

Direct Electrocatalytic Oxidation of Hydrogen Peroxide Based on Nafion and Microspheres MnO₂ Modified Glass Carbon Electrode

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Film of microspheres MnO₂ and Nafion composite fabricated on glass carbon electrode (GCE) were active for electrocatalytic oxidation of H₂O₂ in phosphate buffer solution (PBS). The amperometric response to H₂O₂ obtained at +0.8V (vs. Ag/AgCl) was rapid and highly sensitive. Under the optimized condition, the linear range for the detection of H₂O₂ was 10.0×10⁻⁶ to 15.0×10⁻⁵ M with a detection limit of 2.0×10⁻⁶ M and a fast response time of within 5s. In addition, good reproducibility and long-term stability of the sensor make it valuable for further application.

Keywords: microspheres MnO₂, Nafion, Glass carbon electrode, Electrocatalytic oxidation, H₂O₂

1. INTRODUCTION

The detection of H₂O₂ is very important in various fields including clinic, food, pharmaceutical and environmental analyses, because H₂O₂ is a chemical threat to the environment and the production of enzymatic reactions, at the same time, it has been recognized as one of the major factors in the progression of important diseases [1]. Accurate and reliable determination of H₂O₂ has been widely investigated using chromatography [2], chemiluminescence [3] and electrochemistry [4] technologies. Among these methods, electrochemical detection is a most promising approach to achieve accurate, separate, and rapid H₂O₂ monitoring [5]. Most of the H₂O₂ biosensors developed till date are based on enzymes [6-8]. However, the immobilized enzyme on the surface of the electrode is facilitated to denature, which leads to such modified electrodes suffer from a poor enzyme activity, a low reproducibility and stability [9]. To remedy these problems, many efforts have been tried for the electrochemical measurements of H₂O₂ without using enzyme [10-13]. Although some chemically

modified electrodes have been proposed to reduce the large overpotential required for the direct oxidation of H_2O_2 , it is interesting to develop new materials with high efficiency and small dimensions for the detection of H_2O_2 .

Among various oxide materials, manganese dioxides (MnO_2) are a kind of attractive inorganic materials and have great potential as selective heterogeneous catalysts, adsorbents, and battery materials [14, 15]. In recent years, several kinds of MnO_2 nanoparticles were synthesized and used to construct biosensors. Schachl et al. reported the amperometric determination of H_2O_2 with a carbon paste electrode modified with commercially available MnO_2 using flow injection analysis [16]. Lin et al. reported low potential amperometric determination of H_2O_2 with a carbon paste electrode modified with nanostructured cryptomelane-type manganese oxides [17]. Hu et al. synthesized MnO_2 nanoparticles by rheological phase reaction and dispersed them in dihexadecyl hydrogen phosphate for amperometric determination of H_2O_2 [1]. Porous films of MnO_2 nanoparticles and PDDA or myoglobin by layer-by-layer adsorption was fabricated by J. F. Rusling group [18]. They also fabricated films of polyions and octahedral layered manganese oxide nanoparticles on carbon electrode by layer-by-layer adsorption for electrochemically catalyze styrene epoxidation [15]. Beyene et al. reported biosensors based on manganese dioxide-modified carbon substrates [19]. All these researches are based on the excellent catalytic ability of MnO_2 nanoparticles modified electrode.

In the present work, we constructed a novel functional hybrid film of nafion and MnO_2 microspheres on a glass carbon electrode as a catalytic layer for H_2O_2 detection, taking advantage of MnO_2 microspheres as catalysts and microscopic network structure of nafion. MnO_2 microspheres, which have great surface area and excellent catalytic ability to H_2O_2 , were employed to enhance electron transfer. Nafion, due to its exceptional chemical stability and good biocompatibility, has been widely selected as the immobilization matrix for catalysts [20, 21]. Tests show that MnO_2 microspheres exhibit a remarkable electrocatalytic activity for the oxidation of H_2O_2 . The proposed sensor possesses high sensitivity and high stability. So it has the promising future for practical application.

