Supporting Information

Label-free Si Quantum Dots as Photoluminescence Probe for Glucose Detection

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Instruments and chemicals

SiQDs synthesis was conducted on a CHI660A electrochemical workstation (CHI Instrument Inc., USA). The electrochemical system composed of silicon wafer with 5.0 cm length (area ~ 5 cm^2) as anode and carbon rod (diameter of 5 mm) as cathode. Transmission electron microscopy (TEM) images, high resolution transmission electron microscopy (HRTEM) and electron diffraction (ED) patterns were collected on a JEOL-1230 transmission electronic microscope (JEOL, Japan). Fourier transforms infrared (FTIR) spectra were collected on a Nicolet Nexus 670 FTIR instrument (Nicolet Instrument Co., USA). UV-Vis and fluorescence spectra were recorded on a UV-2450 spectrophotometer (Shimazu Co., Japan) and an F-4500 fluorescence spectrophotometer (Hitachi Co., Japan), respectively.

D-glucose and Glucose oxidase (GOx, 200 U mg^{-1}) were purchased from Shanghai Sangon Biotechnology Co. Ltd. (Shanghai, China). Carbon rods (diameter of 5 nm) were purchased from Shanghai Moyang electronic and carbon Co. Ltd. (Shanghai, China). Silicon wafer (phosphorus-doped (p-type), 8Ω resistivity) and phosphomolybdic acid (POM) were purchased from Sigma-Aldrich. Anhydrous ethanol (analytical grade), hydrofluoric acid (HF) and hydrogen peroxide (H_2O_2, 30%) were purchased from Shanghai Chemical Reagent. Human serum samples were provided by the hospital of Hunan Normal University (Changsha, China). All other chemicals used in this work were of analytical grade. Except the specific statement, the detection buffer was PBS buffer (pH 7.4, 5 mM sodium phosphate). Milli-Q ultrapure water (Millipore, ≥ 18 MΩ□ cm) was used throughout.

Experimental section

Synthesis of SiQDs: Photoluminescence SiQDs were synthesized by the POM-assisted electrochemical etching of bulk Si.[1] 0.015g POM was dissolved in 35 mL anhydrous ethanol, and then 35 mL H_2O_2 and 10 mL HF were added under stirring. Till the solution became transparent, silicon

wafer and carbon rod (length of 5 cm) were immerged in, of which silicon wafer worked as anode and carbon rod served as cathode. Amperometric i-t Curve was selected, the current density was kept in the range of 4-10 mA cm^{-2}. After etching about 1 hour, large amounts of SiQDs formed on the surface of silicon wafer. Without complicated centrifugation and filtration, just ultrasonication fracturing the etched silicon wafer in absolute ethanol, and then SiQDs with excellent fluorescence is obtained.

The procedure for the determination of the fluorescence quantum yields: Photoluminescence (PL) quantum yields of the silicon quantum dots were obtained by using the comparative method of Williams et al.[2] The quantum yield of SiQDs, Q_x, is calculated according to the following equation:

$$Q_X = Q_R \cdot \frac{A_R}{A_X} \cdot \frac{F_X}{F_R} \cdot \left(\frac{n_X}{n_R} \right)^2$$

where Q_R is the quantum yield of the standard, A is the absorbance of the solution, F is the corrected emission intensity and n is the average refractive index of the solution. Subscripts R and X refer to the reference and SiQDs, respectively. Quinine sulfate is used as the standard for the quantum yield correction. Fletcher[3] reported that the relative fluorescence quantum yield of quinine sulfate have no unexplainable deviations from a constant value with the excitation range set from 240 to 400 nm. The maximum excitation wavelengths of silicon quantum dots are at ~360 nm. Therefore, we chose 360 nm as the excitation wavelength. The quinine sulfate (Q_R = 0.54) was dissolved in 0.1 M H_2SO_4 (refractive index (n_R) of 1.33) and the SiQDs was dissolved in absolute ethanol (n_X= 1.003).[4] To minimize re-absorption effects, the absorbances of SiQDs and quinine sulfate solution were adjusted never exceed 0.1 at the excitation wavelength. The measurement results are as follows: A_R=0.053, A_x=0.045, F_X=2259, F_R=8729, $\frac{n_X}{n_R} = 0.7541$. The PL quantum yields of SiQDs were up to ~9.4%. As shown in Fig. 7S, the linear response of PL quantum yields of the SiQDs versus concentrations of glucose was obtained as well.

