Supplementary Data

Electron Transfer Quenching by Nitroxide Radicals of the Fluorescence of Carbon Dots

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Intermolecular quenching of CDs' fluorescence by TEMPO

Assuming the average binding sites on CDs surface are n, the electrostatic binding between CDs and 4-AT produce a non-fluorescent conjugate CD@TEMPO

$$[CD] + n[4\text{-}AT] \rightarrow [CD\text{-}(AT)_n] \qquad (3)$$

Where $[CD\text{-}(AT)_n]$ stands for the concentration of CD@TEMPO. The apparent binding constant for (3) is given as

$$K_S = \frac{[CD\text{-}(AT)_n]}{[CD] \bullet [4\text{-}AT]^n} \qquad (7)$$

And the mass conservation law gives

$$[CD]_0 = [CD] + [CD\text{-}(AT)_n] \qquad (8)$$

Where $[CD]_0$ stands to the initial concentrations of CDs. Considering that the fluorescence intensities are proportional to the concentrations of CDs, the apparent binding constant can be rewritten as

$$K_s = \frac{F_0 - F}{F \bullet [4\text{-}AT]^n} \qquad (9)$$

Hence, we obtain the following relationship:

$$\frac{F_0}{F} = 1 + K_S [4\text{-}AT]^n \qquad (10)$$

The following equation exists,

$$[4\text{-}AT] = [4\text{-}AT]_0 - n[CD\text{-}(AT)_n] \qquad (11)$$

Where $[4\text{-}AT]_0$ is the initial concentrations of 4-AT. Considering $[4\text{-}AT]_0$ is far greater than $[CD\text{-}(AT)_n]$, $[4\text{-}AT]$ can be approximated to $[4\text{-}AT]_0$. Then (8) can be rewritten as

$$\frac{F_0}{F} = 1 + K_S [4\text{-}AT]_0^{\ n} \qquad (12)$$

Inversion of equation of (8) gives the fraction of unbound CDs.

$$\frac{F}{F_0} = \frac{1}{1 + K_S [4\text{-}AT]_0^{\ n}} \qquad (13)$$

As shown in the lifetime quenching experiments, a small portion of dynamic quenching contributed to the quenching of the fluorescence intensities of CDs. The fraction of CDs not quenched by collisional encounter is

$$\frac{F}{F_0} = \frac{1}{1 + K_D [4\text{-}AT]_0} \qquad (14)$$

Then the corrected fluorescence remaining can be given by the product of the fraction of free CDs and the fraction not quenched by collisional encounters, and gives

$$\frac{F}{F_0} = \frac{1}{1 + K_D [4\text{-}AT]_0} \bullet \frac{1}{1 + K_S [4\text{-}AT]_0^{\ n}} \qquad (15)$$

Rearrangement of (13) yields

$$\frac{F_0}{F} = 1 + K_D[4\text{-}AT]_0 + K_S[4\text{-}AT]_0{}^n + K_D[4\text{-}AT]_0{}^{n+1} \qquad (4)$$

The value of K_D is 28.2 M^{-1}, as determined by lifetime quenching experiments. The modified Stern Volmer equation (4) fit quite well with the experiment data (figure 2(b)) and gives a Ks of 3.73×10^2 M^{-1} and a n of 1.9. It demonstrates that the quenching mechanism can be well described by the multiple binding sites and combined dynamic and static quenching model.
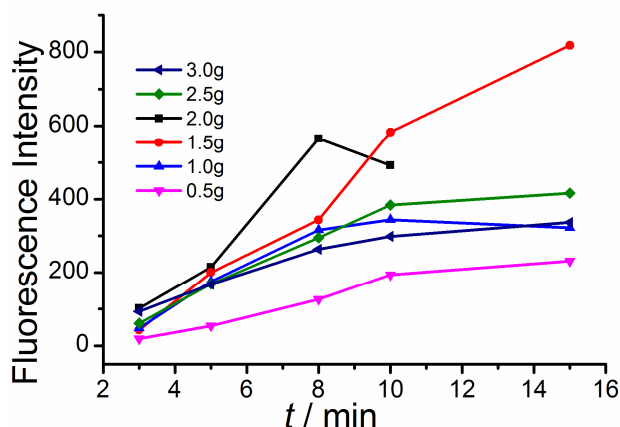

