A sensitive nonenzymatic hydrogen peroxide sensor based on Fe₃O₄–Fe₂O₃ nanocomposites

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Abstract. The Fe₃O₄–Fe₂O₃ nanocomposites were prepared by the co-precipitation method and followed by calcination process. The products were synthesized and characterized by X-ray diffraction, scanning electron microscopy, transmission electron microscopy and energy-dispersive X-ray analysis. The obtained Fe₃O₄–Fe₂O₃ nanocomposites were then applied to study the electrocatalytic reduction of hydrogen peroxide (H₂O₂) in 0.01 M pH 7.0 phosphate buffer medium. Then the Fe₃O₄–Fe₂O₃ nanocomposites were used as active electrode material of electrochemical sensors for H₂O₂ detection. The detection sensitivity of the sensor was 20.325 μA mM⁻¹, and the detection limit was estimated to be about 0.2 mM.

Keywords. Fe₃O₄; Fe₂O₃; nanocomposites; hydrogen peroxide; sensor.

1. Introduction

Owing to its strong oxidizing property, hydrogen peroxide (H₂O₂) is widely used in many fields. For example, H₂O₂ is useful for food production, sterilization, clinical applications and environmental analyses. Further, H₂O₂ has emerged as an important by-product of enzymatic reactions in the field of biosensing. Thus, accurate and reliable determination of H₂O₂ has been widely investigated using spectrometry, chemiluminescence and electrochemistry technologies. Among these methods, electrochemical method has been extensively applied due to its simple, accurate and fast analytical process. Many enzyme-based electrochemical biosensors towards H₂O₂ reduction have been made. However, the immobilized enzyme/protein on the surface of the electrode is facilitated to denature, which leads to such modified electrodes that suffer from a poor enzyme/protein activity, a low reproducibility and stability. Nanomaterials can play an important role in improving sensor performance, due to their large specific surface areas, excellent conductivities and compatibilities. In recent years, nanomaterials have been regarded as excellent substitutes for enzymes. Single crystal and vertically aligned Co₃O₄ nanowalls were synthesized, and the Co₃O₄ nanowall electrode was applied for the amperometric detection of H₂O₂ and showed a fast response and high sensitivity. Gu et al. have synthesized Cu–Ni(OH)₂ nanocomposites and applied it as the fast and sensitive H₂O₂ sensor material. Ag nanoparticles were synthesized on indium tin oxide conducting glass substrate using the electrochemical deposition method, and the developed Ag nanoparticles sensor had excellent electrocatalytic activity for H₂O₂ detection. The electrocatalytic activity of CuO flower-like nanostructured electrode was investigated in terms of its application to enzymeless amperometric H₂O₂ sensors.

Transition metal oxide nanomaterials are one of the promising candidates for the active electrode material of non-enzymatic electrochemical sensors. Magnetite (Fe₃O₄), which is chemically stable, non-toxic and non-carcinogenic, has a high magnetic saturation value. Hematite (α-Fe₂O₃), the most stable iron oxide under ambient condition with low-cost, non-toxicity and environmental-friendly features, is of great scientific and technology importance. Fe₃O₄ and Fe₂O₃ have been widely fabricated as gas sensor because of its good stability, lower cost and easy availability. Yu et al. reported the application of chitosan–Fe₃O₄ nanocomposite-modified glassy carbon electrodes for the amperometric determination of bisphe-nol A. A novel imprinted sol–gel electrochemical sensor based on multi-walled carbon nanotubes doped with chitosan film on a carbon electrode has been developed. La-doped Fe₂O₃ nanotubes are synthesized by an electrospinning method and followed by calcination, and the nanotubesshow a good selectivity to acetone.

