Electrochimica Acta 65 (2012) 64–69

Contents lists available at SciVerse ScienceDirect

Electrochimica Acta

journal homepage: www.elsevier.com/locate/electacta

A highly sensitive non-enzymatic glucose sensor based on nickel and multi-walled carbon nanotubes nanohybrid films fabricated by one-step co-electrodeposition in ionic liquids

Aili Sun[a,b], Jianbin Zheng[a,*], Qinglin Sheng[a]

[a] Institute of Analytical Science/Shaanxi Provincial Key Laboratory of Electroanalytical Chemistry, Northwest University, Xi'an, Shaanxi 710069, PR China
[b] Department of Chemistry and Chemical Engineering, Xinxiang University, Xinxiang 453000, PR China

ARTICLE INFO

Article history:
Received 20 September 2011
Received in revised form 1 January 2012
Accepted 4 January 2012
Available online 11 January 2012

Keywords:
Non-enzymatic glucose sensor
Nanohybrid films
Carbon nanotubes
Ionic liquids

ABSTRACT

In this paper, nickel was combined with multi-walled carbon nanotubes (Ni–MWNTs) to fabricate nanohybrid films on a conventional glassy carbon electrode using simultaneous electrodeposition of $NiCl_2$ and the MWNTs in ionic liquids (ILs). The morphologies and elemental compositions of the nanohybrid films were investigated with scanning electron microscopy and energy dispersive spectroscopy. A novel non-enzymatic glucose sensor based on the Ni–MWNT nanohybrid film-modified glassy carbon electrode was described, and its electrochemical behaviors were investigated. The proposed sensor exhibited high electrocatalytic activity and good response to glucose. Under optimal conditions, the sensor showed high sensitivity ($67.2\,\mu A\,mM^{-1}\,cm^{-2}$), rapid response time (<2 s) and a low detection limit (0.89 μM; signal/noise ratio of 3). In particular, the upper glucose concentration limit produced a linear response of 17.5 mM. Thus, the Ni–MWNT nanohybrid films represent promising sensor materials for non-enzymatic glucose sensing in routine analyses.

1. Introduction

The determination of glucose has attracted much attention due to its significant index in clinical diagnoses, regulation of metabolism, and biochemical analyses [1–3]. Although previous studies regarding enzyme-modified electrodes have made some considerable progress, common and serious disadvantages, such as rigorous operating conditions, complicated immobilization techniques, chemical instability, and high cost remain [4,5]. Therefore, the pursuit of non-enzymatic glucose sensors with rapid responses and precise measurements is a vigorous and competitive area of research.

In recent years, carbon nanotubes (CNTs) have shown great potential for use as sensing materials owing to their unique advantages, including good biocompatibility, enhanced electronic properties, and rapid electrode kinetics [6,7]. Recently, CNTs have been successfully combined with nanoparticles and applied to the fabrication of enzyme-free glucose sensors. Jiang et al. developed a novel glucose biosensor based on electrodeposition of cupric oxide (CuO) nanoparticles onto MWNTs arrays [8]. In addition, Shamsipur et al. demonstrated that a glassy carbon disc electrode modified with MWNTs and nickel (II) oxide (NiO) could be used for the electrochemical oxidation of glucose with a linearity range of 0.2 mM–10 mM and a detection limit of 0.16 mM [9]. The methods used to construct this non-enzymatic glucose sensor were time consuming or technically complex and often involved surface immobilization, which formed nanoparticles and were therefore unstable. However, to date, few reports have demonstrated the one-step electrodeposition of metals combined with MWNT nanohybrid films to construct non-enzymatic glucose sensors. The reason for this is that MWNTs are largely inert and cannot disperse well in aqueous solutions, which makes uniform deposition of the MWNTs in the metal composites difficult without the addition of surfactants or dispersants [10]. Therefore, exploring the possibilities of finding a compatible conductive solvent that can simultaneously show good dispersion stability for MWNTs remains significant.

To the best of our knowledge, MWNTs and $NiCl_2$ form stable dispersions in ethaline ionic liquids. Recent studies demonstrated that composite films synthesized in ILs possessed superior properties of significantly enhanced electrochemical activity, greater conductivity, and superior mechanical behavior [11–13]. These methods, the simultaneous electrodeposition of $NiCl_2$ and MWNTs in ILs, are simpler and time efficient. Ni–MWNT nanohybrid films have not been explored in sensor applications and may prove to be a novel approach for fabricating novel non-enzymatic sensors.

In this study, we present a novel, simple, one-step co-electrodeposition method to deposit Ni and MWNTs in ionic liquid

---

* Corresponding author. Tel.: +86 29 88302077; fax: +86 29 88303448.
E-mail address: zhengjb@nwu.edu.cn (J. Zheng).

