Supporting Information

Water-Dispersible Silicon Dots as Peroxidase Mimetics for High-Sensitive Colorimetric Detection of Glucose

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Instruments and chemicals

Silicon wafer (phosphorus-doped (p-type), 8 Ω resistivity) and phosphomolybdic acid (POM) were purchased from Sigma-Aldrich. Carbon rods (5 mm in diameter) were purchased from Shanghai Moyang electronic and carbon Co. Ltd. (Shanghai, China). H_2O_2 (30 wt %), and hydrofluoric acid (HF) were purchased from Shanghai Chemical Reagent. Glucose, glucose oxidase (GOx, 200 U mg^{-1}) were purchased from Shanghai Sangon Biotechnology Co. Ltd. (Shanghai, China) and stored in a refrigerator at -18 °C. 3′,3′,5,5′-tetramethylbenzidine dihydrochloride (TMB·2HCl) was purchased from Aladdin chemistry Co. Ltd. Fructose, lactose, maltose, and galactose were purchased from Shanghai Zhongqin Chemical Reagent Company (Shanghai, China). Human serum samples were provided by the hospital of Hunan Normal University (Changsha, China). All other chemicals were analytical reagent grade and used without further purification. The water used throughout was purified through a Millipore system and nitrogen saturated before use (Millipore, ≥ 18 MΩ cm).

A CHI660A electrochemical workstation (CHI Instrument Inc., USA) was used for Si-dots synthesis. A three-electrode system was employed, including silicon wafer with 5.0 cm length (area~5 cm^2), a carbon rod and a saturated calomel electrode (SCE), which served as the work electrode, the counter electrode and the reference electrode, respectively. 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 an UV-2450 spectrophotometer (Shimadzu Co., Japan) and an F-4500 fluorescence spectrophotometer (Hitachi Co., Japan), respectively.

Experimental section

Synthesis of SiQDs: Si-dots were prepared by electrochemical etching method[1]. Briefly, 0.015 g POM was dissolved in 35 mL anhydrous ethanol, and then 35 mL H_2O_2 and 10 mL hydrofluoric acid (HF) were added under stirring. Till the solution became transparent, silicon wafer and carbon rod were immerged in and amperometric i-t curve was conducted in condition of keeping the current density in the range of 4~10 mA cm^{-2}. After etching about 1 hour, large amounts of Si-dots formed on the surface of silicon wafer. Ultrasonicating the etched silicon wafer in absolute ethanol and Si-dots were obtained.

Label-free Si-dots Peroxidase Mimetic-Based Colorimetric Assay: The colorimetric assay was performed as follows: a) 1 μL of 5 μg mL^{-1} GOx and 40 μL glucose with different concentrations in 0.1 mM Na_2HPO_4 buffer (pH 7.0) were incubated at 37 °C for 30 mins; b) 8 μL of 20 mM TMB, 10 μL Si-dots stock solution (50 μg mL^{-1}) and 470 μL of 0.2 M NaAc buffer (pH 4.0) were added into the above glucose solution (50 μL); and c) the mixed solution was incubated at 40 °C for 10 mins and kept in an ice-water bath for 10 mins to terminate the reaction, then the standard curve measurement was conducted.

Analysis of glucose in serum samples: For glucose detection in serum, the samples were first treated by ultrafiltration with 5 kDa in the amicon cell at 3000 rpm for 30 mins. 70 μL of the filtrate and 100 μL of 10 μg mL^{-1} GOx was added into 930 μL of 10 mM Na_2HPO_4 buffer (pH 7.0)，then incubated at 35 °C for 30 mins. After reaction, 50 μL of 20 mM TMB, 30 μL Si-dots stock solution and 2.92 mL of 0.2 M NaAc-HAc buffer (pH 4.0) were added. The mixed solution was incubated at 40 °C for 30 mins and then used for the glucose detection. In the control experiments, 10 mM maltose, 10 mM lactose, and 10 mM fructose were used instead of glucose.

