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Nanoporous platinum–cobalt alloy for electrochemical sensing for ethanol, hydrogen peroxide, and glucose

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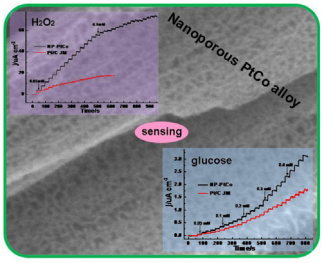
HIGHLIGHTS

- NP–PtCo alloy is fabricated by dealloying PtCoAl alloy in mild alkaline solution.
- NP–PtCo alloy exhibits hierarchical three-dimensional nanoporous structure.
- NP–PtCo shows good sensing performances toward ethanol, H_2O_2, and glucose.
- NP–PtCo shows good anti-interference toward UA, AA, and DA for H_2O_2 detection.

GRAPHICAL ABSTRACT

Nanoporous (NP) PtCo alloy was easily fabricated by dealloying of PtCoAl ternary alloy in a mild alkaline solution. Selectively etching of Al resulted in a hierarchical three-dimensional network nanostructure with a narrow size distribution at 3 nm. The as-made NP–PtCo alloy shows superior sensing ability toward ethanol, H_2O_2, and glucose with highly sensitive response and wider linear range compared with Pt/C catalyst. NP–PtCo also exhibits excellent amperometric durability and long-term stability for H_2O_2 as well as a good anti-interference toward ascorbic acid, uric acid, and dopamine.



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ABSTRACT

Nanoporous platinum–cobalt (NP–PtCo) alloy with hierarchical nanostructure is straightforwardly fabricated by dealloying PtCoAl alloy in a mild alkaline solution. Selectively etching Al resulted in a hierarchical three-dimensional network nanostructure with a narrow size distribution at 3 nm. The as-prepared NP–PtCo alloy shows superior performance toward ethanol and hydrogen peroxide (H_2O_2) with highly sensitive response due to its unique electrocatalytic activity. In addition, NP–PtCo also exhibits excellent amperometric durability and long-term stability for H_2O_2 as well as a good anti-interference toward ascorbic acid, uric acid, and dopamine. The hierarchical nanoporous architecture in PtCo alloy is also highly active for glucose sensing electrooxidation and sensing in a wide linear range. The NP–PtCo alloy holds great application potential for electrochemical sensing with simple preparation, unique catalytic activity, and high structure stability.

1. Introduction

Highly sensitive detection toward some small molecules such as ethanol, H_2O_2, glucose is very desirable due to its widespread application in the fields of food industry, life science, and medical diagnosis [1–4]. Electrochemical sensing technology based on electrocatalytic activity of advanced nanomaterials has attracted

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great attention due to the easy operation and fast detection [5,6]. Among various nanomaterials, nanoscaled Pt has fueled numerous research interests in terms of high sensitivity and good selectivity due to their unique electrocatalytic performance toward the oxidation of many small molecules [7,8]. At present, a majority of the reported Pt sensing catalysts are mainly in a form of dispersed nanoparticles on graphene, carbon nanotubes, carbon powder, and nanofibers, etc. [1,7–10], which are usually fabricated by wet-chemical reduction processing of Pt salt precursors. The carbon support has drawbacks as a transducer in electrochemical sensing because of the problem of de-adhesion between support and nanoparticles [11].

Recently, Pt-based nanoporous structures and their electrochemical sensing performances have attracted great attention due to their high surface area and interconnected porous channels [12–14], which are preferable for unblocked mass and electron transport. For instance, Wang et al. prepared three-dimensional nanoporous (NP) PtPb networks by reducing H_2PtCl_6 and $Pb(NO_3)_2$ in formaldehyde solution on etched Ti substrates at 180 °C, finding unique nonenzymatic electrochemical glucose sensing performance [15]. Liu et al. prepared NP–PtNi nanowires by electrodepositing PtNi alloy into aluminum oxide template followed by dealloying of Ni and template removal [16], and found that the resulted nanostructure showed high H_2O_2 sensing activity. Being indeed quite successful in achieving high activity, however, the preparation of these nanoporous nanostructures is complicated involving a multi-step operation. For instance, their preparation process usually involves the usage of excessive organic agents or applied potential to reduce the metal salts, additionally which also needs careful operation and high temperature processing with low production yield. The stated above are not desirable in terms of the ever-demanding concerns for green synthesis, environmental protection, and a low fabrication cost.