2. EXPERIMENTAL PART

2.1. Reagents and apparatus

Microscale manganese dioxide was synthesized according to reference [22]. Analytical grade $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ (0.3380g, 2mmol), $(\text{NH}_4)_2\text{S}_2\text{O}_8$ (0.4564g, 2mmol) and 2mL concentrated sulfuric were mixed in 50mL distilled water at room temperature. The 1mL of 10mL AgNO_3 (0.1052g, 0.059mmol) solution was added. After the homogeneous solution was allowed to stand for 1-2 days, the products were filtered off, washed with absolute ethanol and distilled water respectively for several times, and then dried in vacuum. Electrochemical experiments were performed with CHI 440A electrochemical analyzer (ChenHua Instruments Co. Ltd., Shanghai, China) with conventional three-electrode cell. The working electrode was a MnO_2 microspheres modified glass carbon electrode. An Ag/AgCl and a

platinum electrode were used as the reference and the auxiliary electrode, respectively. Images of scan electron microscopy (SEM) were obtained using a Hitachi X-650 microscope (Japan).

Analytical grade $\text{MnSO}_4 \cdot \text{H}_2\text{O}$, $(\text{NH}_4)_2\text{S}_2\text{O}_8$, H_2O_2 (30%) and concentrated sulfuric acid were purchased from Shanghai Chemical agent Co. Other chemicals were of analytical reagent grade. All the solutions were prepared with double distilled water and were deaerated with high purity nitrogen. Experiments were carried out at room temperature.

2.2. Electrode modification

The dispersed MnO_2 microspheres on the electrode were fabricated by the following way: Firstly, the glass carbon electrode (GCE, $\Phi=3\text{mm}$) was polished with a 1700# diamond paper and washed successively with double distilled water and ethanol in an ultrasonic bath, then 15 cyclic scans were carried out in the potential of 2.0 to -2.0 V (vs. Ag/AgCl) in the solution of 1.0 mol/l H_2SO_4 . Secondly, Nafion was diluted with ethanol to 0.1%. 3 mg MnO_2 microspheres was dispersed in 2 ml Nafion solution. Next, 20 μl of MnO_2 /Nafion solution (1.5 mg/ml) was cast on the surface of GCE and dried in air. Thus microspheres- MnO_2 /nafion modified GCE was obtained.

3. RESULTS AND DISCUSSION

3.1. Characterization of the as-prepared MnO_2 microspheres

The morphologies of the products were then studied by the field emission scanning electron microscope. Fig. 1 (left) indicated that the product consisted of microspheres with diameters of 1-2.5 μm . There are numerous nanorods on the surface of the MnO_2 microspheres. Fig. 1 (right) showed that nanorods with uniform diameters around 20-40 nm were fixed on the surface of the spheres, and they were densely packed and spherically aligned.

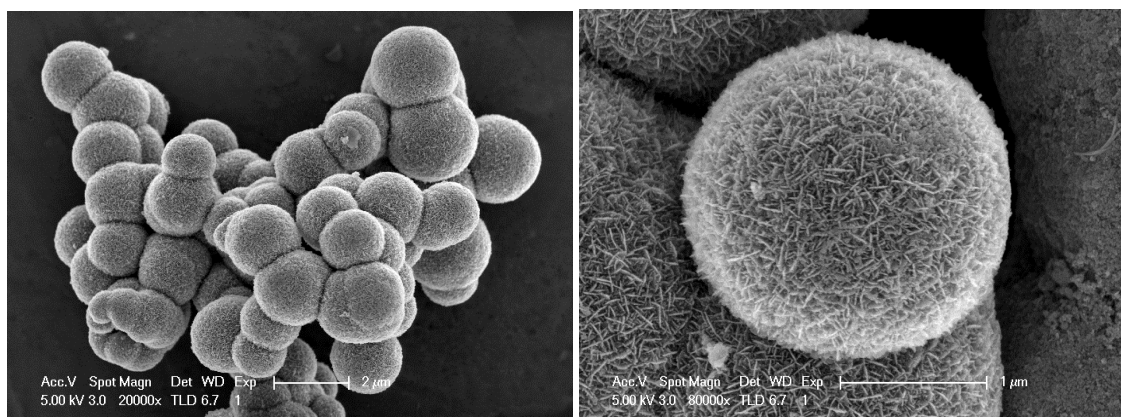


Figure 1. SEM images of as-prepared MnO_2 microspheres with low (left) and high magnification (right).

