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Double-template electrosynthesis of platinum nanomaterials for sensing application

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ABSTRACT

Platinum nanomaterials were synthesized through a double-template electrochemical deposition. Scanning electron microscope, energy dispersive X-ray spectroscopy and X-ray diffraction was used to investigate the morphology and ingredient changes during the fabrication process of platinum nanoparticles (PtNPs)/nanozinc oxide (nanoZnO) modified glassy carbon electrode (GCE). Electrochemical methods were adopted to characterize the sensing properties of the proposed modified electrode towards hydrogen peroxide (H_2O_2) and hydrazine hydrate (N_2H_4). The results indicated that the PtNPs/nanoZnO/GCE showed synergistic electrochemical effect for electrocatalytic reduction of H_2O_2 and electrocatalytic oxidation of N_2H_4. Take N_2H_4 sensing for example, the modified electrode displayed a fast response (<4 s), high sensitivity (110 $\mu A\,mM^{-1}\,cm^{-1}$) and broad linear in the range from 0.5 to 1300 μM and 1300 to 6000 μM with a relatively low detection limit of 0.2 μM (S/N = 3). Zero current potentiometry was used for in situ probing the changes of the interfacial potential during the electrocatalytic oxidation of N_2H_4 on the modified electrode.

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1. Introduction

As a class of materials, nanomaterials offer a variety of opportunities to investigate the evolution of material properties with particle dimensions [1]. They possess large surface areas and usually exhibit high surface concentrations of edges, corners, defect sites, and other unusual structural features [2], which are different from those of bulk materials. Nanostructures present several advantages in analytical sciences when used as transducers or as a component of the recognition layer in a micro-sized sensing device [3]. The large surface to volume ratio and high surface activity, enable nanomaterials to use as ideal candidates for catalysis and sensing devices [4]. Thus, analysts in this field are always enthusiastic about finding new materials with good compatibility to improve sensors' performance [5,6].

Metal nanoparticles (MNPs) are technologically important materials due to their unique optical, electronic, magnetic and catalytic properties [7], which have significant application in display, microelectronics, data storage, drug delivery, imaging and sensing [8]. The hot research points in MNPs always focus on the synthesis of noble metal such as gold (Au), sliver (Ag), patinum (Pt), palladium (Pd), ruthenium (Ru) and their alloys [9]. Various wet-chemical methods as well as template assisted methods have been developed to synthesize noble metal of specific architectures nanoforms. Among these, the template assisted method suits materials for catalysis best. It is imperative to isolate nanoparticles on supports so that unique physical and morphological properties of the nanoforms are retained with minimal leaching in harsh catalytic conditions [10].

At present, the design and synthesis of nanoscale Pt architectures have been explored extensively for applications ranging from heterogeneous catalysis to fuel cells [11]. Electrochemical deposition for the preparation of Pt nanoparticles (PtNPs) is simplicity, low cost and favorable in controlling the purity, particle size and composition of the resulting composites. Moreover, different methods used for the electrodeposition may affect the morphology and electrochemical behavior of the resulting metal [12]. The gas bubble dynamic template electrodeposition is a relatively new technique for the preparation of nanomaterials. The self-supported 3D metal foams of copper (Cu) [13], tin (Sn) [14], Ag [15], zinc (Zn) [16,17] and Au [18] prepared with this method had been reported. Gas bubble assisted deposition of PtNPs was carried out by galvanic replacing process between the deposited Cu and an aqueous chloroplatinic acid (H_2PtCl_6) solution [19,20]. Here, Multi-Potential Steps method was employed to complete the replacement reaction of H_2PtCl_6 with CuNPs. This is the first attempt to realize the template sacrifice deposition and gas bubble electrodeposition at the same time. CuNPs can take replacement reaction with chloroplatinic acid ($H_2PtCl_6{\cdot}6H_2O$). When a negative potential applied to this process, hydrogen (H_2) evolution (dynamic template) is formed at

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the same time. CuNPs and H_2 can play a role as double-template for the deposition of PtNPs. The hydrogen bubbles functioned as the dynamic template for the electrodeposition of PtNPs arising from the electrochemical reduction of H^+ at CuNPs surface more was more easily than that of the bare glassy carbon electrode (GCE). Furthermore, CuNPs played the role as nucleus for the electrodeposition process. CuNPs can kill two birds with one stone. On the one hand, CuNPs accelerated the formation of H_2; on the other hand, it can enhance the electrodeposition of PtNPs by a replacement reaction with H_2PtCl_6. with CuNPs. The double-template electrosynthesis we reported here, not only overcomes troublesome procedures to remove the traditional template, but also it is a simple, cost-effective, and potent method to prepare Pt nanomaterials for applications.

Hydrogen peroxide (H_2O_2) is necessary for the metabolism of proteins, carbohydrates, fats, vitamins and minerals [21]. What's more, H_2O_2 helps regulate blood sugar and the cellular energy production. Oxidative damages in the body are caused by the cellular H_2O_2 imbalance as it plays an important role in cell signaling and communication. Hydrazine hydrate (N_2H_4) is a basic and strong reducing agent and its salts are used in the pharmaceutical industry as an intermediate to produce drugs with different therapeutic effects including decarboxylase inhibitors, antihypertensives and antibacterials [22]. However, N_2H_4 is toxic and thought to be possible human carcinogen. Thus, a simple, fast and low cost way is needed for the determination of H_2O_2 and N_2H_4. Electrochemical detection techniques have a series of advantages, such as rapid response, ease of use and low-cost small-sized commercial detectors [23], which can satisfy the demands mentioned above. PtNPs have been demonstrated to lower the H_2O_2 and N_2H_4 oxidation/reduction overvoltage efficiently [24–26]. Thus, PtNPs are an ideal sensor platform for the determination of H_2O_2 and N_2H_4.