0013-4686/$ – see front matter © 2012 Elsevier Ltd. All rights reserved.
doi:10.1016/j.electacta.2012.01.007

onto a glassy carbon electrode (GCE). A novel non-enzymatic glucose sensor was constructed based on Ni–MWNT nanohybrid films for the first time. A comparative study regarding Ni and the Ni/MWNT-modified electrodes were performed using the same conditions. The sensors fabricated with Ni–MWNT nanohybrid films demonstrated enhanced electrocatalytic activity, selectivity for glucose detection and a wide linearity range.

2. Experimental

2.1. Reagents

Multi-wall carbon nanotubes (MWNTs, >95% purity) were purchased from Chengdu Organic Chemicals Co. Ltd. Prior to use, the MWNTs were treated with concentrated nitric acid to introduce carboxylic acid groups according to Ref. [14]. $NiCl_2{\cdot}6H_2O$ was dried in a vacuum oven at 120 °C for 24 h. Sodium hydroxide, ethylene glycol, choline chloride, glucose, L-ascorbic acid (AA), uric acid (UA) and all other chemicals were of analytical grade and were used without further purification. Distilled water was used in all experiments.

2.2. Apparatus

All of the electrochemical experiments were performed using a CHI660D electrochemical workstation (Shanghai Chenhua Instrument Co. Ltd., China) using a three-electrode system. A silver–silver chloride electrode (Ag/AgCl) as reference electrode (SCE), a platinum wire electrode as the auxiliary electrode, and a modified glassy carbon electrode (GCE) as the working electrode. All the potentials given in this paper were referred to the SCE. Scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS) images were acquired with a JEOL JEM-3010 (JEOL, Japan) high-resolution transmission electron microscope using an accelerating voltage of 200 kV.

2.3. Preparation of the nanohybrid films coated electrode

2.3.1. Nanohybrid film-coated electrode preparation

The ionic liquids, ethaline, were synthesized according to previous work [15] with a slight modification. Briefly, ethylene glycol and choline chloride (2:1) were heated while stirring constantly for 20 min until a homogeneous, colorless liquid formed. Prior to use, a GCE (Φ = 4 mm) was polished with 0.3-μm and 0.05-μm alumina slurries to obtain a mirror-like surface and was then ultrasonically and thoroughly cleaned in ethanol and water. The material was then allowed to dry at room temperature. Ten mg of the acid-treated MWNTs and 3.0 mmol $NiCl_2$ were ultrasonically dispersed within 10 mL ionic liquid ethaline for 30 min to obtain a homogeneous black-blue solution. Then, stable dispersions of MWNTs and $NiCl_2$ in ionic liquids were used for the electrodeposition of the Ni–MWNT nanohybrid films. The potential for multiple cyclic voltammetry (CVs) experiments ranged from 0.0 V to 1.6 V (vs. SCE) with a scan rate of 20 mV s^{-1} and scan number of 20, similar to previously reported [16]. The resulting electrode was washed with distilled water. The effect of the Ni–MWNT nanohybrid film electrodeposition cycles on the electrochemical response of glucose was investigated after injecting the same amount of glucose under the same condition. As a result, the peak current changed with the cycles. At 20 cycles, the peak current reached its maximum. Thus, the optimal cycles for further studies were selected in 20 cycles.

For comparison, a Ni/MWNT/GCE was prepared as follows: 5 μL (1 mg·mL^{-1}) of MWNTs were delivered to a cleaned GCE surface and dried with air; Ni was then electrodeposited in ionic liquid ethaline. The Ni/GCE was similarly prepared, without the MWNTs. These modified electrodes were stored at 4 °C for further use.

3. Results and discussion

3.1. Ni–MWNTs/GCE characterization

SEM was used to characterize the morphologies of the Ni–MWNT nanohybrid films. From Fig. 1B, the majority of the Ni nanoparticles were spherical and clearly had an average diameter of approximately 50 nm. The MWNTs were combined with Ni for each other and the Ni nanoparticles showed good adhesion to the MWNT surfaces. The EDS spectrum (Fig. 1C) indicted the presence of Ni and C. These results demonstrated that the Ni–MWNT nanohybrid films were successfully electrodeposited onto indium oxide glass (elements Ca, Si, O and In were detected due to the indium oxide glass).

The mechanism of electrodeposition was previously described [16]. Firstly, nickel cations could be reduced and generated as Ni nanoparticles on the GCE under cathodic polarization. Secondly, the well-dispersed MWNTs that were close to the Ni nanoparticles were deposited on it and entrapped as individual nanotubes or aggregates. Then, increasing amounts of nickel cations were electrodeposited onto the Ni nanoparticles and also onto the incorporated MWNTs. Finally, increasing amounts of the MWNTs were deposited along with the Ni nanoparticles and were then progressively linked together to form the Ni–MWNT composites. The electrodeposition process of the nanohybrid films is shown in Scheme 1.

