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Short communication

A model of interface-related enhancement based on the contrast between Co_3O_4 sphere and cube for electrochemical detection of hydrogen peroxide

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ABSTRACT

Co_3O_4 spheres and cubes have been prepared for the electrochemical determination of hydrogen peroxide. The Co_3O_4 cube/nafion electrode has shown better sensitivity and lower detection limit than that of Co_3O_4 sphere electrode. The models of the interface of Co_3O_4 and glass carbon electrode were presented and the mechanism of interface-related enhancement was investigated.

1. Introduction

Accurate determination of hydrogen peroxide (H_2O_2) is critically important in the field of food, pharmaceutical, and environmental analysis [1–4]. Among many techniques that have been developed so far, the electrochemical detection method featuring non-noble metal oxide (such as NiO and Co_3O_4) materials-based electrode has received enormous attention due to their low cost, superior of abundance and ease of fabrication [5,6].

On the other hand, non-spherical structures e.g. stars, sheets, octahedrons, cubes, wires, rods, and belts have attracted considerable interest because of their widespread applications in energy conversion and storage, magnetic separation, sensor devices and catalysis [7–10]. Recently, efforts have been dedicated to the rational design of non-spherical structures with well-defined facets and morphologies in view of their unique electrochemical properties [11–14]. However, most reports mainly focus on the effects of facets on the electrochemical properties of the material. To data, there are few reports about the non-facet related enhancement on the electrochemical properties.

Herein, we report a model of interface-related enhancement based on the contrastive study of Co_3O_4 sphere and cube for electrochemical detection of hydrogen peroxide. The Co_3O_4 cube/nafion electrode has shown better sensitivity and lower detection limit than that of Co_3O_4 sphere.

2. Experimental

2.1. Reagents

$Co(NO_3)_2 \cdot 6H_2O$ and NaOH were obtained from Shanghai Chemical Reagent Manufacturing Co. All other reagents were of analytical grade and used as received without further purification. Ultrapure fresh water was obtained from a Millipore water purification system (MilliQ, specific resistivity > 18 MΩ cm, S.A., Molsheim, France) and used in all runs.

2.2. Synthesis of Co_3O_4

Co_3O_4 cubes were synthesized according the literature with some modifications [15]. In brief, 4.4 g $Co(NO_3)_2 \cdot 6H_2O$ and 0.15 g NaOH were dissolved in 15 mL H_2O in a 20 mL Teflon-lined autoclave. Then the mixed reactants were heated at 180 °C for 5 h and then allowed to cool to room temperature. Afterwards, the obtained products were washed with ethanol several times and distilled water several times, which were further dried at 60 °C. Finally, Co_3O_4 were calcined at

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500 °C for 3 h. For the Co_3O_4 sphere, the amount of $Co(NO_3)_2 \cdot 6H_2O$ and NaOH were 8.7 g and 0.15 g, respectively. After they were dissolved in 15 mL H_2O in a 40 mL autoclave, the Co_3O_4 sphere were prepared by the same method as the Co_3O_4 cubes described above.

2.3. Apparatus

All electrochemical measurements were performed on a CHI 660C electrochemical workstation (Chenhua Instrument Co. Shanghai, China). A conventional three-electrode electrochemical cell was used, a modified glass carbon electrode (GCE, diameter 3.0 mm) as the working electrode, a saturated calomel electrode (SCE) as the reference electrode and a platinum wire as the auxiliary electrode. X-ray diffraction (XRD) analysis was performed with a Rigaku Dmax-2000 diffractometer using Cu Kα radiation. The morphologies of the samples were characterized by scanning electron microscopy (SEM) measurements from a JSM-6390LV microscope (JEOL). Transmission electron microscopy (TEM) was conducted at 200 kV with a JEM-2100F field emission TEM.

2.4. Preparation of modified electrode

Before each modification, the bare GCE was sequentially polished with 0.3 and 0.05 μm alumina power slurries to a mirror-shiny surface and sonicated in ethanol and ultrapure water. Co_3O_4/Nafion/GCE was performed in the following manner: 5.0 μL of Co_3O_4 ethanol (5 mg/ml) solution was dripped onto the surface of a freshly polished glassy carbon electrode. The electrode was allowed to dry, and then 2.0 μL of 0.05%w/w nafion solution was pipetted onto it. The electrode was then allowed to air-dry at room temperature.

3. Results and discussion

It was reported that the morphology of Co_3O_4 strongly depends on the amount of $Co(NO_3)_2 \cdot 6H_2O$ and NaOH. When the amount of $Co(NO_3)_2 \cdot 6H_2O$ is increased and the amount of NaOH is kept unchanged, the shape of the resultant Co_3O_4 changes from cube to sphere. Fig. 1A and D shows the panoramic view of the Co_3O_4 spheres and cubes with the particle size of 300 nm, respectively. Further morphology characterization of the sphere-shaped and cube-shaped sample was performed on TEM, as shown in Fig. 1B and E, which is in good agreement with the results of SEM. To avoid the observation effects caused by overlapping, a single sphere and cube was clearly revealed in Fig. 1C and F, respectively. As shown in Fig. 1H and I, both Co_3O_4 spheres and cubes disperse on the surface of the electrode like scattered islands and have about one to seven layers on the surface of the modified electrode. Fig. 1G shows the XRD patterns of Co_3O_4, whose diffraction patterns match Co_3O_4 (JCPDS: 78-1970) and the sketches of Co_3O_4 are inserted. The diffraction peaks of Co_3O_4 cubes are consistent with Co_3O_4 spheres and no impurity peaks are detected showing that the products are pure phase.