To the best of our knowledge, H₂O₂ electrochemical sensor based on the Fe₃O₄–Fe₂O₃ nanocomposites has never been reported before. In this study, Fe₃O₄–Fe₂O₃ nanocomposites are synthesized by the co-precipitation method and followed by calcination process. The Fe₃O₄–Fe₂O₃ nanocomposites

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were applied for the sensitive amperometric detection of \( \text{H}_2\text{O}_2 \). The proposed sensor possesses high sensitivity and high stability.

2. Experimental

2.1 Sample preparation

\( \text{Fe}_3\text{O}_4–\text{Fe}_2\text{O}_3 \) nanocomposites were synthesized by the co-precipitation method and followed by calcination. Typically, 2.2 g of \( \text{FeCl}_3·6\text{H}_2\text{O} \) and 2.3 g of \( \text{FeSO}_4·7\text{H}_2\text{O} \) were dissolved in 30 ml of 0.01 M HCl to form a transparent solution. When the solution became clear, the mixture was then added drop-wise to 40 ml of 3 M \( \text{NH}_3·\text{H}_2\text{O} \) with the reaction mixture vigorously stirred at 80°C for 150 min. The final products were collected, followed by calcination at 350–500°C for 4 h.

2.2 Electrode preparation

Glassy carbon (GC) disks were polished with 0.03 mm \( \text{Al}_2\text{O}_3 \) powders. A typical suspension of the \( \text{Fe}_3\text{O}_4–\text{Fe}_2\text{O}_3 \) nanocomposites was prepared by suspending 6 mg \( \text{Fe}_3\text{O}_4–\text{Fe}_2\text{O}_3 \) nanocomposites in 3 ml 0.5% Nafion solution, and sonicated for 15 min. The suspension was transferred to the surface of the polished GC disk and dried at 80°C for 5 min.

2.3 Characterization

Scanning electron microscopy (SEM, Hitachi S-4700) was used to characterize the morphology of the \( \text{Fe}_3\text{O}_4–\text{Fe}_2\text{O}_3 \) nanocomposites. The chemical compositions of the products were detected using an energy-dispersive X-ray spectrometry (EDS, Thermo Noran VANTAG-ESI). The obtained samples were characterized by X-ray powder diffraction (XRD) using a Rigaku D/Max-??B X-ray diffractometer with graphite monochromatized Cu K\( \alpha \) radiation (\( \lambda = 1.54178 \) Å) operated at 40 kV and 80 mA. Electrochemical measurements were performed using a computer-controlled CHI 660C electrochemical workstation in a standard three-electrode configuration, including \( \text{Fe}_3\text{O}_4–\text{Fe}_2\text{O}_3 \) nanocomposite electrodes as the working electrode, an Ag/AgCl reference electrode and a platinum counter electrode. \( \text{H}_2\text{O}_2 \) measurement was carried out in 0.01 M, pH 7.0, phosphate buffer containing 0.2–1.8 mM \( \text{H}_2\text{O}_2 \).

3. Results and discussion

In our study, the calcination temperature is varied from 350 to 450°C to investigate its influence on the structure. Figure 1a shows the XRD patterns of the as-obtained products at 350°C. All the diffraction peaks in figure 1a can be readily indexed to \( \text{Fe}_3\text{O}_4 \) of spinel structure (JCPDS Card no. 19-0629). Figure 1b shows the XRD pattern of the as-obtained product at 400°C. All of the peaks of the XRD pattern in figure 1b can be indexed to a mixed phase of \( \text{Fe}_3\text{O}_4 \) (JCPDS Card no. 19-0629) and \( \alpha-\text{Fe}_2\text{O}_3 \) (JCPDS Card no. 19-0629).
A sensitive nonenzymatic \( \text{H}_2\text{O}_2 \) sensor based on \( \text{Fe}_3\text{O}_4-\text{Fe}_2\text{O}_3 \) (39-1346). This reveals that \( \text{Fe}_3\text{O}_4-\text{Fe}_2\text{O}_3 \) composites were obtained at 400°C. When calcination temperatures are above 450°C, it can be easily found from figure 1c that besides the diffraction peaks of \( \text{Fe}_3\text{O}_4 \), strong diffraction peaks of \( \alpha-\text{Fe}_2\text{O}_3 \) are observed. Figure 1d shows the XRD patterns of the as-synthesized samples at 500°C, all the reflection peaks can be readily indexed to \( \alpha-\text{Fe}_2\text{O}_3 \) (JCPDS Card no. 39-1346). The XRD patterns indicate that \( \text{Fe}_3\text{O}_4-\text{Fe}_2\text{O}_3 \) composites were obtained in the calcination temperature range under investigation (350–450°C).