Analytes sensing by PL detection: For all tests and reactions, the experiments were repeated at least three times to ensure the accuracy of the measurement. All of the PL spectra were recorded on a fluorescence spectrophotometer. The emission spectra were recorded under a fixed excitation wavelength of 360 nm at a scan rate of 20 nm/s. For the study of the quenching effect of H_2O_2 on SiQDs, SiQDs was diluted with 5 mM phosphate buffer (PBS, pH 7.4), and a certain volume of H_2O_2 solution was added into the diluted SiQDs solution. For the detection of glucose, 30 μL of GOx (0.2 mg/mL) was mixed with 400 μL diluted SiQDs solution, then the glucose solutions with different concentrations were added into the SiQDs/GOx mixture, and then the mixed solution was diluted with PBS to 600 μL. The mixture was incubated at 40 °C for 30 min and measured by using fluorescence

spectrophotometer.

Analysis of glucose in serum samples: 30 μL of GOx (0.2 mg/mL), 400 μL diluted SiQDs 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 °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 360 nm.

Data Normalization Method: In order to make the data referenceable, all of the PL spectra were normalized. The peak intensity of PL spectra at 435 nm was selected as a standard. The normalized intensity was the ratio of I and I_0, where I and I_0 are the PL intensities of the SiQDs in the presence and absence of analytes, respectively. For investigating the effect of pH, temperature and time to the stability of SiQDs, the normalized intensity was obtained by using the maximum intensity of measurement as reference.

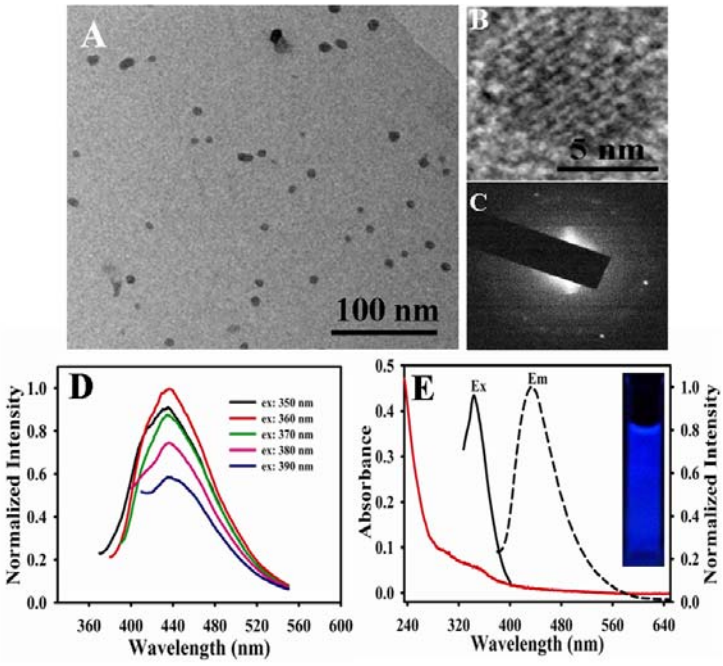

Figure S1 Typical TEM (A), HRTEM (B) and ED (C) images of SiQDs. (D) The normalized PL spectra of SiQDs at different excitation wavelength. (E) UV-vis absorption and excitation spectra (solid line) and emission spectra (dot line) of SiQDs; the inset shows the photo of SiQDs illuminated by UV light of 365 nm.

