Carbon dot-based fluorescence turn-on sensor for hydrogen peroxide with a photo-induced electron transfer mechanism

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Experimental

Materials

Ethylenediamine, dihydrochloride 2-(diphenylphosphino)ethylamine, 2,2'-azobis(2-amidinopropane), citric acid, 3-(ethyliminomethyleneamino)-N,N-dimethyl-propan-1-amine (EDC), N-hydroxysuccinimide (NHS), 2,4,6-trinitrotoluene (TNT), 2,4-dinitrotoluene (DNT), N,N-diethylaniline (DEA), dopamine, fluorescein disodium, 4-(2-hydroxyethyl)-1-piperazineethanesulfonic acid (HEPES), DMSO, KO_2, $NaNO_2$, $NaClO$, $FeCl_2$, H_2O_2 were purchased from Sigma-Aldrich Co. LLC. Distilled water was obtained through a Millipore water purification system.

Characterizations

The UV-Vis absorption spectra were measured by Shimadzu 1700 spectrophotometer, while the fluorescence measurements were performed using Perkin-Elmer LS-50B luminescence spectrometer. Lifetime measurements were performed on LP920-KS Laser Flash Photolysis Spectrometer (Edinburgh Instruments Ltd. Livingston, UK). The excitation source was 355 nm output from a Nd:YAG laser. X-ray photoelectron spectroscopy (XPS) analysis was based on a VG ESCALAB 220i-XL surface analysis system and the indium particles were used as the substrate. Atomic force microscopy (AFM) images were acquired from NanoScopeⅢa MultiMode AFM under tapping-mode. The X-ray diffraction (XRD) pattern of CDs was recorded by the X-ray diffractometer (Bruker, D2 PHASER). Fourier transform infrared spectroscopy (FTIR) was performed on an IFS 66 V/S (Bruker) IR spectrometer. Transmission electron microscopy (TEM) and high-resolution TEM images were taken on a JEOL JEM-2100F operated at an acceleration voltage of 150 kV. Fluorescence quantum yield was

calculated using quinine sulfate in 0.1 M H_2SO_4 as the standard. The pH value of the solution was measured by a pH-meter (Eutech PH 700).

Preparation of fluorescent CDs

Fluorescent CDs were synthesized by microwave-assisted hydrothermal method using citric acid and ethylenediamine as precursors. 0.25 g of citric acid and 12 μL of ethylenediamine were dissolved into 15 mL distilled water to form a clear solution. Then the mixture was putted into the microwave reactor and reacted at 180 °C for 30 min. After cooling to room temperature, reddish brown solution was obtained. Filtering the large particles using a 0.22 μm membrane, the filtrate was dialyzed in distilled water for two days. Afterwards, CDs aqueous solution was collected for future use.

Sensor fabrication and its application for detecting H_2O_2

The synthesis route for the sensor is shown in Scheme 1. The surface of as-prepared CDs is carboxyl groups-riching. 2-(diphenylphosphino) ethylamine was covalently coupled onto the surface of the CDs with the assistant of EDC and NHS. The definite means are as follows: 20 mg EDC and 10 mg NHS were added into 3 mL CDs aqueous solution in an ice bath under stirring for 1 h. 3 mL DMF contains 5 μL 2-(diphenylphosphino) ethylamine was added into the CDs aqueous solution. After reacting for 24 h, the sensor (CDs-P) was purified through dialyzing in distilled water. To detect H_2O_2 quantitively, 100 μL of CDs-P aqueous solution was added into 900 μL HEPES buffer solution (pH 7.2), and then added H_2O_2 by a calculated amount.

Synthesis of various ROS

Superoxide ($O_2^{\bullet-}$) was generated using solid KO_2. Hydrogen peroxide (H_2O_2) and hypochlorite (OCl^-) can be obtained from 35.5% and 13% aqueous solution, respectively. Hydroxyl radical ($\bullet OH$) was created by the reaction of Fe^{2+} and H_2O_2 (1:1). Peroxy radical (ROO•) was obtained by 2,2'-azobis(2-amidinopropane) dihydrochloride stirred at 25 °C for 1 h. Nitrite (NO_2^-) was generated by $NaNO_2$. Peroxynitrite ($ONOO^-$) was synthesized as reported: 0.6 M of $NaNO_2$ aqueous solution mixed with 0.7 M H_2O_2 with the same volume containing 0.6 M HCl.[S1]

Table S1 Comparison of CDs based fluorescent sensors for H_2O_2 detection.

