

# Direct electrochemistry and electrochemical biosensing of glucose oxidase based on CdSe@CdS quantum dots and MWNT-modified electrode

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**Abstract** The direct electron transfer of glucose oxidase (GOx) was achieved based on the immobilization of CdSe@CdS quantum dots on glassy carbon electrode by multi-wall carbon nanotubes (MWNTs)-chitosan (Chit) film. The immobilized GOx displayed a pair of well-defined and reversible redox peaks with a formal potential ( $E^0$ ) of  $-0.459$  V (versus Ag/AgCl) in  $0.1$  M pH 7.0 phosphate buffer solution. The apparent heterogeneous electron transfer rate constants ( $k_s$ ) of GOx confined in MWNTs-Chit/CdSe@CdS membrane were evaluated as  $1.56$  s $^{-1}$  according to Laviron's equation. The surface concentration ( $\Gamma^*$ ) of the electroactive GOx in the MWNTs-Chit film was estimated to be  $(6.52 \pm 0.01) \times 10^{-11}$  mol cm $^{-2}$ . Meanwhile, the catalytic ability of GOx toward the oxidation of glucose was studied. Its apparent Michaelis–Menten constant for glucose was  $0.46 \pm 0.01$  mM, showing a good affinity. The linear range for glucose determination was from  $1.6 \times 10^{-4}$  to  $5.6 \times 10^{-3}$  M with a relatively high sensitivity of  $31.13 \pm 0.02$   $\mu$ A mM $^{-1}$  cm $^{-2}$  and a detection limit of  $2.5 \times 10^{-5}$  M ( $S/N=3$ ).

**Keywords** Glucose oxidase · CdSe@CdS quantum dots · Multi-walled carbon nanotubes · Glucose biosensor

## Introduction

The direct electron transfer between the redox site of enzymes and the electrodes is a great goal which researchers have been pursuing recently, because it can establish a

desirable and ideal model for the fundamental study of the redox behavior of the enzymes in biological systems [1–4]. However, it is difficult for the redox proteins to exchange electron with electrode surface because the denaturation and loss of electrochemical activities occurred when the proteins adsorbed on the electrode surface [5]. Therefore, searching for a material with good biocompatibility for redox proteins immobilization on electrode surface is important to obtain their direct electrochemical reaction and keep their bioactivities.

Because of their unusual physical and chemical properties, nanomaterials have been intensively applied in various fields in recent years. The immobilization of redox proteins on the biocompatible nanoparticles could not only help the proteins to obtain favored orientation but also facilitate the direct electron transfer between them and the electrode [6]. As one of the promising nanoparticles, semiconductor quantum dots (QDs) have drawn intense research interest because of their interesting optical and electronic properties [7]. Quantum dots, which can also be called nanocrystals, are generally applied to semiconductor particles whose sizes are of the order of a few to hundreds of angstroms. They often have an inorganic core and a capping shell, such as CdSe@CdS core-shell QDs. CdSe@CdS QDs are ideal candidates for sensing applications because of their high quantum yield, photostability, extremely large surface-to-atom ratio, and sensitivity to surface ligands [8–10]. Some studies showed that the CdSe@CdS QDs have been used to immobilize hemoglobin (Hb) on a glassy carbon electrode (GCE) [11].

In this article, we developed a new biosensor by using the composite membrane of MWNTs-Chit [12] and the core@-shell CdSe/CdS QDs to immobilize GOx on the surface of glassy carbon electrode. The composite nanomaterials composed of MWNTs-Chit and CdSe/CdS could play an

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important role in adsorbing the GOx onto the electrode surface. A pair of well-defined quasi-reversible redox peaks of glucose oxidase were obtained at MWNTs-Chit/CdSe@CdS-based enzyme electrode. Meanwhile, this new electrochemical system can utilize synergy effect between MWNTs and CdSe@CdS to facilitate electron-transfer processes and retain the good bioactivity of GOx. This biosensing platform based on MWNTs-Chit/CdSe@CdS electrode responded preferable sensitively and selectivity to glucose.

## Experimental

### Reagents

GOx and uric acid (UA) were purchased from Sangon Chemical Co. Ltd. The MWNTs (>95 % purity) were purchased from Shenzhen Nanoport Co. Ltd. Chitosan (deacetylation, >95 %) was obtained from Sanland Chemical Co. Ltd. Dopamine (DA), Nafion (5 wt.%), and ferrocenemethanol were purchased from Aldrich Chemical Co. Ltd. Mercaptoacetic acid (MA) were obtained from Alfa Aesar-A Johnson Matthey Company (Heysham, UK). Glucose, ascorbic acid (AA), cadmium chloride (CdCl<sub>2</sub>), sodium sulfide, and selenium were obtained from Beijing Chemical Reagent Co. (Beijing, China). Sodium borohydride was purchased from Tianjin Chemical Reagent Co. (Tianjin, China). The supporting electrolyte was 0.1 M KCl. The 0.1-M phosphate buffer solutions (PBS) with various pH values were prepared by mixing stock standard solutions of Na<sub>2</sub>HPO<sub>4</sub> and NaH<sub>2</sub>PO<sub>4</sub>. All other chemicals were of analytical grade and were used without further purification. All solutions were made up with double-distilled water.

