Colloids and Surfaces B: Biointerfaces 111 (2013) 726–731

Contents lists available at ScienceDirect

Colloids and Surfaces B: Biointerfaces

journal homepage: www.elsevier.com/locate/colsurfb

Glucose oxidase-loaded amorphous FeNi–Pt fan-shaped nanostructures and their electrochemical behaviors

Na Wang[a], Ming Wen[a,b,*], Qingsheng Wu[a,b]

[a] Department of Chemistry, Key Laboratory of Yangtze River Water Environment, Ministry of Education, Tongji University, Shanghai 200092, China
[b] Shanghai Key Lab Development & Application MetalFunction Material, Tongji University, Shanghai 200092, China

ARTICLE INFO

Article history:
Received 22 January 2013
Received in revised form 27 May 2013
Accepted 5 June 2013
Available online 17 June 2013

Keywords:
Amorphous nanostructure
GOD
Chitosan
Electrode material
Electrochemical

ABSTRACT

Glucose oxidase (GOD) loaded amorphous FeNi–Pt fan-shaped nanostructures with the average length of ~7 μm have been synthesized for improving the electrochemical activity of enzyme electrode materials. The electrochemical oxidation of glucose solution has been successfully facilitated using FeNi–Pt fan-shaped nanostructures to load GOD due to their fan-shaped constitution and amorphous nanostructure. Chitosan could provide better response of nanostructure electrode than nafion. Compared with glassy carbon electrode (GCE) modified by chitosan/$Fe_{40}Ni_{40}$–Pt_{20}/GOD/GCE (GOD-loaded $Fe_{40}Ni_{40}$–Pt_{20} nanoalloys using chitosan as immobilization-agent), chitosan/$Fe_{45}Ni_{45}$–Pt_{10}/GOD/GCE presents smaller oxidation and reduction peak potential separation at 0.2912 V. No any electrochemical response can be observed when FeNi–Pt was absent in this electrode system. Additionally, a group of parallel experiments were tested when chitosan was changed to nafion. When $Fe_{40}Ni_{40}$–Pt_{20} nanostructure was employed to the electrode system, the oxidation and reduction peaks potentials were −0.7341 V and −0.4943 V, respectively, with a peak potential separation of 0.3371 V.

1. Introduction

Up to now, enzyme electrode materials have attracted considerable attention with the development of enzyme full cell. The nanostructure electrode materials could facilitate the direct electron transfer between enzyme and electrode [1]. However, enzyme has a short life and poor stability due to its fragile natural activity. And its macromolecular size can result in low catalytic density. Because the activity sites were buried, the electron cannot be efficiently transferred. As a result, the electrode material is flawed by low catalytic activity [2–6]. Therefore, it is still a challenging work for the development of effective enzyme electrode material.

Nowadays, a great effort has been made to fabricate amorphous alloy nanomaterials [7–11], owing to their short-range order and long-range disorder in structure. The advantage of the short-range orderly structure is that atoms can keep short-range orderly in several lattice constant ranges and form atomic cluster structure, which benefit for the reactivity. In addition, the long-range disordered structure facilitates the chaos arrangement of surface atomic. This behavior leads to a number of atoms in coordination unsaturated state and results in dislocation and defects, which can provide more active centers on the surface and abound in reactivity [12–15].

Additionally, amorphous alloy is porous structure at microscopic, which is good at making it easier for the adsorption of reagents and improving the catalytic density due to the increased activity sites. On the other hand, the porous structure can couple up the active center atom and enzyme by coordination effect to achieve the stabilization of enzyme, meanwhile the activity sites of amorphous alloy play a role for synergy catalysis to enhance the catalytic activity of enzyme. Investigations for the synthesis of binary alloy nanoparticles have been recently reported, such as FePt, CoPt, AuCu, NiCo and so on [16–23], which are of great interest owing to their unique magnetic and structural properties. At the same time, some of the nanostructures were also utilized as electrode materials for phosphoric acid and proton exchange membrane fuel cell. However, to the best of our knowledge, no report has focused on using 3D hierarchical amorphous alloy nanostructure as the electrode materials to research the electrochemical of enzyme electrode.