System	FL signal	pH range	Respone time	LOD (nM)	Ref.
B-CDs	Turn-off	7.4	N/A	~25000	S2
CDs-Fe^{2+}	Turn-off	5	1 h	3800	S3
GQDs-Fe^{2+}	Turn-off	N/A	1 min	~1000	S4
CDs	Turn-off	N/A	N/A	700	S5
CDs-HRP	Turn-off	7.0	18 min	200	S6
CDs-Fe^{2+}	Turn-off	3	10 min	50	S7
CDs-Fe^{2+}	Turn-off	3	10 min	10	S8
CDs	**Turn-on**	**4~12**	**40 s**	**84**	**This work**

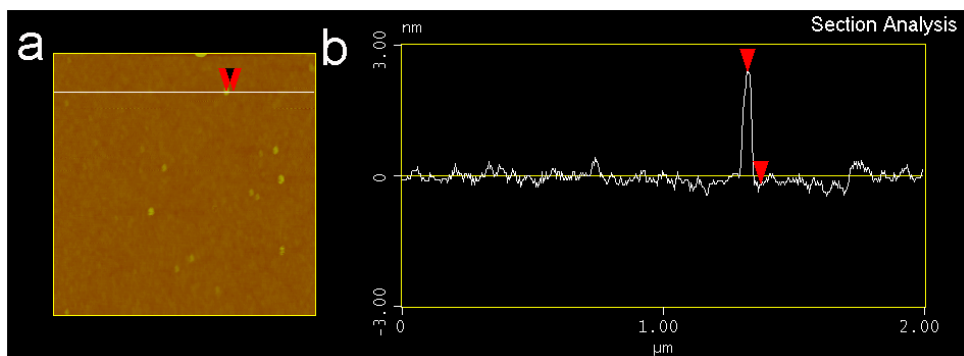*N/A:* no data; *GQDs*: graphene quantum dots.

Fig. S1 (a) AFM image of CDs on a silica substrate. (b) The height profile plot along the line in (a).
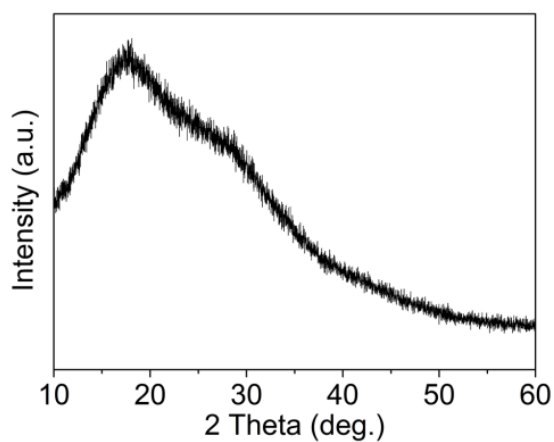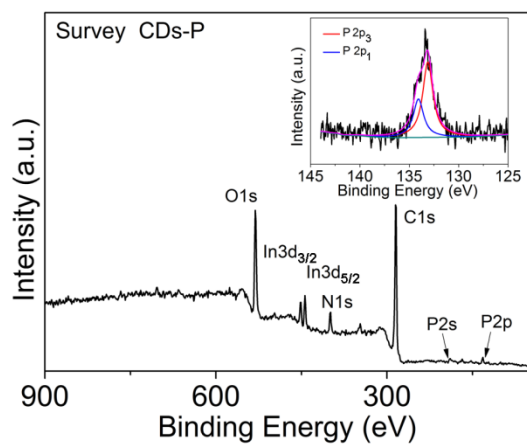

Fig. S2 XRD pattern of the CDs.

