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Direct electrochemistry and reagentless biosensing of glucose oxidase immobilized on chitosan wrapped single-walled carbon nanotubes

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ABSTRACT

Single-walled carbon nanotubes (SWCNTs) selectively wrapped by a water-soluble, environmentally friendly, biocompatible polymer chitosan (CHI) were employed for the construction of a bioelectrochemical platform for the direct electron transfer (DET) of glucose oxidase (GOD) and biosensing purposes. Scanning electron microscopy and Raman spectroscopy were used to investigate the properties of the SWCNT–CHI film. The results show that the preferentially wrapped small-diameter SWCNTs are dispersed within the CHI film and exist on the surface of the electrode as small bundles. The DET between GOD and the electrode surface was observed with a formal potential of about ca. −460 mV vs. SCE in phosphate buffer solution. The heterogeneous electron transfer rate constant and the surface coverage of GOD are estimated to be 3.0 s^{-1} and 1.3×10^{-10} mol/cm^2, respectively. The experimental results demonstrate that the immobilized GOD retains its catalytic activity towards the oxidation of glucose. Such a GOD/SWCNT–CHI film-based biosensor not only exhibits a rapid response time, a wide linear rang and a low detection limits at a detection potential of −400 mV but also shows the effective anti-interference capability. Significantly improved analytical capabilities of the GOD/SWCNT–CHI/GC electrode could be ascribed to the unique properties of the individual SWCNTs and to the biocompatibility of CHI.

1. Introduction

Glucose oxidase (GOD), from Aspergillus or Penicillium, is a homodimer with a molecular weight of about 150–180 kDa containing two tightly bound Flavine adenine dinucleotide (FAD) cofactors [1], and can catalyze the electron transfer from glucose to oxygen accompanying the production of gluconic acid and hydrogen peroxide. The most important application of GOD is in biosensor for the quantitative determination of glucose in food analysis and bioprocess monitoring. In order to investigate the electrochemical properties of GOD and to fabricate glucose enzyme electrode, GOD has been usually immobilized on the surface of the electrode. As an important enzyme molecule, it is of great importance to study the direct electron transfer because it could help us not only to understand the intrinsic redox behavior of GOD, but also to exploit application of biosensor [2]. Unfortunately, it is difficult for GOD to carry out a direct electrochemical reaction at the electrode surface because a thick protein layer surrounds its flavin redox center [3]. Efforts to this end have involved the chemical modification of GOD with electron-relay groups [4], the immobilization of the enzyme into biopolymer matrix [5] or silicon material [6] and the adsorption of GOD onto different nanomaterials, such as Au nanoparticles [7] and carbon nanotubes (CNTs) [8]. Such surface modifications promote the direct electrochemistry of GOD and facilitate the biosensing application for glucose detection.

The first glucose enzyme electrode was proposed in 1962 by Clark and Lyons [9]. In the past 40 years, major achievements have been made for enhancing the capabilities and improving the reliability of measuring devices [2]. Research efforts have aimed at an increase in a wide linear range with a high sensitivity. The discovery of various novel nanomaterials, such as CNTs, has been the focus for the development of glucose enzyme electrode [10], because these nanomaterials could provide a desirable microenvironment between the redox sites of an enzyme and the electrode surface.

Both multiwalled carbon nanotubes (MWCNTs) and single-walled carbon nanotubes (SWCNTs) have attracted enormous attention since their first discovery. Their unique structural, mechanical and electrical properties have made them very attractive candidates for many obvious, important applications, such as serving as active elements in field emission devices [11], as hydrogen storage materials [12], as scanning-probe microscopy tips [13,14], as well as several other uses. More specifically, the high accessible surface area, low electrical resistance, and high chemi-

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cal stability suggest that SWCNTs would be suitable materials for electrodes and supports in biosensor applications. The majority of this effort is devoted to the immobilization of some enzymes on the surface of SWCNTs [15,16]. The SWCNT-modified electrodes have shown excellent catalytic properties as compared to the other materials.

