Supporting Information

A highly efficient, rapid, room temperature synthesis method for coal-based water-soluble fluorescent carbon dots and its use in Fe^{3+} ion detection

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1. Experimental section

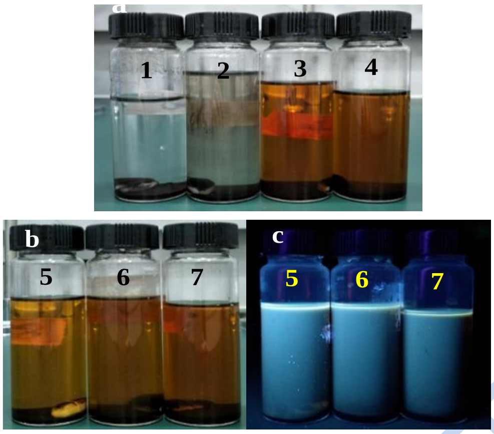

Fig. S1 The (a), (b) day light and (c) 365 nm UV light irradiation photographs of synthesized products under different conditions, the detail reaction conditions see Table S1. (The aqueous solutions are without dilution or enrichment).

Table S1. The comparison experiments conditions.

	Coal/mg	H_2O_2/mL	Formic acid/mL	Time/h	Yield/%
1	200	30	0	24	Trace
2	200	0	30	24	Trace
3	200	5	25	24	65.5%
4	200	3	30	24	43.5%
5	200	5	25	12	54%
6	200	5	25	36	77%
7	200	5	25	48	92.5%

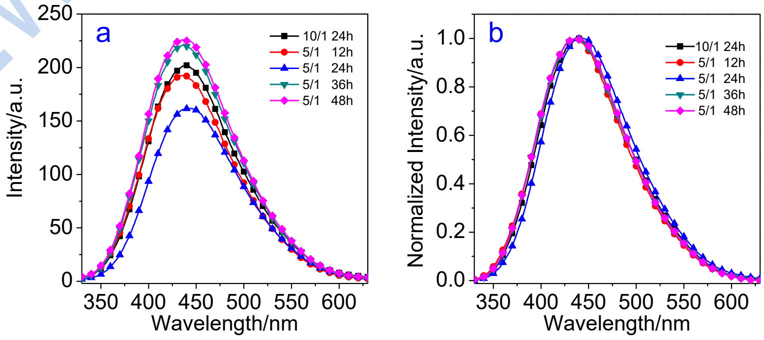

Fig. S2 Fluorescence emission spectra of CDs (λ_{ex} = 320 nm), (a) aqueous solution of CDs under different reaction conditions; (b) the normalized fluorescence emission spectra of CDs under different reaction conditions.

