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Enzyme free glucose sensing by amino-functionalized silicon quantum dot

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ABSTRACT

Silicon quantum dots have become one of the most popular nanomaterials in biological applications for their excellent biocompatibility and optical properties. Herein, we synthesized amino-functionalized silicon quantum dots (NH_2@SiQDs) via a simple microemulsion method, in which silicon tetrachloride and allylamine were used as source of silicon and functional group. NH_2@SiQDs exhibits good water-solubility, high fluorescence quantum yield and optical stability. A non-enzymatic biosensor of glucose was developed based on the fluorescence quenching of NH_2@SiQDs in response to glucose. The fluorescence response was linearly proportional to glucose in the concentration range of 1.0×10^{-6}–9.0×10^{-5} mol/L and the detection limit was determined to be 3.0×10^{-7} mol/L. The developed glucose sensor was successfully applied in blood glucose analysis of human serum. Satisfactory result that agreed very well with traditional method was obtained.

1. Introduction

Glucose is the most widely distributed and important monosaccharide in nature, and plays an important role in biological metabolisms [1–4]. Glucose has the function of strengthening memory, stimulating calcium absorption and increasing intercellular communication. High concentration of glucose however easily increases insulin levels and sequentially leads to obesity and diabetes [5,6], while a low level may induce hypoglycemia and even insulin shock (diabetic coma) [7,8]. Therefore, strict control of glucose content in the blood is essential to prevent long-term chronic diseases, including neurological diseases, cardiovascular diseases, color blindness and etc. [9,10]. To date, the detection of glucose are mainly conducted by principles of electrochemistry [11–14], spectrophotometry [15,16], capillary electrophoresis [17] and high performance liquid chromatography (HPLC) [18]. Recently, various enzymatic biosensors [19–21] have attracted increasing interests for their high sensitivity, selectivity and simplicity. However, enzyme is fragile to be inactivated, and sensitive to temperature and external conditions, which would lead to poor reproducibility in glucose sensing accuracy. Meanwhile, enzyme-based sensors are also of relatively high cost and short shelf life.

Research in developing novel nanomaterials today is attractive. People now are provided with a wide range of choices of nanomaterials based on their desired properties. For example, SiQDs are made of non-toxic and abundant material, offering one of the broadest spectrally ranges with emission tunabilities. Furthermore, colloidal SiQDs are feasible for low-temperature deposition on any substrates (such as glass, plastic, wood, and textile) using techniques like printing, roll-to-roll, stamping, spraying, or painting. Given their bright and tunable emission, colloidal SiQDs are found useful in large-area (flexible) displays, new types of lighting, and third generation photovoltaics-as "light paint" or "solar paint". Additionally, the nontoxicity and biodegradability of SiQDs opens up new opportunities for applications in fields of strict environmental/health concerns, for instances, in-vivo bioimaging, drug delivery, lab-on-chip sensing, optoelectronic toys, smart textiles, photocatalysis for water/waste/food sterilization, phototherapeutics, cosmetics and etc.

Silicon quantum dots (SiQDs) has excellent biocompatibility and can be readily functionalized and conjugated with biomolecules by various chemical modifications [22,23], making it suitable for labeling and detection in vivo [24–26]. Nevertheless, most native SiQDs are rather poor in water-solubility or incompatible with hydrophilic solvents due to the surface Si—H bonds [27], which limits its applications in biological and biomedical field [28,29]. However, appropriate functionalization of SiQDs would provide active morphology for beneficial electron and charge transport [30–33]. Hence, native SiQDs have to be modified with hydrophilic ligands to boost their water dispersibility and photostability, as well as fluorescence quantum yield if appropriate. In this paper, water-soluble allylamine-modified silicon quantum dots (NH_2@SiQDs) were synthesized by the micro-emulsion method [34]. They were further applied to construct a simple enzyme-free biosensor

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for sensitive glucose detection. The newly developed strategy not only eliminates the use of an enzyme, but also offers high stability, good reproducibility and cost-effectiveness for glucose sensing.

