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A novel nonenzymatic hydrogen peroxide sensor based on MnO_2/graphene oxide nanocomposite

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ABSTRACT

A new electrocatalyst, MnO_2/graphene oxide hybrid nanostructure was successfully synthesized for the nonenzymatic detection of H_2O_2. The morphological characterization was examined by scanning electron microscopy and transmission electron microscopy. The MnO_2/graphene oxide based electrodes showed high electrochemical activity for the detection of H_2O_2 in alkaline medium. The nonenzymatic biosensors displayed good performance along with low working potential, high sensitivity, low detection limit, and long-term stability, which could be attributed to the high surface area of graphene oxide providing for the deposition of MnO_2 nanoparticles. These results demonstrate that this new nanocomposite with the high surface area and electrocatalytic activity offers great promise for new class of nanostructured electrode for nonenzymatic biosensor and energy conversion applications.

1. Introduction

Since reliable and fast determination of H_2O_2 is important in many areas such as medicine, food control, environmental protection, and a key factor in the development of efficient biosensors, the study of electrochemical H_2O_2 sensor has attracted extensive attention [1,2]. Horseradish peroxidase, cytochrome C, hemoglobin, and myoglobin have been widely used to construct various amperometric biosensors for H_2O_2 detection due to their high sensitivity and selectivity [3–8]. However, there are several disadvantages of the enzyme-modified electrodes, such as instability, high cost of enzymes and complicated immobilization procedure. The activity of enzymes can be easily affected by temperature, pH value, and toxic chemicals. In order to solve these problems, considerable attention has been paid to develop nonenzymatic electrodes, for instance, noble metals, metal alloys, and metal nanoparticles [9–11]. However, these kinds of electrodes have displayed the drawbacks of low sensitivity, poor selectivity and high cost. Therefore, the development of a cheap and highly sensitive catalyst for nonenzymatic H_2O_2 detection is still greatly demanded.

Recently graphene has attracted tremendous attention because of its unique electronic, optical and chemical properties and many potential applications in nanomaterials and nanotechnology [12–14]. Graphene oxide (GO), one of the most important derivatives of graphene, with two-dimensional plane and oxygen functional groups bearing on the basal planes and edges, provide it with a large specific surface area for the immobilization of large amount of substances including a wide range of metals, nanoparticles, biomolecules, drugs, *etc.* [15–17]. It has been reported that carboxyl-modified GO possess intrinsic peroxidase-like activity that can catalyze the reaction of peroxidase substrate [18].

Manganese dioxide (MnO_2) is a kind of attractive inorganic material and can catalyze the electrocatalytic ability towards H_2O_2 [19,20]. Several kinds of MnO_2 nanomaterials have been utilized in the fabrication of biosensors based on measuring H_2O_2 [21–23].

In this paper, we prepared GO/MnO_2 nanocomposite for nonenzymatic H_2O_2 biosensor. To the best of our knowledge, there are rare reports on the application of GO/MnO_2 in the electrochemical biosensor. The GO/MnO_2 electrode presents high sensitivity, low potential and long-term stability towards the detection of H_2O_2, which is promising for the development of nonenzymatic H_2O_2 sensor.

2. Experimental section

2.1. Reagents and apparatus

H_2O_2 solution (30%) was purchased from Changsha Chemical Reagent Factory (Changsha, China). All chemicals used were of analytical grade.

GO was prepared from powdered flake graphite by a modified Hummers method [24]. 50 mg of GO and certain amount of $KMnO_4$ (0.05 M) aqueous solution were dispersed in 50 mL of deionized water with ultrasonication for 1 h. Subsequently, the slurry was

