

Cobalt oxide nanoparticles anchored to multiwalled carbon nanotubes: Synthesis and application for enhanced electrocatalytic reaction and highly sensitive nonenzymatic detection of hydrogen peroxide



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ARTICLE INFO

Article history:

Received 11 November 2013

Received in revised form 6 January 2014

Accepted 8 January 2014

Available online 21 January 2014

Keywords:

Cobalt oxide

Co₃O₄

Multiwalled carbon nanotubes

Hydrogen peroxide

Electrocatalysis

ABSTRACT

Cobalt (II) dicobalt (III) oxide nanoparticles anchored to multiwalled carbon nanotubes were synthesized for the first time by a microwave decomposition method using cobalt nitrate as a precursor and multiwalled carbon nanotubes as a scaffold. The nanostructure was then employed as the modifier of a carbon paste electrode. The kinetics of the charge transfer process across the modified electrode/solution interface was studied. The modified electrode was then applied to fabricate an enzyme-less hydrogen peroxide biosensor. The mechanism and kinetics of the electrocatalytic reduction and oxidation reactions of hydrogen peroxide on the modified electrode surface were studied by cyclic voltammetry and chronoamperometry. The catalytic rate constants of the hydrogen peroxide electroreduction and electrooxidation processes by an active cobalt species, and the diffusion coefficient of hydrogen peroxide were reported. An amperometric method was developed for determination of hydrogen peroxide based on its electrocatalytic reduction with a sensitivity of 1002.8 mA mol⁻¹ dm³ cm⁻² and a limit of detection of 2.46 μmol dm⁻³. The sensor had the advantages of high electrocatalytic activity and sensitivity, with a simple fabrication method without complications of immobilization steps and using any enzyme or reagent.

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1. Introduction

Transition metal oxides show excellent electrochemical properties leading to a number of interesting applications. Among these oxides, cobalt oxides (and hydroxides) are important magnetic materials [1], catalytic materials [2] ionic exchangers [3] as well as electrode materials [4–8]. As an electrode material, cobalt oxides are greatly appealing due to different applications in electrocatalysis, electroanalysis, sensors and biosensors, and energy-related materials [4–10]. Up to now, various methods have been employed to synthesize cobalt oxides including electrodeposition [4–6,8], hydrothermal synthesis [11], solvothermal and polyol method in

the presence of soft templates or shape-directing agents [12–14] and thermal decomposition [15,16].

Tuning the size, shape and structure of transition metal oxides is one of the important research areas, because the physical and chemical properties of the oxide nanostructures strongly depend on their size and shape [17–23]. In this regard, nanoflakes [4,6], nanoparticles [5,8,16], nanoflowers [10], nanosheets [11], whisker-like nanostructure [12], nanocrystals [13], hollow nanospheres [14] and nanowires [15] of cobalt oxides have been synthesized. In addition, nanocomposites of cobalt oxides with carbon nanofibers [24], carbon nanotubes [25], graphene [26] and conducting polymers [27] have also been fabricated.

Hydrogen peroxide has wide applications in industrial process and plays a fundamental role as an intermediate in many biological reactions. The applications of hydrogen peroxide include antisepticing or disinfection in medical or packaging purposes, bleaching of cellulose, papers and fibers, deodorizing of waste treatment, and cleaning agent in the semiconductor manufactures [28,29]. Therefore, development of simple, sensitive, selective and accurate determination methods of hydrogen peroxide is important

Abbreviations: MWCNTs, Multi wall carbon nanotubes; PANI, Polyaniline; NPs, Nanoparticles; SWCNTs, Single wall carbon nanotubes; PoPD, Poly(o-phenylene diamine); PPy, Polypyrrole.