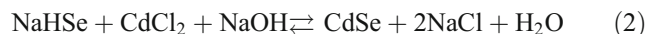
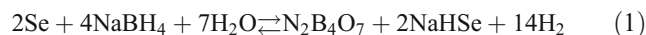
### Apparatus

UV-vis spectra were recorded on a GBC Cintra 10e UV-Visible spectrometer. All electrochemical measurements were performed at room temperature using a CHI 660C electrochemical workstation (Chenhua Instrument Co., Shanghai, China). A conventional three-electrode system was used with an Ag/AgCl (saturated KCl) electrode as the reference electrode, a platinum wire as the counter electrode, and a modified GCE (3 mm in diameter) as the working electrode. Cyclic voltammetric measurements were performed in a static cell while amperometric experiments were carried out in a stirred system. All solutions were purged with high-purity nitrogen for at least 20 min prior to experiments, and a nitrogen environment was then kept over the solution in the cell. Aliquots of glucose solution were added successively to

the solution in amperometric experiments. Current-time data were recorded after a steady-state current had been achieved.

### Synthesis of CdSe@CdS quantum dots

All glassware used in the procedures was firstly washed with freshly prepared HNO<sub>3</sub>/HCl (1:3, v/v), then rinsed thoroughly with double-distilled water, and dried prior to use. CdSe@CdS quantum dots were prepared as previously reported using the reaction between CdSe QDs and Na<sub>2</sub>S solution [13]. Firstly, NaHSe solution was obtained by using the reaction between selenium and sodium borohydride. CdSe QDs was synthesized by adding freshly prepared NaHSe solution to N<sub>2</sub>-saturated CdCl<sub>2</sub> solution in the presence of mercaptoacetic acid as a stabilizer at pH 11. Reactions are as follow:



The precursors were converted to CdSe nanocrystals by refluxing the reaction mixture for 5 min at 90 °C under open-air conditions with condenser attached. Then Na<sub>2</sub>S solution was added slowly before further refluxing for 1–2 h at 90 °C. The molar ratio between S and Se was controlled to be 1:1. The samples collected were then dialyzed against double-distilled water for 5 h to remove excessive MA. The final solution was stable when stored in a refrigerator at 4 °C for 2.5 months.

### Preparation of MWNTs-Chit/GOx/CdSe@CdS/GCE

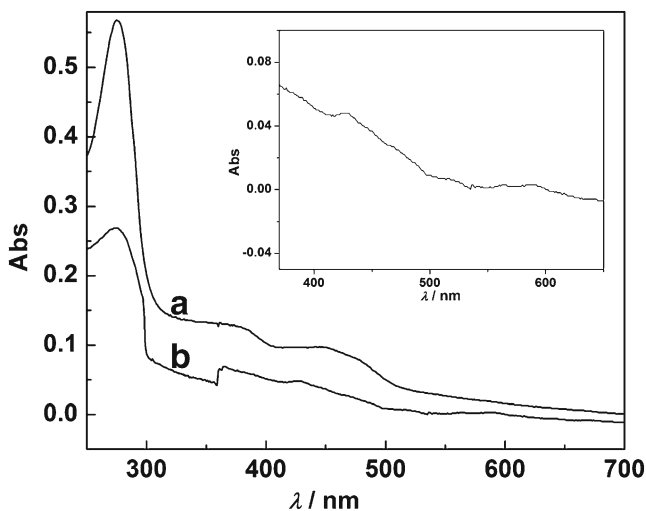
Glassy carbon electrode (3 mm diameter) were polished firstly with 1.0-, 0.3-, and 0.05- $\mu\text{m}$  alumina slurry. After rinsing thoroughly with double-distilled water, they were sonicated in absolute ethanol and double-distilled water for about 1 min, respectively. Upon putting 25 mg of MWNTs into 5 mL of a chitosan solution (1 wt.%), ultrasonic agitation for a few minutes gave a black suspension. GOx solution was obtained by dissolving 6.0 mg of GOx in 3 mL of 0.1 M pH 6.5 PBS, and the CdSe@CdS was used as prepared. Then 10  $\mu\text{L}$  mixture of GOx and CdSe@CdS (v/v=1:1) was dropped onto the surface of a cleaned glassy carbon electrode with a microsyringe and allowed to dry at 4 °C for 12 h. After the GCE was cooled, it was smeared evenly with 8  $\mu\text{L}$  of a MWNTs-chitosan (1 wt.%) solution by a microsyringe and then dried at a temperature of 4 °C for another 12 h. The solvent was allowed to evaporate before use. The final electrode was taken as the

MWNTs-Chit/GOx/CdSe@CdS/GCE. The similar procedures were employed to fabricate the MWNTs-Chit/GOx/GCE and MWNTs-Chit/CdSe@CdS/GCE. All resulting electrodes were stored at 4 °C when not in use.