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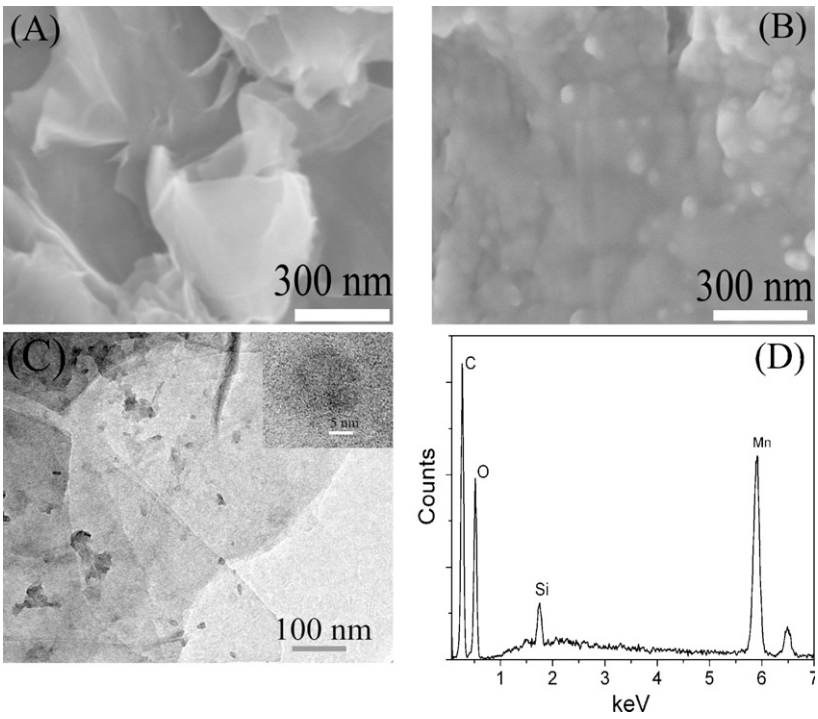

Fig. 1. SEM images of bare graphene oxide (A) and gaphene oxide/MnO_2 (B). TEM image of gaphene oxide/MnO_2, the inset is the corresponding high-resolution TEM image (C). EDS spectrum of the gaphene oxide/MnO_2 nanocomposite (D).

heated to about 160 °C in a water cooled condenser with vigorous stirring, and 3 mL of citric acid (0.1 M) was added dropwise into the above boiling solution. After refluxing for 12 h, the solution was cooled down to room temperature. Finally, the composite products were obtained through filtering, water washing and drying process.

The scanning electron microscopic (SEM) image was carried out by Hitachi 4800 (Hitachi, Japan). The transmission electron microscopic (TEM) image was performed on JEM 2010 high-resolution transmission electron microscopy. Surface elemental composition of the synthesized samples was characterized by an energy-dispersive X-ray spectrometer (EDS). Electrochemical experiments were performed at room temperature on a CHI 660B electrochemical station (CHI Instruments Inc., USA) with a conventional three-electrode system. The composite modified glassy carbon (GC) electrode was used as the working electrode. The Pt wire and saturated calomel electrode acted as the counter and reference electrodes. The solutions were purged with highly purified nitrogen gas for at least 30 min prior to the electrochemical experiments.

2.2. Electrode modification

Prior to the electrode modification, the GC electrodes were polished with 1.0, 0.3, and 0.05 μm alumina powder, respectively, and then sonicated in ethanol and water, each for 2 min. The modified electrodes were prepared by a simple casting method. Typically, 6 μL of the composite solution (1 mg/mL, ethanol) was cast onto the GC electrode and then dried in air at room temperature.

3. Results and discussion

3.1. Characterization of the synthesized GO and GO/MnO_2 composite

The morphology of the prepared GO and GO/MnO_2 are depicted in Fig. 1A and B. It is observed that the surface of GO/MnO_2 becomes rough in compared with bare GO sheets. More detailed structure was performed by TEM, as shown in Fig. 1C. Some of MnO_2 nanoparticles were floc and uniformed covered on the surface of GO sheets. And some crystalline MnO_2 nanoparticles were found from high-resolution TEM images, as depicted in the inset of Fig. 1C. EDS measurements further reveal that the sample contains the elements of manganese and oxygen. The peak of silicon in the spectrum was from the substrate, as shown in Fig. 1D. This result confirmed that MnO_2 has been coated on the GO sheets.