3.2. Electrocatalytic oxidation of H_2O_2 at microspheres $MnO_2/Nafion/GCE$

Fig. 2 (A) shows the cyclic voltammetric behavior of a Nafion/GCE and the microspheres $MnO_2/Nafion/GCE$ in the absence of H_2O_2 in PBS (pH 7.0, 0.1M) at the scan rate of 10 mV/s. At the Nafion/GCE, no obvious oxidation and reduction peak was found in the potential range of 0-1.1 V (curve a). At the microspheres $MnO_2/Nafion/GCE$, a couple of small reduction and oxidation peaks are observed (curve c) at around 0.5 V and 0.8 V, which are assignable to the reduction of MnO_2 to Mn (II or III) and the oxidation of Mn (II or III) to MnO_2 [23]. Fig. 2 (B) shows the cyclic voltammetric behavior of a Nafion/GCE and the microspheres $MnO_2/Nafion/GCE$ in the absence and presence of different concentrations of H_2O_2 in PBS (pH 7.0, 0.1M) at the scan rate of 10 mV/s. At the Nafion/GCE, a slight oxidation current of 1.5 mM H_2O_2 (curve b) was obtained at about 1.0 V. At the microspheres $MnO_2/Nafion/GCE$, sensitive oxidation peaks at around 0.86 V (curve d and e) were found in the presence of 1.5 mM H_2O_2 and 3 mM H_2O_2 . According to the experimental results, the oxidation current of Mn (II or III) to MnO_2 was significantly increased when increasing the concentration of H_2O_2 .

