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Amperometric glucose sensor based on catalytic reduction of dissolved oxygen at soluble carbon nanofiber

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Abstract

This work shows excellent catalytic activity of soluble carbon nanofiber (CNF), which was obtained with a simple nitric acid treatment, toward the electroreduction of dissolved oxygen at a low operating potential. Thus the CNF was applied in the construction of amperometric biosensors for oxidase substrates using glucose oxidase as a model. The good dispersion of CNF led to convenient preparation and acceptable repeatability of the proposed sensors. UV–vis spectra, Fourier transform infrared spectra, X-ray photoelectron spectra and titration curves demonstrated that the good dispersion resulted from the large numbers of surface oxygen-rich groups produced in the treatment process. The membrane of CNF showed good stability and provided fast response to dissolved oxygen with a linear range from 0.1 to 78 μM and detection limit of 0.07 μM. The proposed glucose biosensor could monitor glucose ranging from 10 to 350 μM with detection limit of 2.5 μM and sensitivity of 36.3 nA cm^{-2} μM^{-1}. The coefficients of variation for intra-assay were 4.7 and 3.2% at glucose concentrations of 20 and 210 μM, respectively. The use of a low operating potential (−0.3 V) and Nafion membrane produced good selectivity toward the glucose detection. CNF-based biosensors would provide wide range of bioelectrochemical applications in different fields.

Keywords: Biosensors; Carbon nanofiber; Dissolved oxygen; Glucose; Electrochemistry

1. Introduction

Recent trends in development of biosensors have increasingly emphasized on the application of various nanomaterials to improve their analytical performance. (Niemeyer, 2001; Katz and Willner, 2004; Zayats et al., 2005). Carbon nanomaterials have attracted considerable attention for the construction of biosensors due to their electrical conductivity, unique structural and catalytic properties, high loading of biocatalysts, good stability and excellent penetrability (Boussaad et al., 2003; He and Dai, 2004; Lee et al., 2005; Niwa, 2005). As one of the most interesting carbon nanostructures, carbon nanotubes (CNTs) have been extensively used in electrocatalysis and biosensing (Baughman et al., 1999; Wang et al., 2003a,b; Moore et al., 2004; Chen et al., 2007; Qu et al., 2007). However, the insolubility of CNTs in most solvents limits their application in designing CNTs-based biosensing devices (Salimi et al., 2004). Carbon nanofiber (CNF), possessing excellent mechanical characteristics such as high tensile strength and elastic modulus, and high thermal and electric conductivity (Arai and Endo, 2003), has been used as catalyst, catalyst support (Werner et al., 2005; Qiu et al., 2006) and probe tip (van der Lee et al., 2005). Compared with CNTs, CNF has intrinsic advantages such as low production cost and mass production (Cui et al., 2004), better mechanical stability (Jang et al., 2005), and easier surface functionalization for obtaining hydrophilic groups and good solubility. Particularly, CNF possesses more edge sites on the outer wall than CNTs (Kim and Lee, 2004), which facilitates the electron transfer of electroactive analytes. The oxidation treatment of CNF with acid can produce a range of oxygen-rich groups without degradation of the structural integrity of its backbone (Li and Lukehart, 2006), leading to better dispersion and wettability than CNTs (Werner et al., 2005). This work used a simple nitric acid treatment process to obtain soluble CNF for convenient preparation of CNF-modified electrode. The modified electrode showed excellent electrocatalytic activity for reduction of dissolved oxy-

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gen and could highly sensitively detect dissolved oxygen at a low potential.

The sensitive detection of dissolved oxygen is becoming increasingly important because of its wide applications in biochemistry (Komai, 1998), neuroscience (Andreasen et al., 1997) and physiology (Osborne, 1997). Many materials such as palladium (Lin et al., 2005), platinum (Cui et al., 2005) nanoparticles and CNTs (Ye et al., 2004) have been used as catalysts for the electroreduction and electrochemical detection of dissolved oxygen. A CNF-coated nickel mesh electrode has also been prepared with a chemical vapor deposition method to show electrocatalysis to oxygen reduction with a peak or applied potential of −0.5 V (versus Hg/Hg_2SO_4) (Maldonado and Stevenson, 2004, 2005).