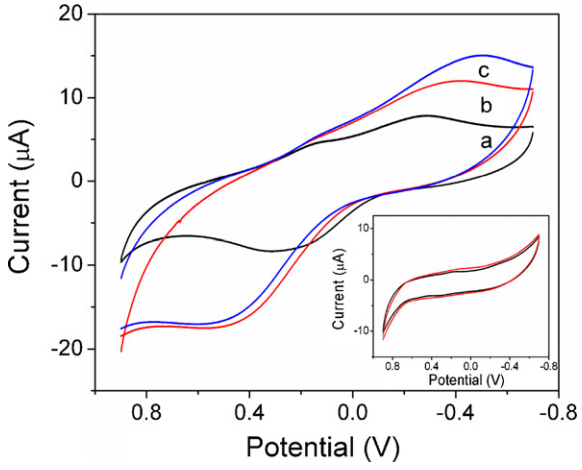

Fig. 2. CVs of gaphene oxide/MnO_2 electrode in the absence (a) and presence of 10 μM (b) and 20 μM (c) H_2O_2 in 0.1 M NaOH solution at the scan rate of 100 mV s^{-1}. Inset: bare graphene oxide in the absence (solid line) and presence (dash line) of 100 μM H_2O_2 under the same situation.

3.2. Electrochemical properties of the GO/MnO_2 composite film modified GC electrode

Fig. 2 shows the cyclic voltammograms (CVs) of the GO/MnO_2 electrode in the absence (a) and presence of 10 μM (b) and 20 μM

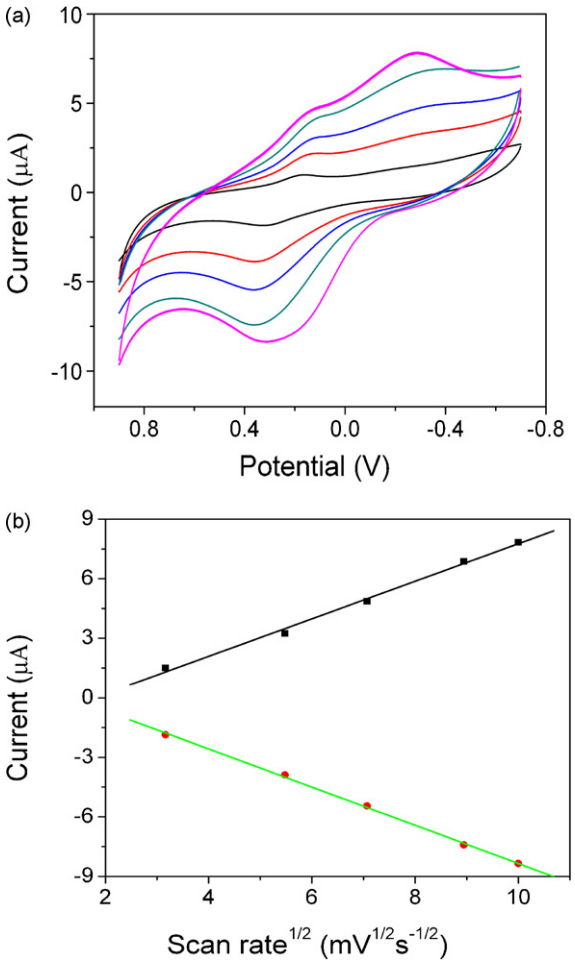

Fig. 3. CVs of the gaphene oxide/MnO_2 electrode at different scan rates (10–100 mV s^{-1}) in 0.1 M NaOH solution (a) and peak current as a function of different scan rate (b).

(c) H_2O_2 in 0.1 M NaOH solution. In the absence of H_2O_2, obvious peaks are observed at the electrode, which can be assigned to the oxidation of Mn(II) to MnO_2, and then the reduction of MnO_2 to Mn(II) species. When H_2O_2 was added into the solution, the voltammetric behavior of the modified electrode changed dramatically. Both the oxidation and reduction currents increased with the concentration of H_2O_2. MnO_2 is chemically reduced to bivalent species by H_2O_2 (Eq. (1)), and then Mn(II) is oxidized to Mn(IV) (Eq. (2)):

$$MnO_2 + H_2O_2 \rightarrow Mn(OH)_2 + O_2 \quad (1)$$

$$Mn(OH)_2 + 2OH^- \rightarrow MnO_2 + H_2O_2 + 2e^- \quad (2)$$

The inset is the CVs of the bare GO sheets modified electrode in the absence (solid line) and presence of 100 μM H_2O_2 (dash line) in the solution. No obvious current for the oxidation of H_2O_2 was observed. These results indicated that the modification of MnO_2 on the surface of GO sheets significantly improved the electrocatalytic activity towards the reduction of H_2O_2.

The CVs of GO/MnO_2 modified GC electrode at various scan rates are shown in Fig. 3(a). It is found that both the cathodic and anodic peak currents increase with the scan rate and enhancements of both currents are linear to the square root of scan rate as shown in Fig. 3(b). The facts indicated that the electrochemical kinetics was a reversible and diffusion-confined electrochemical process.