Fig.S1 Fluorescence intensity (λ_{ex}=415 nm, λ_{em}=510 nm) of the CDs solution measured at different reaction time, synthesized at different sucrose concentration(3.0 g, 2.5 g, 2.0 g, 1.5 g, 1.0 g, 0.5 g sucrose in 10 mL water, respectively) and the concentration of H$_2$SO$_4$ was 0.5 M.
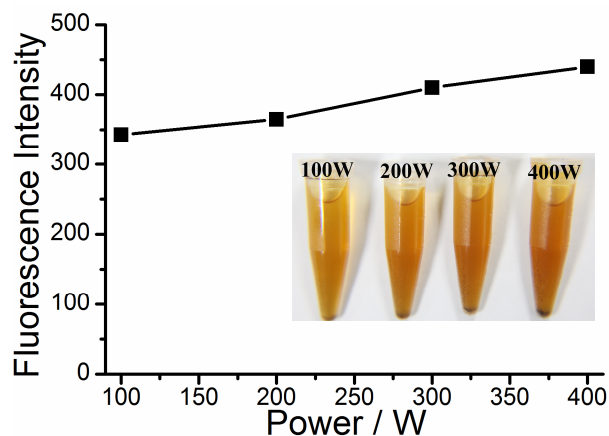

Fig. S2 Fluorescence intensity (λ_{ex}=415 nm, λ_{em}=510 nm) of the CDs synthesized with different microwave power. (Synthesized by using 20% sucrose solution and 0.5 M H$_2$SO$_4$, and a reaction time of 15 min). With increasing power, carbonization of sugar is accelerated and the fluorescence of CDs increased fast, but we also notice that more black and non-fluorescent particle