

Label-free carbon quantum dots as photoluminescence probes for ultrasensitive detection of glucose

Supporting Information

Experiments section

1. Instruments and chemicals.

All the chemicals were used as received from Sigma-Alsrich and Beijing Chemical Reagent (Beijing, China). All solid samples were dried under vacuum at 60°C for 8-10 h before the measurements. The transmission electron microscopy (TEM) image was obtained with a FEI/Philips Tecnai F20 transmission electron microscope at an acceleration voltage of 200 kV. The Fourier transform infrared (FT-IR) spectrum of CQDs was obtained by a Varian Spectrum GX spectrometer. The PL study was carried out on a Horiba JobinYvon (FluoroMax 4) Luminescence Spectrometer and an optical fluorescent microscope (Leica DM4500B), while UV-visible spectra were measured by an Agilent 8453 UV-vis Diode Array Spectrophotometer. The fluorescence lifetimes of samples were measured by a FluoroLog 3-211-TCSPC.

2. Preparation of CQDs.

In this experiment, 8.0 g sodium hydroxide was added to a mixed solution of 200 mL polyethylene glycol and 10 mL deionized water to form a clarified solution. Then the solution was given an electrochemical treatment for 4 h at room temperature (cell potential: 25-40 V) with continuous stirring. Pt rods (diameter of 0.2 cm) were used as the cathode and anode. The CQDs were synthesized when the current intensity was in the range of 200-260 mA cm⁻². In order to remove the non-fluorescent deposit, the resultant solution was centrifuged (15000 rpm) for 15 min. The obtained solution was underwent a dialysis treatment using a semi-permeable membrane. Finally, the solution became brown, which was demonstrated the CQDs had been obtained.

3. The calculation of quantum yield.

The quantum yield (QY) of CQDs was measured according to the method described in the references.^{S1} Briefly, quinine sulfate (0.1 M H₂SO₄ as solvent) was chosen as a reference standard (QY = 54 %). The CQDs were dissolved in distilled water. The absorbance for the standard sample, the CQDs and the fluorescence spectra of the solutions were measured respectively. The integrated fluorescence intensity (that is, the area of the fluorescence spectrum) from the fully corrected fluorescence spectrum was calculated. The areas of the integrated fluorescence intensity vs. absorbance were plotted. The plot obtained should be a straight line with a gradient M, which was used to calculate the quantum yield according to the following equation:

$$\phi_x = \phi_s \left(\frac{M_x}{M_s} \right) \left(\frac{\eta_x}{\eta_y} \right)^2$$

Where the subscripts s and x denote standard (such as quinine sulfate) and test samples respectively, Φ is QY, and η is the refractive index of the solvent. It should be noted that the excitation wavelength for measurements of QY was set at the excitonic absorption peak of the CQDs samples in our experiments.

4. Analytes sensing by PL detection.

For all tests and reactions, the experiments were repeated five times to ensure the accuracy of

the measurement. For the study of fluorescence enhancement of CQDs by H_2O_2 , CQDs were diluted with 5 mM phosphate buffer (PBS, pH 7.4), and a certain volume of H_2O_2 solution was added into the diluted CQDs solution. For the detection of glucose, 45 μL of GO_x (0.2 mg/mL) was mixed with 400 μL diluted CQDs solution, and then the glucose solutions with different concentrations were added into the CQDs/ GO_x mixture. The mixed solution was diluted with PBS to 600 μL . The mixture was incubated at 40 $^\circ\text{C}$ for 30 min and then measured by fluorescence spectrophotometer. The emission spectra were recorded under an excitation wavelength of 420 nm.

5. Analysis of glucose in serum samples.

For the detection of glucose in serum samples, the experiments were performed as follows. In details, 45 μL of GO_x (0.2 mg/mL), 400 μL diluted CQDs solution and 60 μL serum samples were added to a 1.5 mL calibrated test tube. The mixture was diluted with PBS to 600 μL , mixed thoroughly, and incubated in a water bath of 40 $^\circ\text{C}$ for 30 min. Then, the mixture was taken out from the water bath and allowed to cool to room temperature for 5 min for PL measurements at an excitation wavelength of 420 nm.