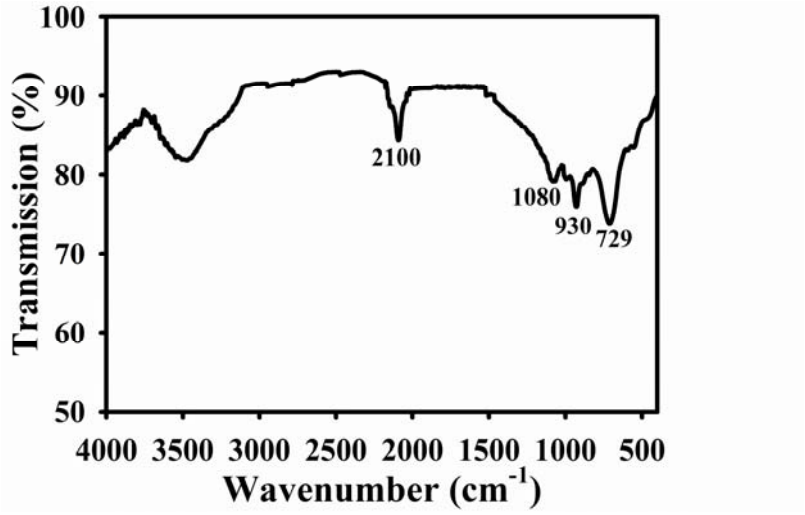

Figure S2 FTIR spectra of SiQDs

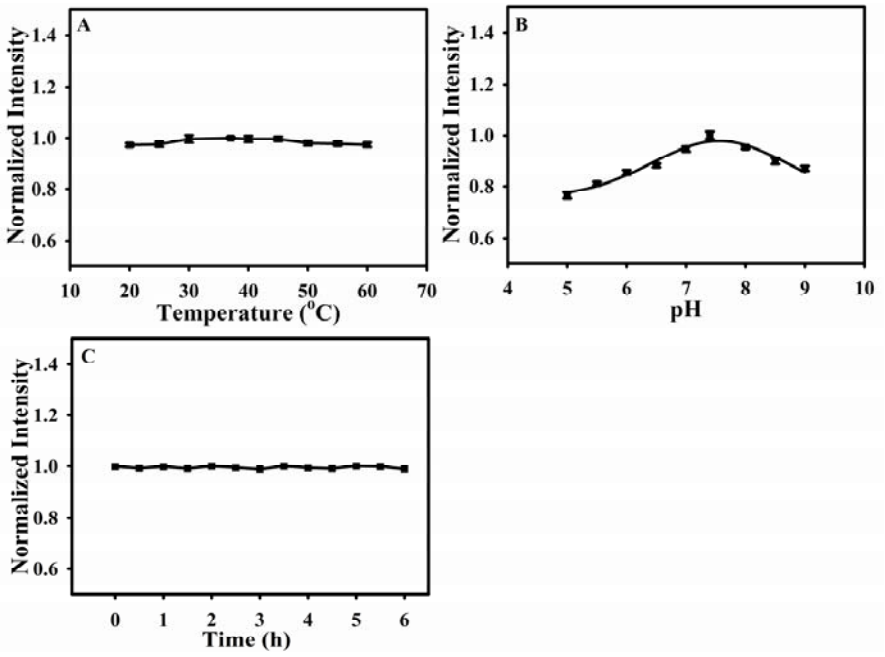

Figure S3 Effects of temperature (A), pH (B) and photostability (C) on the normalized PL intensity of SiQDs solution.

