15.4
3	180	5	1	18.1
4	180	8	1	18.5
5	180	5	4	17.3
6	180	5	0.25	19.3
7	200	5	1	17.9

Table S 2. Comparison of different methods for HClO/ClO^- detection

Detection Limit	Dynamic Range	Detection Method	Ref.
1 μM	0.01-10 mmol·L^{-1}	UV	s1
0.81 μM	0-70 μmol·L^{-1}	Colorimetric	s2
0.4 mg·L^{-1}	2-54.1 mg·L^{-1}	Chemiluminescence	s3
10 mg·ml^{-1}	47–200 mg·ml^{-1}	HPLC	s4
-	0.05– 200 ppm	Electrochemistry	s5
0.05 μM	0.05 - 10 μmol·L^{-1}	Fluorescence	s6
0.05 μM[a]	0.1 -300 μmol·L^{-1}[a]	Fluorescence	This work
0.06 μM[b]	0.1 -300 μmol·L^{-1}[b]		

[a] Downconversion fluorescent property

[b]Upconversion fluorescent property

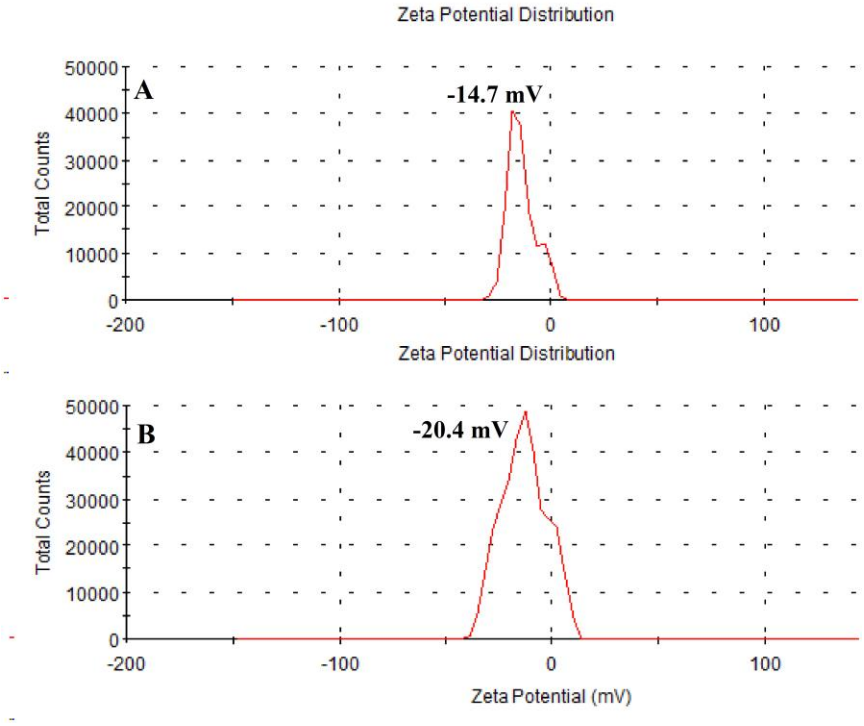

Fig. S 1 Zeta potential of C-dots in the (A) absence and presence of (B) 0.4 mmol·L^{-1} hypochlorite