Previous studies have revealed that the electrocatalytic activity of Ni-constructed electrodes for glucose oxidation was based on the formation of a nickel oxyhydroxide surface film [17]. To reach a stationary state before being used for glucose detection measurements, the Ni–MWNT nanohybrid films were explored in an aqueous solution containing 0.1 M NaOH by 50 consecutive CV scans over the potential range of +0.0 V to +0.8 V at a scan rate of 0.1 V s^{-1}. From Fig. 2, both the anodic and cathodic current densities progressively increased after consecutive potential-sweeping cycles. Changes in the peak current density were likely due to the changes in the crystal structures of the nickel hydroxide and nickel oxyhydroxide [18,19].

3.2. Electrocatalytic oxidation of glucose

The electrochemical responses of the Ni–MWNT/GCE films were further investigated with the scan rates (υ) ranging from 0.1 V s^{-1} to 1.4 V s^{-1}, and the results are shown in Fig. 3. The peak current was proportional to the square root of the scan rate (Fig. 3, inset) with a linear regression equation of I_{pa} (μA) = −75.37 − 440.1 $\upsilon^{1/2}$ (m $V^{1/2}$ $s^{-1/2}$) (n = 14, r = 0.9992) and I_{pc} (μA) = 71.98 + 239.0 $\upsilon^{1/2}$ (m $V^{1/2}$ $s^{-1/2}$) (n = 14, r = 0.9989). These results indicated that the electrochemical kinetics signified a diffusion-controlled process rather than a surface-controlled process at these scan rates, which is an ideal case for quantitative analyses in practical applications. Meanwhile, the cathodic and anodic peaks shifted to high potentials, and the peak currents shifted to lower values with the increase in scan rates. These results were due to the nucleation of NiO(OH) and the following increase of activation sites (Ni^{2+} or Ni^{3+}) [20–24].

$$Ni(OH)_2 + OH^- \rightarrow NiO(OH) + e^- + H_2O$$

Applied potential strongly affects the amperometric response of a biosensor. To improve the performance of the sensor, the effect of the applied potential on the response current of the sensor is illustrated in Fig. 4. When the applied potential was increased from