Dissolved oxygen is usually consumed during the enzymatic reactions between most oxidases and their substrates, thus its detection is also very interesting for the development of biosensors to monitor oxidase substrates and the activity of oxidases. Although a CNF-based glucose biosensor has been proposed based on the oxidation of hydrogen peroxide produced in enzymatic cycle (Vamvakaki et al., 2006), the CNF is used only for loading of enzyme and transducing of electrochemical signal, and the sensor shows low sensitivity (mmol magnitude) and slow response (60 s to reach steady state), and cannot avoid the interference of ascorbic acid (AA) and uric acid (UA). Herein, we further used the CNF-modified electrode to construct a biosensor for oxidase substrate using glucose oxidase as a model. The obtained biosensor shows fast response (10 s to reach steady state) and low detection limit. Thus it can be used in different fields such as food-stuffs, beverages and fermentation liquor for glucose monitoring. In view of these intrinsic advantages CNF would become a nanostructure matrix extensively applied in protein immobilization and biosensing.

2. Experimental

2.1. Chemicals

CNF was a gift from WPI (Sarasota, USA). Glucose oxidase (GOx) from *Aspergillus niger* with an activity of 39800 U mg^{-1} was purchased from Sigma. Nafion (product no. 27470-4) was obtained from Aldrich. CNTs (>95%, 10–20 nm diameter) were purchased from Shenzhen Nanotech Port Ltd. Co., (Shenzhen, China). Other reagents were of analytical reagent grade. All solutions were prepared with twice-distilled water. The buffer for assay was 0.2 M phosphate buffer saline (PBS) prepared by mixing stock-standard solution of K_2HPO_4 and KH_2PO_4. The O_2-saturated standard solution was produced by bubbling double distilled water with pure O_2 at room temperature for 1 h, in which the O_2 content was 2.6×10^{-4} M calculated from its saturated solubility (Ju and Shen, 2001).

2.2. Apparatus

Electrochemical measurements were performed on a CHI 660 electrochemical analyzer (Co., CHI, USA) with a conventional three-electrode system comprised of platinum wire as auxiliary electrode, saturated calomel electrode as reference electrode and glassy carbon electrode (GCE, diameter 3 mm) as working electrode. UV–vis absorbance spectroscopy was performed using a UV–vis-3100-NIR Recording Spectrophotometer (Shimadzu, Japan). Fourier transform infrared spectrum was recorded on a Nicolet Magna-IR 750 spectrometer. X-ray photoelectron spectrum (XPS) was recorded on an ESCALAB MKII X-ray photoelectron spectrometer. The glucose levels in fresh plasma samples were firstly analyzed in a local hospital with Hitachi 7060 Automatic Analyzer. A pH glass electrode (868, Thermo Orion) was used for pH titration.

2.3. Preparation of soluble CNF and electrode

Twenty milligrams of CNF was dispersed in 30 mL of 30% HNO_3 and then refluxed for 24 h at 140 °C. The resulting suspension was centrifuged and the precipitate was washed with water to obtain carboxylic group functionalized CNF, which could be completely dissolved in water at pH 1.0 to obtain 5 mg mL^{-1} CNF solution (Wu et al., 2007). This solution was stable and could be used as stock solution for all experiments. For comparison, similar acidic treatment was adopted for CNTs.

The GCE was successively polished to a mirror finish using 0.3 and 0.05 μm alumina slurry (Beuhler) followed by rinsing thoroughly with twice-distilled water. After successive sonication in 1:1 nitric acid, acetone and twice-distilled water, the electrode was rinsed with twice-distilled water and allowed to dry at room temperature. Three microlitres of CNF solution was dropped on the pre-treated GCE and dried in a silica gel desiccator. After 40 min a uniform CNF film was formed to obtain a sensor for dissolved oxygen.

Enzyme solution was prepared by dissolving 10 mg GOx in 1.0 mL 0.2 M pH 7.0 PBS. The GOx solution was thoroughly mixed with pH 7.0 CNF solution at a volume ratio of 1:1. Three microlitres of this mixture was dropped on the pretreated GCE and dried in a silica gel desiccator to form a GOx–CNF membrane. After 3.0 μL 1% Nafion solution was dropped on the membrane to maintain the stability of the GOx–CNF membrane, a biosensor for glucose was obtained. The biosensor was stored in 0.2 M pH 7.0 PBS at 4 °C. Different stock concentrations of β-D-glucose were prepared in 0.2 M pH 7.0 PBS and stored at 4 °C to allow mutarotation for at least 24 h before use.

