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Leaf-templated synthesis of 3D hierarchical porous cobalt oxide nanostructure as direct electrochemical biosensing interface with enhanced electrocatalysis

Lei Han [a,b], Da-Peng Yang [a,*], Aihua Liu [a,b,*]

[a] *Laboratory for Biosensing, Qingdao Institute of Bioenergy & Bioprocess Technology, and Key Laboratory of Biofuels, Chinese Academy of Sciences, 189 Songling Road, Qingdao 266101, China*

[b] *University of Chinese Academy of Sciences, 19A Yuquan Road, Beijing 100049, China*

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ABSTRACT

A novel three-dimensional (3D) hierarchical porous cobalt oxide (Co_3O_4) architecture was first synthesized through a simple, cost-effective and environmentally friendly leaf-templated strategy. The Co_3O_4 nanoparticles (30–100 nm) with irregular shapes were interconnected with each other to form a 3D multilayer porous network structure, which provided high specific surface area and numerous electrocatalytic active sites. Subsequently, Co_3O_4 was successfully utilized as direct electrochemical sensing interface for non-enzymatic detection of H_2O_2 and glucose. By using chronoamperometry, the current response of the sensor at +0.31 V was linear with H_2O_2 concentration within 0.4–200 μM with a low limit of detection (LOD) of 0.24 μM (S/N=3) and a high sensitivity of 389.7 μA mM^{-1} cm^{-2}. Two linear ranges of 1–300 μM (with LOD of 0.1 μM and sensitivity of 471.5 μA mM^{-1} cm^{-2}) and 4–12.5 mM were found at +0.59 V for glucose. In addition, the as-prepared sensor showed excellent stability and anti-interference performance for possible interferents such as ascorbic acid, uric acid, dopamine, acetaminophen and especially 0.15 M chloride ions. Similarly, other various metal oxide nanostructures may be also prepared using this similar strategy for possible applications in catalysis, electrochemical sensors, and fuel cells.

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1. Introduction

Recently, functional nanostructured or nano-composited metal oxides continued to receive great attention due to their outstanding physicochemical properties such as high specific surface area, excellent semi-conductivity, enhanced electrocatalysis and good biocompatibility, which can be found a wide range of applications in sensing (Zamborini et al., 2011; Hayat and Andreescu, 2013; Liu et al., 2013a, 2013b), energy storage (Jiang et al., 2012; Meyer et al., 2012), field-effect transistor (Ferain et al., 2011) and catalysis (Wei and Wang, 2013; Lin et al., 2014). Particularly, the progress in creating novel nanoscale materials has pushed on the rapid development of analytical chemistry to meet the increasing demands in improving the response time, sensitivity, selectivity, and stability (Liu et al., 2005, 2006; Liu, 2008; Soleymani et al., 2009; Solanki et al., 2011). To date, various synthesis strategies of the nanomaterials had been adopted, such as solvothermal synthesis (Mai et al., 2011), sol-gel method (Debecker and Mutin, 2012), electrospinning method (Liu et al., 2004) and lithography technique (Cen et al., 2009). However, these strategies generally require complex technologies, expensive equipments and harmful organic reagents or surfactants, which might further hinder their application. Hence, it is highly desirable to explore facile synthesis strategies which are cost-effective, simple and environmentally friendly to get “green” nanomaterials. To address this issue, one alternative approach is to learn from nature. The magical nature offers us an enormous library of micro/nano-structured biomaterials with complex morphology, porous structures as well as special functionality. This has stimulated scientists to draw more and more inspiration to take advantage of the intrinsic structures of biomaterials and consider them as templates for fabricating micro/nano-structures conveniently (Sotiropoulou et al., 2008; Jones et al., 2011). Among these bio-templates, DNAs (Berti and Burley, 2008), peptides (Chen and Rosi,

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[*] Corresponding authors at: Chinese Academy of Sciences, Qingdao Institute of Bioenergy and Bioprocess Technology, and Key Laboratory of Biofuels, Laboratory for Biosensing, 189 Songling Road, Qingdao 266101, China.
Tel.: +86 532 8066 2758; fax: +86 532 8066 2778.
E-mail addresses: liuah@qibebt.ac.cn (A. Liu), yangdp@qibebt.ac.cn (D.-P. Yang).

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2010), proteins (Katz and Willner, 2004; Dickerson et al., 2008), viruses (Dujardin et al., 2003; Knez et al., 2003; Nam et al., 2006), bacteria (Berry et al., 2005), diatoms (Rosi et al., 2004), and butterfly wings (Huang et al., 2006) have been explored because of their morphologically complex architectures. However, these biomolecules and organisms are either expensive or insufficient as sources for the large-scale production. In contrast, the leaves are cheap, reproducible and abundant biomass, which can be used for scale-up production of biotemplated materials. Meanwhile, leaves exhibit excellent light-harvesting efficiency because of the 3D architecture of the highly interconnected, nano-layered thylakoid membranes at the nanoscale (Shimoni et al., 2005), and the porous framework of veins at the micrometer (Zhou et al., 2010). These interesting morphologies and characteristics had stimulated researchers to fabricate leaf-templated magnetic iron carbide (Fe_3C), titanium dioxide (TiO_2), magnesium oxide (MgO), platinum (Pt) and silver (Ag) micro/nanomaterials, which are applied to the field of electrodes (Schnepp et al., 2010), photocatalysts (Li et al., 2009; Zhou et al., 2010), water purification (Yang et al., 2013) and antimicrobials (Huang et al., 2011). These materials exhibited many unusual properties. For example, the artificial TiO_2 "leaf" was demonstrated to carry higher light-harvesting performance and photocatalytic activity than those prepared with classic routes[16]. The leaf-templated MgO has the enhanced charged property and adsorption capacity for dye (Yang et al., 2013). The magnetic Fe_3C "leaf" was used as the electrode material which was hard to be passivated by oxygen (Schnepp et al., 2010). The leaf extract-templated Pt or Ag nanoparticals exhibited excellent biocompatibility (Huang et al., 2011; Zheng et al., 2013).