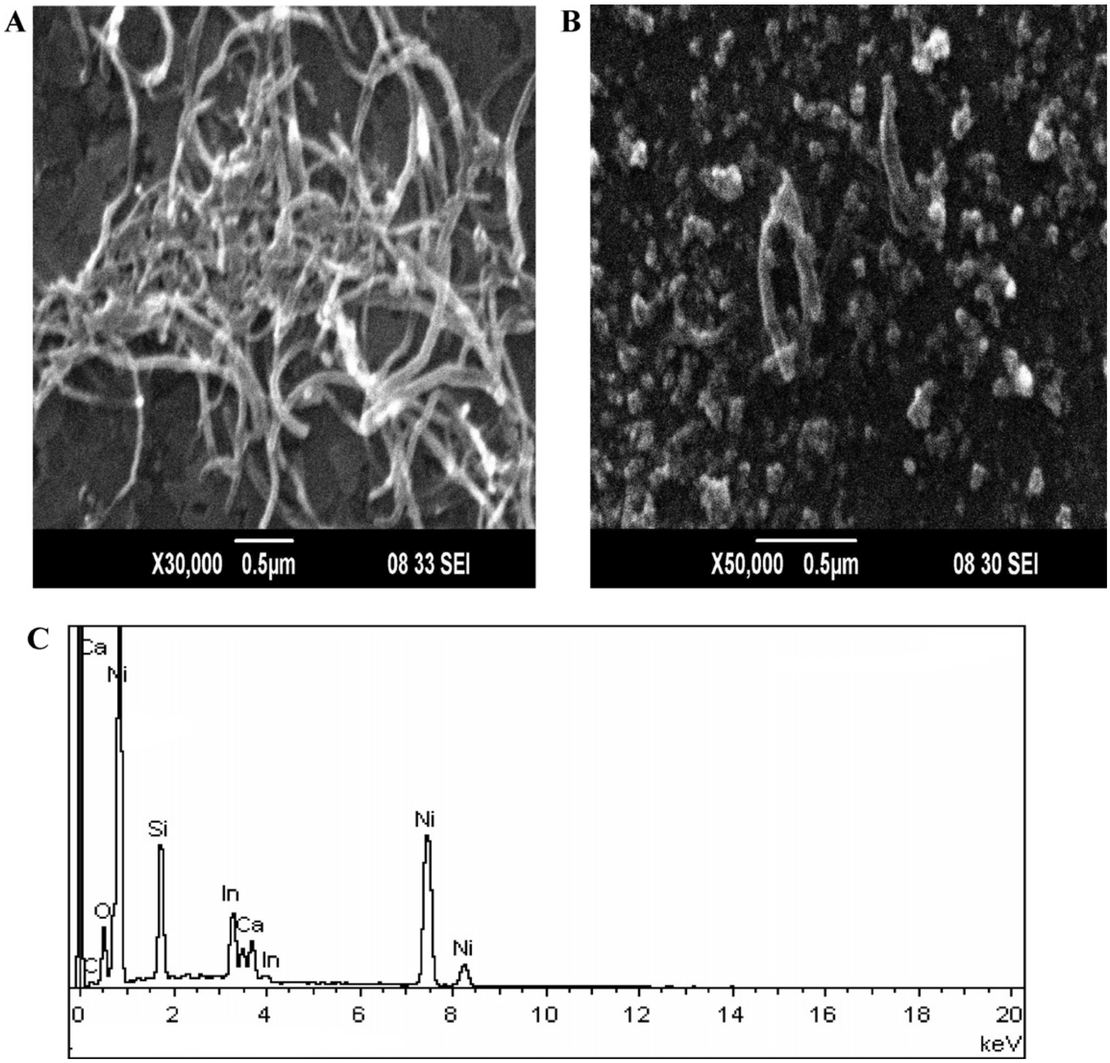
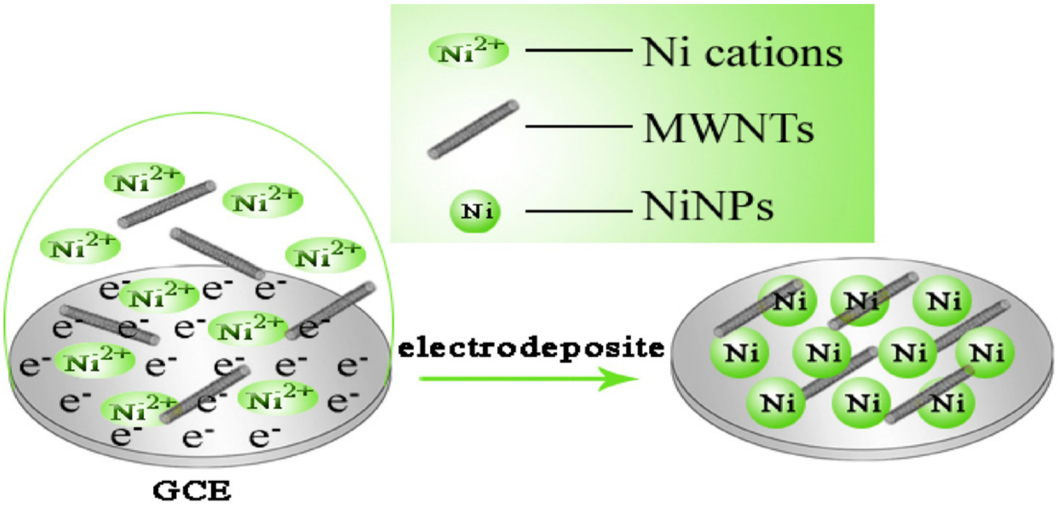


Fig. 1. (A) SEM images of MWNT and (B) Ni–MWNT nanohybrid films, and (C) EDS analyses of Ni–MWNT nanohybrid films.



Scheme 1. An illustration describing the electrodeposition process of modified electrodes.

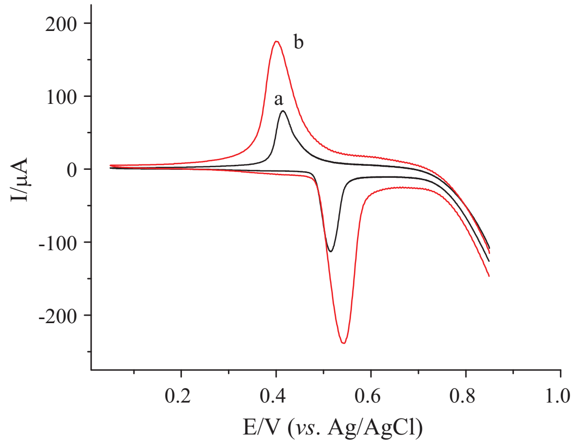


Fig. 2. CVs of the Ni–MWNT/GCE films in 0.1 M NaOH at 0.1 V s^{-1} after (a) 1 and (b) 50 consecutive CVs.

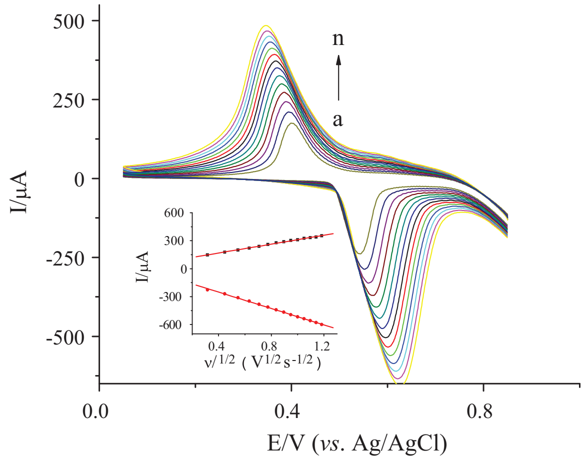


Fig. 3. CV responses of the Ni–MWNT/GCE films at various scan rates in 0.1 M NaOH. Scan rates (from a to n): 0.1, 0.2, 0.3, 0.4 0.5, 0.6, 0.7, 0.8, 0.9, 1.0, 1.1, 1.2, 1.3 and 1.4 V s^{-1}, respectively. The inset represents the plots of I_{pc} and I_{pa} vs. scan rates.