Fig. S3 XPS survey spectrum of the CDs-P. The inset shows the high-resolution P2p spectrum.
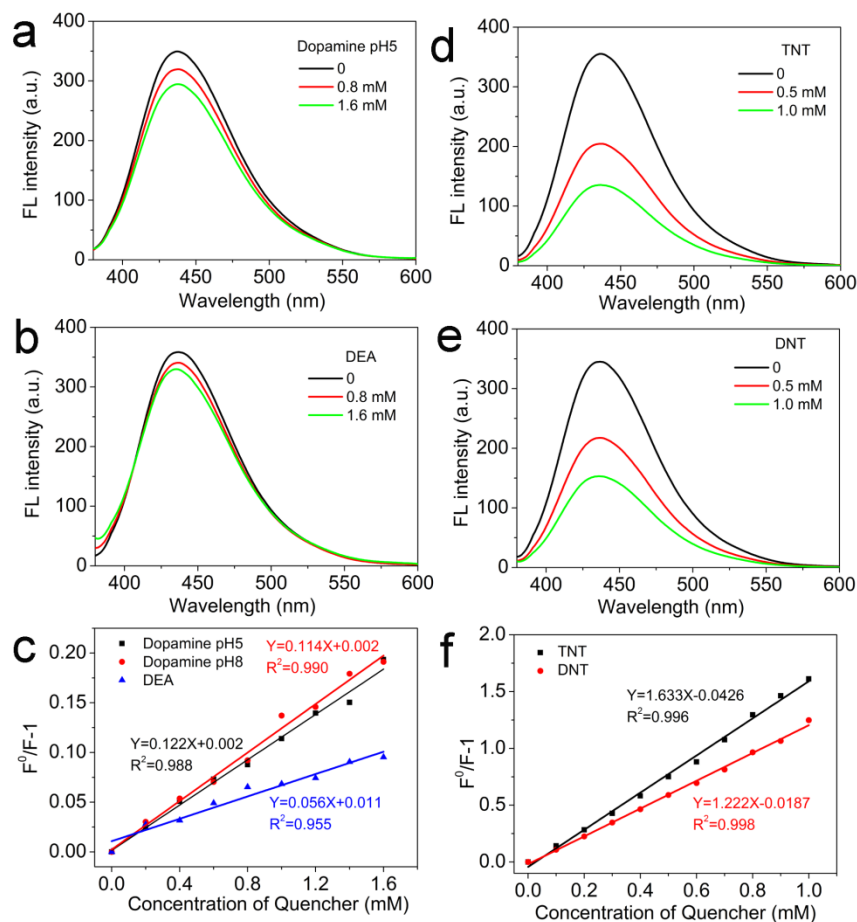
Fig. S4 FL spectra of CDs in HEPES buffer solution with the gradual addition of (a) dopamine, (b) *N,N*-diethylaniline (DEA), (d) 2,4,6-trinitrotoluene (TNT), and (e) 2,4-dinitrotoluene (DNT), λ_{ex} = 350 nm. Stern-Volmer plots for the quenching of fluorescence intensity at 437 nm of CDs by (c) dopamine (pH5, black squares, pH8, red dots) and DEA (blue triangle), and (f) TNT (black squares) and DNT (red dots). F^0 and F are the fluorescence intensities of the CDs at 437 nm in the absence and presence of quenchers, respectively.
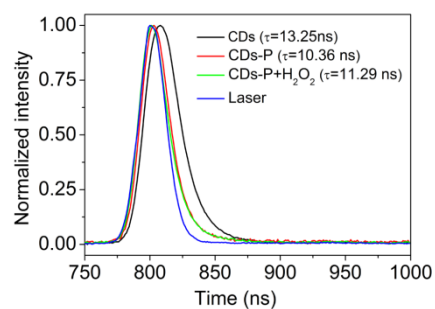

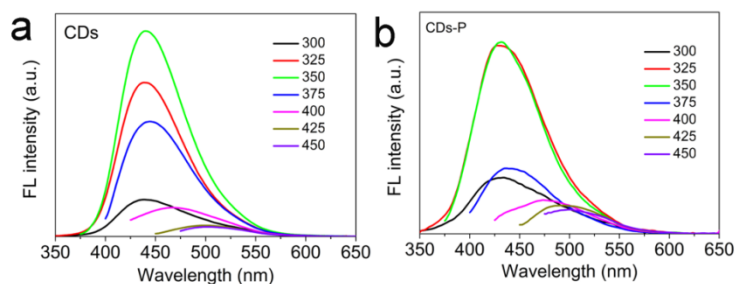**Fig. S5** Time-resolved fluorescence decay curves of CDs, CDs-P and CDs-P/H_2O_2.

