Non-enzymatic hydrogen peroxide sensor based on Co₃O₄ nanocubes

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Abstract. The Co₃O₄ nanocubes were prepared by using hydrogen peroxide (H₂O₂) as oxidant, Co(NO₃)₂·6H₂O as a cobalt source. The products were characterized in detail by multiform techniques: scanning electron microscopy (SEM), transmission electron microscopy (TEM) and X-ray diffraction (XRD). The prepared Co₃O₄ nanocubes were applied to study the electrocatalytic reduction of hydrogen peroxide (H₂O₂) in 0.01 M pH 7.0 phosphate buffer medium. The Co₃O₄ nanocubes exhibit remarkable electrocatalytic activity for H₂O₂ reduction. Furthermore, the obtained Co₃O₄ nanocubes have been employed as electrode materials for electrochemical sensing H₂O₂.

Keywords. Co₃O₄; nanocubes; hydrogen peroxide; sensor.

1. Introduction

Hydrogen peroxide (H₂O₂) is widely used in the synthesis of various organic compounds, food production, pulp and paper bleaching, sterilization and clinical applications (Salimi *et al* 2007; Yang and Hu 2010). Thus, the monitoring of H₂O₂ with a reliable, rapid and economic method is of great significance. Several analytical methods have been developed to detect and quantify H₂O₂, including spectrometry (Tanner and Wong 1998), titrimetry (Klassen *et al* 1994), chemiluminescence (Diaz *et al* 1998) and electrochemistry (Cui *et al* 2008). Among these, electrochemical methods have emerged as preferable due to their relatively low cost, efficiency, high sensitivity and easy operation. Many enzyme-based electrochemical biosensors for H₂O₂ reduction have been made. However, the enzyme-based biosensors were found to have disadvantages (Liu *et al* 2010). In recent years, taking advantage of catalytic activities, stability and convenience of electron transfer, nanomaterials have been regarded as excellent substitutes for enzymes. Song *et al* (2011) reported the growth of Ag nanoparticles on ITO substrate by simple electrochemical deposition, and described their application in the development of an electrochemical sensor for H₂O₂ detection. The Ag nanorods were prepared by a simple hydrothermal process, and the obtained Ag nanorods showed good electrocatalytic activity for the H₂O₂ reduction, and had been applied to detect H₂O₂ (Song *et al* 2012). The Ni(OH)₂ nanoplates had been successfully synthesized by a simple hydrothermal method,

and the Ni(OH)₂ nanoplates sensor was highly selective to H₂O₂ (Zhao and Song 2011). The Co₃O₄ nanowalls electrode was applied for the amperometric detection of H₂O₂ and showed a fast response and high sensitivity (Jia *et al* 2009).

Transition-metal oxide nanoparticles have received widespread interest recently because of their envisioned applications in electronics, optics and magnetic properties (Tang *et al* 2008; Tripathy *et al* 2008). Among these oxides, Co₃O₄ belongs to the spinel crystal structure based on a cubic close-packing array of oxide ions, and has attracted extra attention due to their broad range of applications such as chemical sensors, magnetic data storage systems, catalysts and intercalation compounds for energy storage (Zhao *et al* 2008; Yuan *et al* 2009; Al-Tuwirqi *et al* 2011). The Co₃O₄, when falling in the nano-sized regime, is expected to lead to even more attractive applications in the conjunction of their traditional arena and nanotechnology (Feng and Zeng 2003). Spinel structure Co₃O₄ nanoparticles display a considerable activity and good stability for electrochemical performance. Co₃O₄ nanowire arrays supported on nickel foam substrate were prepared via a template-free synthesis method, and this self-supported binderless nanowire array electrode showed much higher specific capacitance (Gao *et al* 2010). Recently, monodisperse Co₃O₄ nanocubes have been prepared by a microwave-assisted solvothermal method, and the Co₃O₄ nanocubes show good gas-sensing performance towards xylene and ethanol vapours with rapid and high responses at a low-operating temperature (Sun *et al* 2011). The excellent electrochemical performance coupled with the low cost renders Co₃O₄ nanotube very promising for practical application in

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supercapacitors (Xu *et al* 2010). To the best of our knowledge, H_2O_2 electrochemical sensor based on the Co_3O_4 nanocubes has never been reported before. In this study, hydrothermal method was used for the synthesis of Co_3O_4 nanocubes. The obtained Co_3O_4 nanocubes show good electrocatalytic activity for H_2O_2 reduction, and has been applied to detect H_2O_2 .