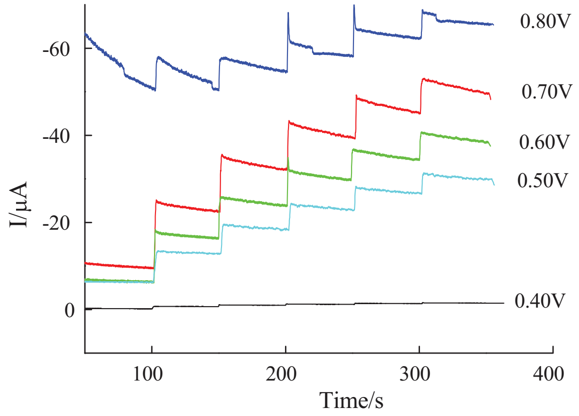


Fig. 4. Steady-state current–time responses of the Ni–MWNT/GCE films to 0.01 mM glucose in 0.1 M NaOH at various potentials.

0.4 to 0.8 V, very little current was observed at an applied potential 0.4 V; however, a large increase was observed from 0.5 to 0.7 V. Therefore, 0.6 V was selected as the optimum applied potential for the amperometric detection of glucose in subsequent studies.

The electrochemical oxidation of glucose was investigated in 0.1 M NaOH at the modified electrodes using CVs. As shown in Fig. 5, increased glucose concentrations induced apparent enhancements in the oxidation peak currents and decreases in the cathodic peak currents. These results indicated that glucose had been oxidized by the active Ni–MWNT nanohybrid films via a cyclic mediation redox process. The reason that the anodic peak potential shifted to a high potential might be attributed to the diffusion limitation of glucose at the electrode surface [25]. The current deviated from linearity at higher glucose concentrations, most possibly due to the passivation of the electrode and formation of glucose isomers, which is known to occur in alkaline media [26]. The mechanism of electrocatalytic oxidation of glucose due to the existence of Ni(II) ions are described with the following reactions [27]:

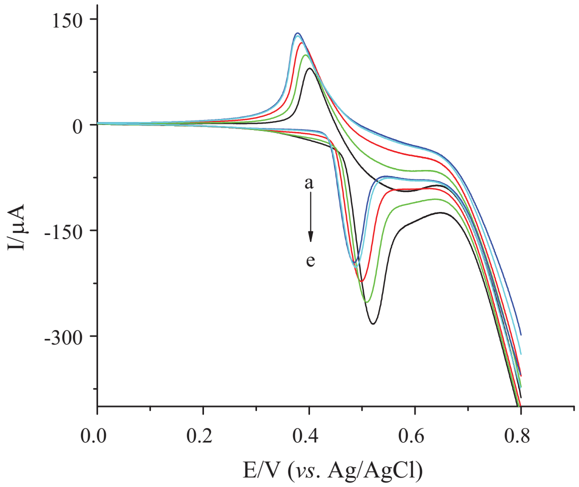


Fig. 5. CVs of the Ni–MWNT/GCE films at different concentrations of glucose: (a) 0.0, (b) 0.5, (c) 1.0, (d) 2.0, (e) 3.0 mM in 0.1 M NaOH.

$$\mathrm{Ni(OH)_2 + OH^- \rightarrow NiO(OH) + e^- + H_2O}$$

$$\mathrm{NiO(OH) + glucose \rightarrow Ni(OH)_2 + glucolactone}$$

The inset represents the corresponding calibration curve at (a) Ni–MWNT/GCE, (b) Ni/MWNT/GCE and (c) Ni/GCE modified glucose sensors.