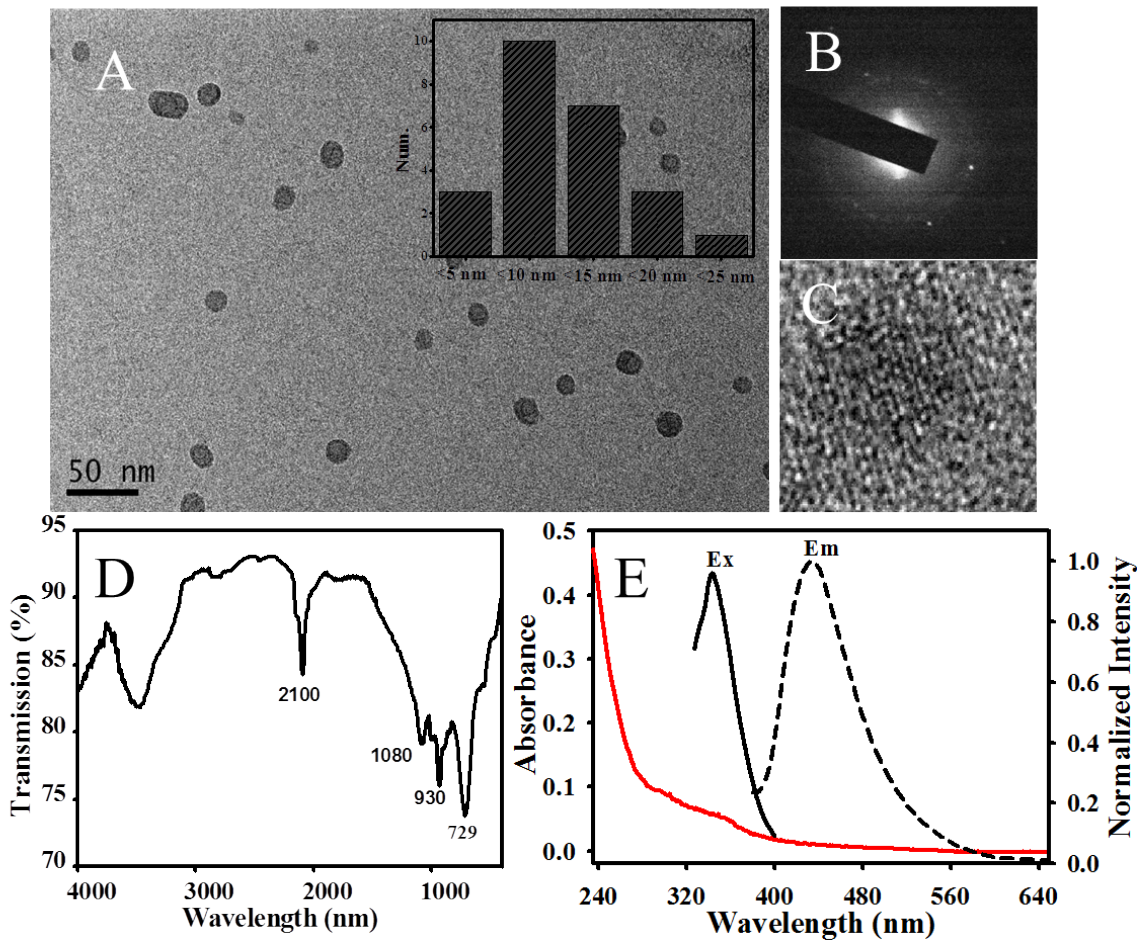

Fig. S1 Typical TEM (A), ED (B) and HRTEM (C) images of Si-dots. (D) FTIR spectra of Si-dots. (E) UV-vis absorption and excitation spectra (solid line) and emission spectra (dot line) of Si-dots; Inset: The corresponding particle size distribution histogram of the products.

spectra (dot line) of SiQDs; the inset shows the photo of SiQDs illuminated by UV light of 365 nm.