Considering the significance of these properties to the field of electroanalytical chemistry, it makes sense to explore the leaf-templated metal oxide micro/nano materials as direct electrochemical biosensing interface. On the direct electrochemical biosensing interface, redox reaction would occur under the catalysis of the interface and electron directly transfers from analytes to the electrode without mediators, so that the electrochemical response would be fast and sensitive. Here, we select cobalt oxide (Co_3O_4), an important transition metal oxide, as model for the application of leaf-templated materials into electrocatalysis and biosensing due to their excellent catalytic (Xie et al., 2009), electronic (Dong et al., 2012) and electrochemical properties (Ding et al., 2010; Lang et al., 2013). The synthesis is simple, cheap, and environmentally friendly. The as-prepared Co_3O_4 inherited the 3D hierarchical porous and interconnected structure from leaves. Further, it was applied to the direct electrochemical non-enzymatic sensor for hydrogen peroxide (H_2O_2) and glucose, which was cost-effective, rapid, sensitive, selective, reliable and stable. To the best of our knowledge, this is the first report to address the leaf-templated nanomaterials for electrochemical sensing. The concept of this work may be applicable to prepare other metal oxides for a series of applications including sensing, supercapacitor and catalysis, and also represent an important first step towards the design of novel non-enzymatic biofuel cells.

2. Materials and methods

2.1. Chemicals and materials

Cobalt acetate ($Co(COOH)_2 \cdot 4H_2O$), sodium hydroxide (NaOH) and D-glucose were purchased from Sinopharm Chemical Reagent Corporation (Shanghai, China). Nafion® perfluorinated resin solution (5 wt% in mixture of lower aliphatic alcohols and water) were purchased from Sigma-Aldrich. All other reagents are of analytical grade and were used without purification. All aqueous solutions were prepared with Milli-Q water (18.2 MΩ cm). The mature gingko leaves were collected from the local park. H_2O_2 and glucose solutions with different concentrations were diluted from their respective stock solution with 0.1 M NaOH solution.

2.2. Synthesis of 3D porous Co_3O_4

The mature gingko leaves were treated with 2 M hydrochloric acid solution for 3 h. After rinsing thoroughly with water and subsequent drying at 60 °C for 3 h, the leaves were subsequently immersed in 0.1 M $Co(CH_3COO)_2$ solution at room temperature overnight. After drying at 60 °C, the leaves were calcined in air at 400 °C for 3 h and then naturally cooled to room temperature. The remaining powder was washed several times with water and collected by centrifugation. After drying at 60 °C overnight, the black Co_3O_4 was obtained. The powder was finely ground in an agate mortar and stored at room temperature. For the control experiment, non-templated Co3O4 was prepared from $Co(CH_3COO)_2$ solution by the same method except that the leaf template had not been used.

2.3. Preparation of the Co_3O_4 modified sensor

Before surface modification, the glassy carbon electrode (GCE, 3 mm in diameter) was polished with 0.05 μm alumina slurry, and sonicated in ethanol and water, respectively. After thorough rinse with water and drying in air, 5 μL of 2 mg/mL as-synthesized porous Co_3O_4 aqueous suspension was dropped onto the surface of the inverted electrode and dried in air. Finally, 5 μL of Nafion solution (0.1 wt% in ethanol) was dropped onto the electrode in order to entrap Co_3O_4. The as-prepared modified electrode was denoted as Nafion/Co_3O_4/GCE. Before use, the modified electrodes were washed with water to remove any loosely combined modifiers. The Nafion-coated GCE (Nafion/GCE) and the Nafion/non-templated Co_3O_4/GCE were also prepared as a control electrodes by the same process.

2.4. Apparatus and electrochemical measurements

The morphology of the as-prepared Co_3O_4 was observed by the field emission scanning electron microscopy (FE-SEM, HITACHI S-4800) and transmission electron microscopy (TEM, HITACHI H-7650). X-ray diffraction (XRD) patterns were recorded on a Bruker-AXS Micro-diffractometer (D8 ADVANCE) at room temperature. Electrochemical measurements were performed on a CHI 660E electrochemical workstation (CH Instruments, Chenhua, Shanghai, China). All electrochemical measurements were carried out at room temperature in a conventional three-electrode system with a modified GCE as the working electrode, a platinum wire as the counter electrode and a saturated calomel electrode (SCE) as the reference electrode. For chronoamperometry, all measurements were performed at appropriate potential on successive injection of analytes in stirring 0.1 M NaOH solution and the effect of dilution on the final concentration had been taken into consideration.

3. Results and discussion

3.1. Synthesis and structure of Co_3O_4 from leaf biotemplates

Here, we developed a simple, environmentally friendly and cost-effective method for the synthesis of 3D hierarchical porous Co_3O_4 with leaf template. The gingko leaf was selected as template, because gingko trees are widely planted in our country and their leaves are available easily. Meanwhile, this kind of leaf has relatively uniform texture without thick vein, which is favorable

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