To fabricate the SWCNT-modified electrodes, SWCNTs must be temporarily dispersed in some solvents such as dimethylformamide and acetone and then cast on the electrode, as SWCNTs are insoluble in essentially all the common solvents. This procedure for electrode preparation is complicated, and its application in biosensors is quite limited because of the use of organic solvents. To surmount the inherent insolubility of SWCNTs, nanotubes can be dispersed into solutions through either covalent [17] or noncovalent [18] interactions to improve solubility and, as well, to unbundled the aggregate ropes that are formed from intertube van der Waals interactions. However, chemisorption, which results in covalently bonded SWCNTs, although potentially enhancing solubility, generally alters the nanotube's electronic properties. To maintain electronic properties of the tubes, physisorption of polymer or surfactant is often used, resulting in formation of individual or very small bundle (ca. 2–5 tubes) of wrapped nanotubes.

The biopolymer chitosan (CHI) is a kind of matrix for enzyme immobilization with attractive properties that include high permeability toward water, good adhesion and biocompatibility [19]. As a good film formation material, CHI has been extensively utilized to fabricate the biosensors [20–22]. Recently, with the help of CHI, an aqueous dispersion and diameter-selective separation of SWCNTs has been accomplished with small-diameter SWCNTs existing in the solution [23]. Due to the high reactivity of small-diameter SWCNTs [24], such SWCNT–CHI system could exhibit unique film properties to fabricate glucose biosensor with a high activity. Generally, SWCNTs existed as bundles are insoluble in essentially all the common solvents, which limits their use in biosensors due to the fact that the amount of enzymes that can be immobilized is limited, providing matrixes with sensitivities and stability properties that are not fully optimized. However, the utilization of CHI wrapped individual SWCNTs in this paper could maximize the contact between SWCNTs and enzyme molecules; thus may be beneficial to an increase in sensor sensitivity and stability.

The research focus in this work is to construct a bioelectrochemical platform for the DET of GOD and for the detection of glucose based on SWCNTs and biocompatible polymer CHI. Within the film, the small-diameter SWCNTs are preferential wrapped by CHI verified by Raman spectroscopy. The direct electrochemistry and bioelectrocatalysis of GOD on the modified electrode were studied. The immobilization of GOD molecules into chitosan wrapped SWCNT film is shown to be an efficient method for the development of a new class of very sensitive, stable, and reproducible electrochemical biosensors.

2. Experimental

2.1. Reagents

Purified HiPco SWCNTs were purchased from Carbon Nanotechnologies, Inc. (Houston, TX, USA). Chitosan (85% deacetylation, average molecular weight = 1×10^6 g/mol) and glucose oxidase (from *Aspergillus niger*, E.C. 1.1.3.4) were obtained from Sigma–Aldrich Corp. All the other chemicals were of reagent grade and used as received. The buffer solution used was 0.1 M Na-phosphate buffer solution (PBS) with a pH value of 7.4. Glucose stock solutions were allowed to mutarotate overnight at room temperature before used. All solutions were prepared with pure water obtained using a Millipore Q water purification apparatus with the resistivity over 18 MΩ/cm.

2.2. Preparation of SWCNT–CHI solution

A 0.5 wt.% CHI solution was prepared by dissolving an appropriate amount of CHI powder in 0.05 M HCl aqueous solution at a temperature of ca. 80–90 °C. Then the solution was immediately filtered and cooled, the pH of the CHI solution was adjusted to 5.0 with NaOH. This stock CHI solution was stored in a refrigerator before use. 2.5 mg of HiPco SWCNTs and 5.0 mL of 0.5 wt.% CHI solution were then added to a vial and mixed ultrasonically in an ice bath for more than 5 h to accomplish dispersion. The resultant black solution with a calculated concentration of 0.5 mg/mL SWCNTs was separated after overnight standing. The resultant SWCNT–CHI solution appears homogenous and stable.

2.3. Fabrication of the SWCNTs–CHI/GC and GOD-modified SWCNT–CHI/GC electrodes

A measured volume (5 μL) of 0.5 mg/mL SWCNTs–CHI solution was transferred via a syringe onto a freshly polished glassy carbon (GC) disk (3 mm in diameter). After solvent was evaporated at room temperature, the resultant electrode was denoted as the SWCNT–CHI/GC electrode. The obtained SWCNT–CHI/GC electrode was immersed into 5 mg/mL GOD solution at 4 °C for 10 h. After that, the GOD immobilized SWCNT–CHI/GC electrode was transferred to 0.1 M PBS for 15 min before use.