2. Experimental section

2.1. Material

Tetraoctylammonium bromide (TOAB, 98%), carbon tetrachloride ($SiCl_4$, 99.5%), lithium ($LiAlH_4$, 97%) and chloroplatinic acid ($H_2PtCl_6 \cdot 6H_2O$) as a reducing and catalytic agents, were obtained from Aladdin. Tetrahydrofuran (THF, allylamine (C_3H_7N, 99%) and isopropyl alcohol (C_3H_8O) were purchased respectively from Tianjin Kaitong, Chengdou Best and Beijing Chemical Company. Anhydrous toluene (C_7H_8), Dopamine (DA), ascorbic acid (AA), cysteine (Cys), glutathione (GSH) sucrose, D-fructose, glucose, sodium chloride (NaCl), potassium chloride (KCl), magnesium chloride ($MgCl_2$), calcium chloride ($CaCl_2$) were purchased from Aladdin. All other chemicals were of analytical reagent grade. Double distilled water (18.25 MΩcm) was used throughout the experiments.

2.2. Synthesis of NH_2@SiQDs

In nitrogen environment, tetraoctylammonium bromide (TOAB, 1.5 g) was dissolved in anhydrous toluene (100 mL), and then mixed with 92 μL carbon tetrachloride (0.8 mmol) and twice excess reducing agent lithium aluminum hydride(1 mol/L)in tetrahydrofuran solution. The mixture was allowed to react at room temperature for 3 h. Then 20 mL anhydrous methanol was slowly added to quench excess reductant. Hydrophilic NH_2@SiQDs particles were formed by modifying the surface silicon–hydrogen bonds by reacting with 2 mL allylamine and 40 μL chloroplatinic acid (H_2PtCl_6 0.05 mol/L) as catalyst in isopropanol. After surface modification, the white precipitate was collected through rotary evaporation and distillation to obtain hydrophilic NH_2@SiQDs. Finally, NH_2@SiQDs was dissolved in double distilled water (50 mL) and further filtered by 0.22 μm filter to remove reminding TOAB. NH_2@SiQDs solution was stocked at 4 °C.

2.3. Characterization of NH_2@SiQDs

The prepared amino-functionalized silicon quantum dots (NH_2@SiQDs) in aqueous solution was dripped on a copper grid and dried over 48 h. Then the feature and size distribution of the NH_2@SiQDs were measured by Transmission Electron Microscope (TEM). The absorption spectra were recorded by ultraviolet visible spectrophotometer (UV–vis) in the wavelength range of 200–600 nm. Infrared spectrum (IR) was measured by Bruker Tensor II Fourier Transform InfraRed spectroscopy (Bruker, Germany). Cary Eclipse fluorescence spectrophotometer (Varian, America) was used to measure fluorescence spectra. The excitation and emission slit was fixed to be 10 nm, respectively. The fluorescence lifetime of the functionalized quantum dots was measured using a FLS 9200 fluorescence spectrometer. The fluorescence quantum yield of quantum dots was calculated by Sankaran formula:

$$\Phi_S = \Phi_R \ (I_S/I_R)(OD_R/O_D) \ (\eta^2{}_S/\eta^2{}_R) \quad (1)$$

where, Φ_R is the fluorescence quantum yield of the standard substance, I_R is the integral area under the fluorescence curve of the standard substance, and η_R is refractive index of standard substance. In this experiment, quinine sulfate in 0.1 mol/L H_2SO_4 was used as the reference to calculate the quantum yield of NH_2@SiQDs, in which the fluorescence quantum yield of quinine sulfate is 0.54, refractive index of water is 1.33.

2.4. Detection of glucose

Silicon quantum dots solution (700 μL) was mixed separately with different amounts of glucose solutions of 5.0 mg/mL (0, 1, 5, 10, 20, 30, 40, 50, 60, 70, 80, 90, 100 and 200 μL) in phosphate buffer (10 mmol/L, pH = 7.0). Total volume was adjusted into 3.00 mL. After the mixture was reacted at 30 °C for 40 min, its emission spectrum was scanned at excitation wavelength of 363 nm with fixed excitation and emission slit 10/10 nm.