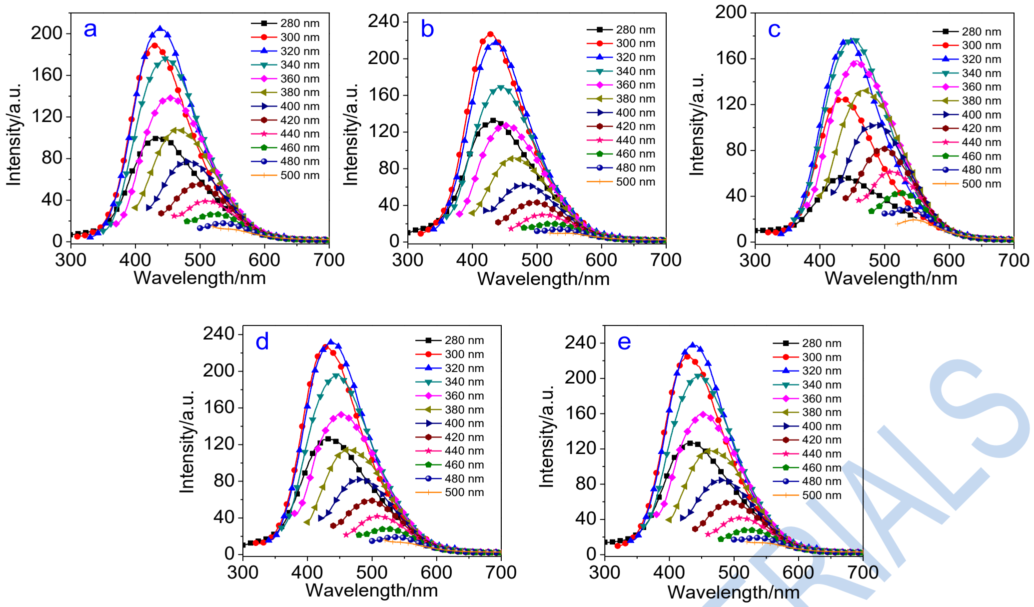

Fig. S3 The fluorescence spectra at different excitation wavelengths ranging from 280 to 500 nm,(a) Formic acid/H_2O_2= 10/1 (V/V), 24 h, (b) Formic acid/H_2O_2= 5/1 (V/V), 12 h, (c) Formic acid/H_2O_2= 5/1 (V/V), 24 h, (d) Formic acid/H_2O_2 = 5/1 (V/V), 36 h, (e) Formic acid/H_2O_2= 5/1 (V/V), 48 h. (c_{CDs} = 0.05 mg/mL).

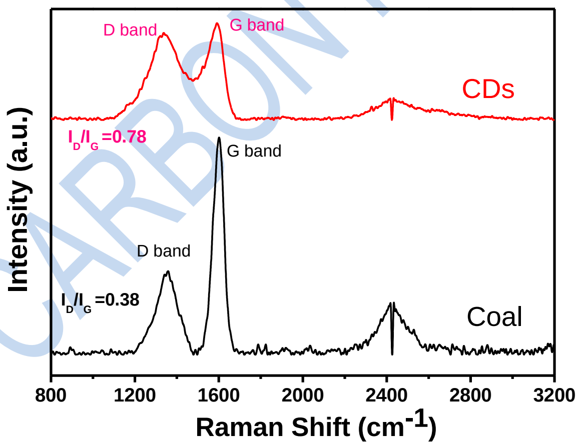

Fig. S4 Raman spectrum of Coal and as-prepared CDs.

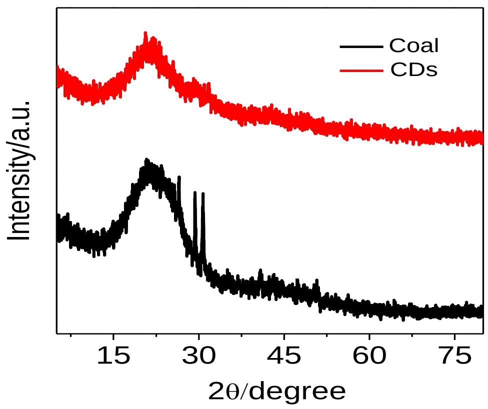

Fig. S5 XRD patterns of Coal and as-made CDs.

Table S2. XPS analysis of Coal and as-made CDs.

		Area (P)	Atomic %
Coal	C1s	279204.02	72.13
	O1s	225637.54	22.47
	N1s	10050.79	1.62
CDs	C1s	155135.69	56.42
	O1s	287274.6	40.26
	N1s	14642.65	3.32

Table S3. The proximate analysis and ultimate analysis of the coal

proximate analysis (wt%)			ultimate analysis (wt%)				
Moisture(M_{ad})	Ash(A_d)	Volatile(V_{daf})	C(C_d)	H(H_d)	O(O_d)	N(N_d)	S($S_{t,d}$)
3.08	1.09	34.01	81.27	4.54	12.02	0.76	0.31

Table S4. The high-resolution XPS-peak-differentation-imitating analysis for C_{1s}

	Peak Binding Energy (eV)	CDs
C–C/C=C (%)	284.78	52.58
Oxygenated Carbon (%)	285.98/288.88	38.11
Nitrous Carbon (%)	286.98	9.31