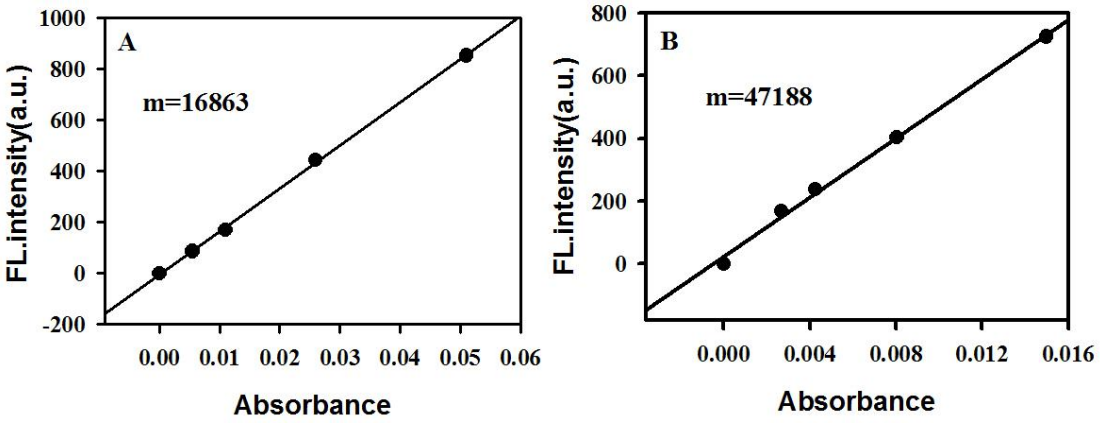

Fig. S 2 Fluorescence and absorbance of the C-dots (A) and quinine sulfate (B).

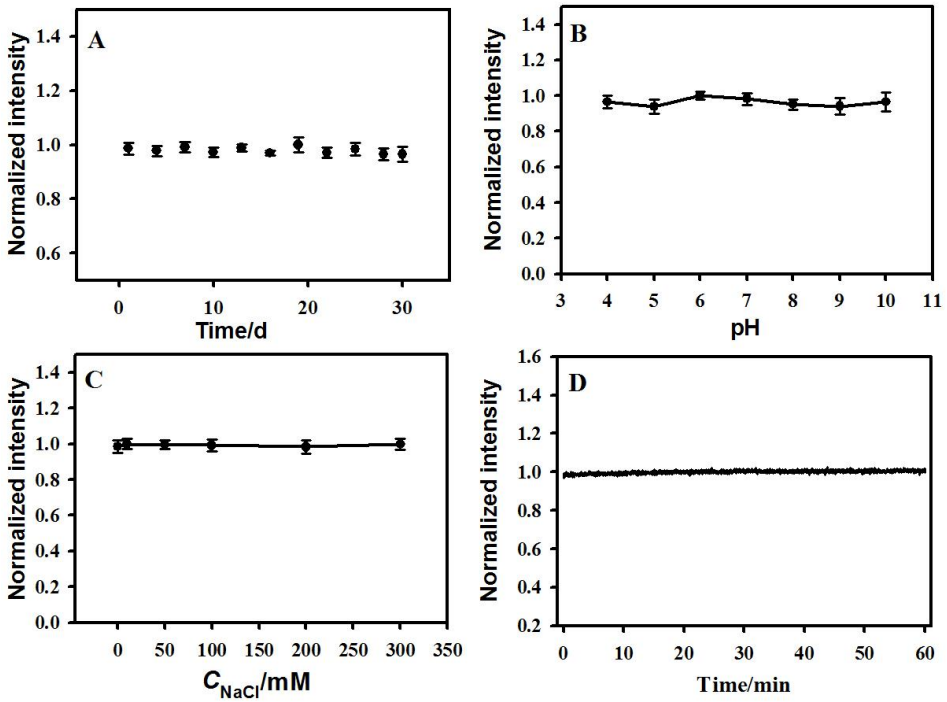

Fig. S 3 (A) The changes of FL intensity of C-dots solution within 30 days. (B) The effect of pH value and (C) the NaCl concentration (0, 10, 50, 100, 200, 300 mmol·L^{-1}) on C-dots fluorescence. (D) Time-course plot of FL intensity from C-dots excited at 360 nm.