All the GOD immobilized electrodes were stored at 4 °C when not in use.

2.4. Apparatus

Raman spectra were obtained using an HR800 Jobin Horiba Raman Microscope. Samples were placed in quartz cuvettes and excited with 514.5 nm laser radiation. All spectra were acquired in 30 s and the incident laser power (at the laser head) was ca. 10 mW. The image of scanning electron microscopy (SEM) was obtained with an S-4700 scanning electron microscope (Hitachi, Japan) at an acceleration voltage of 10 kV.

Electrochemical measurements were performed using a CHI 730B Potentiostat (Shanghai Chenhua Corp., China) and a conventional three-electrode cell. The bare GC or the modified electrode was used as the working electrode. The counter electrode was a Pt wire, and a saturated calomel electrode (SCE) was used as the reference electrode. All potentials were reported with respect to SCE. Amperometric detection of glucose was carried out in PBS by applying a potential of −400 mV. High-purity nitrogen or oxygen was used for deaeration of the solutions. During the measurements, a gentle gas flow was kept above the electrolyte surface.

All electrochemical experiments were performed at a temperature of ca. 20 °C.

3. Results and discussion

3.1. Dispersion of SWCNTs by CHI

In this study, the mixture of SWCNTs and CHI was sonicated for more than 5 h. It is to be noted that only small quantity of black powder spontaneously (overnight) precipitated from dispersion, with the resultant supernatant being homogeneous, stable and of dark color. The precipitate could not be re-dispersed using CHI solution in combination with centrifugation and heating, suggesting a robust method of forming stable SWCNTs in solution.

3.2. Raman spectroscopy characterization

Raman spectroscopy is a useful tool to characterize the properties of SWCNTs. Fig. 1 shows Raman spectra of the raw SWCNT sample, the dispersion of 0.5 mg/mL SWCNTs in CHI solution and the film by casting 0.5 mg/mL SWCNT solution onto GC disk. As can be seen, Raman shifts in curves (b) and (c) are essentially consistent, confirming that the SWCNT–CHI film keeps the same SWCNT properties as those in the solution. From the Raman spectra in the region above 1250 cm^{-1} (i.e., part A), hereinafter also referred to as the high-frequency region, the G band (graphite tangential mode at ca. 1593 cm^{-1}) is associated with the E_{2g} optical mode of graphite, and is characteristic of sp^2 hybridized carbon materials, as are the weak shoulder peaks near the 1551 cm^{-1}. The Raman G-band mode uniquely indicates the presence of SWCNTs. The relative intensity of the disorder-induced peak at ca. 1325 cm^{-1} (the so-called D-band) provides an indication of the relative amount of disordered carbon present; the relatively low intensity of the D-band indicates that the amount of amorphous carbon within these samples is quite low. In part B of Fig. 1, referred to hereinafter as the low-frequency region, bands attributable to radical breathing mode (RBM) vibrations of SWCNTs are clearly seen, which could provide more detailed information about the diameter and structure of SWCNTs. For raw HiPco SWCNTs (curve (a)), there are four distinct peaks at ca. 185, 208, 248 and 264 cm^{-1} (labeled as i, ii, iii and iv, respectively), corresponding to the calculated nanotube diameters of 1.30, 1.14, 0.94 and 0.89 nm, respectively, using the equation d (nm) = 223.5/ν_{RBM} (cm^{-1}) − 12.5 as the correlation between diameter d (nm) and RBM frequency [25]. However, only two RBM bands higher than ca. 240 cm^{-1} in curves (b) and (c) are observed, corresponding to the small-diameter SWCNTs [24,26]. The above observations clearly indicate that smaller-diameter SWCNTs are preferentially wrapped by CHI within the SWCNT–CHI film on the surface of GC electrode.