3. Results and discussion

3.1. Synthesis and characterization

The transmission electron microscopy (TEM) images in Fig. 1a reveals that the NH_2@SiQDs is uniformly dispersed in aqueous solution and its size is approximately 2.0 ± 0.3 nm (50 quantum dots). Fourier infrared spectroscopy (FTIR) of silicon quantum dots modified with allylamines was shown in Fig. 1b. The characteristic peaks at 1460 and 1260 cm^{-1} indicated the presence of Si-CH_2 [35]. The peaks between 2500 and 3500 cm^{-1} are attributed to the vibrational peaks of C-CH_2 and C-NH_2. The peaks between 1000 and 1100 cm^{-1} are attributed to the vibrational stretching of Si-OR. The vibrational peak of Si—H was not observed at 2100 cm^{-1}. It is suggested that amphetamine has been successfully decorated on silicon quantum dots. The fluorescence quantum yield of NH_2@SiQDs is calculated to 10.06% based on fluorescence and ultraviolet measurement. Moreover, the NH_2@SiQDs quantum dots have higher resistance against photobleaching as compared to a traditional fluorescent dyes, Rhodamine 6G (see Fig. 1c). Fig. 1d displays the UV–vis absorption spectra of NH_2@SiQDs, a broad absorption wavelength ranging from 200 to 600 nm was observed, and there were two distinct shoulder peaks at 265 nm and 310 nm. NH_2@SiQDs fluoresces at peak wavelength of 455 nm with the excitation 363 nm. As displayed in Fig. 1d inset, NH_2@SiQDs solution gives strong blue light under the irradiation of 365 nm ultraviolet light. Simultaneously, NH_2@SiQDs shows strong photoluminescence in the visible region, while the maximum emission peak is not affected much by the excitation wavelength (Fig. 1e), which supports that the quantum dots NH_2@SiQDs are appropriate candidate for applications such as bioimaging and biolabeling [36]. (See Scheme 1.)

3.2. Detection of glucose

Here, we report a simple strategy for detecting glucose based on the fluorescence quenching of silicon quantum dots by glucose. Fig. 2 shows the changes in the fluorescence emission of silicon quantum dots with response to different concentrations of glucose. It is clear that the fluorescence intensity of the NH_2@SiQDs gradually declines as of glucose concentrations increases (from 0 to 100 μmol/L), suggesting that glucose has a quenching effect on the fluorescence of NH_2@SiQDs. Moreover, the relative fluorescence intensity of NH_2@SiQDs displayed a good linear relationship with the glucose concentration. According to the Stern-Volmer equation, the linear regression equation is $F/F_0 = -0.00908[C] + 0.98997$. The linear range was 1.0×10^{-6}–9.0×10^{-5} mol/L, and the detection limit (S/N = 3) was estimated to be 0.3×10^{-6} mol/L, which is lower than other reported silicon materials for fluorescence based detection.

3.3. Optimization of the detection conditions

In order to optimize the performance of NH_2@SiQDs for glucose detection, we investigated the effects of reaction temperature, time, and pH value on the glucose sensing condition. The results showed that the temperature and pH value had no significant effect on the fluorescence response. The optimal temperature and pH (PBS buffer solutions) were then determined to be 30 °C and pH 7.0 respectively where