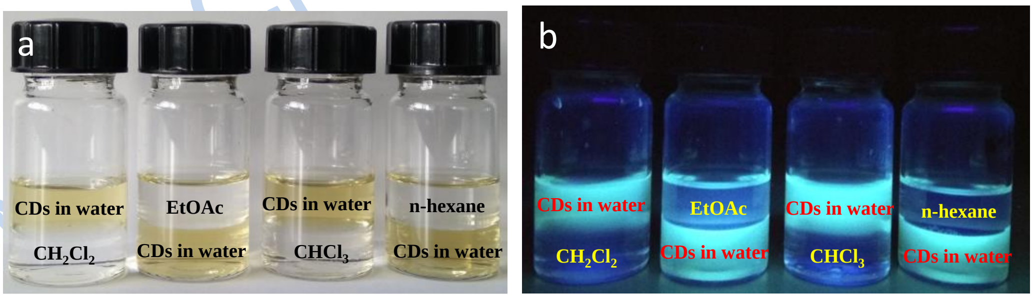

Fig. S6 The photographs of as-synthesized CDs in the mixture of H_2O and CH_2Cl_2, H_2O and EtOAc, H_2O and $CHCl_3$, H_2O and n-hexane, (a) under day light and (b) under 365 nm UV light irradiation.

Table S5 Quantum yields of CDs

Sample	Integrated emission intensity	Absorption at 350 nm (A)	Refractive index of solvent (n)	Quantum yield(Φ)
Quinine sulfate	27008.5	0.042	1.33(default)	54%(known)
CDs	3773.6	0.044	1.33	7.2%

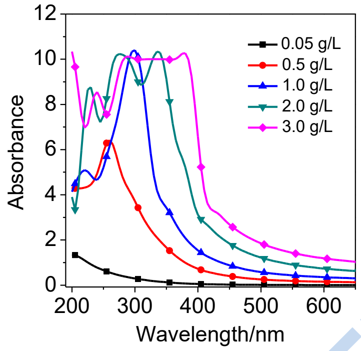

Fig. S7 UV-vis absorption spectra of CDs aqueous solution under different mass concentrations.

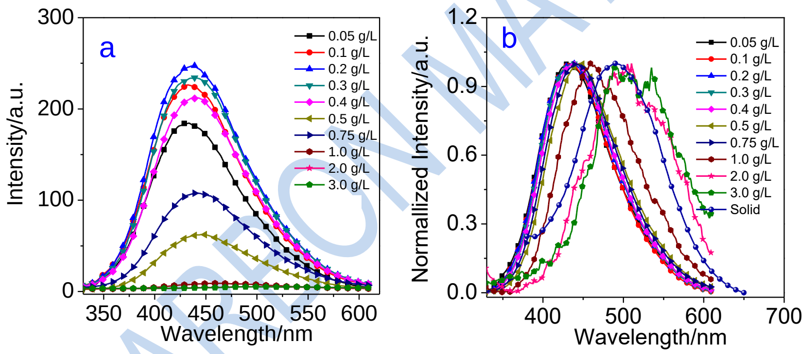

Fig. S8 Fluorescence emission spectra of CDs, (a) powder and aqueous solution under different concentrations, (b) the normalized fluorescence emission spectra of CDs, (λ_{ex} = 320 nm).

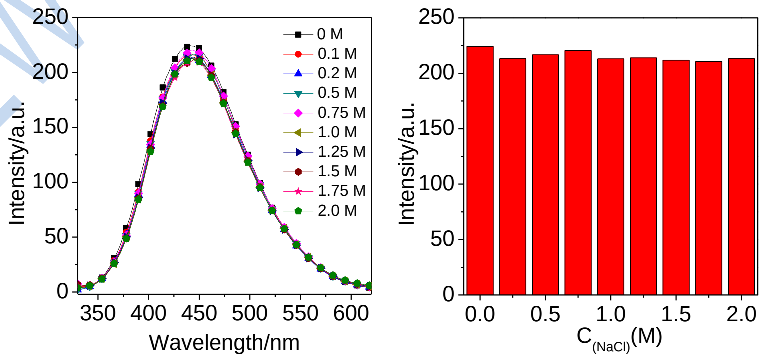

Fig. S9 The fluorescence intensity of CDs in the presence of different concentration of NaCl, (c_{CDs} = 0.2 mg/mL), (λ_{ex} = 320 nm).