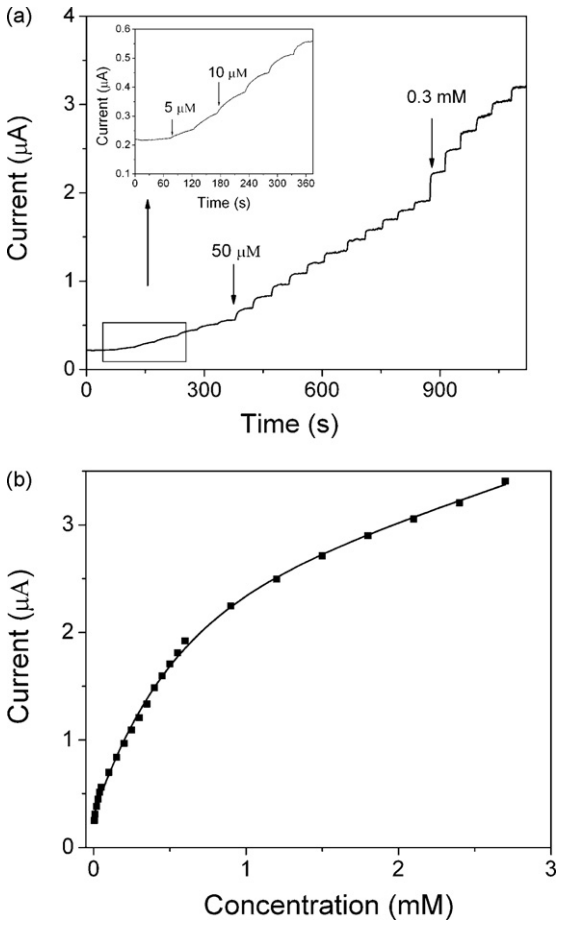

Fig. 4. (a) Amperometric response of the gaphene oxide/MnO_2 electrode upon addition of H_2O_2 at −0.3 V. (b) The corresponding calibration curve between the current response and concentration of H_2O_2.

3.3. Amperometric response of the GO/MnO_2 electrode to H_2O_2

Fig. 4(a) shows typical amperometric response of the GO/MnO_2 electrode to subsequent addition of H_2O_2 in alkaline solution at −0.3 V. It is observed that the GO/MnO_2 electrode responds quickly to the change of H_2O_2 concentration and reaches a steady-state signal within 5 s at higher concentration. The corresponding calibration curve for the H_2O_2 sensor is shown in Fig. 4(b). The sensor displays a linear range of 5–600 μM with a sensitivity of 38.2 μA mM^{-1} cm^{-2} (r = 0.995), and a detection limit of 0.8 μM (signal/noise = 3). Various H_2O_2 sensors have been listed in Table 1 with respect to the detection limit, sensitivity, and linear range. It can be observed that the performance of the sensor is better than the enzyme biosensors or nonenzymatic H_2O_2 sensor using MnO_2 nanorods as electrode in the literature in one or more categories. This may be related to the higher specific surface area of the deposited MnO_2 nanoparticles over the bulk ones. The high surface area of GO sheets provided large amount of anchoring sites for the deposition of MnO_2 during the synthesis of the GO/MnO_2 composite and prevented the aggregation of the nanosized particles.

3.4. Real sample analysis

The possible interference of foreign matters, which might exist in real samples, was investigated with the amperometric determination of H_2O_2. The interference experiments were performed in 0.1 M NaOH by comparing the response currents of 0.5 mM interference and 0.1 mM H_2O_2. The results obtained are listed in Table 2.

Table 1
Comparison of the performance of various H_2O_2 sensors.

Electrode	Detection limit	Sensitivity	Linear range	Reference
Myoglobin/silver nanoparticles	1 μM	20.5 μA mM^{-1}	3–700 μM	[27]
HRP/room temperature ionic liquid	0.1 μM	32 μA mM^{-1} cm^{-2}	0.61–132 μM	[28]
Hemoglobin/kieselgubr	2.1 μM	-	5–300 μM	[29]
Hemoglobin/poly (ε-caprolactone)	6.07 μM	-	2–30 μM	[26]
Cytochrome c/macroporous active carbon	14.6 μM	-	20–240 μM	[6]
MnO_2 nanorods	5 ± 2.5 μM	-	-	[25]
GO/MnO_2	0.8 μM	38.2 μA mM^{-1} cm^{-2}	5–600 μM	This work

Table 2
Interference of external matters to response of the electrode to 0.1 mM H_2O_2 in 0.1 M NaOH.