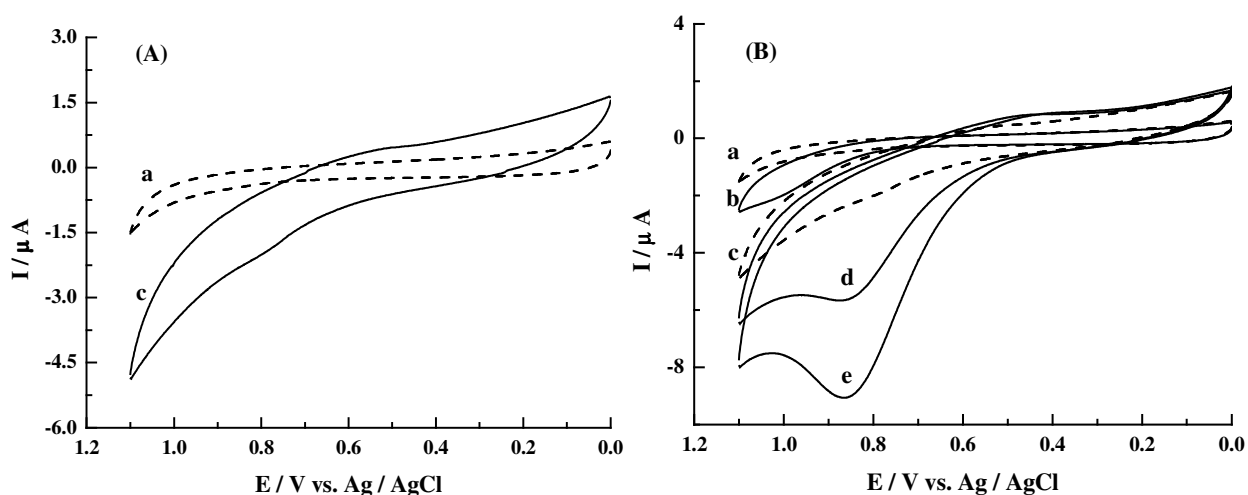


Figure 2. (A) CVs recorded in PBS (pH 7.0, 0.1M) at Nafion/GCE (a) and $MnO_2/Nafion/GCE$ (c). (B) CVs of Nafion/GCE (a, b) and microspheres $MnO_2/Nafion/GC$ electrode (c, d, e) in the absence (a, c) and presence (b, d) of 1.5 mM H_2O_2 , (e) 3.0 mM H_2O_2 in PBS (pH 7.0, 0.1M). Scan rate: 10 mV/s.

3.3 Optimization of the H_2O_2 determination conditions

To improve the performance of the sensor, the effect of the determination conditions such as the concentration of MnO_2 in Nafion solution and the pH value on the response of the microspheres $MnO_2/Nafion/GCE$ to H_2O_2 has been investigated in detail.

The effect of the concentration of MnO_2 in Nafion solution on the response current of the microspheres $MnO_2/Nafion/GCE$ to H_2O_2 is illustrated in Fig. 3 (A). When the concentration of MnO_2

in Nafion solution was changed from 0.1 to 2.0 mg/ml, the maximum response current was observed at 1.5 mg/ml. So the concentration of 1.5 mg/ml was selected as the optimum concentration.

The effect of pH value on the response current of the microspheres $\text{MnO}_2/\text{Nafion}/\text{GCE}$ was also studied between 5.0 and 9.0 in 0.1 M PBS. As shown in fig. 3 (B), the response current increased from 5.0 to 7.0, and a slightly increase from 7.0 to 8.0. In this work, pH 7.0 was selected in the subsequent experiments.

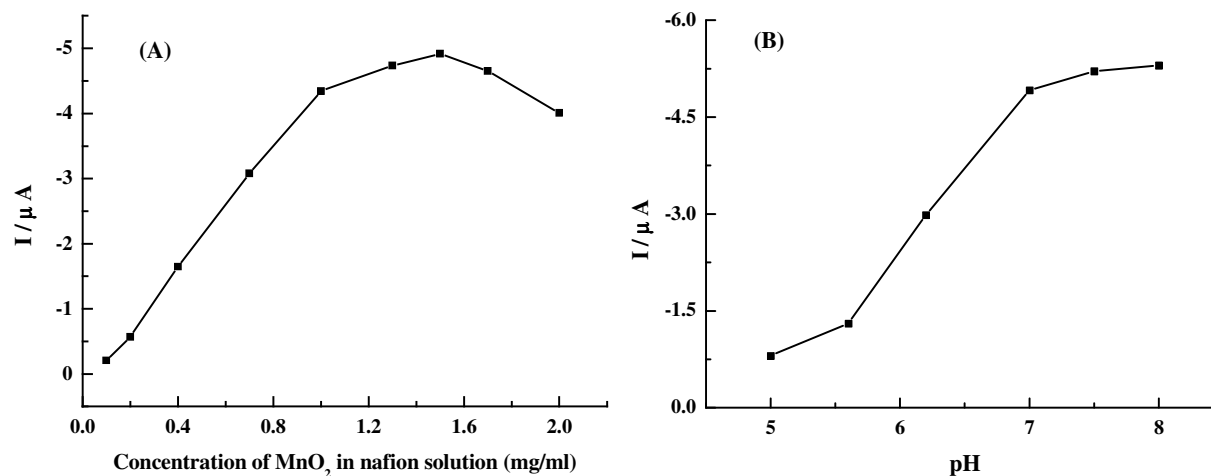


Figure 3. (A) Effect of MnO_2 concentration in Nafion solution on the response current of the microspheres $\text{MnO}_2/\text{Nafion}/\text{GCE}$ to addition of 1.5 mM H_2O_2 to PBS (pH 7.0, 0.1M). (B) Effect of pH solution on the response current of the microspheres $\text{MnO}_2/\text{Nafion}/\text{GCE}$ to addition of 1.5 mM H_2O_2 . Scan rate: 10 mV/s.