formed with higher power. So 200 W was chosen for the synthesis in our procedure. Insert: photographic images of CDs synthesized with different microwave power.
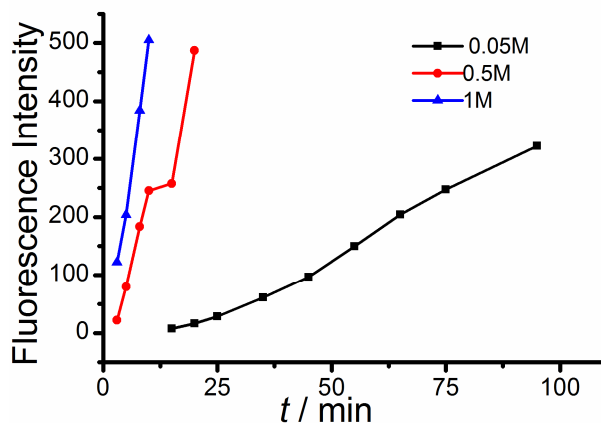
Fig.S3 Fluorescence intensity (λ_{ex}=415 nm, λ_{em}=510 nm) of the CDs solution measured at different reaction time, synthesized by using 20% sucrose solution and different mount of H_2SO_4. Increasing the concentration of H^+ aggravated the carbonization of sugar observably, more black and non-fluorescent particle formed when prolonging the microwave duration. To minimize the by-product, we chose 15 min as the reaction time when the concentration of H_2SO_4 was 0.5 M.
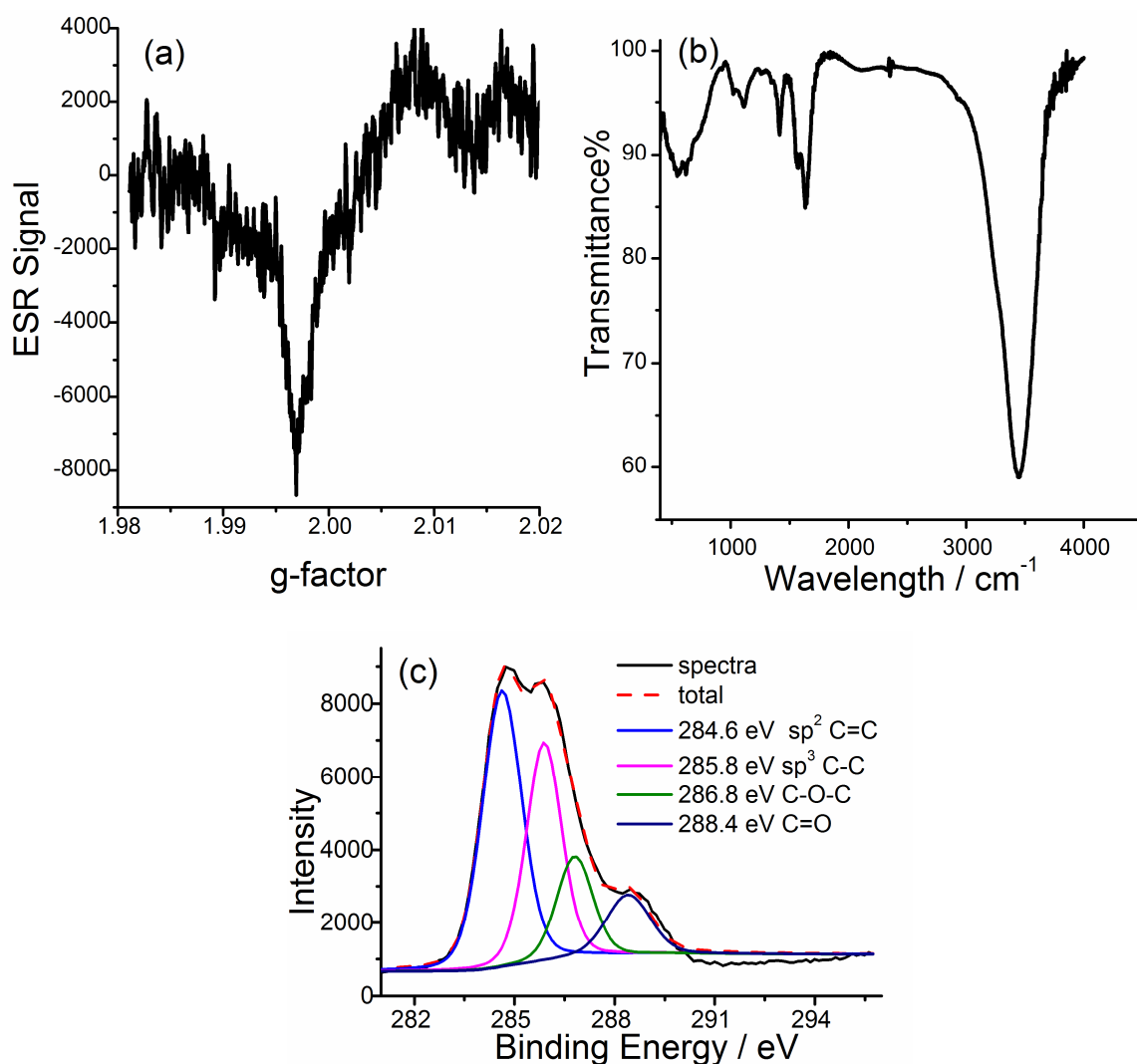

