Synthesis of Co₃O₄ thin films by chemical bath deposition in the presence of different anions and application to H₂O₂ sensing

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Abstract

Co₃O₄ modified electrode was prepared by directly growing layered cobalt carbonate hydroxide (LCCH) on a conducting fluorine-doped tin oxide (FTO) substrate using a simple chemical bath deposition (CBD) technique and then by transforming the LCCH into Co₃O₄ through pyrolysis. Cobalt sources with various anions, including cobalt chloride, cobalt nitrate, cobalt acetate, and cobalt sulfate, were used in the bath solutions of CBD to prepare the LCCH thin films with various morphologies. The composition and grain size of these films were verified by X-ray diffraction (XRD); their morphologies were examined by scanning electron microscopic (SEM) and transmission electron microscopic (TEM) images. Observed from the SEM images, the Co₃O₄ films synthesized from cobalt chloride (C-Co₃O₄), cobalt nitrate (N-Co₃O₄), cobalt acetate (A-Co₃O₄), and cobalt sulfate (S-Co₃O₄) were composed of straight acicular nanorods, bending acicular nanorods, nanosheets, and net-shaped nanosheets, respectively. The four kinds of modified electrodes were applied to detect H₂O₂, and the C-Co₃O₄ modified electrode showed the best electrocatalytic activity toward H₂O₂. The pertinent sensor could be successfully used for the quantification of H₂O₂ by amperometric method. The sensing performance parameters include a linear range up to 2.0 mM, a sensitivity of 66.29 μA/cm²-mM, a remarkable low detection limit of 0.36 μM, and a low applied potential of 0.50 V vs. Ag/AgCl/sat’d KCl.

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1. Introduction

The quantitative detection of hydrogen peroxide (H$_2$O$_2$) is important because H$_2$O$_2$ has emerged as a key by-product for enzymatic reactions in the field of biosensing [1]. Electrochemical methods have been proved to be a simple, fast, inexpensive, and sensitive way for H$_2$O$_2$ determination [1], so it is important to find materials that show high electrocatalytic property and sensing stability toward H$_2$O$_2$ to prepare the modified electrode for electrochemical sensing. Metal oxide nanostructures show the merits of easy preparation, inexpensive price, and thermal stability compared to other materials. Among these metal oxides, cobalt oxide (Co$_3$O$_4$) nanostructures have been attracted considerable interest in the field of electrochemical sensors, mainly due to their excellent electrocatalytic activity [1]. The electrocatalytic property of the Co$_3$O$_4$ thin film is very much dependent on the deposition method. Compared to most deposition methods, chemical bath deposition (CBD) is simple, low-cost, and shows the advantages of the high possibility to fabricate the thin films with different morphologies.

Nanoparticles [1] and nanowalls [2] of Co$_3$O$_4$ had been proposed for H$_2$O$_2$ detection before. In this study, it is the first time to use the Co$_3$O$_4$ acicular nanorods and nanosheets, synthesized by CBD, as H$_2$O$_2$ sensor and discuss the effect of morphology on its sensing. The sensor achieved a remarkable low limit of detection (0.36 $\mu$M), and the low applied potential (0.50 V vs. Ag/AgCl/sat’d KCl) implies the reduction or nullification of the sensing signals from other interferences.

2. Experimental

The Co$_3$O$_4$ modified electrode was prepared by depositing layered cobalt carbonate hydroxide (LCCH) on the FTO glass, using chemical bath deposition (CBD), followed by a pyrolysis treatment to transform the LCCH to cobalt oxide. In the CBD process, an FTO glass substrate (15 x 15 cm$^2$, with an exposed geometric area of 1.5 cm$^2$) was suspended upside-down in a closed bottle with an aqueous solution, containing 6.25 wt% of urea and 0.15 M of cobalt chloride, at 90 °C for 4 h. Identical concentration of cobalt nitrate, cobalt acetate, and cobalt sulfate were used to replace cobalt chloride in the bath solution for each separated experiment to obtain the LCCH films with various morphologies. Thereafter, the LCCH on the FTO was converted to cobalt oxide by pyrolysing it at 400 °C for 30 min in air.

The nanostructures of cobalt oxide were observed by using scanning electron microscope (SEM) and transmission electron microscopy (TEM). The composition of the cobalt oxide thin film was verified by X-ray diffraction patterns (XRD) with Cu K$_\alpha$ radiation.

Cyclic voltammetry (CV) and amperometric experiments were performed in a three-electrode system. An FTO glass modified with Co$_3$O$_4$ thin film (Co$_3$O$_4$/FTO electrode) was used as the working electrode. A Pt foil and a Ag/AgCl/sat’d KCl were used as the counter and reference electrode, respectively.