The electrocatalytic activity of different shapes of Co_3O_4 modified GCE was investigated by cyclic voltammetry for H_2O_2 oxidation in 0.1 M NaOH. As shown in Fig. 2A, without H_2O_2 addition two pairs of redox peaks (I/IV and III/II) were observed which was due to the reversible transition between Co_3O_4 and CoOOH (I/IV) and the transition between CoOOH and CoO_2 (III/II) [6,16]. After H_2O_2 was added, the oxidation current (peak I) related to Co_3O_4/CoOOH of Co_3O_4 cube/Nafion/GCE is much larger than that of Co_3O_4 sphere/Nafion/GCE due to catalytic oxidation of H_2O_2, indicating that Co_3O_4 cube modified electrode has a higher catalytic ability for H_2O_2 oxidation. Herein, there is an interesting phenomenon that Fig. 2A (d) shows that the peak splits into two distinct peaks due to two possible reasons. On the one hand, it may be on account of catalytic oxidation of H_2O_2 [17]. On the other hand, it can be caused by the thin-layer diffusion, as a result of the material's certain mass transport regime. The surface can be thought as a porous layer in which pockets of solution are trapped in between multiple layers of Co_3O_4. Correspondingly, the peak at low potential could be due to "thin layer" diffusion within the Co_3O_4, and the one at higher potential may be a consequence of planar diffusion from bulk solution [18–22]. Fig. 2B shows the electrochemical impedance spectra (EIS) represented as Nyquist plots (Z_{im} vs. Z_{re}) for Co_3O_4 cube/Nafion/GCE and Co_3O_4 sphere/Nafion/GCE, which illustrating that they both contain a liner part at low frequencies relating to diffusion and semicircle portion at high frequencies corresponding to the electron transfer limited process. However, Co_3O_4 cube/Nafion/GCE

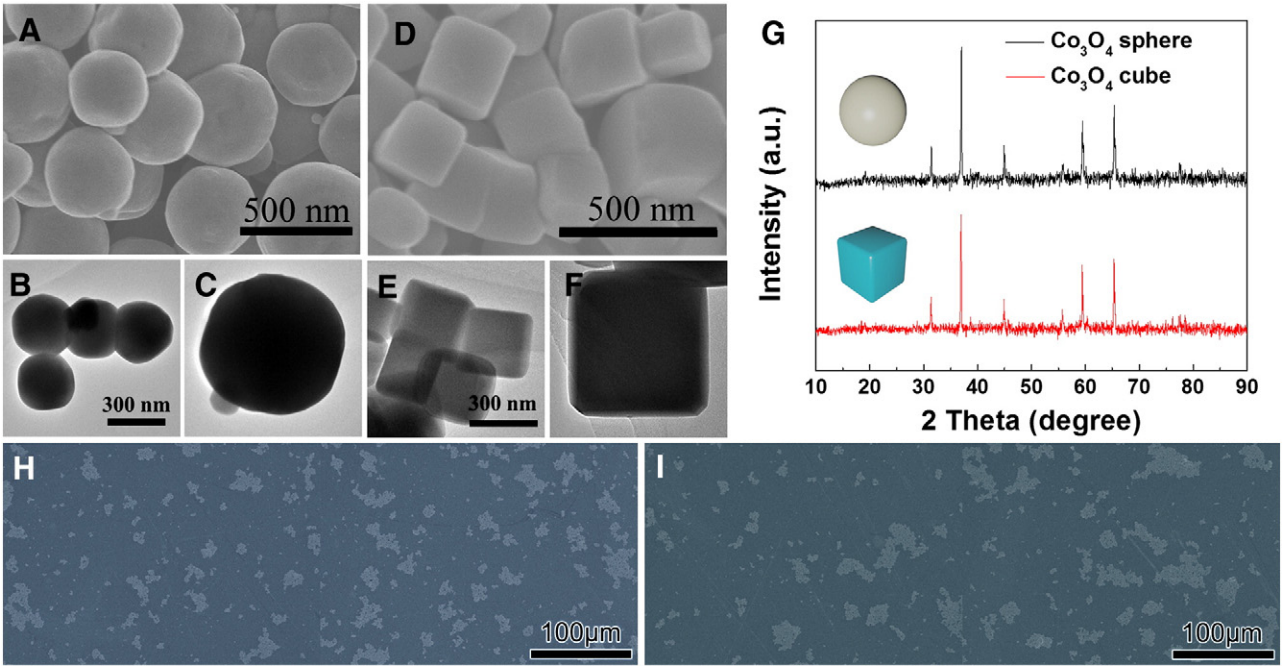

Fig. 1. SEM images (A and D) and TEM images (B, C, D and F) of the as-prepared Co_3O_4 spheres (A, B and C) and Co_3O_4 cubes (D, E and F); (G) XRD patterns of the as-prepared Co_3O_4 spheres and Co_3O_4 cubes (Inserted: sketches of Co_3O_4); the panoramic view of the Co_3O_4 spheres (H) and cubes (I) of the modified electrode.