## Results and discussion

### UV-vis spectroscopy

UV-vis absorption spectra are usually a practical tool which can be used to detect the possible changes of Soret band in heme protein. The changes of Soret band are useful information for the possible structural denaturation of heme groups. Figure 1 shows the UV-vis absorption spectra of pure GOx solution and MWNTs-Chit/GOx/CdSe@CdS composite film on quartz slides. As can be seen in Fig. 1a of GOx solution (native state), an intense band appeared at 285 nm and two well-defined peaks of absorption at 375 and 455 nm could be distinguished. The above peaks could also be observed in the MWNTs-Chit/GOx/CdSe@CdS composite film nearly with no difference in the site or shape, indicating the GOx keeps its natural structure in the composite film. In addition, two distinct absorption bands at about 430 and 520 nm could also be observed in the MWNTs-Chit/GOx/CdSe@CdS composite film (Fig. 1b). The inset shows the section magnified diagram UV-vis absorption spectra of MWNTs-Chit/GOx/CdSe@CdS composite film. According to the previous reports, it should be assigned to CdSe@CdS in the MWNTs-Chit/GOx/CdSe@CdS composite film [14, 15].

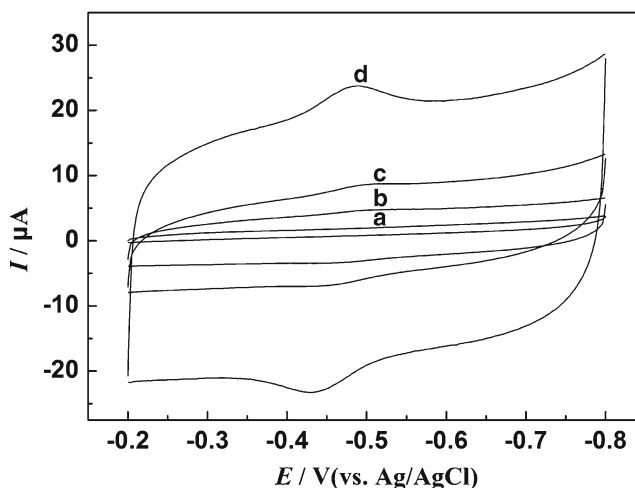


**Fig. 1** UV-vis absorption spectra of **a** pure GOx solution and **b** the MWNTs-Chit/GOx/CdSe@CdS film on quartz slides. *Inset*: the magnified diagram UV-vis absorption spectra of the MWNTs-Chit/GOx/CdSe@CdS film

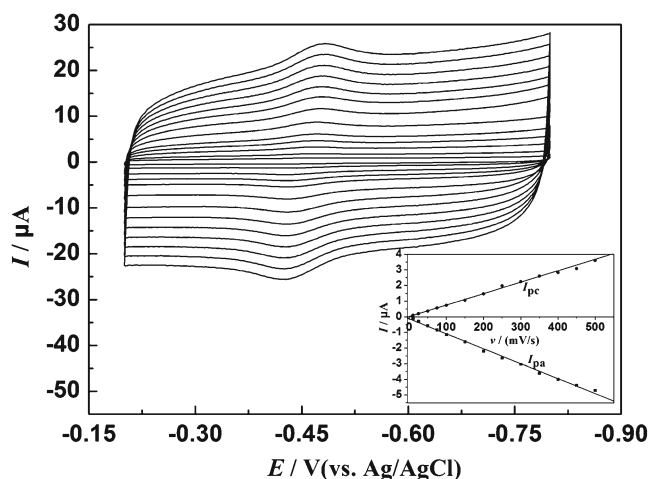
### Direct electron transfer of GOx

Figure 2 shows the cyclic voltammograms of different electrodes in 0.1 M pH 7.0 PBS at 100 mV/s. No redox peaks were observed at bare glassy carbon electrode (Fig. 2a) or at the MWNTs-Chit/CdSe@CdS/GCE (Fig. 2b), which only displayed a small background current. Only a little redox response of GOx was obtained at the Chit-MWNTs/GOx/GCE (Fig. 2c), which suggested that the MWNTs could merely support GOx into much less effective orientation for electron transfer. However, upon addition of CdSe@CdS into the membrane, a pair of well-defined redox peaks were observed at  $-0.488$  and  $-0.430$  V (versus Ag/AgCl) (Fig. 2d), with a formal potential ( $E^{0'}$ ) of  $-0.459$  V (versus Ag/AgCl) and a separation of 58 mV (versus Ag/AgCl), and also, the cathodic and anodic peak currents were stable and nearly equal to each other. In addition, the response of MWNTs-Chit/GOx/CdSe@CdS/GCE showed about 2.5 times larger than that of MWNTs-Chit/GOx/GCE, indicating CdSe@CdS play an important role in maintaining the biological activity of GOx and facilitating the electron transfer between GOx and the electrode surface. This may be attributed to the synergistic effect between MWNTs-Chit substrate and CdSe@CdS, which could provide a favorable microenvironment for GOx and facilitate the direct electron transfer.