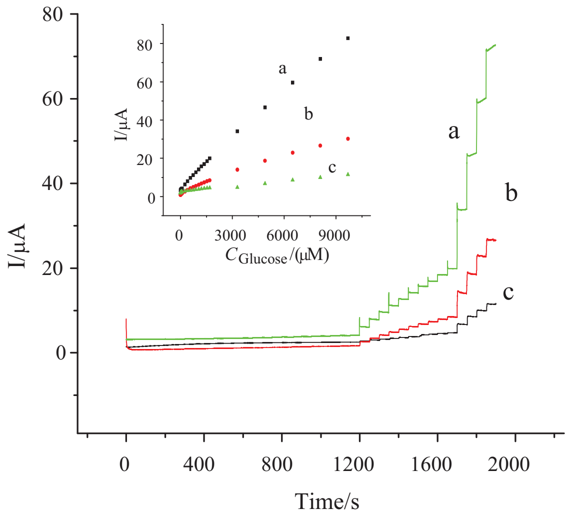


Fig. 6. Amperometric responses of (a) Ni–MWNT/GCE, (b) Ni/MWNT/GCE and (c) Ni/GCE modified electrodes stirring in 0.1 M NaOH after successive glucose additions at an applied potential of 0.60 V. The inset represents the corresponding calibration curve at (a) Ni–MWNT/GCE, (b) Ni/MWNT/GCE and (c) Ni/GCE modified glucose sensors.

Table 1
Performances of the different glucose biosensors.

Electrode	LR	DL	Sensitivity	Stability	References
NiCFP electrode	2 μM–2.5 mM	1 μM	3.30 μA mM^{-1}		[28]
Nickel electrode	100 μM–2.5 mM	0.04 mM	–	–	[21]
Ni powder modified electrode	0.5 μM–5 mM	0.2 μM	40 μA mM^{-1} cm^{-2}	–	[29]
NiO/MWCNTs electrode	10 μM–7 mM	2 μM	1768.8 μA mM^{-1} cm^{-2}	–	[30]
Ni nanoparticle modified carbon paste electrode	1.0 μM–1.0 mM	0.3 μM	–	1 week	[31]
Au/MNE	100 μM–3.0 mM	0.5 μM	2978 μA mM^{-1} cm^{-2}	3–20 days	[32]
Ni–MWNTs	3.2 μM–17.5 mM	0.89 μM	67.19 μA mM^{-1} cm^{-2}	30 days	This work

NiCFP, Ni nanoparticle-loaded carbon nanofiber paste; NiO, nickel(II) oxide; MNE, mesoporous nickel electrodes; LR, linearly range; DL, detection limit.

Fig. 6a shows a typical current–time sensor curve at a constant potential of +0.6 V after the addition of successive glucose in stirring 0.1 M NaOH. A comparative study of injecting the same amount of glucose was conducted by fabricating three types of different modified sensors under the same conditions, using Ni–MWNT/GCE, Ni/MWNT/GCE and Ni/GCE films (Fig. 6a–c, respectively). The amperometric response curves demonstrated that the Ni–MWNT nanohybrid film-modified electrodes presented well-defined, stable and rapid amperometric responses within 2 s and that the sensitivity was higher than that of the Ni/MWNT/GCE and Ni/GCE films. The Ni–MWNT/GCE films better performed the Ni/GCE films, proving that the MWNTs have greatly improved the sensitivity of the electrode. At the same time, when using the Ni/MWNT/GCE films as a control, the results showed that the one-step electrodeposition of metal combined with MWNT nanohybrid films is better than the traditional drop-coating of MWNTs with metal. Thus, the sensors that were constructed with a one-step electrodeposition of metal combined with MWNT nanohybrid films demonstrated better performance. Meanwhile, the calibration curve for the glucose sensor at the Ni–MWNT/GCE was generated and shown in Fig. 7. The sensor displayed a linear range from 3.2 μM to 17.5 mM glucose with a linearly regression equation of $I\,(\text{mA}) = 4.16 + 0.0081\,C_{\text{glucose}}$ (μM) ($R^2 = 0.9954$, in Fig. 7B) and detection limit of 0.89 μM (signal/noise = 3). The linear range for glucose determination at the Ni–MWNT nanohybrid film-modified electrode was comparable and even better than previously reported non-enzymatic glucose sensors [21,28–32]. The results are summarized in Table 1. The wider linear ranges could be explained as follows. Firstly, ionic liquids were used as solvents. MWNTs are inert and cannot disperse in water. The traditional method is to drop carbon nanotubes or film-forming materials to disperse carbon nanotubes onto electrodes. The method used to construct the sensor were time consuming or technically complex. However, MWNTs and NiCl_2 can disperse in ILs. Thus, one-step co-electrodeposition in ionic liquid can be achieved. MWNTs can then serve as effective sites to facilitate the electrodeposition process and nickel matrix reinforcement, which makes the Ni–MWNT nanohybrid films more stable. Meanwhile, direct electrodeposition without using an immobilization matrix offers close contact of the Ni–MWNT nanohybrid films, which is also aids in rapid and sensitive catalytic performance. Secondly, Ni–MWNT nanohybrid films that are electrodeposited in ILs possess potential features, such as enhanced hardness, protection against corrosion and catalytic performance. Finally, the large surface and roughness on the surface of Ni–MWNT nanohybrid films, which is a desirable material for a sensor, also provides more reaction sites.