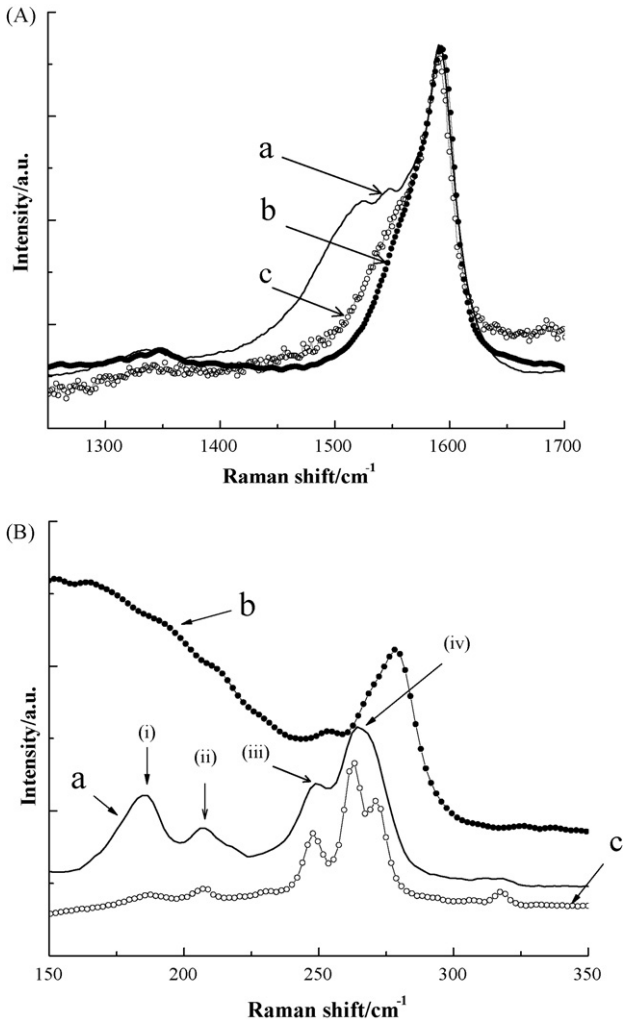

Fig. 1. Part (A) shows Raman spectra using a 514.5 nm excitation in the G-band region: (a) raw HiPco SWCNTs, (b) dispersion of 0.5 mg/mL SWCNTs in chitosan solution, and (c) film of 0.5 mg/mL SWCNTs in chitosan solution by casting onto a GC disk. Part (B) shows Raman spectra in the RBM region for the same samples (a), (b) and (c) as above.

3.3. Immobilization of GOD onto the SWCNT–CHI-modified electrode

Fig. 2 shows SEM images of the SWCNT–CHI and GOD/SWCNT–CHI films. For the SWCNT–CHI film, small bundled SWCNTs with a diameter range from ca. 5 to 15 nm are clearly seen, probably due to rebundling of SWCNTs upon drying, since the SWCNTs exist in the CHI solution as individuals. For the GOD/SWCNT–CHI film, however, one observes that there are some island-like spots attached onto the hair-like SWCNTs, indicating that GOD molecules exist as small islands within the SWCNT–CHI film.

There are two main reasons for the strong interactions between GOD molecule and SWCNTs–CHI composite. Firstly, it is well known