In this work, we used fan-shaped amorphous FeNi–Pt nanostructures as the GOD-loaded electrode materials to investigate the electrochemical behaviors to oxidation glucose solution in detail. The electrode modified with FeNi–Pt fan-shaped amorphous nanostructure shows an obvious increase in reduction and oxidation peaks to the oxidation of glucose solution. FeNi–Pt amorphous nanostructures loaded with GOD using as the electrode materials can give long-life stabilization of GOD and exhibits an excellent

---

* Corresponding author at: Department of Chemistry, Tongji University, 1239 Siping Road, Shanghai 200092, China. Tel.: +86 21 65982653x8544;
fax: +86 21 65981097.
E-mail address: m_wen@tongji.edu.cn (M. Wen).

0927-7765/$ – see front matter © 2013 Published by Elsevier B.V.
http://dx.doi.org/10.1016/j.colsurfb.2013.06.012

catalytic activity for GOD. All of above may be attributed to the special structure of FeNi–Pt amorphous nanostructure.

2. Materials and methods

2.1. Materials

All the reagents used in this work, including $H_2PtCl_6 \cdot 6H_2O$ (99%), $Fe_2(C_2O_4)_3 \cdot 5H_2O$ (95%), $NiCl_2 \cdot 6H_2O$ (99%), ethyl alcohol absolute (C_2H_5OH, 99%), propylene glycol ($C_3H_8O_2$, 99%), glucose, glucose oxidase (GOD), nafion, chitosan were purchased from Sinopharm Chemical Reagent Co., Ltd. (SCRC), and were used without further purification.

2.2. Synthesis of amorphous FeNi–Pt fan-shaped nanostructures

The samples were synthesized and characterized by SEM, TEM, XRD and XPS. Amorphous fan-shaped FeNi–Pt nanostructures were prepared by solvothermal method. $H_2PtCl_6 \cdot 6H_2O$, $Fe_2(C_2O_4)_3 \cdot 5H_2O$ and $NiCl_2 \cdot 6H_2O$ were used as precursors (Replicate times: 3, the length of the product with 2%error). As an example of a typical process, the synthesis process of $Fe_{40}Ni_{40}$–Pt_{20} nanostructure was described as following: 2 mL ethyl alcohol was mixed with 0.024 mmol $Fe_2(C_2O_4)_3 \cdot 5H_2O$, 0.024 mmol $NiCl_2 \cdot 6H_2O$ and 0.012 mmol of $H_2PtCl_6 \cdot 6H_2O$, at room temperature, then added to 10 ml propylene glycol. The mixture was maintained in the autoclave. The reaction system was sealed and treated at a heating rate of 1 °C min^{-1} from 20 °C to 180 °C, and kept for 3 h. After the reaction was cooled to room temperature, the $Fe_{40}Ni_{40}$–Pt_{20} nanostructures were collected at the bottom of the container. The products were alternately washed by deionized water and ethanol mixture with centrifugation thrice, then were redispersed and store in ethanol. The series of FeNi–Pt nanostructures were prepared using the initial molar ratios of Fe^{3+}:Ni^{2+}:Pt^{4+} at 45:45:10, 40:40:20, for the component of $Fe_{45}Ni_{45}$–Pt_{10} and $Fe_{40}Ni_{40}$–Pt_{20} respectively.

2.3. Electrochemical measurements

A glassy carbon electrode (GCE) (3 mm in diameter) and a Pt disk electrode (2 mm in diameter) were first polished with alumina slurries (1 and 0.05 mm, respectively) and then cleaned by sonication in Milli-Q water for approximately 5 min. The dispersed $Fe_{45}Ni_{45}$–Pt_{10} or $Fe_{40}Ni_{40}$–Pt_{20} nanostructures (10 μL) were dropped onto the cleaned GCE by a microliter syringe, followed by the addition of 2–4 μL chitosan or nafion (0.5 wt%) to form a thin film over the nanostructures. The modified electrode was finally rinsed with excessive ethanol and Milli-Q water to remove any loosely bound particles. The $Fe_{45}Ni_{45}$–Pt_{10} or $Fe_{40}Ni_{40}$–Pt_{20} nanostructure-modified GCE was denoted as the $Fe_{45}Ni_{45}$–Pt_{10}/GCE or $Fe_{40}Ni_{40}$–Pt_{20}/GCE. Before recording the voltammograms, the modified surface and the Pt electrode were cleaned in an aqueous solution of N_2-saturated H_2SO_4 (0.5 m) by cycling between −1.5 and 1.5 V (versus Ag/AgCl) until steady cyclic voltammetrics (CVs) were observed. Electrochemical measurements were performed using a computer-controlled CHI 660 electrochemical workstation (CH Instruments) in a conventional three-electrode system. The GCE and modified GCE were used as the working electrode, and a Pt coil was the counter electrode. All potentials were biased versus a KCl-saturated Ag/AgCl electrode. The following parameters were employed for CV (replicate times: 5, ~3%error) and Linear sweep voltammetry (LSV) (replicate times: 5, 3–4%error), respectively: CV: scan rate 100 mV s^{-1}; LSV: 75 mV s^{-1}. GCE is considered to be anode in PBS buffer (pH = 6.8) in which the concentration of glucose is 2 mM as supporting electrolyte solution, while GCE is cathode in PBS buffer (PH = 6.8) as supporting electrolyte solution.