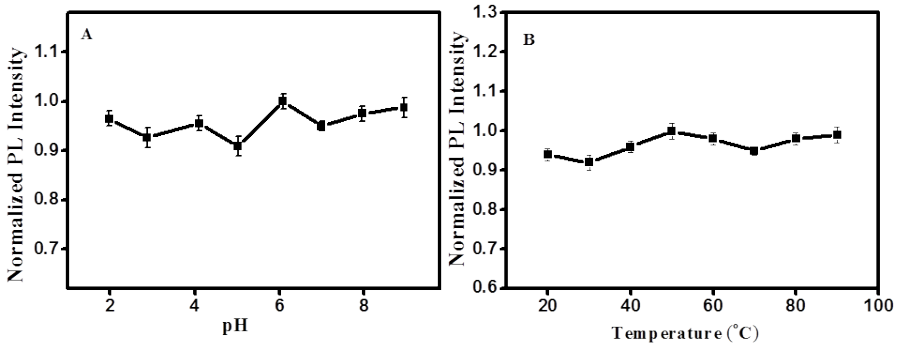

Fig. S2. Effects of temperature (A) and pH (B) on the normalized PL intensity of Si-dots solution. The error bars represent the standard deviation of three measurements.

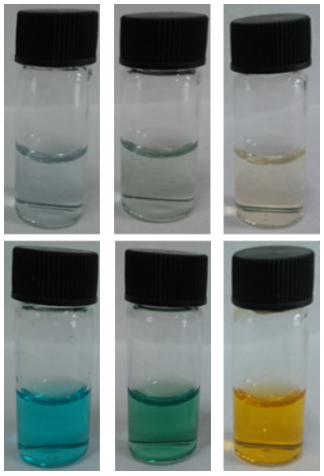

Fig. S3. Images of oxidation color reaction of TMB, OPD, and ABTS by H_2O_2 (from left to right) before (above) and after (below) by the catalysis of Si-dots dots.

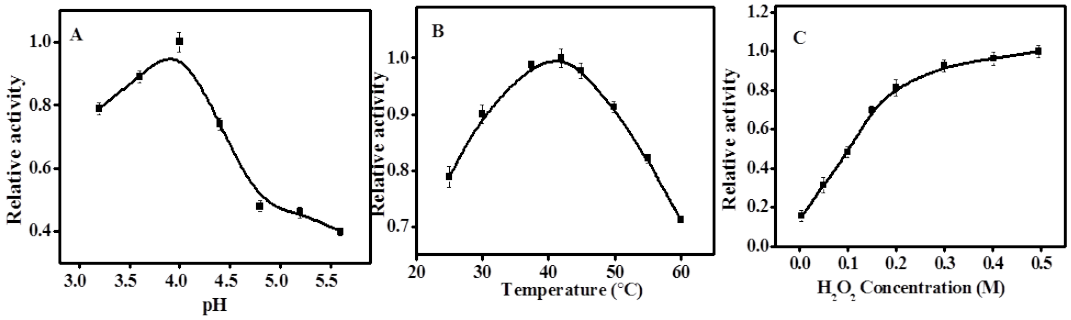

Fig. S4. Si-dots peroxidase-like activity is dependent on A) pH, B) temperature and c) H_2O_2 concentration; Experiments were carried out using 6 μL Si-dots in 580 μL HAc/NaAc buffer (0.2 M, pH 4.0) with 6 μL of 50 mM TMB or 6 μL of 0.01 mM H_2O_2 as substrate at pH 4.0 and 30 ℃ for 10 mins unless otherwise stated. Then the absorbance was read at the maximum absorbance of 652 nm. The maximum point in each curve was set as 1.0. The error bars represent the standard deviation of three measurements.