2.4. Electrochemical measurements

The cyclic voltammetric and amperometric experiments were performed in a thermostated electrochemical cell at 25 °C. Amperometric experiments were carried out in a stirred 0.2 M pH 7.0 PBS by applying a potential step of −0.3 V. When the current reached a steady-state value, substrate was added at one sample per min. Different volumes of O_2-saturated solution were spiked into N_2-saturated PBS for the detection of dissolved oxygen. For the measurement of glucose, different volumes of glucose stock solution were injected into the air-saturated PBS.

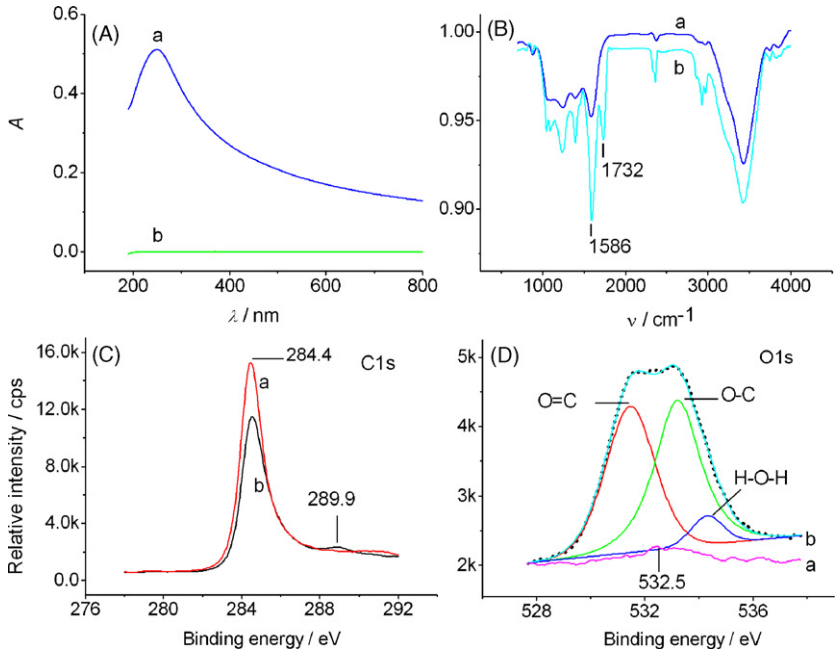

Fig. 1. UV–vis spectra of CNF solution (a) and water (b) (A); Fourier transform infrared spectra of untreated (a) and nitric acid treated (b) CNF (B); C 1s (C) and O 1s (D) XPS spectra of CNF before (a) and after nitric acid treatment (b).

3. Results and discussion

3.1. Physical and chemical characterization of CNF

The UV/vis spectrum of the CNF solution exhibited an absorption band around 230 nm, in a manner analogous to the Nafion-induced solubility of CNTs (Fig. 1A) (Wang et al., 2003a,b). The appearance of the peaks at 1732 and 1586 cm^{-1} in Fourier transform infrared spectrum of CNF indicated the formation of the carboxylic and carboxylate groups in nitric acid treatment process (Fig. 1B) (Luo et al., 2001).

XPS analysis can provide additional information about the oxygen-containing surface groups. The XPS curve for untreated CNF showed a dominant peak structure for C 1s core level at a binding energy of 284.4 eV (Fig. 1C), similar to the carbon shells of CNTs (Martínez et al., 2003). After the CNF was treated, the full width at half-maximum of C 1s peak was obviously broader than that of the untreated sample via extending the peak at the high-binding energy side, attributed to the effect of functional groups. A raised bump around 288.9 eV, similar to that for oxidized CNTs, resulted from the –COO– functional group (Martínez et al., 2003). The corresponding O 1s curve (Fig. 1D) showed that the oxidized CNF gave a much-enhanced O 1s signal around 532.5 eV for untreated CNF. The O 1s signal could be attributed to the contribution of O=C at 531.5 eV, O–C at 533.2 eV, and H–O–H at 534.3 eV, respectively (Martínez et al., 2003; Ma et al., 2006). These results demonstrated that the treated CNF had more oxygen-rich groups. The oxygen–carbon atomic ratio of CNF surface was 14.9 at.% oxygen. As control the CNTs showed an oxygen–carbon atomic ratio of 11.0 at.% oxygen after treated with the same process. However, the untreated CNTs and CNF contained only 1.8 and 1.4 at.% oxygen, respectively. The acidic treatment produced more oxygen-rich groups on CNF surface than CNTs.