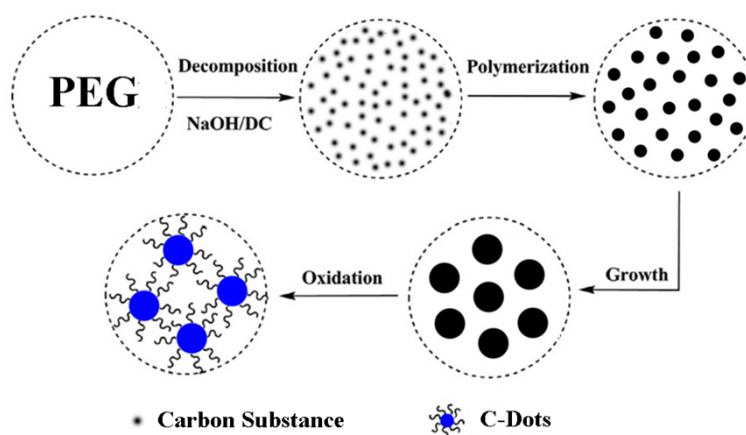


Fig. S1. Schematic growth model of CQDs

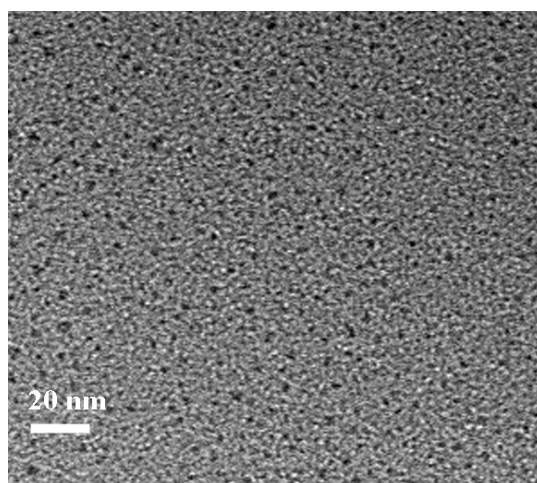


Fig. S2. TEM image of CQDs.

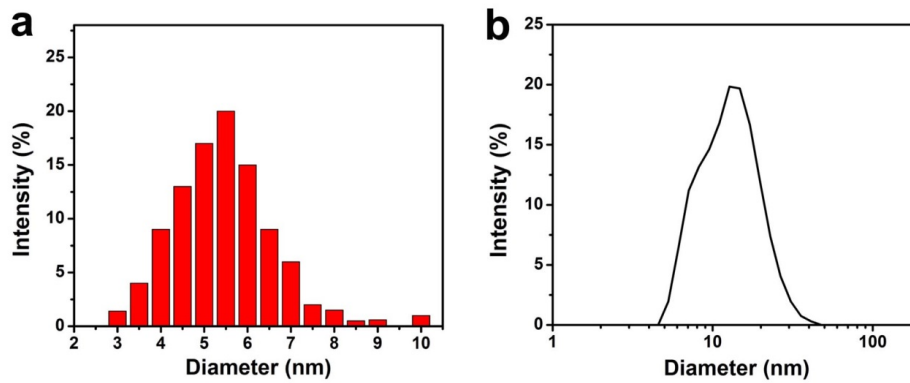


Fig. S3 (a) The size distribution histogram of CQDs. (b) The hydrodynamic diameter of CQDs.

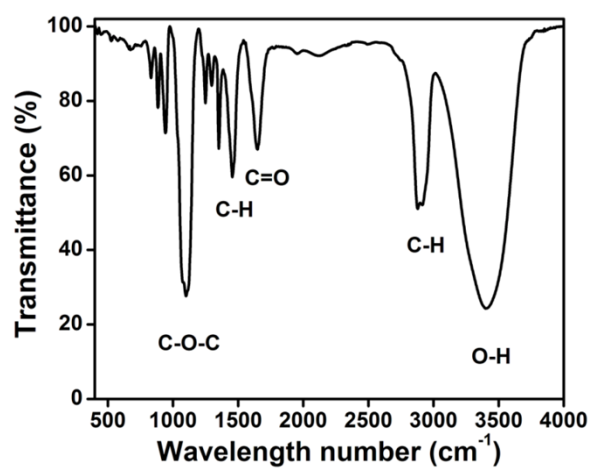


Fig.S4 FTIR spectrum of CQDs.

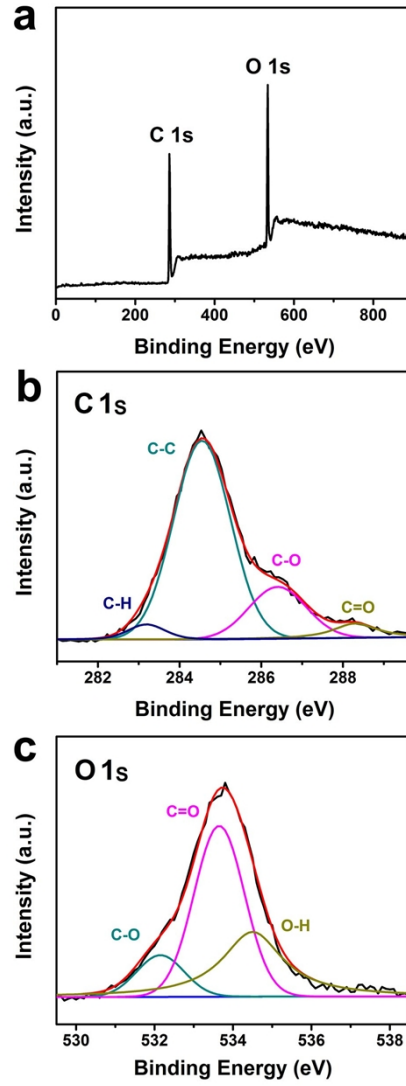


Fig. S5 (a) XPS full spectrum of CQDs. (b and c) High-resolution C 1s and O 1s XPS spectra.