Oxidizable compounds, such as AA and UA, typically co-exist with glucose in physiological fluids on different electrodes, especially on non-enzymatic glucose sensors [33]. According to normal values (physiological), the interference effect of 0.1 mM AA and 0.1 mM UA on the amperometric response of 1 mM glucose was studied. At this level, the current responses produced by AA and DA were 0.21 μA and 0.23 μA, only 3.81% and 4.18% when compared to that of glucose (5.5 μA), respectively. The results showed that the proposed sensor was responsible for good selectivity towards the detection of glucose.

The reproducibility of the sensor was determined by conducting eight successive amperometric measurements of 2.0 mM glucose with a modified electrode. The relative standard deviation (R.S.D.) of the reproducible current was 4.2%. The experimental results confirmed that the electrode was not poisoned by the oxidation products and was highly reproducible. The batch-to-batch reproducibility was estimated from the current responses of six different sensors toward 2.0 mM glucose, and an RSD of 4.5% was obtained, indicating that the proposed method was reliable. The long-term stability is also a significant parameter for evaluating the

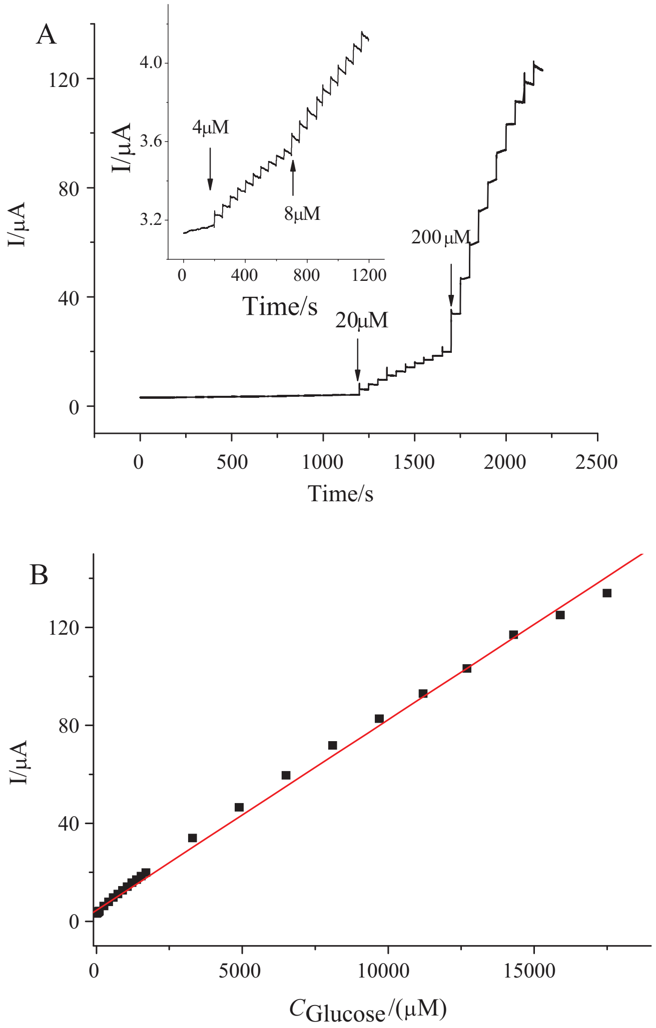


Fig. 7. (A) Amperometric responses of the Ni–MWNT/GCE films to increasing the glucose concentrations with an applied potential of 0.60 V. (B) The corresponding calibration curve at the Ni–MWNT/GCE films.

Table 2
Determination of glucose in human plasma samples by the proposed sensor.

Samples	Measured (mM)	Added (mM)	Measured (mM)	Recovery (%)
1	5.65	2.00	7.62	98.5
2	5.61	2.50	8.20	103.6
3	5.56	3.00	8.61	101.6
4	5.62	4.00	9.70	102.0

performance of the sensor. A response current of 0.2 mM glucose was determined each week. The results showed that the response current was 95% of its initial value after 30 days, which indicated that the stability of the sensor was very good.

The applicability of this glucose biosensor was performed after determining the glucose concentration in real samples, utilizing both the calibration curve and standard addition method. The recovery of glucose was testified using the standard addition method with three times the addition of pure glucose to solutions containing serum samples. The results showed that the sensor produced recoveries in the range of 98.5–103.6%, indicating that the as-prepared Ni–MWNT nanohybrid films hold great potential in real sample analyses (Table 2).

4. Conclusions

In this paper, novel Ni–MWNT nanohybrid films were prepared by the one-step electrodeposition of Ni and MWNTs in ILs and were successfully applied to fabricate a non-enzymatic glucose sensor for the first time. Meanwhile, the experimental results showed that this sensor exhibited rapid responses and a wide linearly range (up to 17.5 mM) when compared to most of the existing non-enzymatic glucose sensors. The high electrocatalytic activity likely raised from the specific large surface area of the Ni–MWNT nanohybrid films. Thus, the present sensors were suitable for glucose determination in real samples.