The aim of the present work is: (1) to electrodeposite PtNPs with a double-template system at CuNPs/nanoZnO modified GCE; (2) investigate the sensing properties of the PtNPs/nanoZnO/GCE towards H_2O_2 and N_2H_4. The coalition of chemical replacement action and template sacrifice electrodeposition will open a new way for the synthesis of novel nanomaterials with unique morphology and properties.

2. Experimental

2.1. Materials and apparatus

$H_2PtCl_6{\cdot}6H_2O$ was obtained from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China). Trisilicate copper nitrate was purchased from Tianjin Basifu Chemical Engineering Co., Ltd. ($Cu(NO_3)_2{\cdot}3H_2O$, Tianjin, China). Zinc chloride was got from Tianjin Tianda Chemistry Reagent Plant ($ZnCl_2$, Tianjin, China). Other reagents were analytical reagent grade and doubly distilled water was used in all the experiments. A 0.1 M pH 7.0 PBS was used in all electrochemical studies unless otherwise stated.

All electrochemical experiments were carried out on a CHI 660D electrochemical workstation (Shanghai CH Instrument Co. Ltd., China) using a three electrode system with a GCE or modified GCE as the working electrode, a saturated calomel electrode (SCE) as reference electrode and a platinum electrode as counter electrode. Scanning electron microscopic (SEM) measurements were carried out on a scanning electron microscope (JEOL, JSM-6700F) at 15 kV. The chemical composition in samples were investigated by an energy dispersive X-ray spectroscopy (EDS) attached to JSM-6390A SEM. X-ray diffraction (XRD) observations were performed using a Rigaku D/max 3C diffractormeter with curved graphite crystal filtered Cu-Kα radiation ($\lambda = 0.15418$ nm). All the electrochemical experiments were conducted at room temperature ($25 \pm 2\,^{\circ}C$).

2.2. Preparation of the PtNPs modified electrode

GCE of 3-mm diameter, before use, was first polished to a mirror-like with 1.0, 0.3 and 0.05 mm Al_2O_3 slurry on a polish cloth, and rinsed with double-distilled water, then ultrasonic treat in ethanol and double-distilled water for 5 min, respectively. The modified process was illustrated in Scheme 1. The first step was the preparation of nanoZnO/GCE: NanoZnO electrodeposits were grown in Multi-Potential Steps method mode at 60 °C in an aqueous solution composed of 0.1 M $ZnCl_2$ with 0.1 M potassium chloride (KCl) as supporting electrolyte under oxygen bubbling. For comparison purpose, electrodeposition was also conducted at the same condition without oxygen bubbling. The second step was the preparation of CuNPs/nanoZnO/GCE: this process was conducted by potentiostatic deposition at −0.5 V for 120 s in an aqueous solution composed of 0.01 M $Cu(NO_3)_2$ with 0.1 M KCl. The third step was the formation of Pt nanomaterials: A template-engaged replacement reaction between the deposited CuNPs and the aqueous H_2PtCl_6 solution was carried out. Multi-Potential Steps method mode was employed to assist the formation of PtNPs at the nanoZnO/GCE according to gas bubble dynamic template method. The PtNPs/nanoZnO/GCE was as stored at 4 °C when not in use.

3. Results and discussion

3.1. Fabrication and characterization of the PtNPs/nanoZnO/GCE

Fig. 1 showed the electrochemical records of each modified step during the fabrication process. The first stage of Multi-Potential Steps method for the deposition of nanoZnO (Fig. 1A) was a nucleation process. When a more negative potential was applied, a remarkable current increase (starting from 2400 s) was observed due to the fast growth of nanoZnO. The current reduce of the Cu deposition indicated the successful composition (Fig. 1B) of CuNPs. The first stage of Multi-Potential Steps method for PtNPs deposition (Fig. 1A) was a template-engaged replacement reaction process. A more negative potential provided a hydrogen gas bubble dynamic template for the subsequent deposition of PtNPs (Fig. 1C).

The fabrication of the PtNPs/nanoZnO/GCE was further characterized by SEM, EDS and XRD. SEM was used to confirm the deposition and measure the size as well as the spatial distribution of the deposited NPs. The morphology of nanoZnO was parallel arrangement nanovalley, as shown in the Fig. 2A. The intermont and surface of the ZnO nanovalleys were porous structure with diameters of 100–200 nm (shown in the Fig. 2C and D). EDS of nanoZnO (Fig. 2E) indicated that the produce was composed of Zn and O without any other metal catalysts or additives. The formation mechanism of ZnO parallel arrangement nanovalley may follow a self-catalyzed growth mechanism [27]. Without the oxygen bubbling, the colour of the production was dinginess (Fig. 2B inset, gray black) comparing with the typical reaction (Fig. 2A inset, tattletale gray). The morphology of the produce was mainly even dispersed thin foliage nanosheets with width range from 0.1 to 0.2 μm and the length range from 9 to 10 μm.

Indium oxide glass (ITO) has many other advantages [28] such as good conductive ability, high optical transmittance, a robust nature, the ability for easy patterning, and an excellent adhesion property to substrates, which make it as an ideal matrix for SEM imaging. Herein, ITO (Hebei Lingxian Gaoke Co. Ltd.) was used as the substrate for the investigation of the morphology and ingredient. Before use, it was cleaned by sonicate treatment sequentially for 20 min in acetone, 10% KOH in ethanol and distilled water. With the deposition of CuNPs, flowers-like structure in the form of clusters distributed over the entire surface of the nanoZnO (as shown in Fig. 3A). Besides a little amount of Cl of electrolyte

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