The titration curves of the untreated CNF, nitric acid treated CNF and CNTs with both HCl and NaOH were shown in Fig. 2. All these curves showed two equivalent points, indicating the presence of different oxygen-containing groups (Vamvakaki et al., 2006). The alkaline groups of untreated CNF suspension, treated CNF solution and treated CNTs suspension with the same content needed 193, 27 and 46 μL 0.01 M HCl to reach the first equivalent points, pH 4.5, 5.8 and 5.7, respectively. Their acidic groups needed 35, 441 and 201 μL 0.01 M NaOH to reach the first equivalent points, pH 7.8, 8.7 and 8.6, respectively. Obviously the nitric acid treatment led to the decrease in alkaline groups and the great increase in acidic groups.

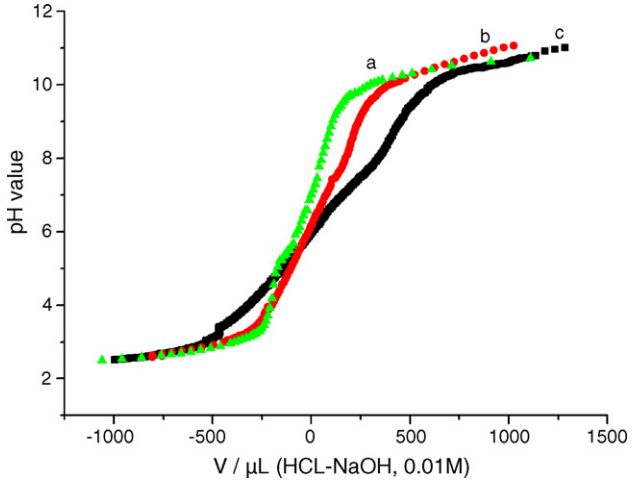

Fig. 2. Titration curves of the untreated CNF suspension (a), CNTs suspension (b) and nitric acid treated CNF solution (c).

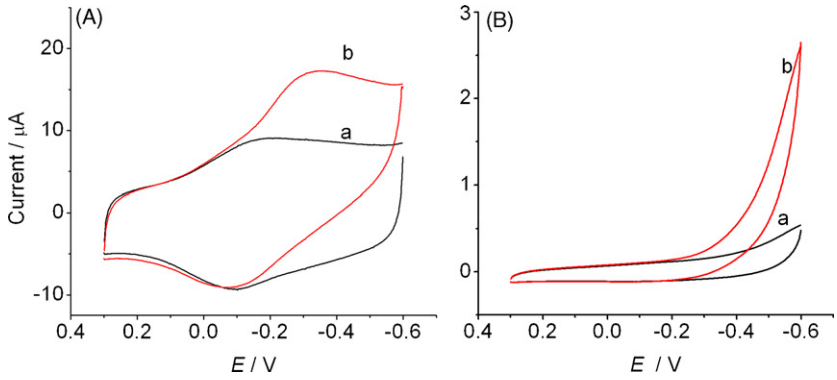

Fig. 3. Cyclic voltammograms of CNF-modified (A) and bare GCE (B) in pH 7.0 N_2-saturated PBS (a) and O_2-dissolved PBS (b). Scan rate: 0.01 V s^{-1}.

After treatment the total amount of these oxygen-containing groups on CNF surface increased twice, which was also twice larger than that on treated CNTs. Thus the treated CNF possessed much better solubility and dispersion ability than treated CNTs.