Figure 3 shows the cyclic voltammograms of MWNTs-Chit/GOx/CdSe@CdS/GCE in pH 7.0 PBS at different scan rates. The voltammograms had well-defined redox peaks, and the peak currents increased gradually with the increase of the scan rates. As illustrated in the inset of Fig. 3, the linear regression equations were as follows— $I_{pc}$  ( $\mu\text{A}$ ) =  $(0.0433 \pm 0.0367) + (0.0071 \pm 0.0001) \nu$  (V/s),  $R = 0.9980$ ;  $I_{pa}$



**Fig. 2** Cyclic voltammograms of **a** bare GCE, **b** MWNTs-Chit/CdSe@CdS/GCE, **c** MWNTs-Chit/GOx/GCE, and **d** MWNTs-Chit/GOx/CdSe@CdS/GCE in pH 7.0 PBS at 100 mV/s



**Fig. 3** Cyclic voltammograms of MWNTs-Chit/GOx/CdSe@CdS/GCE in pH 7.0 PBS at 10, 25, 50, 75, 100, 150, 200, 250, 300, 350, 400, 450, and 500 mV/s (from inner to outer). The inset is relationship between scan rates and the anodic and cathodic peak currents of MWNTs-Chit/GOx/CdSe@CdS/GCE

$(\mu\text{A}) = (0.1340 \pm 0.0498) - (0.0096 \pm 0.0001) v \text{ (V/s)}$ ,  $R = 0.9980$ . The results demonstrate that the redox reaction of GOx at the MWNTs-Chit/GOx/CdSe@CdS/GCE is a surface-controlled process, not a diffusion-controlled process [16]. According to the Laviron equation [17]:

$$I_p = n^2 F^2 A v \Gamma^* / 4RT = nFQv / 4RT \quad (3)$$

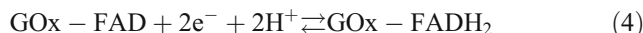
where  $\Gamma^*$  (moles per square centimeter) is the amount of GOx adsorbed on the film electrode surface,  $A$  is the effective area of the modified electrode (square centimeters),  $v$  is the scan rate,  $I_p$  is the peak current,  $n$  is the number of transferred electron,  $Q$  is the charge involved in the redox process, and  $F$  is the Faraday's constant. The average amount ( $\Gamma^*$ ) of GOx adsorbed on the MWNTs-Chit/GOx/CdSe@CdS/GCE was estimated to be  $(6.52 \pm 0.01) \times 10^{-11} \text{ mol cm}^{-2}$ . The large adsorption amount of GOx at the composite film was beneficial to the enlarged surface area of the CdSe@CdS located on MWNTs-Chit and the biocompatibility of the film.

The electron transfer rate constant ( $k_s$ ) has been estimated from the peak potential separation value using the model of Laviron equation [17]. Taking  $\alpha$  of 0.5 and at scan rate of 100 mV/s,  $\Delta E_p = 58 \text{ mV}$ , and then the  $k_s$  was estimated to be  $1.56 \text{ s}^{-1}$ . The results indicate that MWNTs-Chit and CdSe@CdS could provide a suitable microenvironment to increase the electron transfer rate of GOx.

#### Effect of pH on the electrochemistry of GOx

It is well known that the direct electrochemistry of GOx is a two-electron coupled with two-proton reaction, which

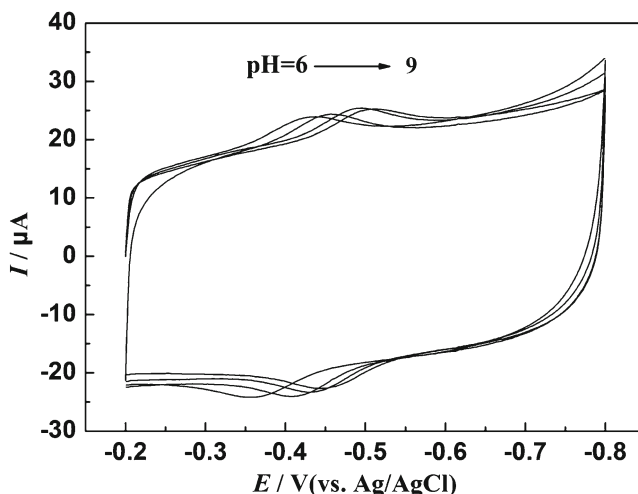
undergoes a redox reaction as follows [18]



Consequently, the pH value of the solution has influence on the electrochemical behavior of GOx at the MWNTs-Chit/GOx/CdSe@CdS/GCE electrode. Figure 4 shows cyclic voltammograms of the MWNTs-Chit/GOx/CdSe@CdS/GCE electrode in the solutions with different pH values. Stable and well-defined cyclic voltammograms could be observed in the pH range of 6.0–9.0. However, the maximum peak current was found at about pH 7.0, which agreed with other reports of GOD-based biosensors [19, 20]. Therefore, pH 7.0 was regarded as the optimum pH of solution in subsequent experiments. Moreover, an increase of solution pH caused a negative shift of both cathodic and anodic peak potentials. Figure 5 displays the effect of solution pH on the formal potential of MWNTs-Chit/GOx/CdSe@CdS/GCE electrode. As can be seen, the formal potential of the MWNTs-Chit/GOx/CdSe@CdS/GCE electrode depended linearly on the pH value in the range of 6.0–9.0 with a slope of  $-46.55 \text{ mV/pH}$  ( $R = 0.985$ ), which was close to the theoretical value of  $58.60 \text{ mV/pH}$  of a two-electron coupled with two-proton reaction [21, 22].