2.4. Characterization

The size, morphology and composition are investigated by field-emission scanning electron microscopy (FE-SEM, Hitachi, S-4800) and transmission electron microscopy (TEM) on a JEOL JEM-1200EX microscope (Japan). Energy dispersive X-ray spectra (EDS) analysis is conducted at 20 keV on a TN5400 EDS instrument (Oxford). The structure is characterized using powder X-ray diffraction on Bruker D8 (German) with a Cu Kα X-ray radiation source with $\lambda = 0.154056$ nm. X-ray photoelectron spectroscopy (XPS) experiments were carried out on a RBD upgraded PHI-5000C ESCA system (Perkin Elmer) using a Al Kα radiation ($h\nu = 1486.6$ eV). The whole spectra (0–1100 eV) and the narrow spectra of all the elements with much high resolution were both recorded using RBD 147 interface (RBD Enterprises, USA) through the AugerScan 3.21 software. Binding energies were calibrated by using the containment carbon (C1s = 284.6 eV). The data analysis was carried out using the RBD AugerScan 3.21 software provided by RBD Enterprises or XPSPeak4.1 provided by Raymund W.M. Kwok (The Chinese University of Hongkong, China). Magnetic property is examined by Vibration sample magnetometry (VSM) on lakeshore 7312 (Replicate times: 3, 2%error). A CHI 660 electrochemical work station (CH instruments, Shanghai, China) was employed in all electrochemical measurements, which were carried out with a conventional two compartment three-electrode electrochemical cell. The reference electrode was a KCl-saturated Ag/AgCl electrode.

3. Results and discussion

3.1. Characterization of amorphous FeNi–Pt fan-shaped nanostructures

The morphology of as-prepared FeNi–Pt fan-shaped nanostructures were characterized by FE-SEM and TEM. It can be observed that the average length of fan-shaped nanostructures are ~7 μm for $Fe_{45}Ni_{45}$–Pt_{10} and ~7 μm for $Fe_{40}Ni_{40}$–Pt_{20} in Fig. 1A and B (a) respectively. TEM images are given in Supplementary materials (SM) in Fig. S1. The selected-area electron diffraction (SAED) pattern recorded from FeNi–Pt nanostructures (Fig. 1A and B (b and c)) exhibiting a diffuse halo indicates that they have amorphous structure, confirming the chemical disorder amorphous structure by two broad halo of (1 1 1) at ~40.02° and (2 0 0) at ~46.24° exhibited in XRD pattern in Fig. S2A (in SM) [24]. Selected area energy dispersive X-ray spectroscopy (EDXS) performed on $Fe_{45}Ni_{45}$–Pt_{10} and $Fe_{40}Ni_{40}$–Pt_{20} shown in Fig. S2B illustrate that the component were consistent with the initial molar ratio of Fe:Ni at ~1:1, but the content of Pt in product is less than that in reactant.

In order to investigate the structure and corresponding electrochemical activity affected by the content of Pt in FeNi–Pt system, a series of fan-shaped nanostructures with different content of Pt element were synthesized, the SEM images were shown in Fig. S3. It can be observed that the $Fe_{48}Ni_{48}$–Pt_4 were not fan-shaped nanostructure. With the increase of Pt element, the fan-shaped nanostructure was gradually formed. In Fig.S3D, when Pt content reached 25%, the fan-shaped nanostructure began to collapse. Fig. S3E gives the SEM image of $Fe_{35}Ni_{35}$–Pt_{30}, it can be found that the Pt element was formed particles and dispersed on the surface of nanostructure. Fig. S3F was the high magnification image about the Pt particles of the $Fe_{35}Ni_{35}$–Pt_{30} nanostructure. With the increase of Pt content, Pt nanoparticles was agglomeration on the surface of