3.2. Electrochemical measurements of dissolved oxygen

In the potential window from +0.3 to −0.6 V, the CNF/GCE exhibited a pair of small redox peaks at −0.168 and −0.102 V at 0.01 V s^{-1} in a detection solution bubbled thoroughly with high purity nitrogen for 5 min (curve a, Fig. 3A), which were ascribed to the reduction and oxidation of the groups on the CNF surface. Dissolved oxygen began to reduce at about 0 V at CNF/GCE in PBS and the cyclic voltammograms showed an obvious reduction peak centered at about −0.308 V (curve b, Fig. 3A), while at bare GCE the oxygen began to reduce after −0.2 V and no reductive peak was observed in the scan range (Fig. 3B).

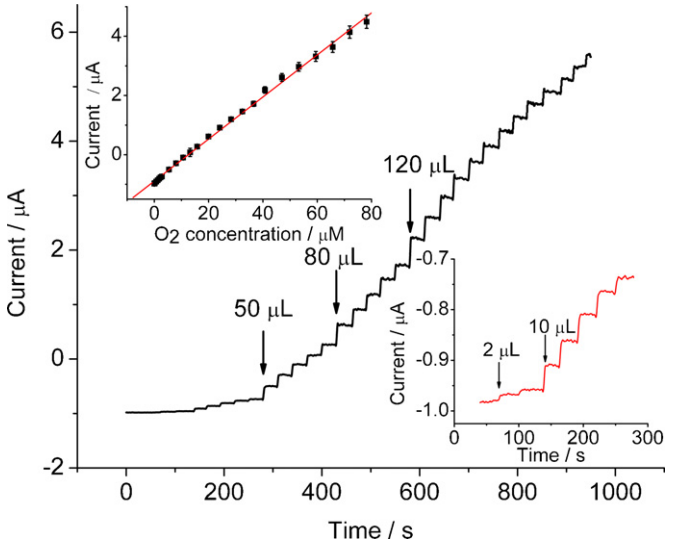

Fig. 4. Typical steady-state current response of the CNF-modified electrode to successive addition of different volumes of O_2-saturated solution into N_2-saturated PBS. Applied potential, −0.30 V. Upper inset: calibration curve of the electrocatalytic current on the concentration of oxygen, lower inset: amplified response curve.

Fig. 4 displayed the amperometric trace of the CNF film-modified electrode recorded at −0.3 V, which is an optimal applied potential from Fig. 3, during the spiking of different volumes of O_2-saturated solution into N_2-saturated solution. The trace illustrated that the modified electrode responds very rapidly to these changes in the O_2 concentration, producing steady-state signals within 5 s. The response displayed a linear range from 0.1 to 78 μM with a correlation coefficient of 0.999 and a slope of 723 nA cm^{-2} μM^{-1}. The limit of detection is 0.07 μM at the signal to noise ratio of 3, which is much lower than 7.8 μM for laccase/CNT–chitosan composite-based biosensor (Liu et al., 2006). The high sensitivity comes from the excellent catalytic activity of CNF.

Repeated use of the electrodes did not affect the long-term stability. The coefficients of variation of the current signals for eight repeated injections of 1.0 and 10 μM O_2 were 3.4 and 2.7%, respectively. The modified electrode showed acceptable preparation reproducibility with a relative standard deviation of 5.5% estimated from the slopes of the calibration plots at six freshly prepared CNF-modified electrodes. The homogeneous CNF solution should have better reproducibility than suspension for biosensor preparation. No obvious decrease in the response to O_2 was observed after three months of storage. The stability is better than the enzyme-based biosensor for O_2 (Liu et al., 2006).

3.3. Amperometric biosensing of glucose

The glucose biosensors are generally based on the detection of the oxidation signal of hydrogen peroxide (Luo et al., 2005) or the reduction signal of dissolved oxygen (Lin et al., 2004), which is produced or consumed in the oxidation process of β-D-glucose to D-glucono-δ-lactone catalyzed by GOx, respectively. The greatly enhanced reduction activity of dissolved oxygen at CNF-based electrochemical transducers makes the CNF extremely attractive for pertinent oxidase-based amperometric biosensors. The measurement principle of these biosensors relies upon the immobilization of oxidase on the surface of various electrodes and the detection of the current associated with decrease of O_2 concentration in the biological reaction. Lin et al. (2004) described a mediator-free biosensor based on CNT nanoelectrode ensembles. Here using GOx as an enzyme model, a CNF–GOx/Nafion-based biosensor for glucose was constructed.