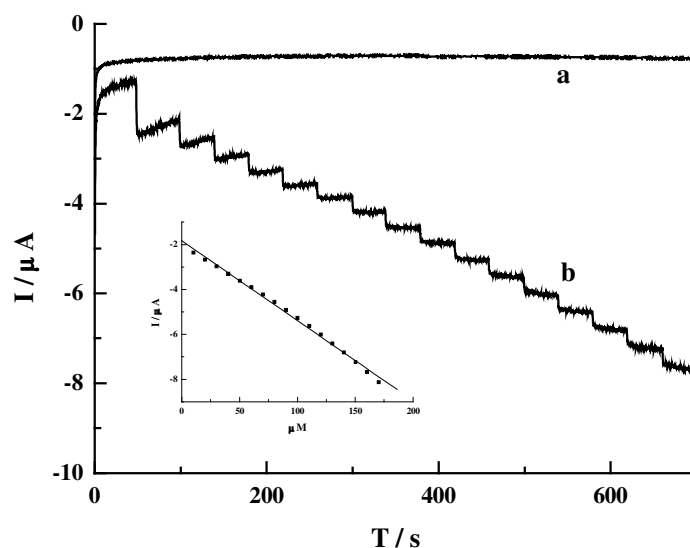


Figure 4. Current-time recording obtained on increasing the H_2O_2 concentration in 10 μM steps at (a) Nafion/GCE and (b) microspheres $\text{MnO}_2/\text{Nafion}/\text{GCE}$ at an operating potential of 0.8 V in PBS (pH 7.0, 0.1M). Inset: calibration curve of the sensor for H_2O_2 concentration from 10.0×10^{-6} to 15.0×10^{-5} M.

3.4 Amperometric response of H₂O₂ at microspheres MnO₂/Nafion/GCE

Fig. 4 compares the amperometric response (at +0.80 V) of the (a) Nafion/GCE and (b) microspheres MnO₂/Nafion/GCE to the successive addition of 10 μM H₂O₂. As expected from the voltammetric data (Fig. 2(B, b)), the Nafion/GCE is not responsive to the addition of H₂O₂. In contrast, the microspheres MnO₂/Nafion/GCE respond rapidly to the changes in H₂O₂ concentration, producing steady-state signals within 5 s (Fig. 4(b)). Such a fast response implies that microspheres MnO₂ can promote the oxidation of H₂O₂. The linear relationship between the catalytic current and the concentration is shown in the inset of the fig. 4. As can be seen, the microspheres MnO₂/Nafion/GCE displays linear response range of 10.0×10⁻⁶ to 15.0 ×10⁻⁵ M (correlation coefficient: 0.997), with a detection limit of 2.0 ×10⁻⁶ M at a signal-to-noise ratio of 3.

The reproducibility and stability of the sensor were also investigated. For 10 replicate measurements of one electrode studied at 50 μM H₂O₂, the relative standard deviation (R. S. D) was 3.2%. We studied the storage stability of the sensor by storing it at room temperature. One week later the response of the sensor still retained 93.5% and the next three weeks the response still retained 89.0% of the initial value. These experiments results confirmed that the modified electrode were highly reproducibility and stability.

3.5 Effect of interferents

The influence of possible interfering species on the current response of the sensor was examined and is given in Table 1. The current response obtained with 10 : 1 concentration ratio of interfering species and H₂O₂ was compared with the results obtained with that of pure H₂O₂ alone. As shown, Uric acid, dopamine and L-cysteine induced slight effect on the steady-state current to H₂O₂. The steady-state current to H₂O₂ was increased to 109% of original response by addition of ascorbic acid. So there was no obvious interference in the measure of the electrode. The modified electrode exhibits great prospects for future biosensor work.