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in environmental, industrial, clinical, pharmaceutical and biomedical analyses [18,30–32]. Up to now, different electrochemical methods have been developed for quantitation of hydrogen peroxide based on direct oxidation or reduction on electrode surfaces, rather than enzymatic electrodes. Enzyme-less hydrogen peroxide sensors have the advantage of simplicity, low cost, high sensitivity, fast response time, and convenient operation. On the other hand, enzymatic and protein-based hydrogen peroxide biosensors have the disadvantage of instability of the immobilized biomacromolecules, complex immobilization process and high costs. In order to attain the entire advantages of enzyme-less sensors, the synthesis and application of novel nanostructured materials has attracted tremendous attention to fabricate hydrogen peroxide electrochemical sensors. In this regard, metals, metal oxides, metal hexacyanoferrates, carbonaceous nanostructures and conducting polymers have been employed for the hydrogen peroxide quantitation [33–35].

In the present study, cobalt oxide nanoparticles anchored to multiwalled carbon nanotubes ($\text{Co}_3\text{O}_4/\text{MWCNTs}$) were synthesized and applied to the electrocatalytic reduction and oxidation and detection of hydrogen peroxide. To the best of our knowledge, this approach has not been carried out successfully so far. Cobalt oxides represent multiple redox transitions at different potentials in alkaline solutions, compared to other metal oxides. Therefore, it can be employed for both electrooxidation and electroreduction of different substances and development of various electrochemical sensors.

2. Experimental

Graphite fine powder with a particle size of $<50\ \mu\text{m}$ was purchased from Merck. All other chemicals were of analytical grade from Merck and used without further purification. Multi-wall carbon nanotubes (MWCNTs) were obtained from US Research Nanomaterials, Inc. All solutions were prepared with doubly distilled water.

$\text{Co}_3\text{O}_4/\text{MWCNTs}$ were synthesized by the microwave decomposition method using the scaffold of MWCNTs. Before use, MWCNTs were pretreated as reported previously [23,36,37]. Briefly, MWCNTs were refluxed in a $2.0\ \text{mol dm}^{-3}$ nitric acid solution for 12 h, washed with redistilled water several times and dried at room temperature. MWCNTs were then sonicated in a 3:1 sulfuric/nitric acid solution for 6 h in an ultrasonic bath at room temperature, and then washed by vacuum filtration with distilled water until neutralization. The obtained sample was taken, and dried overnight at 50°C . This procedure causes scission and carboxylation of MWCNTs and the tubes bear negative surface charges on the outside. An aqueous solution of cobalt nitrate hexahydrate ($9\ \text{mmol dm}^{-3}$) was prepared separately and mixed with $150\ \text{mg}$ of pretreated MWCNT. The mixture was sonicated and then heated in an oven at 80°C for 15 min and continued to heat to dry the sample. Then, the dried mixture was put into a microwave working at $2.45\ \text{GHz}$ and a fixed power level of $900\ \text{W}$. The mixture was $60\ \text{s}$ irradiated following by a $60\ \text{s}$ rest and the microwave irradiation procedure was repeated 40 times to produce $\text{Co}_3\text{O}_4/\text{MWCNTs}$. Based on atomic absorption measurements, $7.6 \pm 0.4\ \text{mg}$ of cobalt was deposited on $1\ \text{mg}$ of MWCNT.

Carbon paste electrode (CPE) was prepared by hand-mixing graphite fine powder and mineral oil with a ratio of 80/20% (w/w). The paste was packed firmly into a cavity ($2.0\ \text{mm}$ diameter) at the end of a Teflon tube. Electrical contact was established by a copper wire.

Modified carbon paste electrodes with $\text{Co}_3\text{O}_4/\text{MWCNTs}$ (MCPE) were prepared by mixing graphite fine powder, mineral oil, and $\text{Co}_3\text{O}_4/\text{MWCNTs}$ with ratios of 60:20:20 by wt%. Before experiments, MCPE was placed in the supporting electrolyte ($100\ \text{mmol}$

dm^{-3} NaOH solution) and 25 potential cycles were applied in a regime of cyclic voltammetry in the potential range of -400 to $550\ \text{mV}$ at a potential sweep rate of $50\ \text{mV s}^{-1}$. This procedure caused the voltammograms of MCPE to become more stable and reproducible.