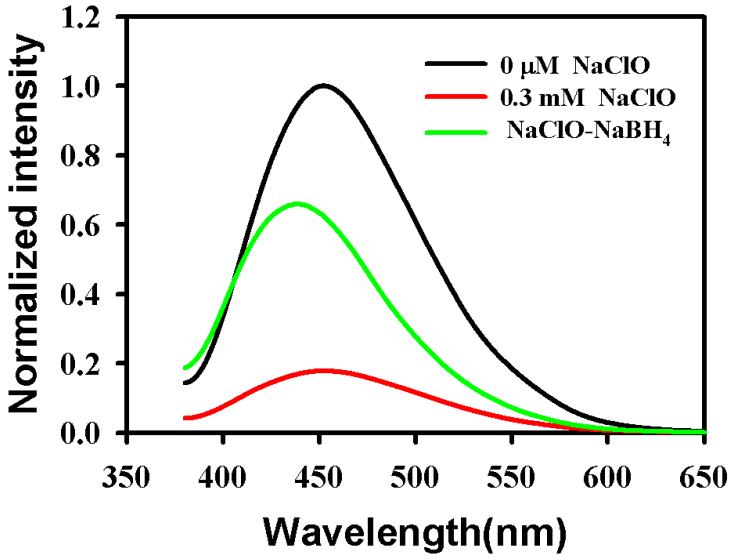

Fig. S 4 Fluorescence emission spectrum of 0.18 mg·mL^{-1} C-dots solution in the absence (black), presence of (red) 0.3 mmol·L^{-1} hypochlorite and (green) adding $NaBH_4$ to the oxidation C-dots excited at 360 nm.

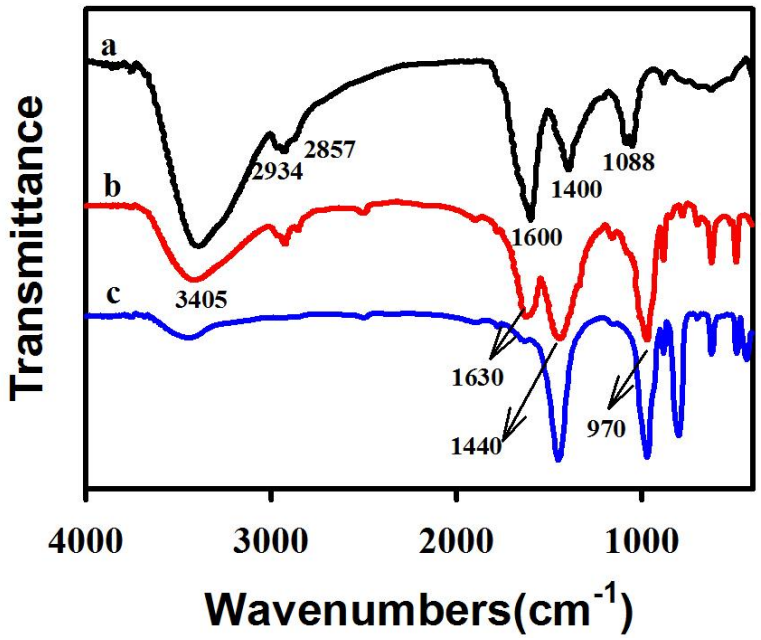

Fig. S 5 FT-IR spectra of (a) the C-dots, (b) the C-dots in the presence of NaClO and (c) NaClO

Reference

1 T. Aoki and M. Munemori, *Anal. Chem.,* 1983, ***55***, 209-212.

2 X. Lou, Y. Zhang, Q. Li, J. Qin and Z. Li, *Chem. Commun.,* 2011, ***47***, 3189-3191.

3 J. Ballesta Claver, M. C. Valencia Mirón and L. F. Capitán-Vallvey, *Anal. Chim. Acta,* 2004, ***522***, 267-273.

4 T. Watanabe, T. Idehara, Y. Yoshimura and H. Nakazawa, *J. Chromatogr., A,* 1998, ***796***, 397-400.

5 S.-y. Kishioka, T. Kosugi and A. Yamada, *Electroanalysis,* 2005, ***17***, 724-726.

6 Y. Dong, G. Li, N. Zhou, R. Wang, Y. Chi and G. Chen, *Anal. Chem.,* 2012, ***84***, 8378-8382.