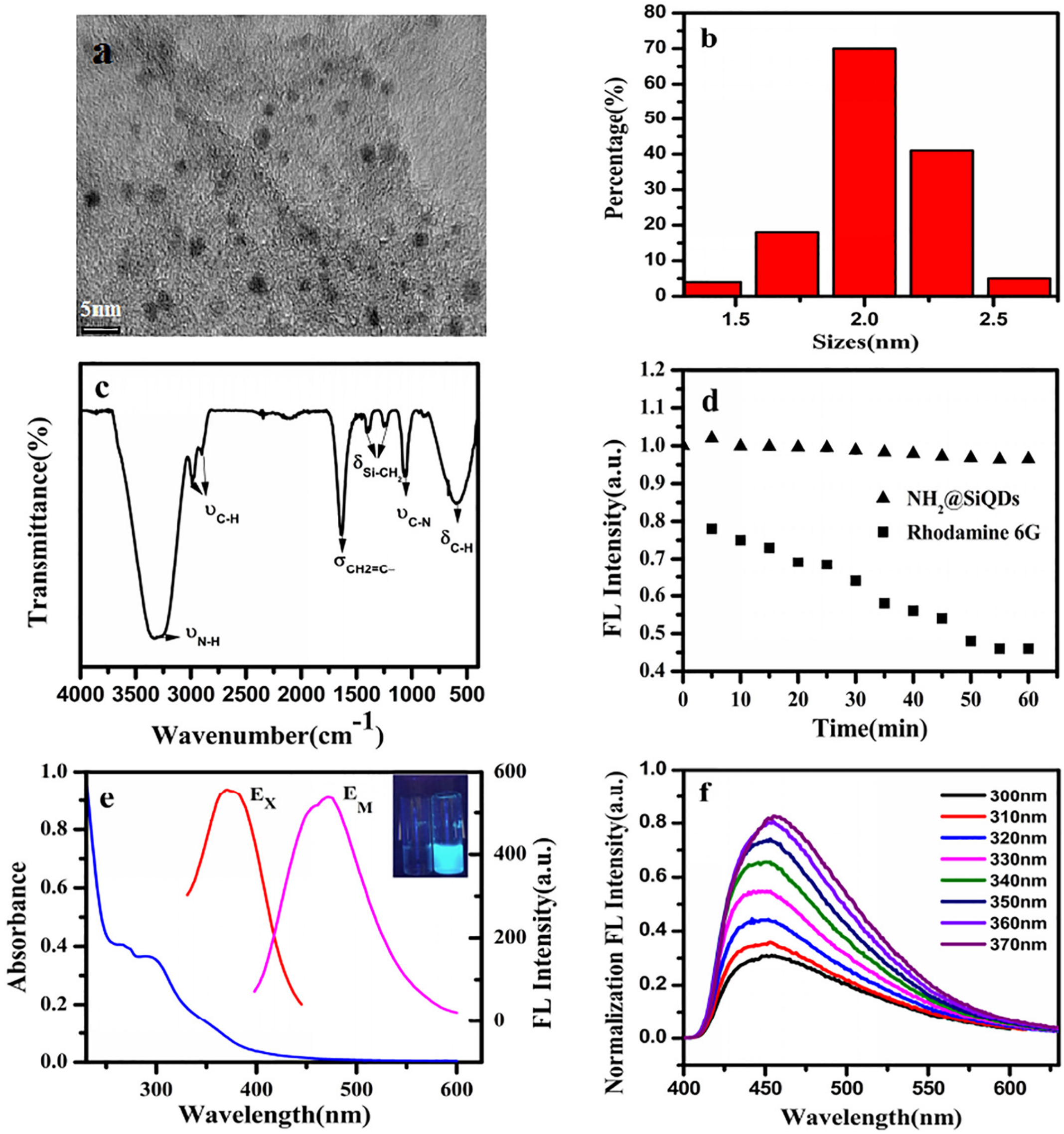
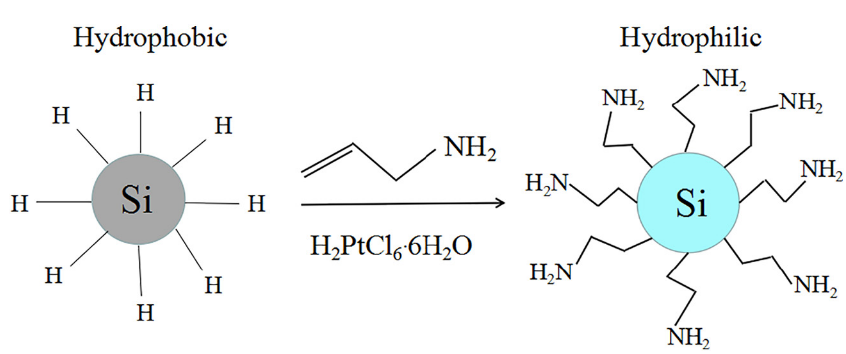