Nafion membrane was used not only to prevent the loss of the immobilized enzyme but also improve the anti-interferent ability of the glucose biosensor. The CNF–GOx/Nafion-based biosensor retained the catalytic activity of the CNF for efficient reduction of dissolved oxygen, allowing for fast and sensitive glucose quantification.

Fig. 5 showed a steady-state response of the biosensor to additions of glucose aliquots to a stirred PBS. Upon addition of an aliquot of glucose the current increased steeply to 95% of the stable value within 10 s, indicating a fast response. The biosensor exhibited a linear response to glucose from 10 to 350 μM with the sensitivity of 36.3 nA cm^{-2} μM^{-1} and a limit of detection of 2.5 μM. The sensitivity was 5 times higher than that for GOx/titania sol–gel-based glucose biosensor (Yu et al., 2003). The detection limit of glucose was slightly lower than 3 μM obtained using chitosan–CNT–glucose dehydrogenase electrode (Zhang et al., 2004). This better performance than CNTs-based biosensors was due to more edge sites on the outer wall of CNF than CNTs (Kim and Lee, 2004), which facilitate the electron transfer of electroactive analytes. The coefficients of variation for intra-assay with this method were 4.7 and 3.2% at glucose concentrations of 20 and 210 μM, respectively. In addition, the relative standard deviation of current signals for measurement of 90 μM glucose at six independently prepared biosensors was 6.1%, which proved good reproducibility of the biosensor preparation.

The stability of the CNF–GOx/Nafion-modified electrode was investigated when stored in 0.2 M pH 7.0 PBS at 4 °C and measured at intervals over several days. No obvious decrease in the response to glucose was observed after 3 weeks of storage. After 30 days the response current was still retained at 95% value of the initial response. This implied that the three-dimensional structure of the CNF–GOx/Nafion membrane was very efficient for retaining the bioactivity of GOx and preventing it from leaking out of the sensor.

The glucose biosensors are often interfered by electroactive compounds such as UA and AA in the analysis of serum samples. The use of a low operating potential (−0.3 V) and Nafion prevented the interference from UA and AA (Burmeister and Gerhardt, 2001), indicating high selectivity toward the glucose substrate. As shown in Fig. 6, the response of the CNF–GOx/Nafion electrode to 0.08 mM glucose was not affected by additions of 0.08 mM uric acid and ascorbic acid.

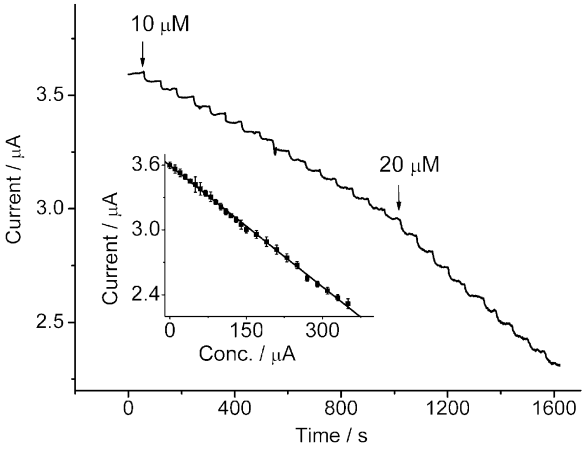

Fig. 5. Successive amperometric response of the CNF–GOx/Nafion-modified electrode to the successive addition of glucose from 10 and 20 μM in stirred air-saturated pH 7.0 PBS at −0.3 V; inset: linear calibration curve for glucose detection.

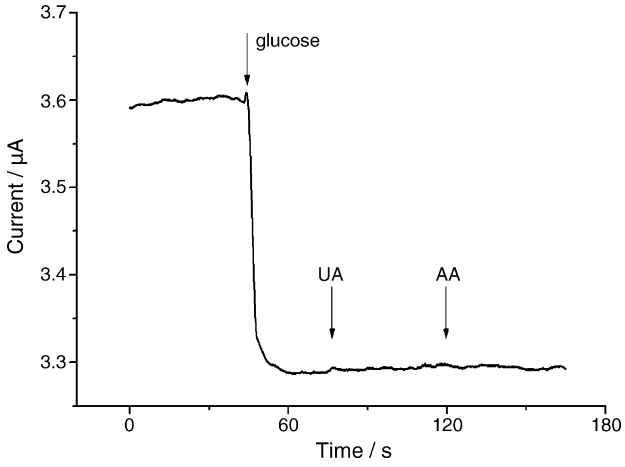

Fig. 6. Amperometric response of CNF–GOx/Nafion-modified electrode to 0.08 mM glucose, UA and AA in pH 7.0 PBS.