2. Experimental

2.1 Sample preparation

All the chemicals were analytic-grade reagents without further purification. In a typical procedure, 1 g of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was dissolved in 45 mL of distilled water. Then, 0.5–1.2 mL of H_2O_2 (30 wt%) was added to the above solution under continuous stirring. When the solution is clarified, pH of the solution was maintained at 9 by adding NaOH. Then, the reaction mixture was charged in a 50-mL capacity autoclave with teflon liner, followed by uniform heating at 180 °C for 12 h. After the reaction is completed, the autoclave was allowed to cool to room temperature naturally. The final products were collected and washed with deionized water and ethanol several times and dried in air at 80 °C.

2.2 Electrode preparation

Glassy carbon (GC) disks were polished with 0.03 mm Al_2O_3 powders. A typical suspension of Co_3O_4 nanocubes

was prepared by suspending 6 mg Co_3O_4 nanocubes 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

The obtained samples were characterized by X-ray powder diffraction (XRD) using a Rigaku D/max- γ B X-ray diffractometer with graphite monochromatized $\text{CuK}\alpha$ radiation ($\lambda = 1.54178 \text{ \AA}$) operated at 40 kV and 80 mA. The morphologies were characterized using scanning electron microscopy (SEM, Hitachi S-4700, 15 kV) and transmission electron microscopy (TEM, JEM200CX, 120 kV). The composition of the products was analysed by energy dispersive X-ray detector (EDS, Thermo Noran VANTAG-ES). Electrochemical measurements were carried out in a standard three-electrode electrochemical cell with Co_3O_4 nanocubes electrodes as the working electrode, saturated Ag/AgCl reference electrode and Pt counter electrode. 0.01 M pH 7 phosphate buffer containing 0.2–1.8 mM H_2O_2 was employed as electrolyte. The electrochemical measurements were performed by using a computer-controlled CHI 660C electrochemical workstation.

3. Results and discussion

The morphologies of the Co_3O_4 samples obtained were examined by SEM and TEM microscopies. Figure 1(a) is

Figure 1. SEM images of products synthesized with different amounts of H_2O_2 : (a) 0.5 mL, (b) 0.8 mL and (d) 1.2 mL. (c) TEM images of products synthesized with 0.8 mL of H_2O_2 .

the SEM image of the Co_3O_4 samples obtained in the presence of 0.5 mL of 30 wt% H_2O_2 . It can be found that the Co_3O_4 products are not uniform cubes with size of about 30–200 nm. Figure 1(b) is the SEM image of the Co_3O_4 sample obtained in the presence of 0.8 mL of 30 wt% H_2O_2 . The result shows that the products synthesized are uniform Co_3O_4 nanocubes with size about 30–50 nm. Figure 1(c) shows the TEM images of the uniform Co_3O_4 nanocubes. TEM images further demonstrate that the obtained products have uniform morphology. Sizes of nanoplates were consistent with SEM results. The selected area electron diffraction (SAED) patterns of Co_3O_4 nanocubes (inserted in figure 1(c)) indicate the single-crystalline nature of the nanocubes. Figure 1(d) is the SEM image of the Co_3O_4 sample obtained in the presence of 1.2 mL of 30 wt% H_2O_2 . This SEM image reveals that the morphologies of the Co_3O_4 nanocubes were similar to Co_3O_4 sample obtained in the presence of 0.8 mL of

Figure 2. XRD pattern of the Co_3O_4 nanocubes.

Figure 3. HRTEM image of the Co_3O_4 nanocubes.

30 wt% H_2O_2 . It is apparent that the concentration of H_2O_2 plays an important role in our synthesis in determining the nanocrystal size of the products.

The crystal phase of the samples was analysed by powder X-ray diffraction. Figure 2 shows the XRD patterns of the Co_3O_4 sample obtained in the presence of 0.8 mL of 30 wt% H_2O_2 . All the diffraction peaks can be readily indexed to the cubic spinel structure Co_3O_4 with the lattice parameters, $a = 8.073 \text{ \AA}$. The results are in good accordance with the standard values (JCPDS card file no. 43-1003). No other phase can be detected, indicating the high purity of the final products.

HRTEM analysis provides more detailed structural information about the Co_3O_4 nanocubes, showing the apparent lattice fringes of the crystal. Figure 3 is an

Figure 4. Cyclic voltammograms of the Co_3O_4 nanocubes synthesized with different amounts of H_2O_2 : (a) 0.5, (b) 0.8, and (c) 1.2 mL.

Figure 5. Cyclic voltammograms of the Co_3O_4 nanocubes at various concentrations of H_2O_2 : (a) 0, (b) 0.2, (c) 0.6 and (d) 1.0 mM.