Fig. 1. (a) The TEM image of NH_2@SiQDs (inset plot of size distribution), the scale bar is 5 nm. (b) The IR image of NH_2@SiQDs. (c) Time-resolved photoluminescence decays of in aqueous solution. NH_2@SiQDs (Triangle) and Rhodamine 6G (square) in aqueous solution under the excitation wavelength at 363 nm. (d) UV–vis absorption spectrum and emission spectrum of the NH_2@SiQDs. (e) Excitation-independent FL behavior of NH_2@SiQDs.

maximal fluorescence quenching was given (Fig. 3a, c). The fluorescence signal of sensing system was stable beyond reaction time of 40 min, indicating a completed reaction (Fig. 3b). Therefore, the optimal conditions for glucose detection were performed at 30 °C, pH 7.0 and reaction time of 40 min.

3.4. Selective sensing of glucose

To evaluate the selectivity of the developed glucose biosensor, a series of major relevant carbohydrates, metal ions and amino acids were



Scheme 1. Schematic diagram of the amino-functionalized silicon quantum dot fabricated by H_2PtCl_6 catalyst.

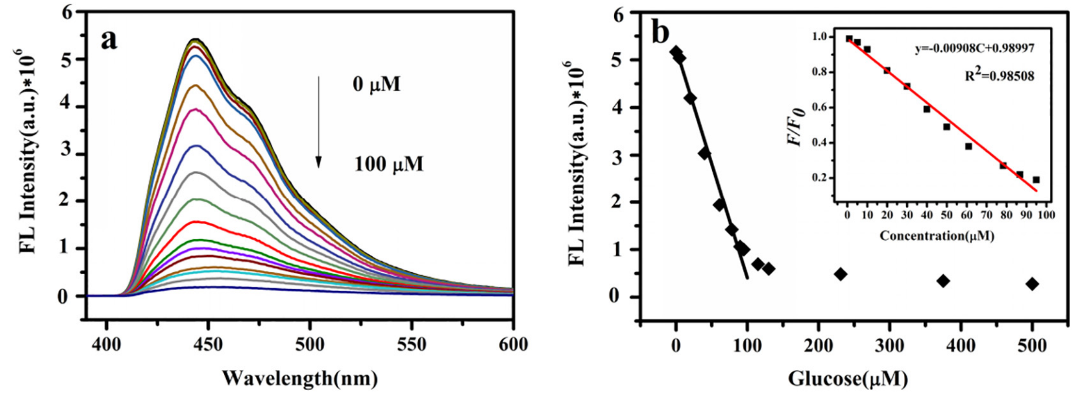


Fig. 2. (a) Fluorescence spectra of NH_2@SiQDs indicated with addition of the concentration of glucose (0–100 μmol/L). (b) The fluorescence intensity NH_2@SiQDs in the presence of glucose solution of different concentrations (excited at 363 nm). Insert: A plot of F/F_0 against the concentrations of glucose. Linear relationship was displayed.