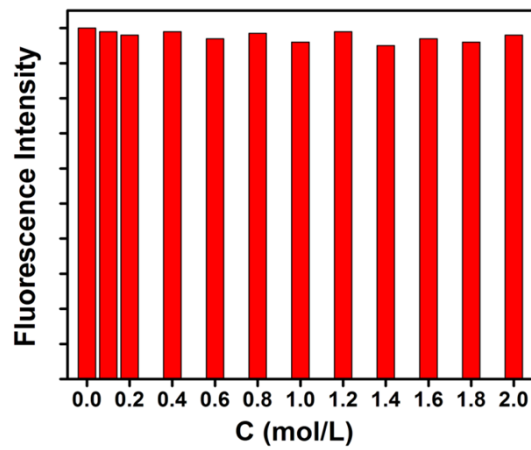


Fig.S6 Fluorescence intensity of CQDs in NaCl aqueous solution against ionic strength.

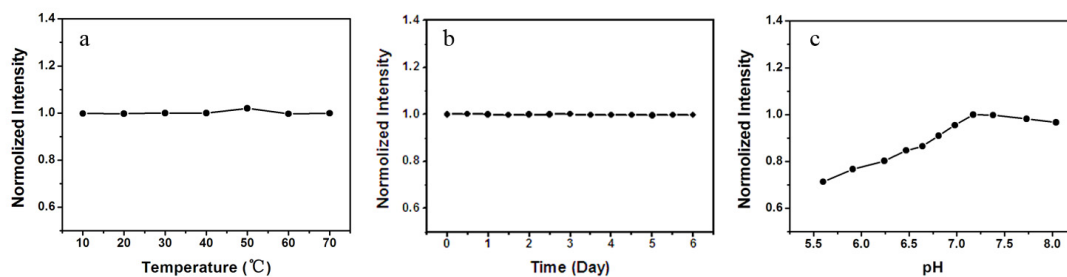


Fig. S7 Effects of temperature (a), stabilization time (b) and pH (c) on the normalized PL intensity of CQDs.

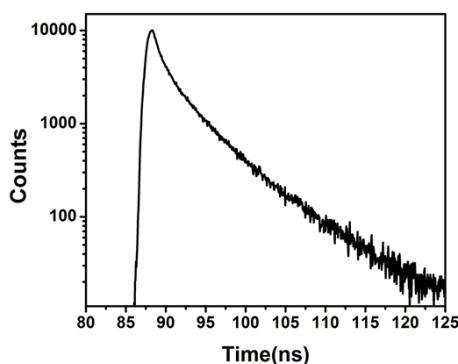


Fig.S8 Fluorescence lifetime of CQDs.

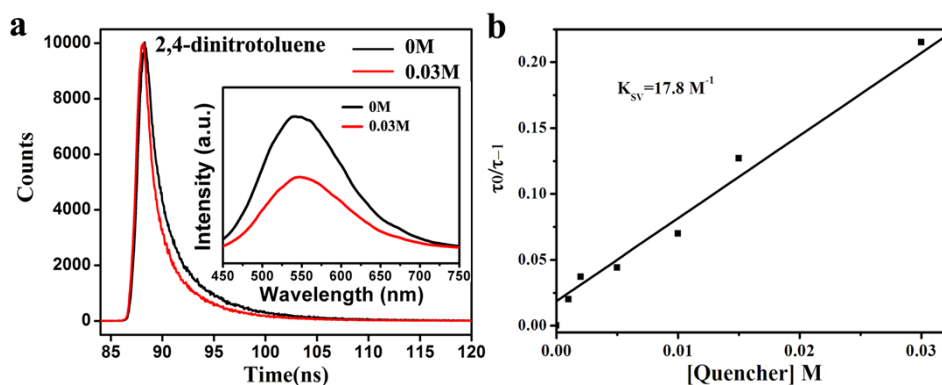


Fig. S9. (a) Luminescence decays (420 nm excitation, monitored with 560 nm narrow bandpass filter) of the CQDs with 2,4-dinitrotoluene. Inset: Luminescence emission spectra (420 nm excitation) of the CQDs in toluene without and with the quenchers (2,4-dinitrotoluene, 0.03 M). (b) Stern–Volmer plots for the quenching of luminescence quantum yields (420 nm excitation) of the CQDs by 2,4-dinitrotoluene.