River water samples were taken from three different local rivers. The water samples were put intact for two days to settle and then filtered by filter paper. The amperometric responses of MCPE were measured by hydrogen peroxide addition of known concentrations to the samples.

Electrochemical studies were performed in a conventional three-electrode cell containing $100\ \text{mmol dm}^{-3}$ NaOH solution as the running electrolyte powered by a μ -Autolab potentiostat/galvanostat, type III, FRA2 (The Netherlands) run by a computer through GPES 4.9 commercial software. An Ag/AgCl/ $3\ \text{mol dm}^{-3}$ KCl and a glassy carbon rod were used as the reference and counter electrodes, respectively.

Powder X-ray diffraction (XRD) patterns were recorded in the 2θ range 10 to 90° at a scanning rate of $2.4^\circ\ \text{min}^{-1}$ by an X-ray diffractometer (Philips X'Pert, The Netherlands) with a Cu $K\alpha$ radiation at $40\ \text{kV}$ and $30\ \text{mA}$. Transmission electron microscopy (TEM) was performed by a Philips CM30 instrument.

All measurements were carried out at room temperature.

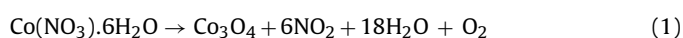
3. Results and discussion

3.1. Characterization of $\text{Co}_3\text{O}_4/\text{MWCNTs}$

Fig. 1 shows typical powder XRD patterns of MWCNTs (A) and $\text{Co}_3\text{O}_4/\text{MWCNTs}$ (B). MWCNTs represent broad diffraction peaks located at 2θ of 27 , 43 and 54° corresponding to (002), (100) and (004) reflections, respectively. The well resolved diffraction peak located at 2θ of 27° in the diffractogram corresponds to (002) planes of the stacked graphene layers in MWCNTs. The diffractogram of $\text{Co}_3\text{O}_4/\text{MWCNTs}$ contained peaks located at 31 , 37 , 53 , 69 , 77 , and 85° . They were related to (220), (311), (422), (440), (533) and (444) reflections, respectively, which confirmed the deposition of Co_3O_4 on the MWCNTs.

Fig. 2 shows TEM images of MWCNTs (A) and $\text{Co}_3\text{O}_4/\text{MWCNTs}$ (B). MWCNTs resemble the filament with an average diameter of $\approx 25\ \text{nm}$. On the other hand, cobalt oxide was deposited on and anchored to the outside of MWCNTs as nanoparticles of $\approx 75\ \text{nm}$ diameter.

Microwave irradiation is one of thermochemical methods employed for the synthesis of nanostructured materials through a decomposition reaction. Microwave irradiation can in depth pass the heat very fast and uniformly, while thermal gradients are minimized and the time for the particle diffusion is reduced. Therefore, the reaction products are produced in a relatively short time [38–40]. Thermal decomposition of nitrate salts of some transition metals results in pure metal oxides [16,23,39,41]. Moreover, the carbonaceous materials, as susceptors, enhance the microwave absorption [39]. In this study, MWCNTs act as both the microwave absorbing agent (the susceptor) and a scaffold. Cobalt oxide is formed through the decomposition of cobalt nitrate and deposited on the outer surface of MWCNTs. The microwave irradiation decomposition reaction of cobalt nitrate can be written as:



Typical cyclic voltammogram of MCPE recorded in the supporting electrolyte with a potential sweep rate of $50\ \text{mV s}^{-1}$ is shown in Fig. 3A. In this voltammogram, two pairs of well-defined peaks appear and the pattern of the voltammogram is similar to those previously reported [42–45]. The formal potentials of the redox transitions were estimated to be ≈ -56 (transition I) and $\approx 173\ \text{mV}$ (transition II) (as an average mid peak of cyclic voltammograms

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