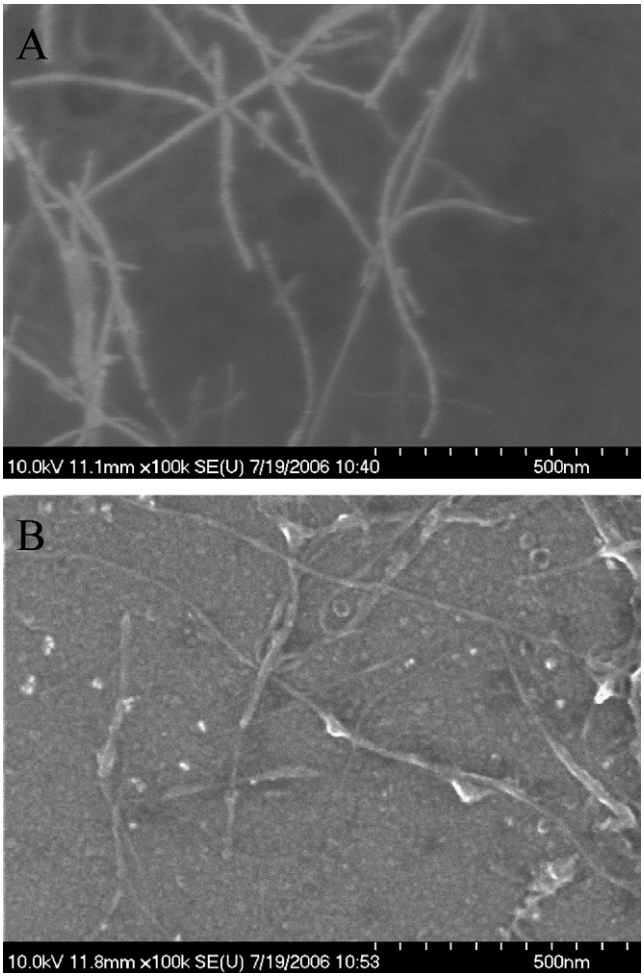

Fig. 2. SEM images of (A) CHI wrapped SWCNT film on GC surface and (B) GOD adsorbed on CHI wrapped SWCNT film on GC surface.

that hydrophobic interactions existed between SWCNTs and GOD lead to a strong adsorption of GOD on the sidewalls of SWCNTs [27]. Secondly, GOD is negatively charged in pH 7.4 PBS solution, whereas the chitosan wrapped SWCNTs composite is positively charged because of $-NH_3^+$ groups existed within the chitosan; therefore, resulting in a strong electrostatic interaction between GOD and SWCNTs–CHI films [28]. It is believed that the strong interactions between GOD and SWCNTs–CHI composite, coming from the synergetic effects of both SWCNTs and chitosan, lead to an enhanced stability of the biosensor.

3.4. Direct electron transfer of glucose oxidase on the modified electrode

Fig. 3 shows the cyclic voltammograms (CVs) of the GOD/SWCNT–CHI/GC (curve a) and GOD/CHI/GC (curve b) electrodes in an N_2-saturated PBS at a scan rate of 100 mV s^{-1}. In comparison with the GOD/CHI/GC electrode, a significantly increased current is clearly observed for the GOD/SWCNT–CHI/GC electrode. The enhancement of the double layer charging/discharging capacitance with SWCNTs could be due to the high surface area, unique structural and electrical properties of small-diameter SWCNTs. As seen in Fig. 3(a), a pair of well-defined redox peaks with a peak potential separation (ΔE_p) of 37 mV at scan rate of 100 mV/s indicates that GOD adsorbed onto the SWCNT–CHI film undergoes a quasi-reversible electron transfer process. In curve b, however, an unobvious direct electrochemical redox peak of GOD is also observed with a ΔE_p of 91 mV also at a scan rate of 100 mV/s, which is much larger than that shown in curve a, showing that GOD adsorbed on the CHI film undergoes an irreversible electron transfer process. Thus, it can be concluded that SWCNTs play an important role in promoting the DET of GOD. By integrating the redox wave area in curve a, the surface coverage of GOD is calculated to be 1.3×10^{-10} mol/cm^2, suggesting that the GOD immobilized on the SWCNT–CHI film might be a monolayer adsorption. Such a surface coverage is about five times higher than that GOD immobilized on the SWCNT–PDDA film with a value of 2.35×10^{-11} mol/cm^2 [29], suggesting that the SWCNT–CHI film provides a high active area and favorable microenvironment for enzyme immobilization. However,