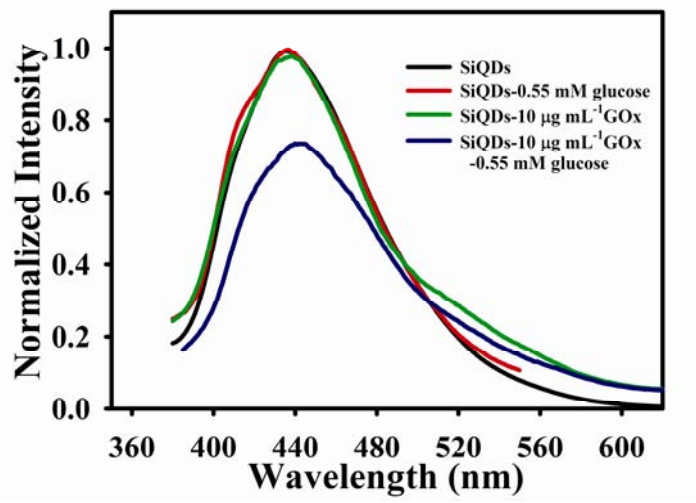

Figure S4 The normalized PL spectra of SiQDs (black line), SiQDs in the presence of 0.55 mM glucose (red line) and 10 μg mL^{-1} GOx (green line), blue line shows the PL apectra of SiQDs containing 10 μg mL^{-1} GOx after the addition of 0.55 mM glucose. All of the spectra were recorded after mixing the components for 30 min.

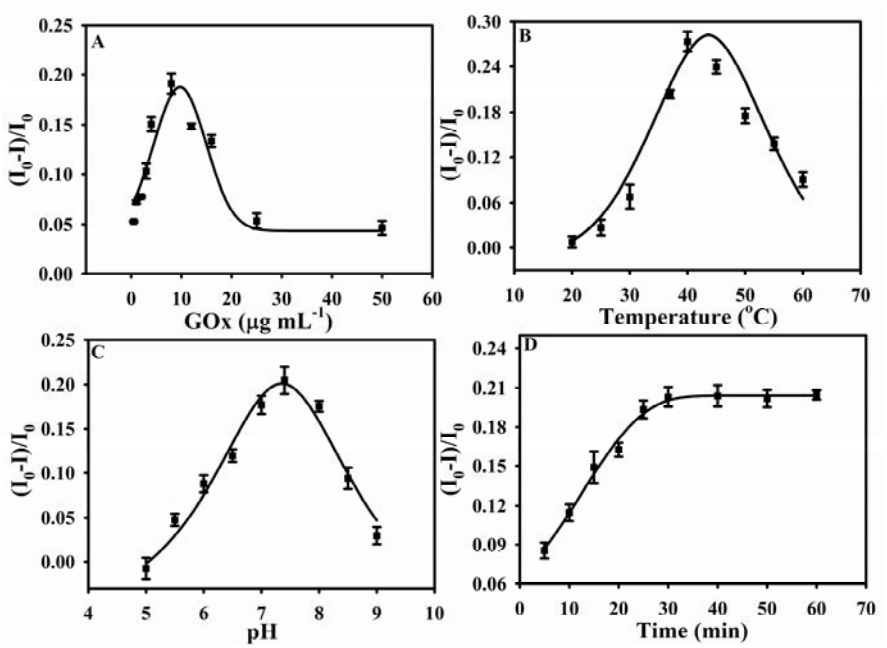

Figure S5 Effects of GOx concentration (A) temperature (B), pH values (C) and incubation time (D) on the quenched efficiency of the SiQDs in the presence of 0.55 mM glucose containing 10 μg mL^{-1} GOx.

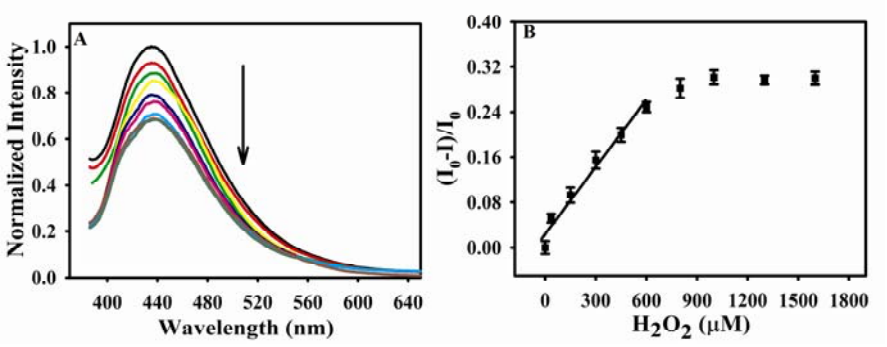

Figure S6 (A) The normalized PL spectra of SiQDs upon stepwise addition of H_2O_2 (from top to bottom, 0, 35, 150, 300, 450, 600, 800, 1000, 1300, 1600 μM). (B) The linear response of the quenching efficiency $(I_0 - I) / I_0$ of the SiQDs versus concentrations of H_2O_2. I_0 and I are the PL intensities of the SiQDs in the absence and presence of H_2O_2, respectively.

