Electronic Supplementary Information

B-doped carbon quantum dots as a sensitive fluorescence probe for hydrogen peroxide and glucose detection

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Instruments and chemicals

For UV-Vis and Fluorescence analysis, BCQDs were first dissolved in alcohol, and then were diluted with buffer to the desired concentration. For determination of the quantum efficiency of fluorescence (Ff), were calculated using the integrated emission intensity of quinine sulfate as standard. The UV–Vis absorption spectra were obtained with a Perkin Elmer Lambda 950 spectrometer. Fluorescence experiments were recorded on a Perkin Elmer LS 45 luminescence spectrometer.

All reagents were of analytical grade and without any further purification. Boron tribromide, hydroquinone, glycol, diamine, glucose oxidase (GOx), glucose, H_2O_2 (30wt%) and acetone were purchased from Aladin Ltd. (Shanghai, China). All spectra detections were carried out at pH 7.4 phosphate buffer solution (PBS), which was prepared by mixing stock solutions of NaH₂PO₄ and Na₂HPO₄. A fresh solution of H_2O_2 was prepared daily and distilled water was used in the whole experimental process.

Experimental section

Synthesis of B-doped carbon quantum dots. 2.58 mL of BBr₃, 1.0 g of hydroquinone and 5 mL of acetone were placed into a 25 mL Teflon equipped stainless steel autoclave, and then the mixture was heated solvothermally at 200 °C for 2 h using a blast oven. After the reaction completed, the autoclave was cooled down to room temperature, the solution was condensed by rotary evaporation and the obtained product was B-doped CQDs. This product was denoted as BCQDs.

Synthesis of pristine carbon quantum dots. 5 mL of CCl₄, 5.708 g of hydroquinone, 2.0736 g of NaOH and 5 mL of ethanol were placed into a 25 mL Teflon equipped stainless steel autoclave, and then the mixture was heated solvothermally at 200 $^{\circ}$ C for 1 h using a blast oven. When the autoclave cooled down to room temperature, the solution was condensed by rotary evaporation and the obtained product was pristine CQDs.

Characterization methods. The morphologies of the products were characterized by transmission electron microscopy, which was performed on a JEOL-2100F instrument with accelerating voltage of 200 KV. Samples were prepared by dropping ethanolic or aqueous

suspensions of the separated fractions of oxidized products onto Cu TEM grids coated with a holey amorphous carbon film and following solvent evaporation in a dust protected atmosphere. The X-ray photoelectron spectroscopy analyses were conducted using a Kratos Axis ULTRA X-ray photoelectron spectrometer with a 165 nm hemisphereical electron energy analyzer. The incident radiation came from monochromatic Al X-ray (1486.6 eV) at 15 kV and 3 mA. Wide survey scans were taken at an analyzer pass energy of 160 eV over a 1400-0 eV binding energy with 1.0 eV step and a dwell time of 100 ms, while narrow multiplex higher resolution scans were performed at a pass energy of 20 eV with 0.05 eV step and a dwell time of 200 ms. The pressure in analysis chamber was less than 7.5×10^{-9} Torr during sample analysis. Atomic concentrations were calculated using Vision software and a Shirley baseline. The UV-Vis spectra were carried out on a Perkin Elmer Lambda 950 spectrometer, in which the products were dispersed in solvent after ultrasonication for 30 min. The photoluminescence spectra were conducted on a PerkinElmer LS-45 fluorescence spectrometer.

Determination of the quantum yields. Determination of the quantum yields of these oxidized products was accomplished by comparison of the wavelength integrated intensity of these functionalized products to that of the standard quinine sulfate. The optical density was kept below 0.05 to avoid inner filter effects. The quantum yields of these oxidized products were calculated using

$$\Phi = \Phi_{\rm s} \left[(\mathbf{I} \cdot \mathbf{A}_{\rm s} \cdot \mathbf{n}^2) / (\mathbf{I}_{\rm s} \cdot \mathbf{A} \cdot \mathbf{n}_{\rm s}^2) \right]$$

where Φ is the quantum yield, I is the integrated intensity, A is the optical density and n is the refractive index of the solvent. The subscript S refers to the standard reference of known quantum yield. Quinine sulfate was chosen as the standard, whose quantum yield is 0.577 and nearly constant for excitation wavelength from 200 nm to 400 nm.

Fluorescence experiments. All fluorescence spectra were recorded on a Perkin Elmer LS 45 luminescence spectrometer at pH 7.4 buffer solutions. The emission spectra were recorded under the excitation wavelength of 315 nm at a scan rate of 200 nm/min. The slot widths of the excitation and emission were both 10 nm. For the study of the quenching effect of H_2O_2 on BCQDs, 2 mL of BCQDs were diluted with phosphate buffer solution (PBS, pH 7.4), and

a certain volume of H_2O_2 solution was added into the diluted BCQDs. For the detection of glucose, 100µL of GOx (20µg/mL) were mixed with 2 mL of BCQDs, and diluted with PBS (pH 7.4). Then the glucose solutions with different concentrations were added into the BCQDs mixture for fluorescence detection.



Fig. S1 Selected regions of XPS spectra of BCQDs (A). The enlarged regions for B1s, C1s and O1s of BCQDs (B,C and D).



Figure S2. The excitation and emission spectra of BCQDs



Figure S3. The excitation and emission spectra of CQDs



Figure S4. The different quenching effect of O_2 and H_2O_2 on fluorescence of BCQDs. Concentration of O_2 is the saturated concentration in solution.



Figure S5. The response time of fluorescence of BCQDs to H_2O_2



Figure S6. The response time of fluorescence of BCQDs to glucose with aid of GOx.



Figure S7. The recovery of quenched fluorescence of BCQDs in the presence of small amount of MnO_2 . The presence of MnO_2 not only can remove the hydrogen peroxide and reactivate the sensor, but also can not influence the fluorescence of BCQDs.



Figure. S8 The fluorescence spectra of B-CQDs (black line), B-CQDs in the presence of 0.2 mM glucose (red line) and 10 μ g/mL GOx (blue line), B-CQDs in the presence of 10 μ g/mL GOx after the addition of 0.2 mM glucose (green line). All of the spectra were recorded after mixing the components for 30 min.

Table S1. The fluorescence parameters of BCQDs and CQDs				
Sample	$\lambda_{\rm ex}{}^a$ (nm)	$\lambda_{em} b(nm)$	Φ_{f}^{c} (%)	$\tau^{d}(ns)$
BCQDs	316	370	14.8	2.2
CQDs ^e	372	440	3.4	8.4

^{*a*} The excitation wavelength. ^{*b*} The central emission wavelength. ^{*c*} The fluorescence quantum yield determined with quinine sulfate (0.577) as reference. ^{*d*} The average lifetime. ^{*e*} From Ref. 17.