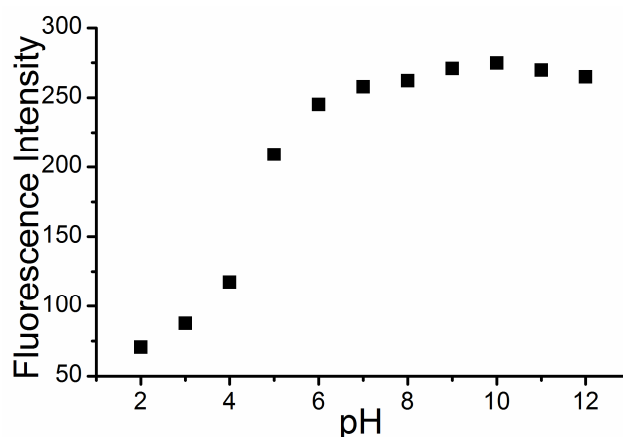**Fig.S4** (a) ESR (b) FT-IR and (c) XPS spectra of the as-prepared CDs.

Fig.S5 pH-dependent fluorescence intensity (λ_{ex}=420 nm, λ_{em}=511 nm) when pH is switched between 2 and 12 in B-R buffer.

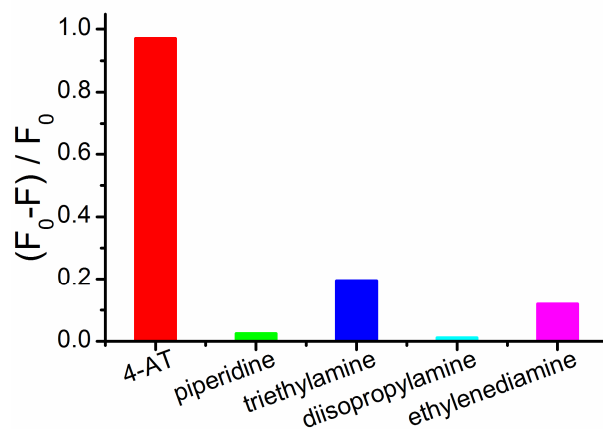**Fig.S6** Intermolecular fluorescence quenching (λ_{ex}=415 nm，λ_{em}=511 nm) of CDs by piperidine, triethylamine, diisopropylamine and ethylenediamine (performed in pH 7.4, 0.2 M borate buffer, the concentration for each of triethylamine, diisopropylamine and ethylenediamine piperidine was 25 mM. F_0 and F stand for fluorescence intensity of CDs in the absence and presence of amine, respectively).
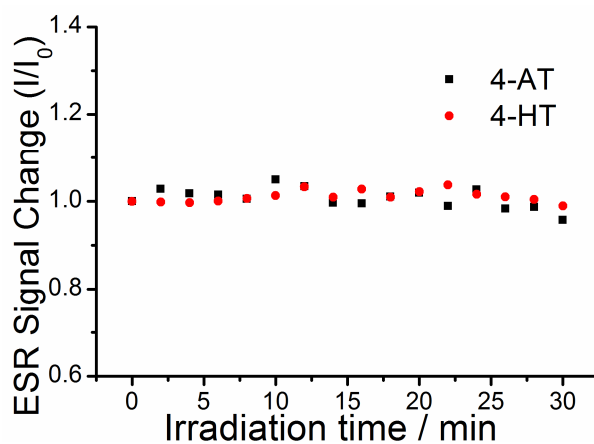

Fig.S7 ESR signals of CDs as a function of UV irradiation duration in the presence of 4-AT (■) and 4-HT (●), respectively, in pH 7.4 boric buffer solution ([4-AT] =2.67 mM, [4-HT]= 33.3 mM, I_0 and I stands for ESR signals of mixture solution of CDs and TEMPO in the initial and under different UV irradiation duration, respectively).

Table S1. Quenching constants of CDs by 4-AT and 4-HT

	4-AT	4-HT
	K_D / M^{-1}	K_{SV} / M^{-1}
0.2 M borate buffe(pH 7.4)	28.2	23.4
DMF	23.5	21.6

Tab.S1 K_{SV} is the Stern-Volmer constant which is related to the quenching efficiency at lower concentration of TEMPO calculated by (1), K_D was obtained by a linear Stern–Volmer equation between τ_0/τ and concentration of TEMPO as described in (2).
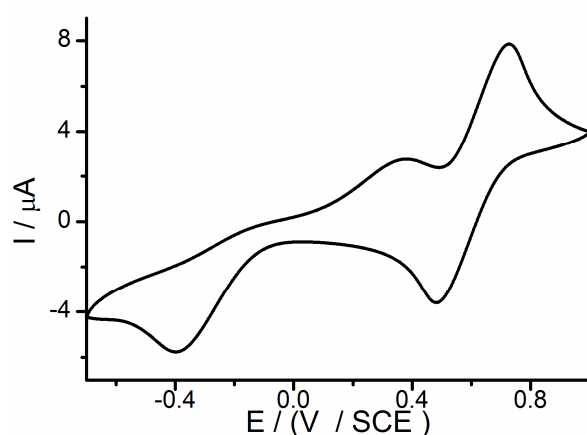

Fig.S8 The cyclic voltammogram of 4-AT in 0.2 M borate buffer (pH 7.4), with glassy carbon electrode as the working electrode (scan rate: 50 mV·s^{-1}).