Fig. S6 FL emission spectra of (a) CDs and (b) CDs-P obtained at different excitation wavelengths with a 25 nm increment from 300 nm to 450 nm.
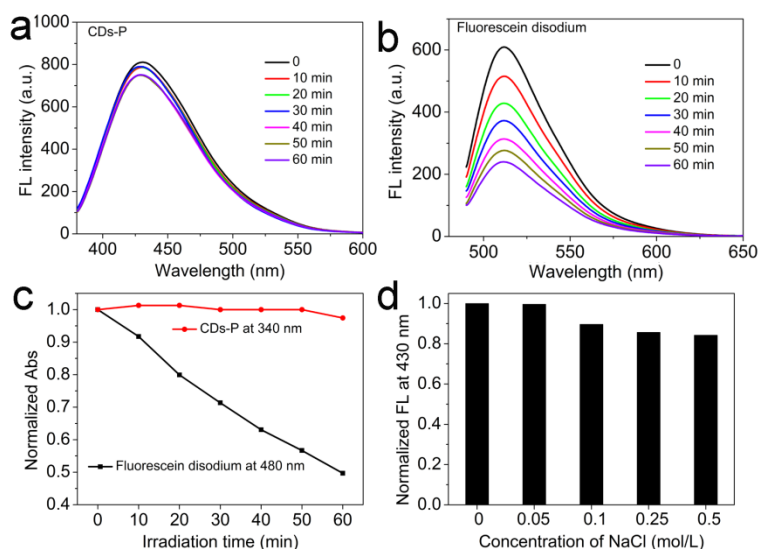

Fig. S7 The fluorescence spectra of (a) CDs-P and (b) fluorescein disodium under irradiation by a 500 W xenon lamp for different time. (c) A comparison on the photostability characteristics of CDs-P and fluorescein disodium. All samples were continuously irradiated using a 500 W xenon lamp and the absorbance was normalized. (d) The effect of concentration of NaCl on the FL intensity of the CDs aqueous solution.
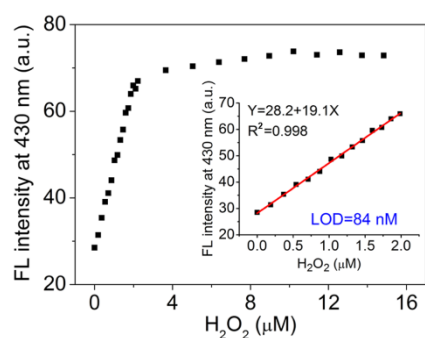

Fig S8 The FL intensity of CDs-P solution at 430 nm versus the concentration of H_2O_2 (0~15 μM). Inset graph showing the linear relation between FL intensity and the concentrations of H_2O_2 from 0 to 2.0 μM.
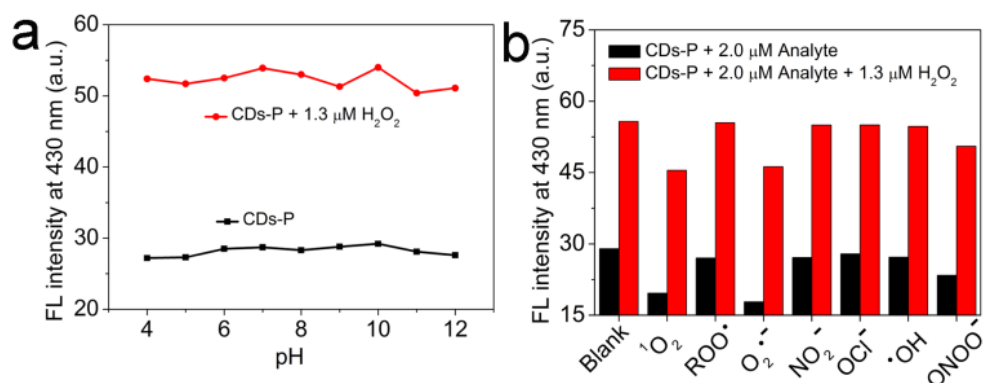
Fig. S9 (a) Influence of pH on FL intensity of CDs-P at 430 nm in the absence (black line) and presence (red line) of 1.3 μM H_2O_2. (b) Selectivity of CDs-P to H_2O_2 in the presence of other ROS in HEPES buffer solution. The black and red columns refer to the CDs-P solution in the absence and presence of 1.3 μM H_2O_2, respectively. Blank refers to free CDs-P solution. The synthesis of these ROS is shown in supporting information.
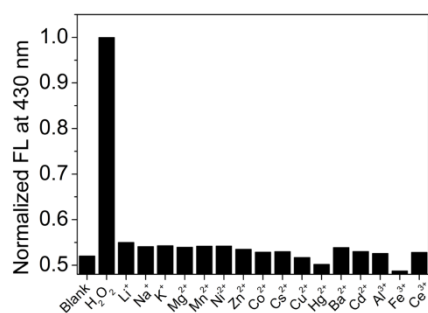

Fig. S10 The selectivity of CDs-P to H_2O_2 (1.3 μM) compared with other metal ions (50 μM) in 10 mM HEPES buffer solution.

References

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S6. Y. M. Zhang, X. J. Yang and Z. Q. Gao, *RSC Adv.*, 2015, **5**, 21675.

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