#### Electrocatalytic behavior of MWNTs-Chit/GOx/CdSe@CdS/GCE for the oxidation of glucose

In order to investigate whether GOx immobilized on the CdSe@CdS and MWNTs-Chit substrate retained its electrocatalytic activity for the oxidation of glucose, the cyclic voltammetric experiments were carried out in 0.1 M PBS (pH=7.0) containing 0.5 mM ferrocenemethanol with and without the presence of glucose, respectively, as shown in Fig. 6. Curves a and b are the cyclic voltammetric responses of the MWNTs-Chit/GOx/CdSe@CdS/GCE in 0.1 M



**Fig. 4** Cyclic voltammograms of the MWNTs-Chit/GOx/CdSe@CdS/GCE in 0.1 M PBS at different pH (6, 7, 8, 9); scan rate, 100 mV/s

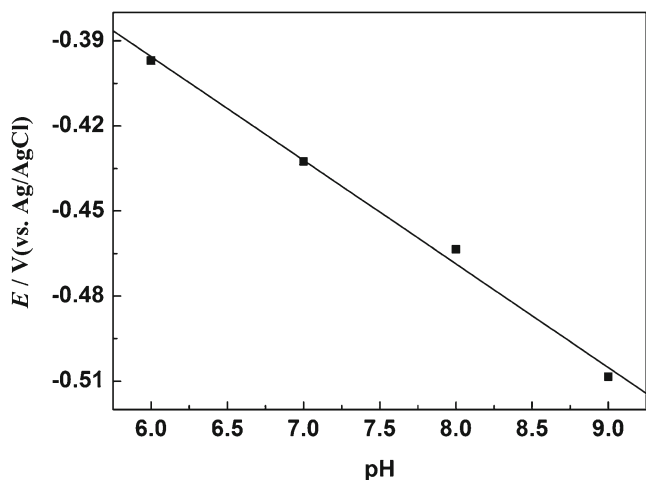


Fig. 5 Influence of pH on the cathodic peak current (*I*<sub>pc</sub>)

pH 7.0 PBS in the absence and presence of 0.5 mM ferrocenemethanol. No electrochemical response was observed in the absence of ferrocenemethanol (curve a). However, a pair of well-reversible redox waves was observed in the presence of ferrocenemethanol (curve b), which corresponds to the redox reaction of Fc<sup>+</sup>/Fc. Adding glucose to above solution, a well-defined sigmoidal catalytic wave was developed as a consequence of the GOx catalytic oxidation of glucose, and the electrocatalytic current increased with the increase of the concentration of glucose in buffer (Fig. 6, curves c, d, and e). The above results indicate that the immobilized GOx maintained its electrocatalytic activity for the oxidation of glucose.

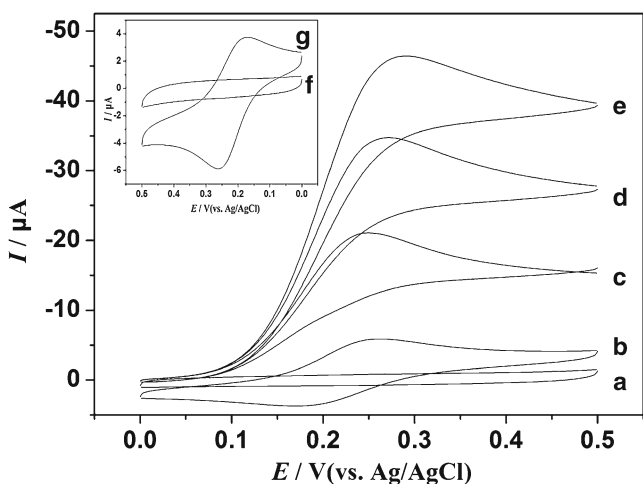
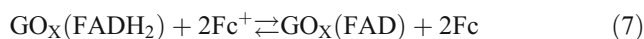
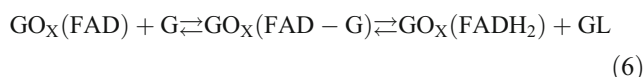


Fig. 6 Cyclic voltammograms of MWNTs-Chit/GOx/CdSe@CdS/GCE in 0.1 M pH 7.0 PBS without a and with b 0.5 mM ferrocenemethanol, c 0.5 mM ferrocenemethanol +10 mM glucose, d 0.5 mM ferrocenemethanol +20 mM glucose, and e 0.5 mM ferrocenemethanol +30 mM glucose; scan rate, 10 mV/s. Inset: Cyclic voltammograms of MWNTs-Chit/CdSe@CdS/GCE in 0.1 M pH 7.0 PBS with f 20 mM glucose and g 0.5 mM ferrocenemethanol +20 mM glucose; scan rate, 10 mV/s

Controlled experimental results showed that electrocatalytic oxidation of glucose did not occur on the MWNTs-Chit/CdSe@CdS/GCE (without GOx) whether the ferrocenemethanol was present (curve g) or absent (curve f) in solution. These results indicate that the GOx immobilized on the CdSe@CdS and MWNTs-Chit substrate could not only occur in the direct electron transfer reaction but also remained in the electrocatalytic activities and catalyzed the oxidation of glucose. The result further supports that the redox peak of Fig. 2d was the result of the direct electron transfer of native GOx not free FAD. The reaction is a typical dependent enzyme catalytic reaction and can be described by the following mechanism [23]:



Where GO<sub>x</sub>(FAD) and GO<sub>x</sub>(FADH<sub>2</sub>) represent oxidized and reduced forms of glucose oxidase, Fc and Fc<sup>+</sup> the reduced and oxidized forms of ferrocenemethanol mediator, and G and GL are glucose and glucose-lactone, respectively.