Acknowledgment

The authors appreciate the financial support from the National Natural Science Foundation of China (No. 20875076).

References

[1] E. Crouch, D.C. Cowell, S. Hoskins, R.W. Pittson, J.P. Hart, Biosens. Bioelectron. 21 (2005) 712.
[2] C. Nan, Y. Zhang, G. Zhang, C. Dong, S. Shuang, M.M.F. Choi, Enzyme Microb. Technol. 44 (2009) 249.
[3] J.B. Jia, B.Q. Wang, A.G. Wu, G.J. Cheng, Z. Li, S.J. Dong, J. Anal. Chem. 74 (2002) 2217.
[4] R. Wilson, A.P.F. Turner, Biosens. Bioelectron. 7 (1992) 165.
[5] X.H. Kang, Z.B. Mai, X.Y. Zou, P.X. Cai, J.Y. Mo, Anal. Biochem. 363 (2007) 143.
[6] D. Eder, Chem. Rev. 110 (2010) 1348.
[7] C.B. Jacobs, M.J. Peairs, B.J. Venton, Anal. Chim. Acta 662 (2010) 105.
[8] J. Yang, L.C. Jiang, W.D. Zhang, S. Gunasekarana, Talanta 82 (2010) 25.
[9] M. Shamsipur, M. Najafi, M.R.M. Hosseini, Bioelectrochemistry 77 (2010) 120.
[10] C. Chen, B. Liang, A. Ogino, X. Wang, M. Nagatsu, J. Phys. Chem. C 113 (2009) 7659.
[11] Q. Wang, Y.B. Yun, J.B. Zheng, Microchim. Acta. 167 (2009) 153.
[12] M.C. Li, C.A. Ma, B.Y. Liu, Z.M. Jin, Electrochem. Commun. 7 (2005) 209.
[13] K. Sekiguchi, M. Atobe, T. Fuchigami, J. Electroanal. Chem. 557 (2003) 1.
[14] M.L. Guo, J.H. Chen, L.H. Nie, S.Z. Yao, Electrochim. Acta 49 (2004) 2637.
[15] A.P. Abbott, J.C. Barron, K.S. Ryder, Trans. Inst. Met. Finish 87 (40) (2009) 201.
[16] P. Martis, V.S. Dilimon, J. Delhalle, Z. Mekhalif, Electrochim. Acta 55 (2010) 5407.
[17] P.F.F. Luo, T. Kuwana, Anal. Chem. 66 (1994) 2775.
[18] A.A. El-shafei, J. Electroanal. Chem. 471 (1999) 89.
[19] Q.F. Yi, J.J. Zhang, W. Huang, X.P. Liu, Catal. Commun. 8 (2007) 1017.
[20] B. Ballarin, R. Seeber, D. Tonelli, A. Vaccari, J. Electroanal. Chem. 463 (1999) 123.
[21] C. Zhao, C. Shao, M. Li, K. Jiao, Talanta 71 (2007) 1769.
[22] M. Jafarian, M.G. Mahjani, H. Heli, F. Gobal, M. Heydarpoor, Electrochem. Commun. 5 (2003) 184.
[23] L.W. Wang, C.X. Yin, L.Y. Zhang, R. Gao, J. Phys. Chem. C 114 (2010) 4408.
[24] R.S. Schrebler Guzmán, J.R. Vilchel, A.J. Arvíal, Appl. Electrochem. 8 (1978) 67.
[25] L.M. Lu, L. Zhang, F.L. Qu, H.X. Lu, X.B. Zhang, Z.S. Wu, S.Y. Huan, Q.A. Wang, G.L. Shen, R.Q. Yu, Biosens. Bioelectron. 25 (2009) 218.
[26] J.F. Robyt, in: C.R. Cantor (Ed.), Springer Advanced Texts in Chemistry, Springer, New York, 1998, p. 48.
[27] H. Zheng, H.G. Xue, Y.F. Zhang, Z.Q. Shen, Biosens. Bioelectron. 17 (2002) 541.
[28] Y. Liu, H. Teng, H. Hou, T. You, Biosens. Bioelectron. 24 (2009) 3329.
[29] T. You, O. Niwa, Z. Chen, K. Hayashi, M. Tomita, S. Hirono, Anal. Chem. 75 (2003) 5191.
[30] W.D. Zhang, J. Chen, L.C. Jiang, Y.X. Yu, J.Q. Zhang, Microchim. Acta 168 (2010) 259.
[31] X. Cheng, S. Zhang, H. Zhang, Q. Wang, P. He, Y. Fang, Food Chem. 106 (2008) 830.
[32] T.R. Ling, C.S. Li, J.J. Jowb, J.F. Leec, Electrochim. Acta 56 (2011) 1043.
[33] J.H. Yuan, K. Wang, X.H. Xia, Adv. Funct. Mater. 15 (2005) 803.