AN EMPHERICAL APPROACH IN ENHANCING THE SYNTHESIS OF CO_3O_4 THIN FILMS BY CHEMICAL BATH UNDER DIFFERENT WORKING PARAMETERS

JYOTI N. HANDRAL
Research Scholar, Dept. of Physics,
Shri JJT University, Rajasthan.

Dr. A. N. CHATTARKI
Co-Guide, Dept. of Physics,
Shri JJT University, Rajasthan.

Abstract

For the Co3O4 modification, a simple chemical bath deposition (CBD) approach is used to directly develop Co3O4 on an FTO substrate and then change the Co3O4 to Co3O4 via the process of pyrolysis to produce Co3O4-modified electrodes. It was utilised in the bath solution of CBD to make the LCCH thin films with varied shapes of anions from diverse sources, including cobalt sulphate, cobalt chloride, and cobalt nitrate. X-ray diffraction (XRD) confirmed the films' composition and grain size, while scanning electron microscopy (SEM) and transmission electron microscopy (TEM) pictures evaluated their morphologies. As shown in the SEM photos, the Co3O4 films made from cobalt chloride (C-Co3O4), cobalt nitrate (N-Co3O4), cobalt acetate (A-Co3O4), and cobalt sulphate (S-Co3O4) included straight acicular nanorods, bendable nanorods, nanosheets, and net-shaped nanosheets, respectively. The C-Co3O4 modified electrode had the greatest electrocatalytic activity toward H2O2 of the four modified electrodes tested. The amperometric technique may be used to measure H2O2 with the appropriate sensor.

Keywords:*Acicular nanorods; Chemical bath deposition; Cobalt oxide; Hydrogen peroxide sensor; Layered cobalt carbonate; Modified electrode*

1. Introduction

Since enzymatic activities in biosensing generate large amounts of hydrogen peroxide (H2O2) as a by-product, it is critical to accurately measure H2O2 levels. When determining the concentration of H2O2, an electrochemical approach has been shown to be a rapid and economical method, thus it is vital to choose materials that have strong electrocatalytic properties and are stable in the presence of the oxidant. Compared to other materials, metal oxide nanostructures are straightforward to manufacture, affordable, and thermally stable. The outstanding electrocatalytic activity of cobalt oxide (Co3O4) nanostructures in the realm of electrochemical sensors has drawn substantial attention in these metal oxides [1]. This thin layer of Co3O4 is very reliant on the process of deposition. Most deposition processes are complicated and expensive, and CBD has the benefit of being able to make films with a wide range of shapes and sizes.

Before, Co3O4 nanoparticles [1] and Co3O4 nanowalls [2] were suggested for the detection of hydrogen peroxide. The Co3O4 acicular nanorods and nanosheets, produced by CBD, were used in this work for the first time as an H2O2 sensor and the influence of shape was discussed. The sensor's low detection limit (0.36 0) and low applied voltage (0.50 V vs. Ag/AgCl/sat'd KCl) suggest that the detecting signals from other interferences have been reduced or eliminated.

2. Experimental Approach

After depositing layered cobalt carbonate hydroxide (LCCH) on the FTO glass using chemical bath deposition (CBD), the Co3O4 modified electrode was pyrolyzed to turn the LCCH to CoO4. It was done in the CBD method using an FTO glass

substrate (15:/, with an exposed geometric area of 1.5 cm2) hanging upside down in an aqueous solution, which included 6.25wt% Urea (urea) and 0.15m CoCl2 (cobalt chloride). Each separated experiment employed the same concentration of cobalt nitrate, cobalt acetate, and cobalt sulphate to replace cobalt chloride in the bath solution. After that, the LCCH on the FTO was pyrolyzed at 400 °C for 30 minutes in air to produce cobalt oxide.

SEM and transmission electron microscopy (TEM) were used to study the nanostructures of cobalt oxide (TEM). With Cu K radiation, X-ray diffraction (XRD) patterns were used to confirm the cobalt oxide thin film's composition.

A three-electrode setup was used to conduct CV and amperometric studies. The working electrode was an FTO glass modified with a Co3O4 thin layer. Counter and reference electrodes were Pt foil and Ag/AgCl/sat'd KCl.

3. Results and discussion

3.1. *Characterization of the films of LCCH and cobaltoxide*

Layered cobalt carbonate hydroxide (LCCH) films made from cobalt nitrate, cobalt acetate, and cobalt sulphate are shown in Figure 1a by XRD patterns (S-LCCH). Co(CO3)0.5(OH)xx11H2O, as shown in Figure 1(a), is the index for all four types of as-prepared films, according to the Joint Committee on Powder Diffraction Standards (JCPDS, PDF no. 48-0083). Figure 1b shows the XRD patterns of the four films following pyrolysis treatment at 400 °C in Figure 1. After 400 degrees Celsius of pyrolysis, the LCCH thin films may be converted into pure Co3O4.

SEM images of N-Co3O4, C-Co3O4, A-Co3O4, and S-Co3O4 are shown in Figures 2a, 2b, 2c, and 2d. There is a clear distinction between the nanorods of N-Co3O4 and those of C-Co3O4 and A-Co3O4 and S-Co3O4 based on the arrangement of the nanorods.