Amperometric response to glucose

Figure 7 illustrates a typical current-time plot of the MWNTs-Chit/GOx/CdSe@CdS/GCE in pH 7.0 buffer solution containing 0.5 mM ferrocenemethanol at a constant

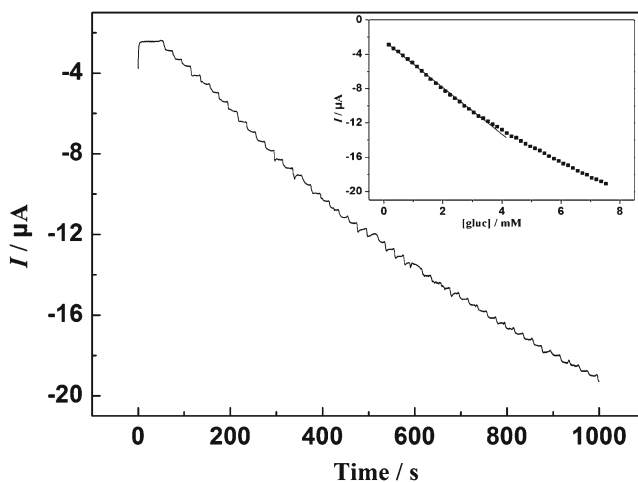


Fig. 7 Amperometric response of MWNTs-Chit/GOx/CdSe@CdS/GCE at +0.26 V (versus Ag/AgCl) upon successive addition of 10 μL 0.2 M glucose to 5.0 mL 0.1 M pH 7.0 PBS with 0.5 mM ferrocenemethanol. Inset: calibration curve of the sensor as a function of glucose concentrations



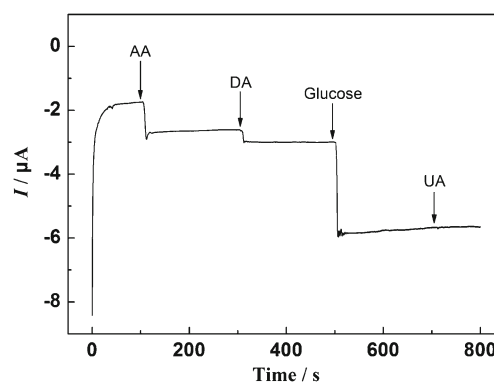
potential of +0.26 V during successive addition of glucose. As the glucose was added to the stirring buffer solution, the oxidation current rises steeply and the steady state was achieved within 6 s. The oxidation current response of the enzyme electrode increased along with glucose concentration. Inset in Fig. 7 presents a calibration plot of the steady-state current versus glucose concentration. The oxidation currents were proportional to the concentration of glucose in the range from  $1.6 \times 10^{-4}$  to  $5.6 \times 10^{-3}$  M, and the detection limit was  $2.5 \times 10^{-5}$  M at a signal-to-noise ratio of 3. In the linear range, the MWNTs-Chit/GOx/CdSe@CdS/GCE had a high sensitivity of  $31.13 \pm 0.02 \mu\text{A mM}^{-1} \text{cm}^{-2}$ , which was higher than the AuNPs-GOD-MWCNTs-PVA/GC electrode [24] and the GOD/CNx-MWCNTs/GCE [25]. When glucose concentration was high, a plateau current was observed, showing the characteristics of the Michaelis–Menten kinetics. The apparent Michaelis–Menten constant ( $K^{\text{app}}_{\text{M}}$ ), an important parameter to reveal enzyme substrate reaction kinetics, could be calculated by the electrochemical version of the Lineweaver–Burk plot [26].

$$1/I_{\text{ss}} = 1/I_{\text{max}}(1 + K^{\text{app}}_{\text{M}}/C) \quad (8)$$

Here,  $I_{\text{max}}$  is the maximum current under saturated substrate condition,  $C$  is the bulk concentrate of glucose.  $I_{\text{ss}}$  is the steady-state current after the addition of substrate, which can be obtained from amperometric experiments. In this work, the  $K^{\text{app}}_{\text{M}}$  value of MWNTs-Chit/GOx/CdSe@CdS modified electrode was estimated to be  $0.46 \pm 0.01$  mM, which is much smaller than those of 4.14 and 5.1 mM obtained in the literature [27, 28]. The smaller ( $K^{\text{app}}_{\text{M}}$ ) value indicates that the immobilized GOD possesses higher enzymatic activity and the MWNTs-Chit/GOx/CdSe@CdS modified electrode exhibits a higher affinity for glucose than that reported in literatures [27, 28]. Therefore, it can be believed that the composite membrane of MWNTs and CdSe@CdS provides favorable microenvironment for retaining the bioactivity of GOD.