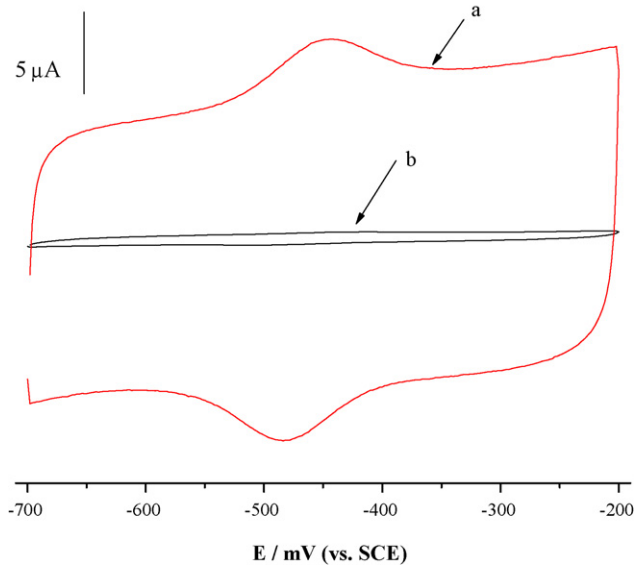

Fig. 3. CVs of (a) the GOD/SWCNT–CHI/GC and (b) GOD/CHI/GC electrodes in an N_2-saturated PBS at a scan rate of 100 mV s^{-1}. The inserts are the magnifying CVs of curve b.

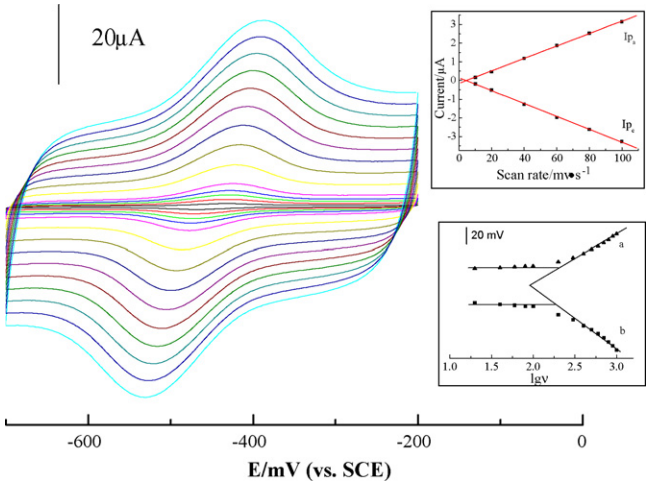

Fig. 4. CVs of the GOD/SWCNT–CHI/GC electrode in an N_2-saturated PBS at various scan rates. The upper insets are the plots of peak current vs. scan rate. The lower insets are the plots of peak potential vs. logarithm of scan rate.

in curve b, the surface GOD coverage is only 2.7×10^{-12} mol/cm^2, which is much lower than that on the SWCNT–CHI/GC film. Such a result demonstrates that SWCNTs significantly enhance the adsorptive capability of GOD molecules on the film.

Fig. 4 shows the CVs of the GOD/SWCNT–CHI/GC electrode in an N_2-saturated PBS at various scan rates. The formal potential is calculated as ca. −460 mV. The peak current increases with scan rate in the range from 20 to 1000 mV/s. The linearly dependent relationship of peak current on low scan rates from 20 to 100 mV/s (see upper insert of Fig. 4) indicates that the electrochemical behavior of GOD has the typical property of a surface electrochemical process. However, the peak potential separation remains almost constant with a value of ca. 37 mV ranged from 20 to 100 mV/s and starts to increase with scan rate from 200 to 1000 mV/s (see lower insert of Fig. 4). By using the model of Laviron [30], with ΔE_p of 100 mV at 600 mV/s, α of 0.58 calculated by the slot of line a and b (see lower insert of Fig. 4), according to the equation of $\lg k_s = \alpha \lg(1-\alpha) + (1-\alpha)\lg\alpha - \lg(RT/nF\upsilon) - \alpha(1-\alpha)nF\Delta E_p/2.3RT$, the heterogeneous surface electron transfer rate constant (k_s) on SWCNTs–CHI is ca. 3.0 s^{-1}, which is higher than that on MWCNTs–PDDA (2.76 s^{-1}) [31], on MWCNT paper (1.7 s^{-1}) [32], on MWCNTs/Nafion (1.53 s^{-1}) [33] and on gold nanoparticles (1.3 s^{-1}) [34], suggesting that SWCNTs are more effective in facilitating the DET of GOD than other nanomaterials Due to SWCNTs which benefits of their electrocatalytic properties and their small size may bring themselves close to the redox centers of GOD [35].