Interference	Response change (%)[a]	R.S.D. (n = 6) (%)
SO_4^-	9	3.1
Cl^-	8.6	2.5
NO_3^-	−2.8	2.8
CO_3^{2-}	6.3	3.3
Glucose	13.5	2.7
Cu^{2+}	11	3.5
Fe^{3+}	14	2.9
Citric acid	7.4	3.6

SO_4^-, Cl^-, NO_3^-, CO_3^{2-}, citric acid did not cause significant interference, indicating that these species did not affect the determination of H_2O_2. The glucose, Fe^{3+} and Cu^{2+} were the main interference for the determination of H_2O_2, which were probably owing to the catalytic ability of MnO_2 toward glucose and the ability of Fe^{3+} and Cu^{2+} to the electrocatalytic reduction of H_2O_2.

In order to verify the applicability of the proposed biosensor for real sample analysis, the application of the biosensor was also evaluated by the determination of H_2O_2 in real samples. In comparison with the classical potassium permanganate titration method, the results determined by the H_2O_2 sensor were in satisfactory agreement (Table 3). These results proved that the sensors had potential applications in the determination of H_2O_2 in real samples.

3.5. Reproducibility and stability

The reproducibility and stability of the GO/MnO_2 modified GC electrodes were performed by measuring the current response of the electrode upon 50 μM of H_2O_2 in 0.1 M NaOH. The average relative standard deviation (RSD) was not more than 4.5%. In a series of 10 sensors prepared in the same way, a RSD of 3.8% was obtained, indicating the reliability of this method. The prepared electrode was stored in air at ambient conditions. In order to understand the stability of the sensor, the current response to 50 μM of H_2O_2 was recorded each 4 days. As shown in Fig. 5, it was found that the current could retain 90% of its original signal after 4 weeks storage, which showed long-term stability.

Table 3
Results of H_2O_2 analysis in real samples determined by the proposed biosensor and the classical titration method.

Samples	(%) (m/v) by biosensor[a]	(%) (m/v) by titration[a]
1	16.4	16.85
2	27.2	26.74
3	48.74	48.26
4	75.31	76.28

[a] The values were obtained by averaging the values from five successive determination.

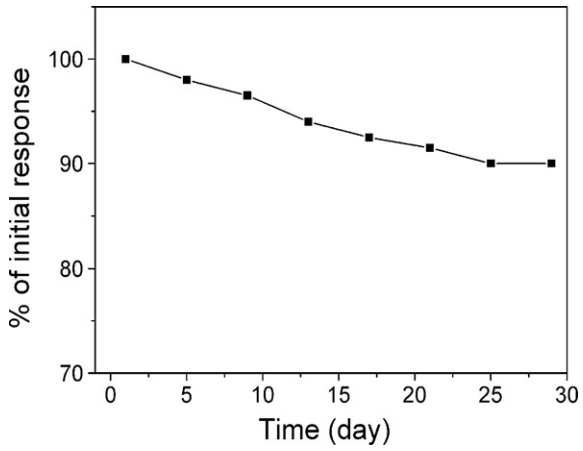

Fig. 5. Long-term stability of the gaphene oxide/MnO_2 electrode with the addition of 50 μM H_2O_2 in 0.1 M NaOH solution. Applied potential: −0.3 V.

4. Conclusion

In summary, a nonenzymatic biosensor based on GO/MnO_2 was fabricated by in situ deposition of MnO_2 on the surface of GO sheets. The electrode exhibited a high electrocatalytic activity for the H_2O_2 detection. A low detection limit, a high sensitivity of and a wide linear range were obtained. Therefore, the catalytic nature of MnO_2 towards H_2O_2, combined with the high surface area of GO make GO/MnO_2 hold the promise for the development of nonenzymatic sensor at low cost.