#### Selectivity, stability, and reproducibility of the biosensor

Anti-interference property is an important factor for sensors. Because the easily oxidative species such as AA, DA, and UA usually co-exist with glucose in human blood [29], the electrochemical response of the interfering species was examined at the MWNTs-Chit/GOx/CdSe@CdS-modified electrode. Comparing the amperometric responses for each of the interferences at the same concentration is a more straightforward way to demonstrate selectivity of sensor. Figure 8 displays the amperometric response to successive additions of 10  $\mu\text{L}$  0.1 M AA, 10  $\mu\text{L}$  0.1 M DA, 10  $\mu\text{L}$  0.1 M glucose, and 10  $\mu\text{L}$  0.1 M UA in 0.1 M PBS at pH 7.0. The current response produced by glucose was far



**Fig. 8** Amperometric response to successive additions of substances in the sequence of 10  $\mu\text{L}$  0.1 M ascorbic acid (AA), 10  $\mu\text{L}$  0.1 M dopamine (DA), 10  $\mu\text{L}$  0.1 M glucose, and 10  $\mu\text{L}$  0.1 M uric acid (UA) in 0.1 M PBS at pH 7.0, the applied potential was +0.26 V (versus Ag/AgCl)

higher than the same concentration of DA, AA, and UA, which implies a good selectivity to determination of glucose. The responses obtained at the modified electrode to AA, DA, and UA alone were only 3.33 %, 11.3 %, and 0.2 % to that of glucose, respectively. The experimental results indicated that these substances showed no obvious interference to the glucose determination, which proved that the biosensor possesses potential application for the determination of glucose in real samples.

In order to improve the precision and practicability, we investigated the stability and reproducibility of the MWNTs-Chit/GOx/CdSe@CdS/GCE by electrochemical method. After the composite membrane electrode was stored in pH 7.0 PBS at 4  $^{\circ}\text{C}$  for 2 weeks, the biosensor retained 95 % of its original current response, indicating the membrane electrode had good stability. Meanwhile, the relative standard deviation of the biosensor response to 0.1 mM glucose was 2.6 % for ten successive measurements. The relative standard deviation for detection of 0.1 mM glucose with six different sensors prepared under the same conditions was 3.7 %. This indicated that the biosensor had good reproducibility.

#### Conclusions

In this paper, we fabricated a glucose biosensor by effectively entrapping GOx into the MWNTs-Chit/CdSe@CdS composite matrix. This composite not only provides a very suitable environment for enzyme entrapment but also establishes efficient electronic communication between GOD and the electrodes. Based on the synergy of MWNTs and CdSe@CdS quantum dots, the composites enhances the electrocatalytic activity of glucose oxidation by GOD and the electric communication between GOD and electrode, resulting in a sensitive amperometric sensor for glucose.

This proposed biosensor exhibited acceptable reproducibility, good selectivity, and long-term stability for the determination of glucose and could offer a new approach for developing a new generation biosensor.