The morphologies of the as-obtained products were examined by SEM microscopy. Figure 2a shows the pattern of the \( \text{Fe}_3\text{O}_4-\text{Fe}_2\text{O}_3 \) composites prepared at 400°C. The SEM image displayed much smaller nanoparticles with diameters of about 40–50 nm. Figure 2b is the SEM image of the sample prepared at 450°C. SEM images revealed that the morphologies of the \( \text{Fe}_3\text{O}_4-\text{Fe}_2\text{O}_3 \) nanocomposites prepared at 450°C were similar to the sample prepared at 350°C.

HRTEM analysis provides more detail structural information about the \( \text{Fe}_3\text{O}_4-\text{Fe}_2\text{O}_3 \) nanocomposites, showing the apparent lattice fringes of the crystal. Figure 3 is an HRTEM image taken from the \( \text{Fe}_3\text{O}_4-\text{Fe}_2\text{O}_3 \) nanocomposites. The observed interplanar spacing is 0.309 and 0.205 nm, which correspond to the (012) atomic spacing of \( \text{Fe}_3\text{O}_4 \) and the (400) atomic spacing of \( \text{Fe}_2\text{O}_3 \), respectively.

The EDS patterns of the \( \text{Fe}_3\text{O}_4-\text{Fe}_2\text{O}_3 \) nanocomposites prepared at 400 and 450°C are shown in figure 4. It can be seen that the main elements in the samples are O and Fe and the peak intensity of Fe decreases with the increasing calcination temperature. Fe and O elements existed in the \( \text{Fe}_3\text{O}_4-\text{Fe}_2\text{O}_3 \) nanocomposites prepared at 400 and 450°C have the molar ratio of 72.9:100 and 70.6:100, respectively. By calculation, the \( \text{Fe}_3\text{O}_4-\text{Fe}_2\text{O}_3 \) molar ratios in the \( \text{Fe}_3\text{O}_4-\text{Fe}_2\text{O}_3 \) nanocomposites are 2.22:1 and 0.67:1.

The electrocatalytic activity of the as-obtained products at different calcination temperature was studied. All samples exhibited the reduction of \( \text{H}_2\text{O}_2 \) starting around −0.5 V. The \( \text{Fe}_3\text{O}_4-\text{Fe}_2\text{O}_3 \) nanocomposites prepared at 400°C exhibited the strongest electrocatalytic ability towards the reduction of \( \text{H}_2\text{O}_2 \). The electro-reduction mechanism of \( \text{H}_2\text{O}_2 \) on

![HRTEM images of the Fe₃O₄–Fe₂O₃ nanocomposites.](image)

**Figure 3.** HRTEM images of the \( \text{Fe}_3\text{O}_4-\text{Fe}_2\text{O}_3 \) nanocomposites.

![EDS patterns of the Fe₃O₄–Fe₂O₃ nanocomposites.](image)

**Figure 4.** EDS patterns of the \( \text{Fe}_3\text{O}_4-\text{Fe}_2\text{O}_3 \) nanocomposites prepared at (a) 400°C and (b) 450°C.