3.4. Sample detection

After sample was diluted for 50 times by addition of sample aliquot to a stirred PBS the biosensor could be used for detection of glucose ranging from 0.5 to 17.5 mM. Thus this sensor could be conveniently used for glucose detection in sera. From the calibration curve the contents of glucose in practical fresh plasma samples were determined at −0.3 V to be 4.25, 4.13, 5.34, 6.43, 7.41, 5.26, 5.73, 4.60, 7.21 and 4.44 mM, respectively, which were close to the control values of 4.33, 4.09, 5.37, 6.48, 7.32, 5.16, 5.60, 4.69, 7.17 and 4.46 mM detected in a local hospital with Hitachi 7060 Automatic Analyzer. The relative errors were −1.8, 4.0, −3.0, −0.8, 1.2, 1.9, 2.3, −1.9, 0.6 and −0.4%, respectively, indicating good agreement and that the presented biosensor could be satisfactorily applied to the clinical determination of glucose levels.

4. Conclusions

The soluble CNF shows excellent electrocatalytic activity toward the electroreduction of dissolved oxygen and can thus be used for highly sensitive detection of dissolved oxygen. With GOx as a model for preparation of pertinent oxidase-based amperometric biosensors, the fabricated CNF–GOx/Nafion-based biosensor can quickly detect glucose ranging from 10 to 350 μM with a detection limit of 2.5 μM. The general interferences that coexisted in human serum sample such as UA and AA do not affect the determination of glucose. The simple nitric acid treatment has been proved to produce a large number of different oxygen-containing groups on CNF surface for improving its solubility and biocompatibility. The soluble CNF attributes to the good preparation reproducibility of biosensor and shows good conductivity for accelerating the electron transfer of electroac-

tive compound and excellent catalytic activity towards reduction of dissolved oxygen, which can be used for continuous monitoring of dissolved oxygen and represents a biocompatible platform for the development of electrochemical biosensors.