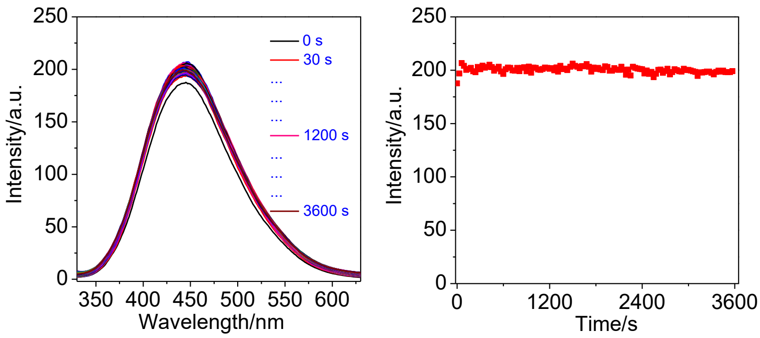

Fig. S10 Photo-bleaching properties of CDs, (c_{CDs} = 0.2 mg/mL), (λ_{ex} = 320 nm).

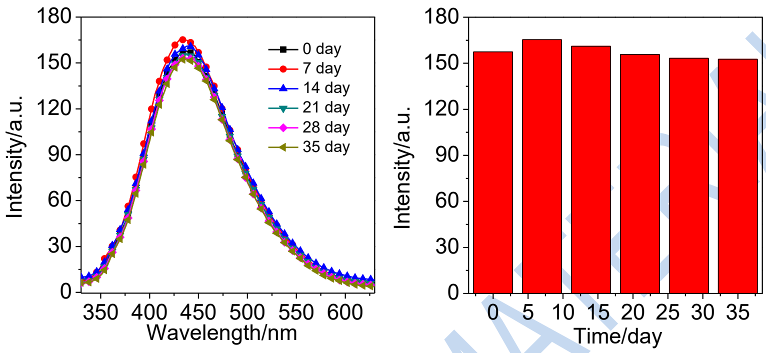

Fig. S11 The fluorescence intensity changes of CDs at room temperature for 35 days, (c_{CDs} = 0.2 mg/mL), (λ_{ex} = 320 nm).

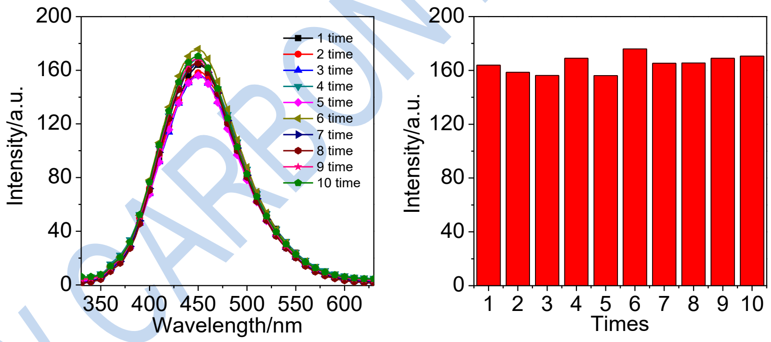

Fig. S12 The fluorescence intensity changes of the CDs (powder) repeatedly disperse in water, (c_{CDs} = 0.2 mg/mL), (λ_{ex} = 320 nm).