Figure 6. (a) Amperometric response of the Co₃O₄ nanocubes sensors with successive additions of H₂O₂ to 0.01 M phosphate buffer at an applied potential of -1 V (vs Ag/AgCl) and (b) its corresponding calibration plot.

Table 1. Comparison of electrochemical sensing H₂O₂ on various electrodes.

Electrodes	Detection limit (mM)	Sensitivity ($\mu\text{A mM}^{-1}$)	Applied potential	References
PB-modified Pt _{nano} /PCNTs	0.1	112.51	-0.2	Zhang <i>et al</i> (2010)
Carbon nanotubes	0.02	0.8	$+0.95$	Valentini <i>et al</i> (2003)
Flower-like gold assembling sphere	0.1	—	-0.2	Guo <i>et al</i> (2009)
CuO nanoflowers	0.5	88.4	-0.2	Song <i>et al</i> (2010)
Ag nanoparticles	1.0	230	-0.4	Song <i>et al</i> (2011)
Ni(OH) ₂ nanoplates	1.0	—	-0.7	Zhao and Song (2011)
Electrochemically roughened silver	0.05	—	-0.3	Lian <i>et al</i> (2009)
Ag nanorods	1	0.77	-0.5	Song <i>et al</i> (2012)

HRTEM image taken from the Co₃O₄ nanocubes obtained in the presence of 0.8 mL of 30 wt% H₂O₂. The observed interplanar spacing is 0.2 nm, which corresponds to the (4 0 0) atomic spacing.

The electrocatalytic activity of the Co₃O₄ nanocubes is studied using cyclic voltammetry (CV). Cyclic voltammograms of the obtained Co₃O₄ nanocubes with different concentrations of H₂O₂ in 0.01 M phosphate buffer (pH 7) containing 1 mM H₂O₂ at a scan rate of 50 mV s⁻¹ are shown in figure 4. All Co₃O₄ nanocubes obtained with different concentrations of H₂O₂ exhibit reduction of H₂O₂ starting around -0.5 V. As can be clearly seen, the Co₃O₄ nanocubes prepared in the presence of 0.8 and 1.2 mL of H₂O₂ exhibit the strongest electrocatalytic ability towards the reduction of H₂O₂. Based on the SEM analysis, it is obvious that the strongest electrocatalytic activity of the Co₃O₄ nanocubes prepared in the presence of 0.8 and 1.2 mL of H₂O₂, compared with those obtained in the presence of 0.5 mL of H₂O₂, may be attributed to its smaller particle size. The smaller particle size is favourable for increasing the interface area between nanocubes and electrolyte, which can result in a higher diffusion rate and faster electrode kinetics.

Figure 5 shows the CVs of the Co₃O₄ nanocubes obtained in the presence of 0.8 mL of H₂O₂ in 0.01 M

phosphate buffer containing H₂O₂ with different concentrations. With increase in the concentration of H₂O₂ (from the top: 0, 0.2, 0.6 and 1 mM), the H₂O₂ reduction current gradually increases, which may be applied as the quantitative analysis. Figure 6(a) shows the typical amperometric responses of the Co₃O₄ nanocubes upon the successive addition of H₂O₂ into the continuous stirring of 0.01 M phosphate buffer. The operating potential was -1 V. The Co₃O₄ nanocubes respond sensitively to the changes in H₂O₂ concentration, reaching a steady-state signal within 2 s. The corresponding calibration plot for the response curve is shown in figure 6(b). There is a linear relation between response current and H₂O₂ concentration with a sensitivity of $13.6175 \mu\text{A mM}^{-1}$ (the linear fitting correction coefficient, $R = 0.99219$). Various H₂O₂ sensors are summarized in table 1 with respect to the operating conditions, sensitivity and the detection limit. It can be seen that the method used in our experiment is simple and has a lower cost.

4. Conclusions

In conclusion, the Co₃O₄ nanocubes have been successfully synthesized by a simple hydrothermal method. The

electrocatalytic activity of the Co₃O₄ nanocubes has been studied using cyclic voltammetry. It is found that the Co₃O₄ nanocubes obtained in the presence of 1 mL of 30 wt% H₂O₂ show maximal electrocatalytic ability for the reduction of H₂O₂. The amperometric response of the electrode is rapid (within 2 s) and has high sensitivity (13.6175 μ A mM⁻¹). The Co₃O₄ nanocubes-based sensors demonstrated in this study show great potential applications in electrochemical sensor development.

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