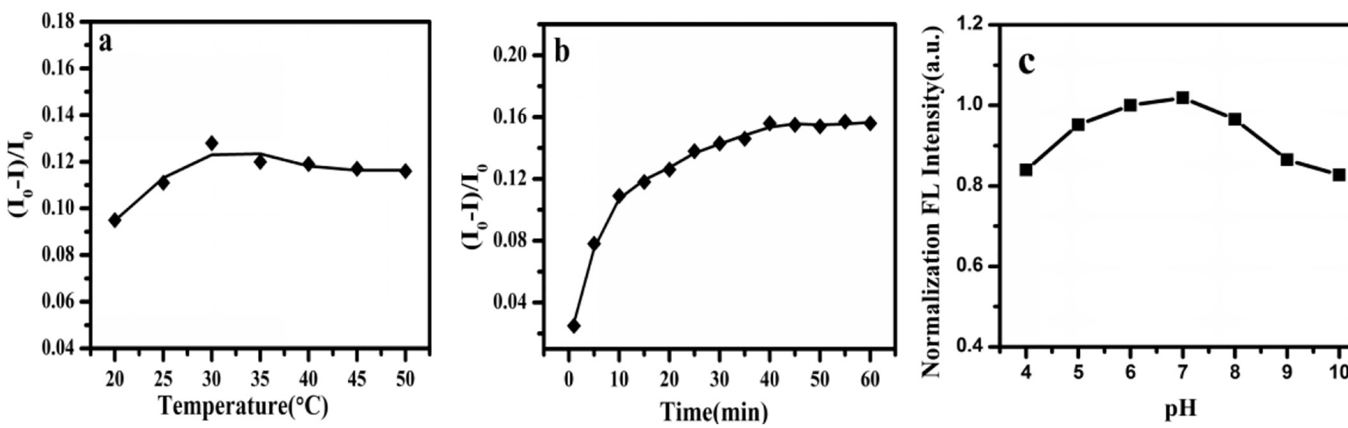


Fig. 3. The effects of temperature (a), incubation time (b), and pH value (c) on the glucose detection performance as indicated by the changes in fluorescence intensity.

adopted and studied under the optimized conditions. As elucidated in Fig. 4, several glucose analogues, such as sucrose and fructose, exhibited little influence on glucose detection even at a concentration 20 times higher than that of glucose. Common metal ions and amino acids also showed minimal interference in glucose determination. These results clearly demonstrated that the NH_2@SiQDs can serve as novel fluorescence probes for highly selective and reliable glucose monitoring.

3.5. Detection mechanism guess

TEM images of the NH_2@SiQDs in the presence of glucose were taken to investigate the sensing mechanism. Comparing the sizes of the particles before and after reaction, the TEM images (Fig. 1a and Fig. 5c) indicated the average size significantly increased in the presence of glucose. It was readily to find large "clusters" of the NH_2@SiQDs (average particle size is 3.59 nm). But the fluorescence lifetime and ultraviolet absorption spectrum of the SiQDs in the absence and presence of glucose were essentially the same, indicating no new material formation. It can be attributed to the fact that glucose molecules linked the NH_2@SiQDs together via H-bonding and hydrophobic interactions that induced the self-aggregation of the QDs and thus quenched the fluorescence (Scheme 2). Upon sonication, the linkage among NH_2@SiQDs and glucose are broken and the fluorescence of NH_2@SiQDs recovered (Fig. 5d). The native fluorescence intensity of NH_2@SiQDs recovered to 98% after 25 min of sonication.

As summarized in Table 1, the performance of the NH_2@SiQDs glucose sensor was compared with other silicon nanomaterials in the aspects of linear range and detection limit. Compared with other enzymatic Si-based fluorescence nanosensors, this sensitive glucose sensor provides an enzyme-free, simple, direct but low-cost detection strategy for glucose detection.