Acknowledgments

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References

[1] A.A. Karyakin, E.E. Karyakina, Russ. Chem. Bull. Int. Ed. 50 (2001) 1811.
[2] I.L. Mattos, K.A. Shiraishi, A.D. Braz, J.R. Fernandes, Quim. Nova 26 (2003) 373.
[3] L.M. Li, S.J. Xu, Z.F. Du, Y.F. Gao, J.H. Li, T.H. Wang, Chem. Asian J. 5 (2010) 919.
[4] X.B. Lu, J.H. Zhou, W. Lu, Q. Liu, J.H. Li, Biosens. Bioelectron. 23 (2008) 1236.
[5] C.H. Wang, C. Yang, Y.Y. Song, W. Gao, X.H. Xia, Adv. Funct. Mater. 15 (2005) 1267.
[6] L. Zhang, Biosens. Bioelectron. 23 (2008) 1610.
[7] H.Y. Liu, J.F. Rusling, N.F. Hu, Langmuir 20 (2004) 10700.
[8] X. Kang, J. Wang, Z. Tang, H. Wu, Y.H. Lin, Talanta 78 (2009) 120.
[9] Y.Y. Song, D. Zhang, X.H. Xia, Chem. Eur. J. 11 (2005) 2177.
[10] J.J. Yu, J.R. Ma, F.Q. Zhao, B.Z. Zeng, Talanta 74 (2008) 1586.
[11] H.F. Cui, J.S. Ye, W.D. Zhang, C.M. Li, J.H.T. Luong, F.S. Sheu, Anal. Chim. Acta 594 (2007) 175.
[12] Y.B. Zhang, Y.W. Tan, H.L. Stormer, P. Kim, Nature 438 (2005) 201.
[13] A.A. Balandin, S. Ghosh, W.Z. Bao, I. Calizo, D. Teweldebrhan, F. Miao, C.N. Lau, Nano Lett. 8 (2008) 902.
[14] X. Kang, J. Wang, H. Wu, I. Aksay, J. Liu, Y.H. Lin, Biosens. Bioelectron. 25 (2009) 901.
[15] Z. Liu, J.T. Robinson, X. Sun, H.J. Dai, J. Am. Chem. Soc. 130 (2008) 10876.

[16] X. Sun, Z. Liu, K. Welsher, J.T. Robinson, A. Goodwin, S. Zaric, H. Dai, Nano Res. 1 (2008) 203.
[17] X.Y. Yang, X.Y. Zhang, Y.F. Ma, Y. Huang, W.S. Wang, Y.S. Chen, J. Mater. Chem. 19 (2009) 2710.
[18] Y.J. Song, K.G. Qu, C. Zhao, J.S. Ren, X.G. Qu, Adv. Mater. 22 (2010) 1.
[19] N.W. Beyene, P. Kotzian, K. Schachl, H. Alemu, E. Turkušić, A. Čopra, H. Moderegger, I. Švancara, K. Vytřas, K. Kalcher, Talanta 64 (2004) 1151.
[20] Y.H. Lin, X.L. Cui, L.Y. Li, Electrochem. Commun. 7 (2005) 166.
[21] X.L. Luo, J.J. Xu, J.L. Wang, H.Y. Chen, Chem. Commun. 16 (2005) 2169.
[22] S.J. Yao, J.H. Xu, Y. Wang, X.X. Chen, Y.X. Xu, S.S. Hu, Anal. Chim. Acta 557 (2006) 78.
[23] E. Turkusica, J. Kalcher, E. Kahrovi, N.W. Beyene, H. Moderegger, E. Sofic, S. Begic, K. Kalcher, Talanta 65 (2005) 559.
[24] W.S. Hummers, R. Offeman, J. Am. Chem. Soc. 80 (1958) 1339.
[25] C.B. McAuley, L. Shao, G.G. Wildgoose, M.L.H. Green, R.G. Compton, New. J. Chem. 32 (2008) 1195.
[26] W. Zeng, J. Li, Y.F. Zheng, Biosens. Bioelectron. 23 (2008) 1562.
[27] X. Gan, T. Liu, J. Zhong, X.J. Liu, G.X. Li, Chem. Bio. Chem. 5 (2004) 1686.
[28] S.F. Wang, T. Chen, Z.L. Zhang, D.W. Pang, Electrochem. Commun. 9 (2007) 1337.
[29] H.Y. Wang, R. Guan, C.H. Fan, D.X. Zhu, G.X. Li, Sens. Actuators B 84 (2002) 214.