The TEM images of N-Co3O4, C-Co3O4, A-Co3O4, and S-Co3O4 are shown in Figs. 3(a), 3(b), 3(c), and 3(d), respectively, for each of the Co3O4 films. Co3O4 nanoparticles were found in all four types of nanorods and nanosheets.

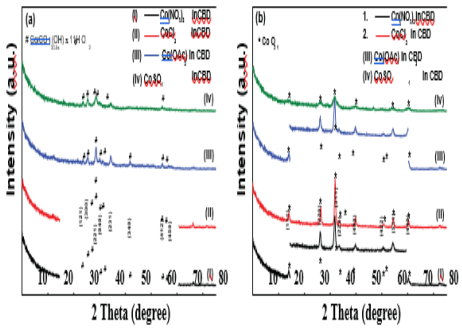

Fig. 1. The XRD patterns of (a) LCCH films and (b) Co3O4 films synthesized from various anions in CBD.

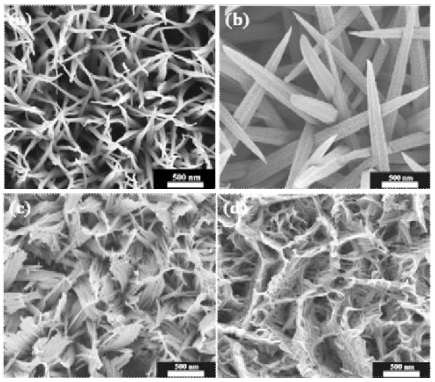

Fig. 2. The SEM images of variousCo3O4films.

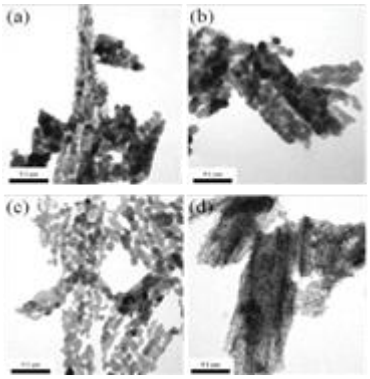

Fig. 3. The TEM images of various Co3O4films.

3.2. *Electrooxidation behavior of hydrogen peroxide at the Co_3O_4/FTOelectrode*

Figure 4(a) shows cyclic voltammetric (CV) responses of the bare FTO electrode and the C-Co_3O_4 modified FTO electrode in 0.1 M pH 7 phosphate buffer solution (PBS) with and without 3.0 mM H_2O_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_2O_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_2O_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_3O_4 modified electrode toward H_2O_2. Figure 4(b) shows the CV responses of C-Co_3O_4 modified FTO electrode in 0.1 M pH 7 PBS containing various concentrations of H_2O_2. The apparent and linear increase in J_{pa} indicates that the modified electrode can be applied for the detection of H_2O_2 with highsensitivity.

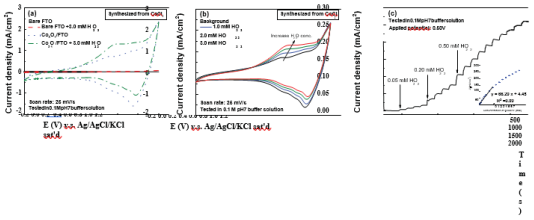

Fig. 4. The CV curves of C-Co3O4 modified electrode (a) compared to bare FTO and (b) with various concentrations of H2O2 addition; (c) The amperometric response of C-Co3O4 modified electrode toward H2O2.

3.3. *Amperometric detection of hydrogenperoxide*

After optimization of sensor performance among the four modified electrodes with different morphologies(notshownhere),C-Co_3O_4wasselectedforfollowingstudy.Linearsweepvoltammetry (modified electrode for successive droppings of the H_2O_2 solution of various concentrations into 0.1MpH 7PBS,at an applied potential of 0.50Vvs.Ag/AgCl/sat'dKCl. 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), 66.293$/FP^2-mM, and 0.3630, respectively.

4. Conclusion

LSV is applied at 0.1mV/s, and the suitable potential for amperometric detection is then determined to be0.5V. Figure4(c) shows an amperometric response, i.e., a current density-time plot, for the C-Co_3O_4 Cobalt carbonate hydroxide (LCCH) thin films were created directly on the FTO conducting glass by CBD approach, and the films were transformed to pure Co3O4 after the pyrolysis treatment at 400 °C was performed. Co3O4 films with different morphologies were synthesised using bath

solutions containing various anions. There were straight acicular nanorods, bending acicular nano rods, nano sheets and net-shaped nano sheets in the films made from cobalt nitrate (N-Co3O4), cobalt acetate (A-Co3O4) and cobalt sulphate (S-Co3O4). Nanoparticles of Co3O4 were found in all four types of Co3O4 nanorods or nanosheets (TEM). The C-Co3O4 modified electrode had the highest electro catalytic activity toward H2O2 of all the tested modified electrodes. The amperometric detection of H2O2 with the C-Co3O4 modified electrode had linear range, sensitivity, detection limit, and an appropriate applied potential of 0.05 - 2.0 mM (correlation coefficient, R2=0.99), 66.29 A/cm2-mM, 0.36 0, and 0.5 V, respectively. According to these results, the C-Co3O4 modified electrode has a potential future as a sensitive H2O2 sensor.

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