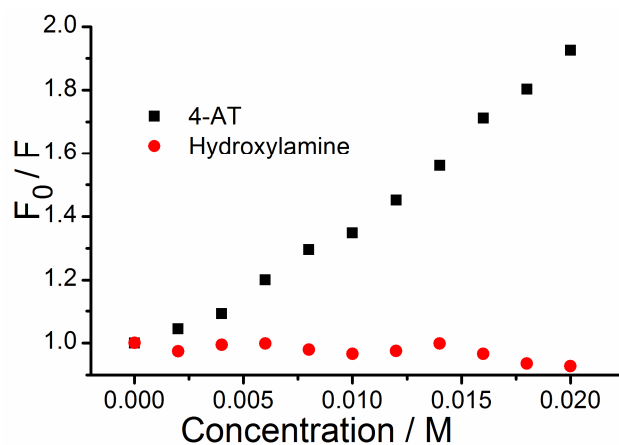**Fig.S9** Fluorescence intensity (λ_{ex}=415 nm, λ_{em}=510 nm) of the CDs upon introduction of 4-AT (■) and hydroxylamine (●) (performed in pH 7.4, 0.2 M borate buffer).
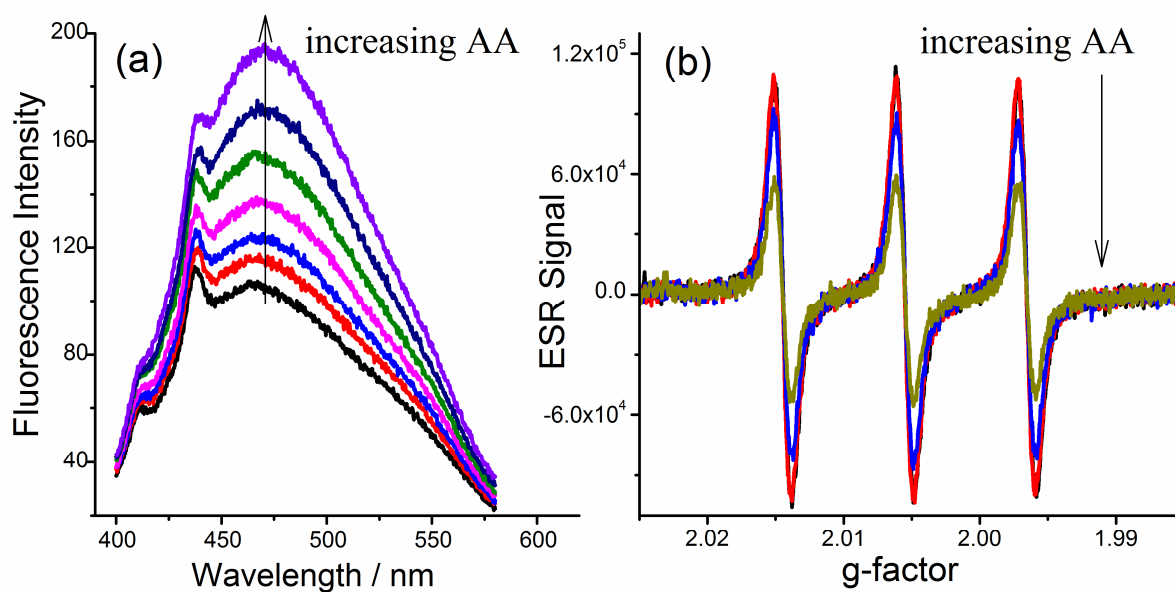
Fig.S10 (a) Fluorescence restoration and (b) decay of the ESR signal of CD@TEMPO upon introduction of AA with concentration changing from 0.80 mM to 1.92 mM (λ_{ex}=385 nm, slit width: 5 nm/5 nm) in DMF.
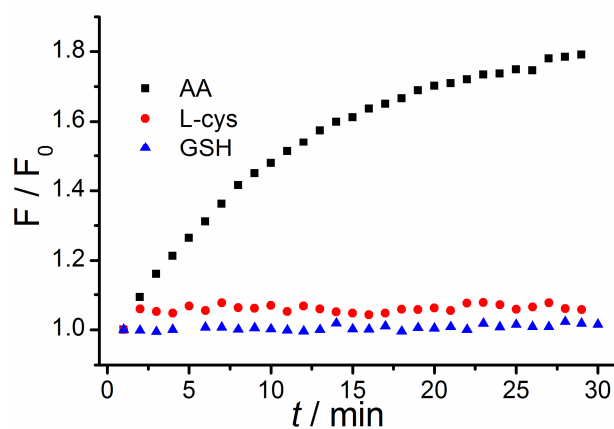

Fig.S11 Time-dependent fluorescence (λ_{ex}=375 nm, λ_{em}=470 nm) following addition of 0.33 mM AA (■), 3.33 mM GSH (▲) and L-Cys (●) to a CDs solution in 0.2 M borate buffer at pH 7.4. F_0 and F represent fluorescence intensities of the spin-labeled CD-TEMPO in the presence and absence of antioxidant, respectively.