In last several decades, dealloying strategy has been demonstrated to be very promising for scaling up the simple preparation of nanoporous metals [17–19]. The dealloyed nanoporous structures represent an ideal class of metallic electrocatalysts which can provide the unblocked mass and electron transport during sensing process [20,21]. Importantly, the interconnected skeleton extending in three dimensions can bypass the particle aggregation and the corrosion of support [22,23]. It is well known that alloy nanomaterials, which combine the advantages of two compositions, have received considerable attention considering their synergistic catalytic effect and saving the Pt loadings [15,24]. Consequently, it is interesting to construct highly sensitive and stable electrochemical biosensors by using Pt-based nanoporous alloy materials.

In this work, NP–$Pt_{55}Co_{45}$ alloy was fabricated by selectively etching the ternary PtCoAl source alloy in a mild alkaline solution. Non-precious Co as a 3d metal has exhibited synergistic catalytic effect on many electrocatalytic reactions such as methanol electrooxidation [18]. In current work, the electrocatalytic activities of the NP–PtCo alloy were studied toward ethanol, hydrogen peroxide, and glucose as models in order to explore the effect of Co on the biosensing ability of Pt with the aim to construct highly sensitive and stable electrochemical sensors.

2. Experimental

2.1. Reagents

PtCoAl alloy was prepared by refining high-purity (>99.9%) Pt, Co, and Al metals in an argon-protected arc furnace, followed by melt-spinning into foils with a typical thickness at ~50 μm. H_2O_2 solution (30%) and D-(+)-glucose were purchased from Sinopharm Chemical Reagent Co., Ltd. The glucose stock solution was kept overnight (at least 24 h) to allow mutarotation. Dopamine (DA), uric acid (UA), and ascorbic acid (AA) were purchased from Sigma–Aldrich. The commercial John–Matthey Pt/C catalyst (20 wt.%) was purchased from Alfa Aesar. Other chemicals were of analytical grade.

2.2. Apparatus

X-ray diffraction (XRD) analysis was conducted on a Bruker D8 advanced X-ray diffractometer using Cu KR radiation at a step rate of $0.04^\circ\ s^{-1}$. The microstructures and composition of the sample were characterized by a JEM-2100 transmission electron microscope (TEM) and a JSM-6700 field-emission scanning electron microscope (SEM) equipped with an Oxford INCA x-sight Energy Dispersive X-ray Spectrometer (EDS). Electrochemical measurements were performed on a CHI 760 D potentiostat in a standard three-electrode cell with a Pt foil as counter electrode and a saturated mercurous sulfate electrode as reference electrode. All potentials were provided according to the reversible hydrogen electrode (RHE) scale for clarity.

2.3. Preparation of the modified electrodes

The NP–PtCo alloy was prepared by dealloying the PtCoAl alloy foils in 1 M NaOH solutions for 48 h at room temperature. Catalyst ink was prepared by sonicating the mixture of 1.5 mg PtCo alloy powder, 1.0 mg carbon powder, 300 μL ethanol, and 100 μL Nafion solution (0.5 wt.%) to form uniform suspension solution. The working electrode was made by placing the catalyst ink on a polished glassy carbon electrode (GCE, 4 mm in diameter).

3. Results and discussion

3.1. Characterization of NP–PtCo alloy

Fig. 1a shows the typical SEM image of the resulted sample after dealloying PtCoAl alloy. It is clear that the island-cracked structure runs through the whole sample surface, which can be deemed to an irregular nanoporous structure composed of the interconnected dendrites-like ligaments and interstices-like pores with the length scales at hundreds of nanometers. From high magnification SEM image (Fig. 1b), the ligaments have an open three-dimensional bicontinuous spongy morphology with the typical ligament size around 3 nm. As shown by cross-sectional SEM image (Fig. 1c), nanoporous structure crosses the whole structure with high structure uniformity. In the TEM image (Fig. 1d) a clear contrast between the dark skeletons and bright central region further indicates the formation of an open 3D bicontinuous spongy structure. Obviously, the resulted sample exhibits bimodal pore/ligament size distributions, which is beneficial for the mass and electron transport during electrochemical sensing.

The crystal structure of the dealloyed sample was examined by XRD. As shown in Fig. 2, three diffraction peaks emerged at around 41.4, 46.7, and 69.8 (2θ), which located in just between the projected 2θ values for pure Pt and Co. These three peaks can be ascribed to the diffraction from the (1 1 1), (2 0 0), and (2 2 0) planes of face-centered cubic (f c c) PtCo alloy structure, respectively. No peaks from Co oxides or Al-based alloy species can be observed, indicating the formation of pure single phase PtCo alloy. EDS results show that the atomic ratio of the resulted nanoporous alloy is $Pt_{55}Co_{45}$ with almost no Al atoms detected, which is also consistent with the initial feeding ratio of Pt and Co in the ternary PtCoAl alloy. Based on the experimental results above, the NP–PtCo alloy with uniform structure was straightforwardly fabricated by means of a simple dealloying procedure. More importantly, this process can effectively pre-define the bimetallic composition of the