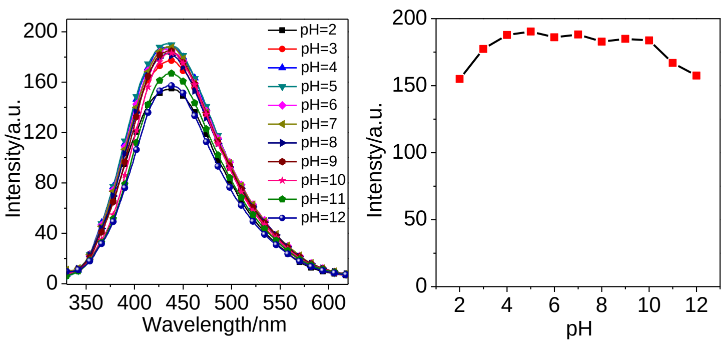

Fig. S13 The variation of fluorescence intensity with pH, (c_{CDs} = 0.2 mg/mL), (λ_{ex} = 320 nm).

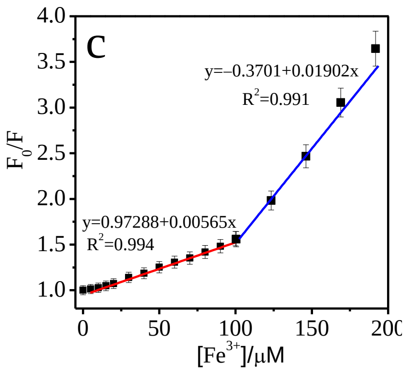

Fig. S14 The relationship between F_0/F and concentration of Fe^{3+} form 2 to 200 μM.

Table S6. Comparison of the sensing performance of different fluorescent probes for Fe^{3+} detection.

Fe^{3+} Fluorescence Probes	Detection limit (μM)	Linear range (μM)	Refs
Carbon dots	2.9	0–250	[1]
Carbon dots	1.3	2–50	[2]
Carbon dots	0.7	5–80	[3]
Carbon dots	0.5	5–100	[4]
Carbon dots	0.239	0–80	[5]
Carbon dots	0.6	2–100	This work

Table S7. The time-resolved photoluminescence decay data for CDs (c_{CDs} = 0.2 mg/mL in water) with different concentration of Fe^{3+}.

pH value	λ_{em} ^{a} [nm]	τ_1 ^{b} [ns]	α_1 ^{c} [%]	τ_2 ^{b} [ns]	α_2 ^{c} [%]	$\bar{\tau}$ ^{d} [ns]	χ^2 ^{e}
0	450	2.57	28.33	9.86	71.67	7.79	1.02
100μM	450	2.52	30.45	9.54	69.55	7.40	1.09
200μM	450	2.51	31.98	9.59	68.02	7.33	1.12

a) Measured emission wavelength; PL peak excited at 340 nm; *b)* PL lifetime; *c)* Fractional contribution of PL decay; *d)* Average lifetime; *e)* Goodness of fit.

Reference:

[1] Y. Song, S. Zhu, S. Xiang, X. Zhao, J. Zhang, H. Zhang, Y. Fu, B. Yang, Investigation into the fluorescence quenching behaviors and applications of carbon dots, Nanoscale 6 (2014) 4676–4682.

[2] M. Zhou, Z. Zhou, A. Gong, Y. Zhang, Q. Li, Synthesis of highly photoluminescent carbon dots via citric acid and Tris for iron(III) ions sensors and bioimaging, Talanta 143 (2015) 107–113.

[3] P. Zhang, Z. Xue, D. Luo, W. Yu, Z. Guo, T. Wang, Dual-peak electro-generated chemiluminescence of carbon dots for iron ions detection, Anal. Chem. 86 (2014) 5620–5623.

[4] W. Zhu, J. Zhang, Z. Jiang, W. Wang, X. Liu, High-quality carbon dots: synthesis, peroxidase-like activity and their application in the detection of H_2O_2, Ag^+ and Fe^{3+}, RSC Adv. 4 (2014) 17387–17392.

[5] L. Rao, Y. Tang, Z. Lia, X. Ding, G. Liang, H. Lu, C. Yan, K. Tang, B. Yu. Efficient synthesis of highly fluorescent carbon dots by microreactor method and their application in Fe^{3+} ion detection, Mater. Sci. Eng. C 81 (2017) 213–223.