![CV of the Fe₃O₄–Fe₂O₃ nanocomposites at various concentrations of H₂O₂.](image)

**Figure 5.** CV of the \( \text{Fe}_3\text{O}_4-\text{Fe}_2\text{O}_3 \) nanocomposites at various concentrations of \( \text{H}_2\text{O}_2 \): (a) 0 mM, (b) 0.2 mM, (c) 0.6 mM and (d) 1.0 mM.
the Fe$_3$O$_4$–Fe$_2$O$_3$ nanocomposites can be illustrated by the equations below

\[
\text{Fe}_3\text{O}_4 + \text{H}_2\text{O}_2 \rightarrow \text{Fe}_2\text{O}_3 + \text{OH}^-, \quad (1)
\]

\[
\text{Fe}_2\text{O}_3 + \text{H}_2\text{O} + e^- \rightarrow \text{Fe}_3\text{O}_4 + \text{OH}^-.
\]

Based on the XRD, HRTEM and FDS analysis, it is obvious that the strongest electrocatalytic activity of the Fe$_3$O$_4$–Fe$_2$O$_3$ nanocomposites may be attributed to its structure with the interface of Fe$_3$O$_4$–Fe$_2$O$_3$. According to the mechanism above, the reaction exists in Fe$_3$O$_4$ and Fe$_2$O$_3$. In Fe$_3$O$_4$–Fe$_2$O$_3$ nanocomposites, there are many Fe$_3$O$_4$–Fe$_2$O$_3$ interfaces, which is favourable for increasing diffusion rate and accelerating electrode kinetics. It is believed that the structure and Fe$_2$O$_3$ content have played an important role in controlling the reduction of H$_2$O$_2$.

Figure 5 shows the CVs of the Fe$_3$O$_4$–Fe$_2$O$_3$ nanocomposites prepared at 400°C in 0.01 M phosphate buffer containing H$_2$O$_2$ with different concentrations. The current sensitivity increases with increasing H$_2$O$_2$ concentration (from the top: 0, 0.2, 0.6, 1.0 mM), which may be applied as the quantitative analysis. Figure 6a displays a typical current–time plot of the Fe$_3$O$_4$–Fe$_2$O$_3$ nanocomposites on the successive addition of H$_2$O$_2$ with various concentrations into stirring phosphate buffer (0.01 M, pH 7.0) at the applied potential of −1.0 V. These Fe$_3$O$_4$–Fe$_2$O$_3$ nanocomposite sensors show a very fast response, as the response reaches 100% of the steady-state value within 2.5 s. The calibration curves of the Fe$_3$O$_4$–Fe$_2$O$_3$ nanocomposites sensor are shown in figure 6b. The sensor has a wide linear range from 0.2 to 1.8 mM with a correlation coefficient of 0.997, and the sensitivity is determined to be as 20.325 μA mM$^{-1}$. The selectivity of the sensor was also evaluated with four species: SO$_4^{2-}$, Cl$, \text{ClO}_3^-$ and CO$_3^{2-}$. When SO$_4^{2-}$, Cl$, \text{ClO}_3^-$ and CO$_3^{2-}$ were injected into the phosphate buffer, no obvious current was observed as shown in figure 7. This suggests that these species have no obvious interference in the reduction of H$_2$O$_2$.

4. Conclusion

In conclusion, the Fe$_3$O$_4$–Fe$_2$O$_3$ nanocomposites have been successfully synthesized by the co-precipitation method and followed by calcination process. The electrocatalytic activity of the as-obtained products at different calcination temperatures was studied by CV. It was found that the Fe$_3$O$_4$–Fe$_2$O$_3$ nanocomposites obtained at 400°C showed maximal electrocatalytic ability for the reduction of H$_2$O$_2$. The amperometric response of the electrode was rapid (within 2.5 s), and had high sensitivity (20.325 μA mM$^{-1}$). The proposed electrochemical sensor based on Fe$_3$O$_4$–Fe$_2$O$_3$ nanocomposites is thus expected to generate new opportunities for monitoring H$_2$O$_2$ concentrations in industry analyses fields.

References

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