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Full Length Article

Fabrication of a novel metal chromite – Carbon nanotube composite for the highly efficient electrocatalytic reduction of hydrogen peroxide

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ABSTRACT

The new electrocatalyst, $ZnCr_2O_4$/MWCNTs composite was successfully synthesized by hydrothermal method followed by calcination at 500 °C. A potential application of $ZnCr_2O_4$/MWCNTs composite modified electrode as enzyme-free sensor to monitor H_2O_2 has been studied. The sensor exhibited a high sensitivity of 1717.14 μA mM^{-1} cm^{-2} and a low detection limit down to 0.11 μM with a linear wide range from 50 μM to 34.8 mM with a fast response time of 2 s. In addition, modified electrode performance was investigated by measuring current responses of the sensor for three weeks to confirm the great stability of the proposed sensor. Along with these considerable analytical advantages, the as-prepared composite showed very high specificity to H_2O_2 with complete elimination of interference from uric acid, ascorbic acid, dopamine and glucose. The sensor gave satisfactory results in a real sample, when employed for determination of H_2O_2 in lens cleaning solution.

1. Introduction

The rapid and accurate detection of H_2O_2 is very important since it is an essential intermediate in both biomedical and environmental fields [1,2]. In the past decades, enzymatic modified electrodes were used for detecting of H_2O_2 due to their good selectivity and sensitivity. However, the relatively high cost, environmental instability and the complicated immobilization procedure limit enzyme-based biosensors applicability. Therefore, the development of non-enzymatic sensors with low detection limit has drawn more attention recently [3–6].

Physical and chemical properties of spinel materials have the potential for a wide range of applications, these materials are subjects of continuing study in materials sciences [7]. Zinc chromite ($ZnCr_2O_4$) nanospinels crystallize in the cubic system, Zn^{2+} and Cr^{3+} occupy the tetrahedral and the octahedral B-sites, respectively. In spite of several reports that showed spinel-type chromites were active materials in water-gas shift reaction, combustion catalysis, humidity sensing and dye absorbance [8–12], there has been no report dealing with this material as hydrogen peroxide sensor. These transition metal ions posses the large surface-to-volume ratio and the increased surface activity which can act as the efficient electrocatalyst in the reduction of hydrogen peroxide and sensing properties. As a suitable support is required to promote the catalytic efficiency of an electrocatalyst, carbon nanotubes (CNTs) was utilized. A wide range of impressive properties such as high aspect ratio, large surface area, great mechanical strengths and good bio-compatibility has made carbon nanotubes (CNTs) a focus of research in many applications in electroanalytical chemistry [13–15].

In this study the spinel composite of $ZnCr_2O_4$/MWCNTs was first time synthesized by means of the thermal treatment method and the catalytic activity of this composite was investigated with respect to the reduction of H_2O_2 using cyclic voltammetry, amperometry, and electrochemical impedance spectroscopy. It is a reliable fabrication of an enzyme free hydrogen peroxide sensor, which could be employed for the real-time electrochemical detection of hydrogen peroxide in environmental or biological samples.

2. Materials and methods

2.1. Characterization and instrumentations

Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) experiments are performed using Hitachi SU 8000 model instrument. Fourier transform infrared spectra (FTIR)

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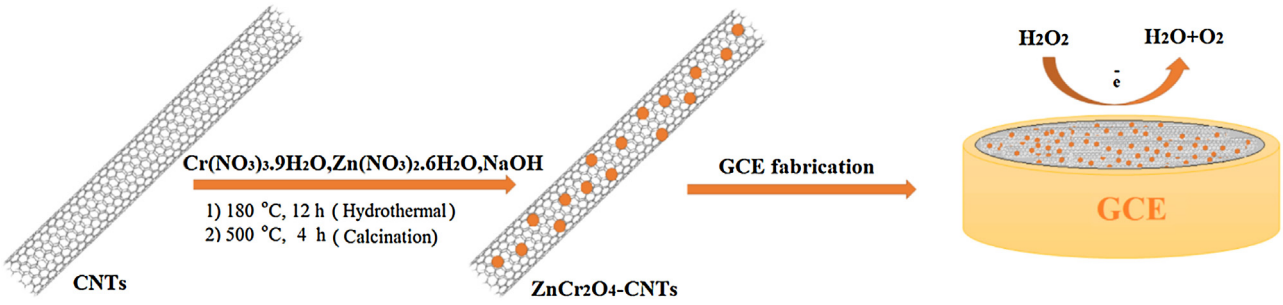

Scheme 1. The synthesis process of the $ZnCr_2O_4$/MWCNTs composite.

of the samples were recorded on a Perkin-Elmer RX1FT-IR spectrometer with a wavenumber resolution of 2 cm^{-1} as potassium bromide (KBr) pellets at a weight ratio. X-ray diffraction patterns (XRD) measurements were recorded using Cu Kα radiation to analyze the nanoparticles and composite structures. All electrochemical measurements were performed using a three-electrode configuration, consisting of the modified glassy carbon (GC) working electrode, a silver chloride (Ag/AgCl) reference electrode, and a platinum wire counter electrode in 0.1 M PBS at pH 7.4 at room temperature.