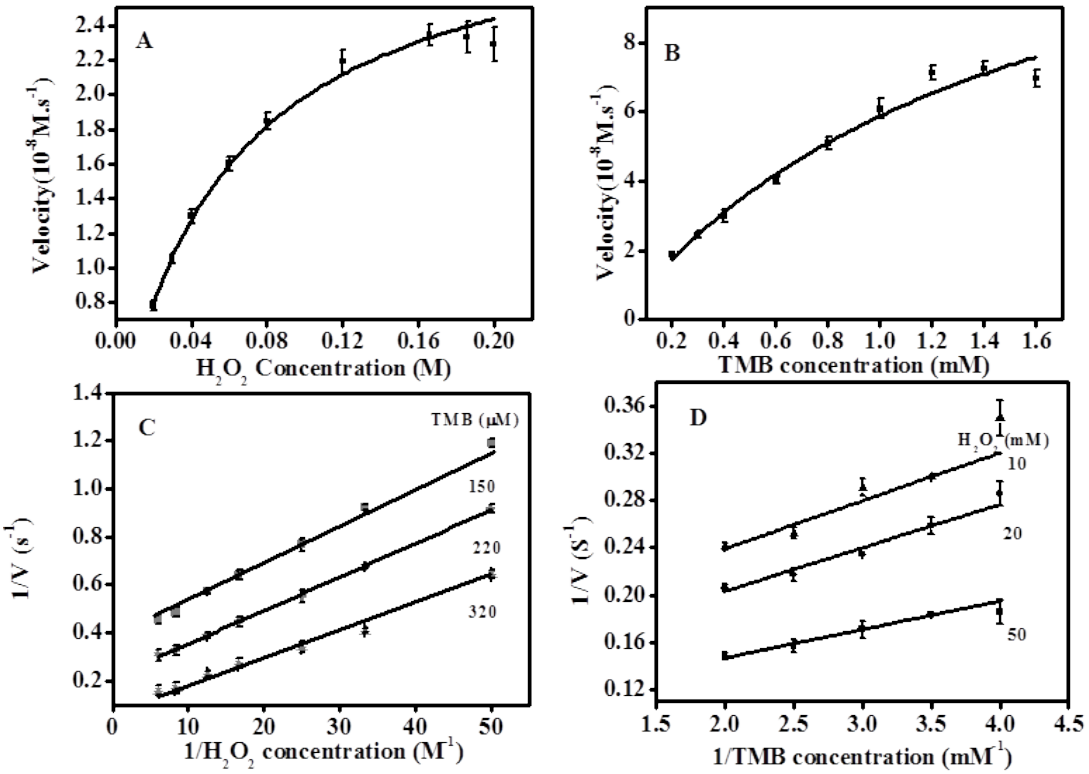

Fig. S5. Steady-state kinetic assay and catalytic mechanism of Si-dots (a–d). The velocity (v) of the reaction was measured using 10 μL Si-dots in 0.5 mL of 0.2 M NaAc/HAc buffer at pH 4.0 and 40 °C. The error bars represent the standard error derived from three repeated measurements. (a) The concentration of TMB was 320 μM and H_2O_2 concentration was varied. (b) The concentration of H_2O_2 was 20 mM and TMB concentration was varied. (c, d) Double reciprocal plots of activity of Si-dots with the concentration of one substrate (TMB or H_2O_2) fixed and the other varied.

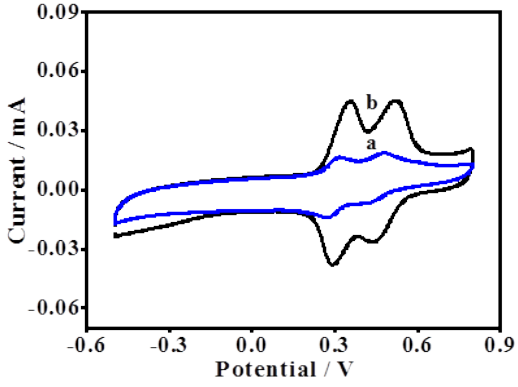

Fig. S6. CV curves of different electrodes in acetate buffer solution (pH 4.0, 0.2 mM KCl,) containing 1 mM TMB, 2.45 μM H_2O_2, scan rate of 100 mV*s^{-1}. a: GCE electrode; b: Si-dots/chitosan/GCE electrode.