Table 1. Possible interferences tested with the modified electrode

Possible interferences	Current ratio ^a
<i>Uric acid</i>	0.985
<i>Dopamine</i>	0.987
<i>L-cysteine</i>	1.002
<i>ascorbic acid</i>	1.090

^a Ratio is the current from a mixture of 1.0 mmol interfering substances and 0.1 mM H₂O₂ versus the current from 0.1 mM H₂O₂ alone. Assay solution: 0.1 M PBS.

4. CONCLUSIONS

A novel functional hybrid film of Nafion and MnO₂ microspheres on a glass carbon electrode was constructed as a catalytic layer for H₂O₂ detection in the present work. Tests show that MnO₂ microspheres exhibit a remarkable electrocatalytic activity for the oxidation of H₂O₂. The proposed sensor possesses high sensitivity and stability, good reproducibility and selectivity. These advantages make it promising for providing a simple method for practical application.

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References

1. S. Yao, J. Xu, Y. Wang, X. Chen, Y. Xu, S. Hu, *Anal. Chim. Acta* 557 (2006) 78.
2. W. M. Weigert, *Chem. Ztg.* 99 (1975) 106.
3. H. Knorre, *Galvanotechnik* 66 (1975) 374.
4. X. M. Miao, R. Yuan, Y. Q. Chai, Y. T. Shi, Y. Y. Yuan, *J. Electroanal. Chem.* 612 (2008) 157.
5. J. Gong, L. Wang, K. Zhao, D. Song, *Electrochem. Commun.* 10 (2008) 123.
6. C. X. Lei, S. Q. Hu, N. Gao, G. L. Shen, R. Q. Yu, *Bioelectrochemistry* 65 (2004) 33.
7. H. Y. Wang, R. Guan, C. H. Fan, D. X. Zhu, G. X. Li, *Sens. Actuators B: Chem.* 84 (2002) 214.
8. Q. L. Wang, G. X. Lu, B. J. Yang, *Sens. Actuators B: Chem.* 99 (2004) 50.
9. Y. Yang, S. Mu, *J. Electroanal. Chem.* 432 (1997) 71.
10. I. L. de Mattos, L. Gorton, T. Ruzgas, *Biosens. Bioelectron.* 18 (2003) 193.
11. T. Y. You, O. Niwa, M. Tomita, S. Hirono, *Anal. Chem.* 75 (2003) 2080.
12. J. Zhang, L. Gao, *Mater. Lett.* 61 (2007) 3571.
13. J. D. Qiu, H. Z. Peng, R. P. Liang, J. Li, X. H. Xia, *Langmuir* 23 (2007) 2133.
14. S. L. Brock, M. Sanabria, J. Nair, S. L. Suib, T. Ressler, *J. Phys. Chem. B* 105 (2001) 5404.
15. L. Espinal, S. L. Suib, J. F. Rusling, *J. Am. Chem. Soc.* 126 (2004) 7676.
16. K. Schachl, H. Alemu, K. Kalcher, J. Jezkova, I. Svancara, K. Vytras, *Analyst* 122 (1997) 985.
17. Y. Lin, X. Cui, L. Li, *Electrochem. Commun.* 7 (2005) 166.
18. Y. Lvov, B. Munge, O. Giraldo, I. Ichinose, S. L. Suib, J. F. Rusling, *Langmuir* 16 (2000) 8850.
19. N. W. Beyene, P. Kotzian, K. Schachl, K. Vytřas, K. Kalcher, *Talanta* 64 (2004) 1151.
20. M. Pan, H. L. Tang, S. P. Jiang, Z. Liu, *Electrochem. Commun.* 7 (2005) 119.
21. M. Pan, H. L. Tang, S. P. Jiang, Z. Liu, *Electrochem. Soc.* 152 (2005) 1081.
22. Z. Li, Y. Ding, Y. Xiong, Q. Yang, Y. Xie, *Chem. Commun.* (2005) 918.
23. E. Turkusic, J. Kalcher, E. Kahrovic, N. W. Beyene, J. Kalcher, *Talanta* 65 (2005) 559.