2.2. Reagents

Zinc nitrate hexahydrate ($Zn(NO_3)_2$.$6H_2O$), chromium nitrate nonahydrate ($Cr(NO_3)_3$.$9H_2O$), sodium hydroxide (NaOH, 96% purity), ethanol (C_2H_5OH, 99.7% purity), Sulfuric acid (H_2SO_4, 98%), D-(+) −glucose, uric acid (UA), ascorbic acid (AA) and dopamine were obtained from Aldrich. Multi-wall carbon nanotubes (30–50 nm diameter and 15 μm length), with >95% purity were obtained from DropSens (Spain). Deionized water was used for all experiments which were carried out at room temperature.

2.3. Preparation of $ZnCr_2O_4$ spinel NPs and $ZnCr_2O_4$/MWCNTs composite

The $ZnCr_2O_4$/MWCNTs nanocomposite with different MWCNTs content (10, 20, 30 wt% and 40%) were synthesized. 34 mg of acid treated-MWCNTs was dispersed in 25 ml of ethanol with sonication for 1 h. $Zn(NO_3)_2$.$6H_2O$ and $Cr(NO_3)_3$.$9H_2O$ were dissolved in 20 ml distilled water to form a clear aqueous solution. The above two solutions were then mixed together and stirred for 30 min. A NaOH aqueous solution (6 M) was added dropwise and the pH of the suspension was maintained at 11 with an attached pH regulator. The obtained suspension was transferred into Teflon-lined 100 ml capacity autoclaves. Hydrothermal reaction was conducted at 180 °C for 12 h in an oven. After the reaction was completed, the product was collected and washed with distilled water several times. The reaction mixture was allowed to cool to room temperature, and the precipitate was filtered, washed with distilled water several times, and dried in a vacuum oven at 60 °C for 12 h. The dried powder specimens were calcined at 500 °C for 4 h. The product was labeled as (10 wt%). For comparison, the same method was used to synthesize pure $ZnCr_2O_4$ NPs without adding MWCNTs. The synthesis process of the composite is shown in Scheme 1.

2.4. Preparation of the modified glassy carbon electrode (GCE) before modification

Prior to the surface coating, the GCE was polished carefully to mirror smoothness with 0.3 and 1.0 μm alumina power and rinsed with deionized water, followed by sonication in ethanol and water successively. The electrode was allowed to dry under nitrogen then 10 μl of $ZnCr_2O_4$ NPs or $ZnCr_2O_4$/MWCNTs composite dispersion was dropped on the surface of the GCE and dried in air before electrochemical experiments.

3. Results and discussion

3.1. Characterization of $ZnCr_2O_4$ spinel NPs and $ZnCr_2O_4$/MWCNTs composite

The FTIR absorption peaks (Fig. 1A) at 1681 and 1415 cm^{-1} in the spectrum of acid-treated MWCNTs (curve a) are the characteristic bands of graphite structure and disordered structure of MWCNTs, respectively. The absorption band related to C—N bond can be observed at 1061 cm^{-1} which indicates the appearance of new amine functional groups upon functionalization process in HNO_3. The peak at 3379 cm^{-1} can be assigned to —OH stretching vibration mode in carboxyl groups or adsorbed water. The shift in characteristic wavenumber to the lower direction indicates the presence of strong hydrogen bonds between –OH groups [16,17]. Observed peak around 2363 cm^{-1} also can be associated to ionic amines C═NH^+. Peak occurred in 2738 cm^{-1} are associated with C—H stretching bond in aliphatic –CH_2 and CH_3 groups. Deformation and bending of different types of C—H bonds are characterized by peaks below 900 cm^{-1} [18]. The appearance of peak at 491 and 605 cm^{-1} are attributed to absorption bands of Cr—O and Zn—O respectively, indicate the formation of spinel $ZnCr_2O_4$ nanoparticles. These two vibration bands Cr—O and Zn—O corresponded to the intrinsic lattice vibrations of octahedral and tetrahedral coordination compounds in the spinel structure, respectively [19]. The absorption band at 1632 cm^{-1} is due to absorbed water on the surface of the nanoparticles. Presence of MWCNTs in $ZnCr_2O_4$/MWCNTs composite makes the diffraction strength of $ZnCr_2O_4$/MWCNTs composite weaker than that of pure $ZnCr_2O_4$ nanoparticles (curve c).

Fig. 1B shows the XRD patterns of the (a) MWCNTs; (b) $ZnCr_2O_4$ NPs and (c) $ZnCr_2O_4$/MWCNTs composite. As displayed in curve a, there is a peak at around $2\theta \approx 25.5^\circ$ which is the strongest diffraction peak and can be indexed as the reflection of the hexagonal graphite structure. The sharpness of the peak confirms that the graphite structure of the MWCNTs was acid-oxidized without significant damage. The other diffraction peaks, are at the angles 2θ of 43.9°, 53.5° indexed to the (100) and (004) reflections [17,20]. Good crystallinity of the $ZnCr_2O_4$ specimens can be confirmed by revealed well-resolved diffraction peaks located at 2θ of 30.25°, 35.5°, 43.34°, 53.45°, 57.21°, 62.59° and 75.04°, respectively. These diffraction peaks corresponding to planes (220), (311), (400), (422), (511), (440) and (533) which provide a clear evidence for the formation of spinel structure of the chromite [11,21]. For $ZnCr_2O_4$/MWCNTs composite (curve c), it was found the diffraction peaks relating to MWCNTs and $ZnCr_2O_4$ NPs were appeared together, implying that the composite was synthesized successfully.