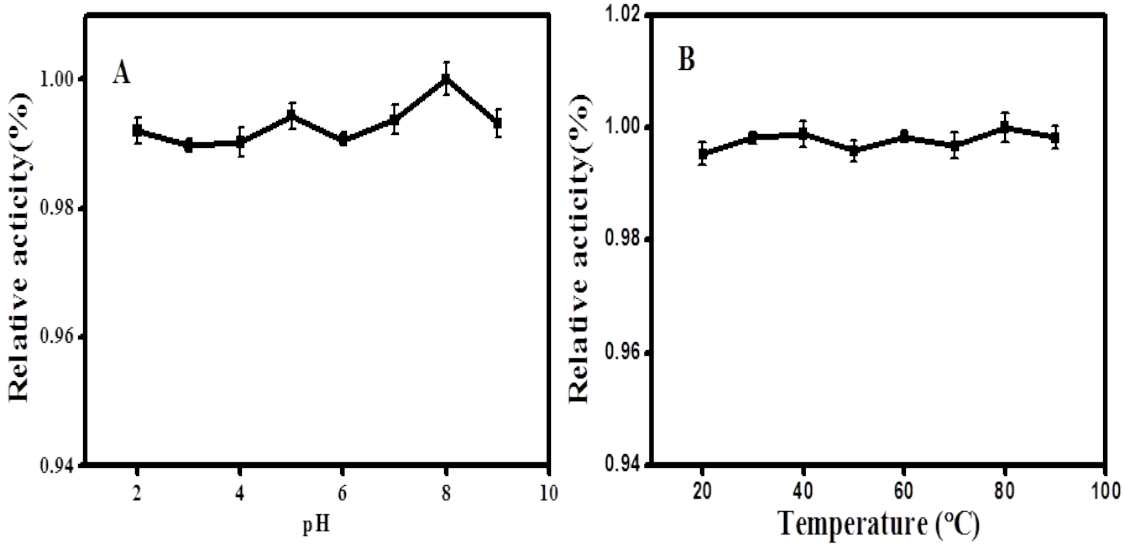

Fig. S7. Relative catalytic activity of Si-dots after incubation at a range of pH values (2-9) (A), and a range of temperatures (20-90 °C) for 2 h (B). The error bars represent the standard deviation of three measurements. The catalytic activity assay is carried out using 6 μL testing Si-dots in 580 μL HAc/NaAc buffer (0.2 M, pH 4.0) with 6 μL of 50 mM TMB or 6 μL of 0.01 mM H_2O_2 as substrate at pH 4.0 and 40 ℃ for 10 mins

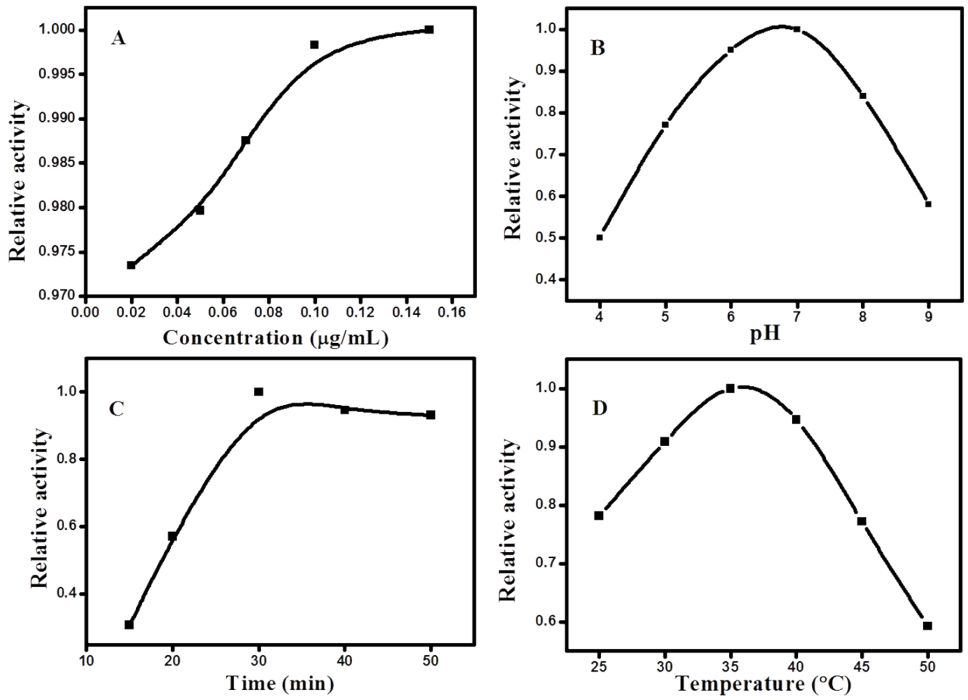

Fig. S8. Effect on activity of GOx in the (A)concentration, (B)pH, (C)accumulation time, and (D)temperature.