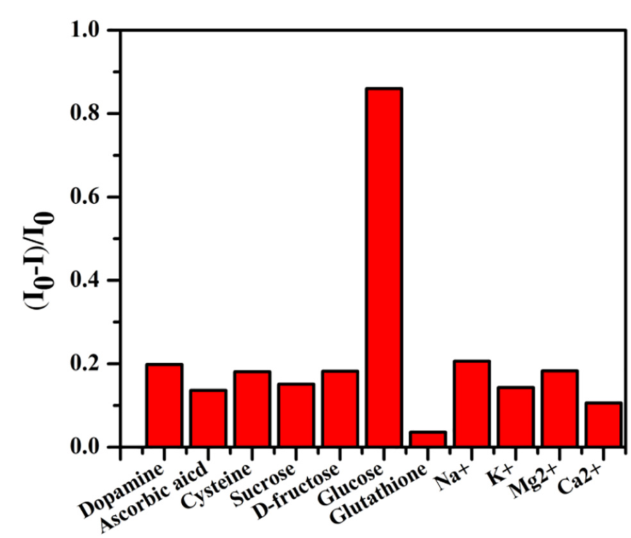


Fig. 4. Selective responses of NH_2@SiQDs to glucose over other relevant carbohydrate, metal ions and amino acids.

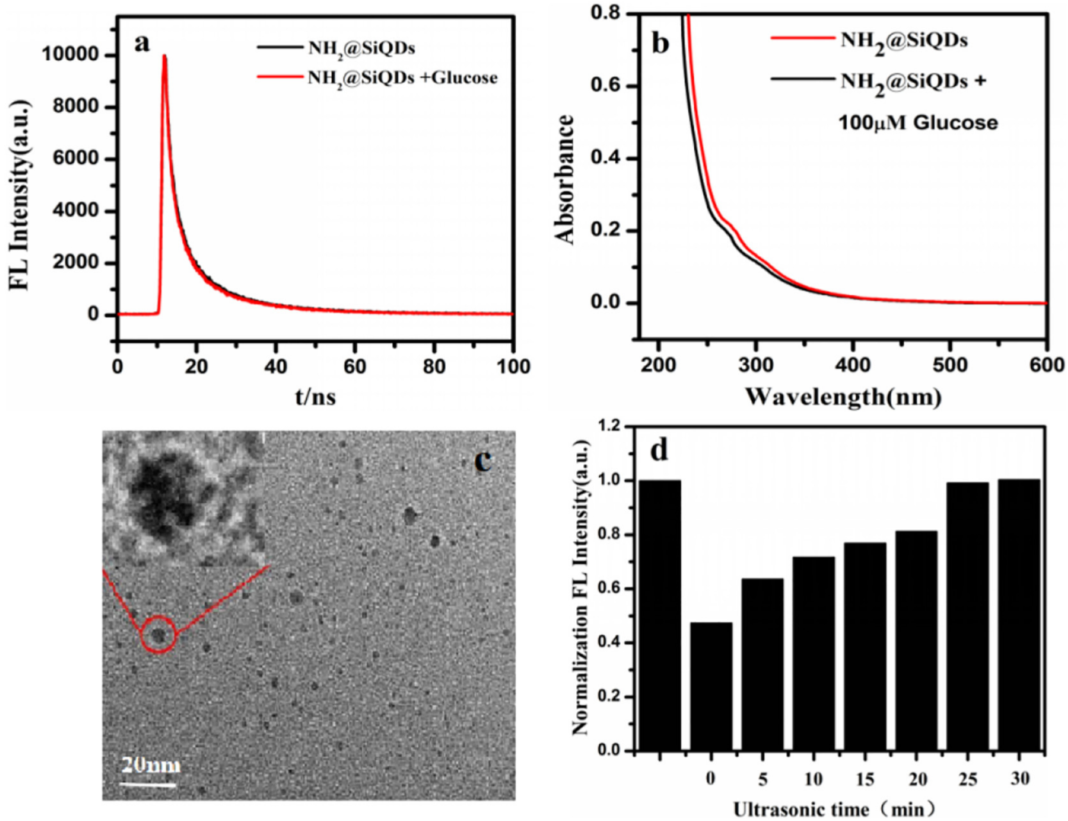
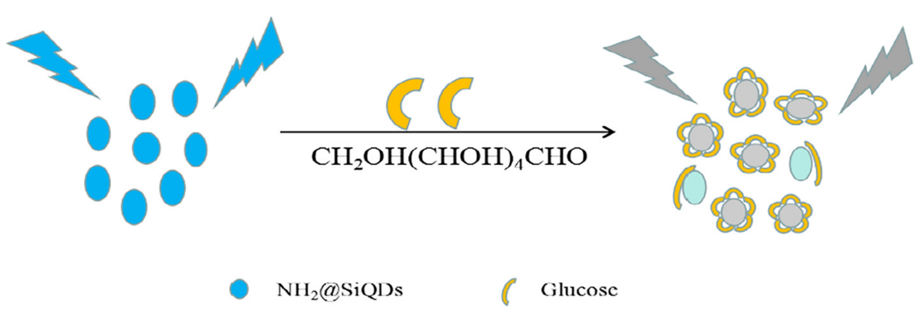