3. Results and discussion

3.1. Characterization of the films of LCCH and cobalt oxide

Figure 1(a) shows the XRD patterns of the as-prepared layered cobalt carbonate hydroxide (LCCH) films synthesized from cobalt chloride (C-LCCH), cobalt nitrate (N-LCCH), cobalt acetate (A-LCCH), and cobalt sulfate (S-LCCH). As revealed in Fig. 1(a), all the diffraction peaks of the four kinds of as-prepared films can be indexed to LCCH, i.e., Co(CO$_3$)$_{0.5}$(OH)$_x$$\cdot$$11$H$_2$O, according to Joint Committee on Powder Diffraction Standards (JCPDS, PDF no. 48-0083). Figure 1(b) shows the XRD patterns of the four films after 400 °C of pyrolysis treatment. It can be observed that the LCCH thin films can be transformed to pure Co$_3$O$_4$ after 400 °C of pyrolysis.
Figures 2(a), 2(b), 2(c), and 2(d) show the SEM images of N-Co$_3$O$_4$, C-Co$_3$O$_4$, A-Co$_3$O$_4$, and S-Co$_3$O$_4$, respectively. It can be seen that the N-Co$_3$O$_4$ is composed of bending acicular nanorods; the C-Co$_3$O$_4$ is composed of large and straight acicular nanorods, with a much larger size and a loose arrangement compared to the nanorods of N-Co$_3$O$_4$; the A-Co$_3$O$_4$ is composed of nanosheets, which are composed of several small nanorods; the S-Co$_3$O$_4$ is composed of net-shaped nanosheets.

TEM was used to observe the microscopic morphologies of each different Co$_3$O$_4$ film, and the TEM images of N-Co$_3$O$_4$, C-Co$_3$O$_4$, A-Co$_3$O$_4$, and S-Co$_3$O$_4$ are shown in Figs. 3(a), 3(b), 3(c), and 3(d), respectively. It can be seen that all these four kinds of nanorods or nanosheets were composed of tiny Co$_3$O$_4$ nanoparticles.

Fig. 1. The XRD patterns of (a) LCCH films and (b) Co$_3$O$_4$ films synthesized from various anions in CBD.

3.2. Electrooxidation behavior of hydrogen peroxide at the Co$_3$O$_4$/FTO electrode

Figure 4(a) shows cyclic voltammetric (CV) responses of the bare FTO electrode and the C-Co$_3$O$_4$ modified FTO electrode in 0.1 M pH 7 phosphate buffer solution (PBS) with and without 3.0 mM H$_2$O$_2$, at a scan rate of 25 mV/s. From Fig. 4(a), it can be observed the current response of the bare FTO electrode for the addition of H$_2$O$_2$ is small and neglectable, and there is a remarkable increase in the anodic peak current density ($J_{pa}$) at the first anodic peak of the modified electrode after the addition of H$_2$O$_2$, with reference to the $J_{pa}$ of the modified electrode before its addition. This increase is indicative of the excellent electrocatalytic activity of the C-Co$_3$O$_4$ modified electrode toward H$_2$O$_2$. Figure 4(b) shows the CV responses of C-Co$_3$O$_4$ modified FTO electrode in 0.1 M pH 7 PBS containing various concentrations of H$_2$O$_2$. The apparent and linear increase in $J_{pa}$ indicates that the modified electrode can be applied for the detection of H$_2$O$_2$ with high sensitivity.
3.3. Amperometric detection of hydrogen peroxide

After optimization of sensor performance among the four modified electrodes with different morphologies (not shown here), C-Co$_3$O$_4$ was selected for following study. Linear sweep voltammetry (LSV) was applied at 0.1 mV/s, and the suitable potential for amperometric detection was determined to be 0.5 V. Figure 4(c) shows an amperometric response, i.e., a current density-time plot, for the C-Co$_3$O$_4$ modified electrode for successive droppings of the H$_2$O$_2$ solution of various concentrations into 0.1 M pH 7 PBS, at an applied potential of 0.50 V vs. Ag/AgCl/sat’d KCl. From the calibration curve shown in the inset of Fig. 4(c), the linear range, sensitivity, and limit of detection were estimated to be 2.0 mM (correlation coefficient, $R^2=0.99$), 66.29 $\mu$A/cm$^2$-mM, and 0.36 $\mu$M, respectively.

4. Conclusions

The thin films of layered cobalt carbonate hydroxide (LCCH) were synthesized directly on the FTO conducting glass by CBD technique, and the films were converted to pure Co$_3$O$_4$ after the pyrolysis treatment at 400 °C. Various anions were used in the bath solutions of CBD to synthesize the Co$_3$O$_4$ films with various morphologies. The Co$_3$O$_4$ films synthesized from cobalt chloride (C-Co$_3$O$_4$), cobalt nitrate (N-Co$_3$O$_4$), cobalt acetate (A-Co$_3$O$_4$), and cobalt sulfate (S-Co$_3$O$_4$) were composed of straight acicular nanorods, bending acicular nanorods, nanosheets, and net-shaped nanosheets, respectively. All four kinds of Co$_3$O$_4$ nanorods or nanosheets were composed of tiny Co$_3$O$_4$ nanoparticles (TEM). These modified electrodes were applied to detect H$_2$O$_2$, and the C-Co$_3$O$_4$ modified electrode showed the best electrocatalytic activity toward H$_2$O$_2$. The C-Co$_3$O$_4$ modified electrode was applied to the amperometric detection toward H$_2$O$_2$, and the linear range, sensitivity, limit of detection, and suitable applied potential were 0.05 - 2.0 mM (correlation coefficient, $R^2=0.99$), 66.29 $\mu$A/cm$^2$-mM, 0.36 $\mu$M, and 0.5 V, respectively. These findings imply the promising probability of the C-Co$_3$O$_4$ modified electrode as a sensitive H$_2$O$_2$ sensor.

References