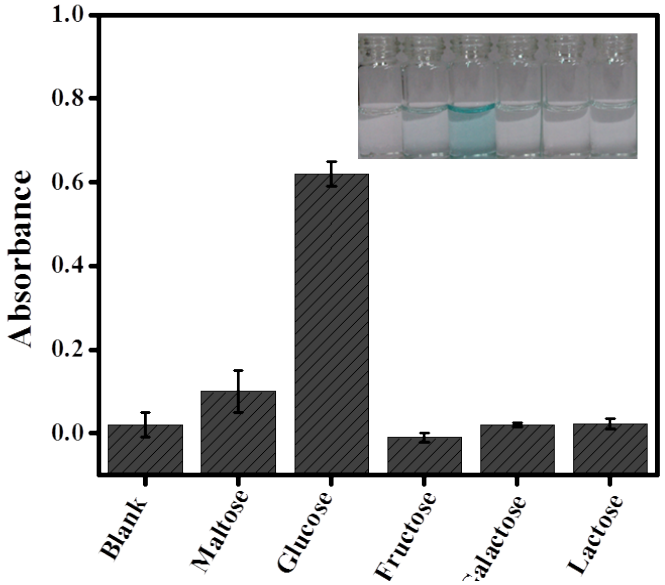

Fig. S9. Selectivity analysis of this system for glucose detection by measuring the absorbance at 652 nm ([maltose]=[fructose]=[galactose]=[lactose]=1 mM, [glucose]=0.1 mM). Error bars represent the standard deviation for three measurements. Inset: photographs of different solutions.

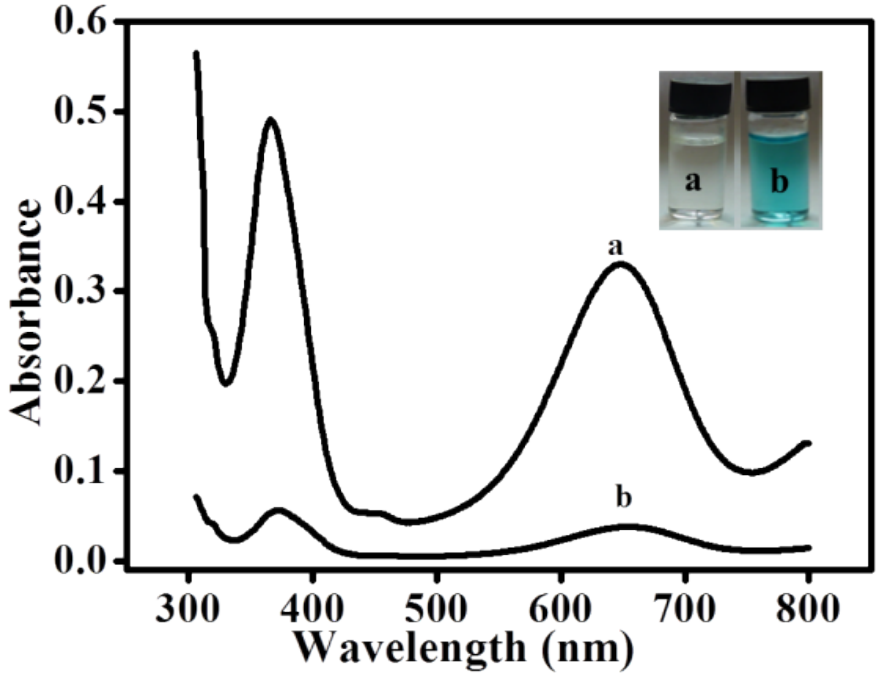

Fig. S10. UV−vis spectra of buffer solution (a) and 60-fold serial dilution of serum sample (b). Inset: Images of production of colored product for buffer solution and serum sample.

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

Method	Linear range	Detect limit	Reference
C-Dots/GOx	1-500 μM	0.4 μM	[2]
CNDs	1-5 μM	0.5 μM	[3]
GO-Fe_3O_4	2-200 μM	0.74 μM	[4]
$ZnFe_2O_4$	1.25-18.75μM	0.3 μM	[5]
Si-dots	0.17-200μM	0.05 μM	This work

Supporting References

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