Fig. 5. (a) Photoluminescence decays of NH_2@SiQDs and NH_2@SiQDs with 0.3 mM glucose in water measured at emission wavelengths 455 nm; (b) UV–vis absorption spectra of NH_2@SiQDs and NH_2@SiQDs with 100 μM glucose; (c) TEM image of the NH_2@SiQDs with 0.3 mM glucose, the scale bar is 20 nm; (d) Fluorescence intensity of NH_2@SiQDs gradually recovered upon lengthened sonication duration (glucose concentration of 50 μM).

3.6. Real sample detection

To evaluate the practicability of NH_2@SiQDs biosensors, glucose content in human serum was determined by standard addition method using NH_2@SiQDs. The sample of human serum was provided by the Hospital of Shanxi University and was diluted by 100 times with ultrapure water for direct determination. As expected, the fluorescence intensity of NH_2@SiQDs was gradually reduced with increasing glucose spiked concentrations (Table 2). The recovery rate was between 92.5%–98.7%, and the RSD value is less than 7%. The result shows that



Scheme 2. Schematic illustration of the free-enzyme biosensor for sensitive glucose detection.

Table 1
Compared with reported silicon nanomaterials for glucose detection.

Method	Detection	Monitoring system	Linear range	Detect limit	Reference
Silica sol-gel	Oxygen sensing/GOx	Fluorescence Enhancement	0.1–5 mM	0.06 mM	[37]
SiQDs	GOx	Fluorescence Quenching	5–650 μM	0.68 μM	[38]
Mesoporous Si NWs	GOx	Fluorescence Enhancement	0.1–50 mM	1.06 μM	[39]
Si NPs	GOx	Fluorescence Quenching	0.01–7 mM	3.5 μM	[40]
Si-dots	GOx	Colorimetric	0.17–200 μM	0.05 μM	[41]
NH_2@SiQDs	Direct Detection	Fluorescence Quenching	1–90 μM	1 μM	This work

Table 2
Adding standard recovery test to detect glucose in human serum ($n = 3$).

	Added (μM)	Detected (μM)	Recovery rate (%)	RSD (%)
1[a]	0	45.8		
2	10	53.4	95.7	5.41
		52.4	93.9	
		55.1	98.7	
3	20	62.1	94.4	6.94
		61.1	92.8	
		66.0	96.5	
4	30	73.3	96.7	5.94
		70.1	92.5	
		73.7	97.2	

[a] Hospital test result was 4.6 mmol/L as measured by commercial blood glucose meter.

this glucose sensor is suitable and promising for the determination of glucose in human serum samples.

4. Conclusion

In summary, we prepared amino-functionalized silicon quantum dots by microemulsion method. (NH_2@SiQDs). The as-prepared NH_2@SiQDs possesses high water solubility, high fluorescence quantum yield and photostability. Additionally, NH_2@SiQDs was demonstrated to be capable of sensing blood glucose without enzyme. The detection range of this method is 1.0×10^{-6}-9.0×10^{-5} mol/L with a detection limit of 0.3 μmol/L. Compared to the existing electrochemical non-enzymatic glucose sensors, its superior selectivity and sensitivity are well elucidated. It provides insights for the further applications of such silicon quantum dots/electrochemical nanomaterials in non-enzymatic glucose biosensing.

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