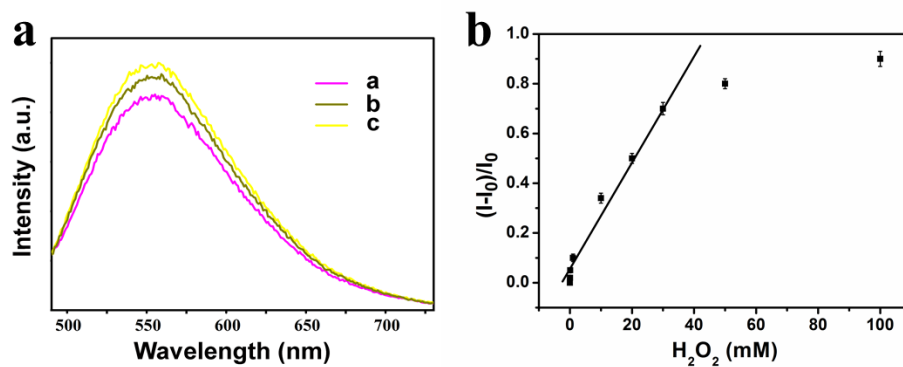


Fig. S10 (a) PL spectra of CQDs in the absence of H_2O_2 or GO_x a), presence of 0.5 mM H_2O_2 , b) and 0.5 mM glucose containing $15 \mu\text{g mL}^{-1}GO_x$ c) in PBS (pH 7.4) for 30 min. (b) The linear response of the enhanced efficiency $(I-I_0)/I_0$ of the CQDs vs. concentrations of H_2O_2 . All spectra were recorded under the identical experimental conditions and excited at 420 nm. I_0 and I are the PL intensities of the CQDs in the absence and presence of glucose, respectively.

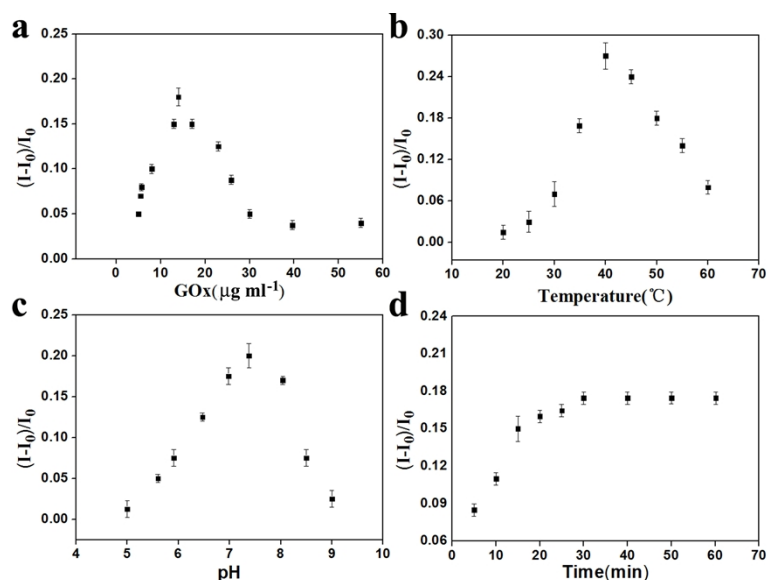


Fig. S11 Effects of GO_x concentration (a), temperature (b), pH values (c) and incubation time (d) on the enhanced efficiency of CQDs in the presence of 1 mM glucose containing GO_x ((b), (c) and (d) contain $15 \mu\text{g mL}^{-1}$).

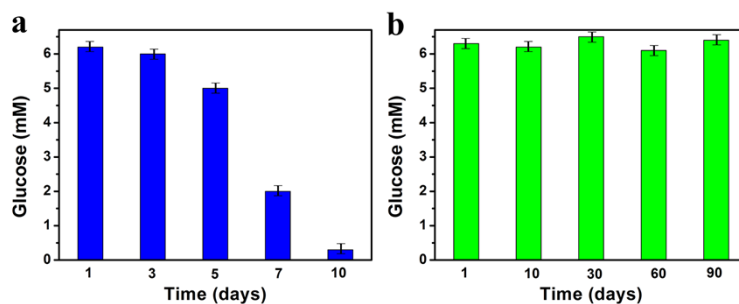


Fig. S12 Detection results of glucose with different time in serum obtained using (a) SiQDs and (b) CQD based on PL method. All measurements were performed in PBS, pH = 7.4, thermostated at 40 $^{\circ}\text{C}$.

°C for 30 min.

References

S1. N. W. Barnett, B. J. Hindson, P. Jones and T. A. Smith, *Anal. Chim. Acta*, 2002, **451**, 181–188.