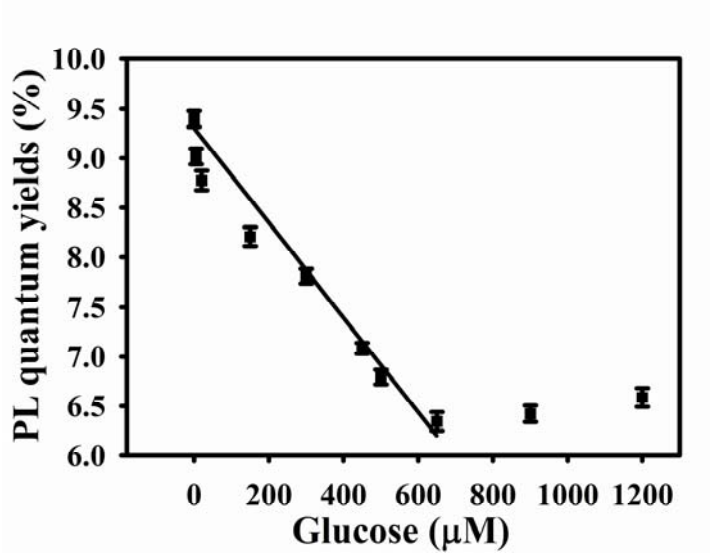

Figure S7 PL quantum yields of the SiQDs versus the concentration of glucose.

Table S1 Comparison of different nanoparticle-based methods for fluorescence detection of glucose.

Method	Enzyme immobilization	Linear range	Detect limit	Reference
Mn-doped ZnS QDs/Glucose Oxidase	Covalent conjugation	10 – 100 μM	3 μM	5
CdTe/CdS QDs/Glucose Oxidase	Not needed	1.8 – 1000 μM	1.8 μM	6
CdSe/ZnS QDs/glucose dehydrogenase	Biotin-avidin conjugation	Not given	10 μM	7
CdTe QDs /glucose oxidase	Covalent conjugation	5.0 – 1000 μM	0.10 μM	8
CdTe QDs/glucose oxidase multilayer film	assembly	0.5 – 16 mM	0.5 mM	9
SiQDs /glucose oxidase	Not needed	5 – 650 μM	0.68 μM	This work

References

1 Z. Kang; Y. Liu; C. H. A. Tsang; D. D. D. Ma; X. Fan; N.-B. Wong and S.-T. Lee, *Adv. Mater.,* 2009, **21**, 661.

2 A. T. R. Williams; S. A. Winfield and J. N. Miller, *Analyst,* 1983, **108**, 1067.

3 A. N. Fletcher, *Photochem. Photobiol.,* 1969, **9**, 439.

4 Q.-L. Zhao; Z.-L. Zhang; B.-H. Huang; J. Peng; M. Zhang and D.-W. Pang, *Chem. Commun.,* 2008, 5116.

5 P. Wu; Y. He; H.-F. Wang and X.-P. Yan, *Anal. Chem.,* 2010, **82**, 1427.

6 M. Hu; J. Tian; H.-T. Lu; L.-X. Weng and L.-H. Wang, *Talanta,* 2010, **82**, 997.

7 L. Bahshi; R. Freeman; R. Gill and I. Willner, *Small,* 2009, **5**, 676.

8 L. Cao; J. Ye; L. Tong and B. Tang, *Chemistry – A European Journal,* 2008, **14**, 9633.

9 X. Li; Y. Zhou; Z. Zheng; X. Yue; Z. Dai; S. Liu and Z. Tang, *Langmuir,* 2009, **25**, 6580.