3.5. Performance of the SWCNT–CHI/GOD film-based biosensor

It is known that the use of low detection potential of a biosensor would be effective for the development of practical glucose amperometric biosensor because it is possible to avoid the interference of uric acid (UA) and ascorbic acid (AA) etc., which coexist with glucose in in vivo detection. The amperometric responses at the each successive addition of 1 mM glucose are presented in Fig. 5 at a detection potential of −400 mV. Inset is the calibration curve. The biosensor displayed a linear response to glucose in the concentration range from 1 to 10 mM with a correlation coefficient of 0.998. The reaction occurring at the biosensor is very fast in reaching a stable value within 10–15 s. The limit of detection, based on the signal-to-noise ratio of 3, was 0.01 mM. It is knowing that the interfering species may influence the response of glucose biosensor. However, we use the detection potential of

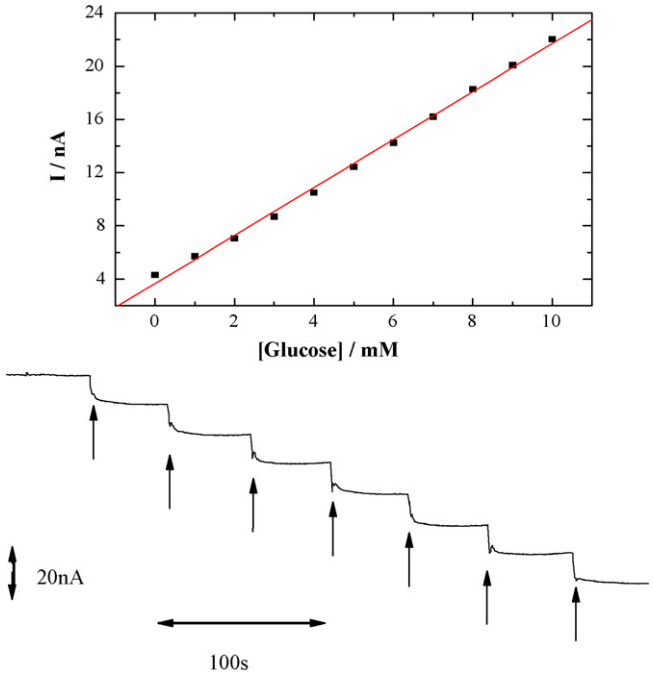

Fig. 5. Amperometric response with an increase in glucose concentration by 1 mM obtained at the GOD/SWCNT–CHI/GC electrode in 0.1 M PBS at a given potential of −400 mV. The inset shows the calibration curve.

−400 mV in this work. So no interference species was observed indicating a high selectivity of such a biosensor toward the glucose detection.

3.6. *Reproducibility and stability*

Importantly, such a biosensor displayed very good reproducibility. The relative standard deviation of nine repetitive measurements is less than 3.0% for 10.0 mM glucose solution. A single sensor could be used consecutively over a week with only ca. 10% diminution in the sensitivity. Meanwhile, there is nearly no any decrease in catalytic current after keeping the biosensor for 15 days at 4 °C. The good stability of such a biosensor should be due to the fact that the formation of network-like nanocomposite film restricts the loss of GOD.

4. Conclusions

The immobilization of enzyme molecules onto chitosan wrapped SWCNT film is shown to be a highly efficient method for the development of a new type of very sensitive, stable, and reproducible electrochemical biosensors. The use of SWCNTs in such a biosensor is based on the fact that SWCNTs can play dual roles, i.e. as immobilization matrixes for GOD molecules and as electrocatalytic material for glucose oxidation. SWCNTs significantly promote the direct electron transfer of GOD. Moreover, the adsorbed GOD is found to retain its catalytic activity toward the oxidation of glucose. Such a GOD/SWCNT–CHI film-based biosensor exhibits a rapid response time of 10–15 s, a high sensitivity, and a good linear range from 1 to 15 mM with a detection limit of 0.01 mM for the glucose detection. Both the unique electrical properties of SWCNTs and the biocompatibility of chitosan enable us to construct an excellent biosensing platform for glucose detection.

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