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References

Andreasen, A., Danscher, G., Juhl, S., Stoltenberg, M., Revsbech, N.P., Jensen, H., Jensen, K.B., 1997. J. Neurosci. Methods 72, 15–21.
Arai, S., Endo, M., 2003. Electrochem. Commun. 5, 797–799.
Baughman, R.H., Cui, C., Zakhidov, A.A., Iqbal, Z., Barisci, J.N., Spinks, G.M., Wallace, G.G., Mazzoldi, A., Rossi, D.D., Rinzler, A.G., Jaschinski, O., Roth, S., Kertesz, M., 1999. Science 284, 1340–1344.
Boussaad, S., Tao, N.J., Hopson, T., Nagahara, L.A., 2003. Chem. Commun. 13, 1502–1503.
Burmeister, J.J., Gerhardt, G.A., 2001. Anal. Chem. 73, 1037–1042.
Chen, S.H., Yuan, R., Chai, Y.Q., Zhang, L.Y., Wang, N., Li, X.L., 2007. Biosens. Bioelectron. 22, 1268–1274.
Cui, H., Kalinin, S.V., Yang, X., Lowndes, D.H., 2004. Nano Lett. 4, 2157–2161.
Cui, H.F., Ye, J.-S., Zhang, W.-D., Wang, J., Sheu, F.-S., 2005. J. Electroanal. Chem. 577, 295–302.
He, P.G., Dai, L.M., 2004. Chem. Commun. 3, 348–349.
Jang, J., Bae, J., Choi, M., Yoon, S.-H., 2005. Carbon 43, 2730–2736.
Ju, H.X., Shen, C.Z., 2001. Electroanalysis 13, 8–9.
Katz, E., Willner, I., 2004. Angew. Chem. Int. Ed. 43, 6042–6108.
Kim, S.-U., Lee, K.-H., 2004. Chem. Phys. Lett. 400, 253–257.
Komai, Y., 1998. J. Exp. Biol. 201, 2359–2366.
Lee, D., Lee, J., Kim, J., Kim, J., Na, H.B., Kim, B., Shin, C.-H., Kwak, J.H., Dohnalkova, A., Grate, J.W., Hyeon, T., Kim, H.-S., 2005. Adv. Mater. 17, 2828–2833.
Li, L., Lukehart, C.M., 2006. Chem. Mater. 18, 94–99.
Lin, Y.H., Lu, F., Tu, Y., Ren, Z.F., 2004. Nano Lett. 4, 191–195.
Lin, Y.H., Cui, X.L., Ye, X.R., 2005. Electrochem. Commun. 7, 267–274.
Liu, Y., Qu, X.H., Guo, H.W., Chen, H.J., Liu, B.F., Dong, S.J., 2006. Biosens. Bioelectron. 21, 2195–2201.
Luo, H.X., Shi, Z.J., Li, N.Q., Gu, Z.N., Zhuang, Q.K., 2001. Anal. Chem. 73, 915–920.
Luo, X.L., Xu, J.J., Wang, J.L., Chen, H.Y., 2005. Chem. Commun. 16, 2169–2170.
Ma, Y.W., Hu, Z., Yu, L.S., Hu, Y.M., Yue, B., Wang, X.Z., Chen, Y., 2006. J. Phys. Chem. B 110, 20118–20122.
Maldonado, S., Stevenson, K.J., 2004. J. Phys. Chem. B 108, 11375–11383.
Maldonado, S., Stevenson, K.J., 2005. J. Phys. Chem. B 109, 4707–4716.
Martínez, M.T., Callejas, M.A., Benito, A.M., Cochet, M., Seeger, T., Ansón, A., Schreiber, J., Gordon, C., Marhic, C., Chauvet, O., Fierro, J.L.G., Maser, W.K., 2003. Carbon 41, 2247–2256.
Moore, R.R., Banks, C.E., Compton, R.G., 2004. Anal. Chem. 76, 2677–2682.
Niemeyer, C.M., 2001. Angew. Chem. Int. Ed. 40, 4128–4158.
Niwa, O., 2005. Bull. Chem. Soc. Jpn. 78, 555–571.
Osborne, P.G., 1997. Physiol. Behav. 61, 485–492.
Qiu, J.S., Zhang, H.Z., Liang, C.H., Li, J.W., Zhao, Z.B., 2006. Chem. Eur. J. 12, 2147–2151.
Qu, F.L., Yang, M.H., Shen, G.L., Yu, R.Q., 2007. Biosens. Bioelectron. 22, 1749–1755.
Salimi, A., Compton, R.G., Hallaj, R., 2004. Anal. Biochem. 333, 49–56.
Vamvakaki, V., Tsagaraki, K., Chaniotakis, N., 2006. Anal. Chem. 78, 5538–5542.
van der Lee, M.K., Jos van Dillen, A., Bitter, J.H., de Jong, K.P., 2005. J. Am. Chem. Soc. 127, 13573–13582.
Wang, J., Deo, R.P., Poulin, P., Mangey, M., 2003a. J. Am. Chem. Soc. 125, 14706–14707.
Wang, J., Musameh, M., Lin, Y.H., 2003b. J. Am. Chem. Soc. 125, 2408–2409.
Werner, P., Verdejo, R., Wollecke, F., Altstadt, V., Sandler, J.K.W., Shaffer, M.S.P., 2005. Adv. Mater. 17, 2864–2869.
Wu, L.N., Zhang, X.J., Ju, H.X., 2007. Anal. Chem. 79, 453–458.
Ye, J.-S., Wen, Y., Zhang, W.D., Cui, H.F., Gan, L.M., Xu, G.Q., Sheu, F.-S., 2004. J. Electroanal. Chem. 562, 241–246.
Yu, J.H., Li, S.Q., Ju, H.X., 2003. Biosens. Bioelectron. 19, 401–409.
Zayats, M., Katz, E., Baron, R., Willner, I., 2005. J. Am. Chem. Soc. 127, 12400–12406.
Zhang, M.G., Smith, A., Gorski, W., 2004. Anal. Chem. 76, 5045–5050.