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## References

- Fan C, Plaxco KW, Heeger AJ, Am J (2002) High-efficiency fluorescence quenching of conjugated polymers by proteins. *J Am Chem Soc* 124:5642–5643
- Gao Q, Guo YY, Liu J, Yuan XQ, Qi HL, Zhang CX (2011) A biosensor prepared by co-entrapment of a glucose oxidase and a carbon nanotube within an electrochemically deposited redox polymer multilayer. *Bioelectrochemistry* 81:109–113
- Kuznetsov BA, Shumakovich GP, Koroleva OV, Yaropolov AI (2001) On applicability of laccase as label in the mediated and mediatorless electroimmunoassay: effect of distance on the direct electron transfer between laccase and electrode. *Biosens Bioelectron* 16:73–84
- Chen D, Li J (2006) Interfacial design and functionalization on metalelectrodes through self-assembled monolayers. *Surf Sci Rep* 61:445–463
- Lu X, Wen Z, Li J (2006) Hydroxyl-containing antimony oxide bromide nanorods combined with chitosan for biosensors. *Biomaterials* 27:5740–5747
- Sun JY, Huang KJ, Zhao SF, Fan Y, Wu ZW (2011) Direct electrochemistry and electrocatalysis of hemoglobin on chitosan-room temperature ionic liquid-TiO<sub>2</sub>-graphene nanocomposite film modified electrode. *Bioelectrochemistry* 82:125–130
- Yu WW, Qu L, Guo W, Peng X (2003) Experimental determination of the extinction coefficient of CdTe, CdSe, and CdS nanocrystals. *Chem Mater* 15:2854–2860
- Peng X, Schlamp MC, Kadavanich AV, Alivisatos AP (1997) Epitaxial growth of highly luminescent CdSe/CdS core/shell nanocrystals with photostability and electronic accessibility. *J Am Chem Soc* 119:7019–7029
- Li J, Wang YA, Guo WZ, Keay JC, Mishima TD, Johnson MB, Peng X (2003) Large-scale synthesis of nearly monodisperse CdSe/CdS core/shell nanocrystals using air-stable reagents via successive ion layer adsorption and reaction. *J Am Chem Soc* 125:12567–12575
- Munro AM, Plante IJ, Ng MS, Ginger DS (2007) Quantitative study of the effects of surface ligand concentration on CdSe nanocrystal photoluminescence. *J Phys Chem C* 111:6220–6227
- Lu Q, Hu SS, Pang DW, He ZK (2005) Direct electrochemistry and electrocatalysis with hemoglobin in water-soluble quantum dots film on glassy carbon electrode. *Chem Commun* 20:2584–2585
- Sajjadi S, Ghourchian H, Rahimi P (2011) Different behaviors of single and multi wall carbon nanotubes for studying electrochemistry and electrocatalysis of choline oxidase. *Electrochim Acta* 56:9542–9548
- Chen H, Li R, Lin L, Guo GS, Lin JM (2010) Determination of L-ascorbic acid in human serum by chemiluminescence based on hydrogen peroxide-sodium hydrogen carbonate-CdSe/CdS. *Talanta* 81:1688–1696
- Liu SQ, Ju HX (2003) Reagentless glucose biosensor based on direct electron transfer of glucose oxidase immobilized on colloidal gold modified carbon paste electrode. *Biosens Bioelectron* 19:177–183
- Ju HX, Liu SQ, Ge B, Lisdat F, Scheller FW (2002) Electrochemistry of cytochrome c immobilized on colloidal gold modified carbon paste electrodes and its electrocatalytic activity. *Electroanal* 14:141–147
- Liu Q, Lu XB, Li J, Yao X, Li JH (2007) Direct electrochemistry of glucose oxidase and electrochemical biosensing of glucose on quantum dots/carbon nanotubes electrodes. *Biosens Bioelectron* 22:3203–3209
- Laviron E (1979) General expression of the linear potential sweep voltammogram in the case of diffusionless electrochemical systems. *J Electroanal Chem* 101:19–28
- Huang YX, Zhang WJ, Xiao H, Li GX (2005) An electrochemical investigation of glucose oxidase at a CdS nanoparticles modified electrode. *Biosens Bioelectron* 21:817–821
- Wang KQ, Yang H, Zhu L, Liao JH, Lu TH, Xing W, Xing SY, Lv Q (2009) Direct electrochemistry and electrocatalysis of glucose oxidase immobilized on glassy carbon electrode modified by Nafion and ordered mesoporous silica-SBA-15. *J Mol Catal B: Enzym* 58:194–198
- Wang KQ, Yang H, Zhu L, Ma ZS, Xing SY, Lv Q, Liao JH, Liu CP, Xing W (2009) Direct electron transfer and electrocatalysis of glucose oxidase immobilized on glassy carbon electrode modified with Nafion and mesoporous carbon FDU-15. *Electrochim Acta* 54:4626–4630
- Deng CY, Chen JH, Chen XL, Xiao CH, Nie LH, Yao SZ (2008) Direct electrochemistry of glucose oxidase and biosensing for glucose based on boron-doped carbon nanotubes modified electrode. *Biosens Bioelectron* 23:1272–1277
- Li JW, Yu JJ, Zhao FQ, Zeng BZ (2007) Direct electrochemistry of glucose oxidase entrapped in nano gold particles-ionic liquid-N,N-dimethylformamide composite film on glassy carbon electrode and glucose sensing. *Anal Chim Acta* 587:33–40
- Bourdillon C, Demaille C, Guerin J, Morieux J, Saveant JM (1993) A fully active monolayer enzyme electrode derivatized by antigen-antibody attachment. *J Am Chem Soc* 115:12264–12269
- Zhang HF, Meng ZC, Wang Q, Zheng JB (2011) A novel glucose biosensor based on direct electrochemistry of glucose oxidase incorporated in biomediated gold nanoparticles-carbon nanotubes composite film. *Sens Actuators B* 158:23–27
- Deng S, Jian G, Lei J, Hu Z, Ju H (2009) A glucose biosensor based on direct electrochemistry of glucose oxidase immobilized on nitrogen-doped carbon nanotubes. *Biosens Bioelectron* 25:373–377
- Kamin RA, Wilson GS (1980) Rotating ring-dish enzyme electrode for biocatalysis kinetic studies and characterization of the immobilized enzyme layer. *Anal Chem* 52:1198–1205
- Wang Y, Yuan R, Chaia YQ, Li WJ, Zhuo Y, YuanYL LJJ (2011) Direct electron transfer: electrochemical glucose biosensor based on hollow Pt nanosphere functionalized multiwall carbon nanotubes. *J Mol Catal B:Enzym* 71:146–151
- Huang YX, Zhang WJ, Xiao H, Li GX (2005) An electrochemical investigation of glucose oxidase at a CdS nanoparticles modified electrode. *Biosens Bioelectron* 21:817–821
- Liu BH, Hu RQ, Deng JQ (1997) Characterization of immobilization of an enzyme in a modified Y zeolite matrix and its application to an amperometric glucose biosensor. *Anal Chem* 69:2343–2348