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Oxidation and sensing of ascorbic acid and dopamine on self-assembled gold nanoparticles incorporated within polyaniline film

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ABSTRACT

Electrochemical biosensors based on conducting polymers incorporated with metallic nanoparticles can greatly enhance sensitivity and selectivity. Herein, we report a facile fabrication approach for polyaniline (PAN) incorporated with a gold nanoparticle (AuNP) composite electrode by electrodeposition of PAN on a self-assembled AuNP layer on the surface of an indium tin oxide electrode. The resulting AuNP/PAN composite electrode exhibits a remarkable synergistic effect on the electrocatalytic oxidation of ascorbic acid (AA) and dopamine (DA). It is demonstrated that the oxidation reaction of AA mainly occurs at AuNPs inside the PAN film as the ascorbate anions are doped into the polymer during the oxidation of the PAN film. Conversely, the oxidation of positively charged DA may only take place at the PAN/solution interface. The different mechanisms of the electrode reactions result in the oxidation of AA and DA occurring at different potentials. As a result, the AuNP/PAN composite electrode can be employed to simultaneously detect AA and DA with a good linear range, high sensitivity, and low detection limit.

1. Introduction

Incorporation of metallic nanoparticles in conducting polymers has attracted significant attention, due to the strong electronic interaction between the nanoparticles and polymer matrices. This may lead to the properties of the composite expected to be different from those of the polymers or metal particles [1,2]. Among the conducting polymers, polyaniline (PAN) has been extensively studied and proven to have a large number of applications in nanoelectronics, inkjet printing, opto-microelectronics, photonics, chemical and electrochemical sensors [3–5]. Especially, the incorporation of gold nanoparticles (AuNPs) into PAN may lead to a combination of the enviable qualities of both components, such as good stability, high conductivity, as well as pH and redox sensitivity from PAN polymer. Therefore, the gold nanoparticle/polyaniline (AuNP/PAN) composites are of particular interest in chemical and electrochemical sensing. Various methods have been employed for preparing AuNP/PAN composite systems, including autoreduction of metal salts by monomer [6–8], spontaneous reduction by electroactive polymers [9,10], electrodeposition of AuNPs on electroactive PAN electrodes [11,12], direct growth of AuNPs on the surface of PAN membrane [13], use of templates for arranging the nanoscopic metal into spatially well-defined structures [14], and Langmuir–Blodgett technique [15]. Pillalamarri and coworkers [8] synthesized polyaniline nanofibers decorated with noble-metal (Ag or Au) nanoparticles. They demonstrated that the electrical conductivity of the composites increased with the loading of metal in the nanocomposites, up to 50 times greater than that of polyaniline fibers alone. Afzal et al. [16] also demonstrated that AuNPs incorporated in PAN showed considerable effects on the electrical properties of PAN by reducing the charge-trapping centers and increasing conducting channels. Granot et al. [17] compared the thin film electrodes of polyaniline/poly(4-styrene-sulfonate) and AuNP/PAN nanoparticles capped with 2-mercaptoethane sulfonic acid. The charge transport in the AuNP/PAN system exhibited a 25-fold enhancement as compared to the analogous polyaniline/poly(4-styrene-sulfonate) system. The AuNP/PAN system revealed superior function as the catalyst for the electrochemical oxidation of ascorbic acid and the bioelectrocatalytic activation of glucose oxidase, because of high surface area of the assembly and enhanced charge-transport properties of the composite material. By using polystyrene/sulfonated polystyrene core/shell gel particles as templates, Feng et al. [14] successfully synthesized AuNP/PAN composite hollow spheres, which exhibited

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high conductivity and excellent catalytic activity for the oxidation of dopamine. Majumdar et al. [18] reported that AuNPs and PAN synthesized on same cation-exchange resin beads can catalyze the oxidation of glucose to gluconic acid by AuNPs. Thus, it is possible to simultaneously detect the formation of the acid by the color change of PAN. Tian [19] constructed polyaniline/mercaptosuccinic-acid-capped AuNP multilayer films by the layer-by-layer method. Such a film system can electrocatalyze the oxidation of NADH and can be utilized to detect DNA hybridization. On the AuNP/PAN nanotube membrane modified glassy carbon electrodes, as demonstrated by Feng [20], the synergistic effect of the two kinds of nanomaterials could enhance dramatically the sensitivity for the DNA hybridization recognition. Spain also [21] developed a DNA sensor based on the AuNP-modified PAN nanofibres. The AuNPs not only increased the area available for DNA immobilization, but also efficiently decreased the interactions between adjacent PAN chains and/or motional broadening, leading to a wide dynamic range, excellent ability to discriminate DNA mismatches, and a high sensitivity. Hung [22] demonstrated that a strong interaction between AuNPs and polyaniline nanofibers may accelerate the redox reactions for both PAN and AuNPs, and enhance the anodic oxidation of H_2O_2, leading to a fast response time (less than 3 s) and a high sensitivity (8.34 mAM^{-1}) for H_2O_2 sensing. Xiang et al. [23] further immobilized cytochrome C on AuNP/PAN nanosphere composite electrodes by a noncovalent strategy. The modified electrode gave an improved electrocatalytic activity toward the reduction of hydrogen peroxide. By further immobilization of glucose oxidase, the authors prepared bienzymatic glucose biosensors.

Nevertheless, detailed mechanisms of the electrode processes involving PAN and metal nanoparticles have scarcely been investigated in those studies. A better understanding of the mechanisms of the electrochemical reactions on the AuNP/PAN composite electrodes would be desirable for proper design of sensors. In this paper, we demonstrated a facile approach for the fabrication of AuNP/PAN composite electrodes by electrodeposition of PAN on a self-assembled AuNP film to form a layer-by-layer structure. The electroxidation of ascorbic acid (AA) and dopamine (DA) were examined on the modified electrodes. Synergistic effect of AuNP and PAN led to different mechanisms of the electrode reactions for the oxidation of AA and DA. As a result, such AuNP/PAN composite electrodes exhibit satisfactory performance in simultaneous detection of AA and DA.

2. Experimental

2.1. Chemicals

Aniline was purchased from Sinopharm Chemical Reagent Co. Ltd. (China) and distilled prior to its use. DA and polyvinylpyridine (PVP) was obtained from Acros Organics Chemical Company Limited. Other chemicals involved were of analytical grade and used without further purification. Water used throughout all experiments was purified with the Milli-Q system having resistivity greater than 18.2 $\Omega\,cm^{-1}$.

2.2. Apparatus

The SEM images were obtained on a Hitachi S4700 field emission scanning electron microscope at an accelerating voltage of 15 kV. All electrochemical measurements were performed on an Autolab electrochemical station (PGSTAT302N). A standard three electrode cell was used in the experiments with a saturated calomel electrode (SCE) and platinum foil as the reference and counter electrodes, respectively. All electrochemical measurements were performed at ambient temperature.

2.3. Fabrication of PAN/ITO and AuNP/PAN electrodes

A gold colloid was prepared according to the literature protocols [24]. Briefly, a solution of 1% sodium citrate (50 mL) was added to a 500 mL solution containing 240 mg $HAuCl_4$. The mixed solution was heated to boiling and kept under magnetic stirring for 1 hour to produce the AuNP colloid. The derivatization of the surface of an indium tin oxide (ITO) electrode was conducted by immersing the ITO slide into a 2% PVP ethanol solution for 12 h. After being thoroughly washed with ethanol and water, the PVP modified electrode was exposed to a colloidal solution of AuNPs for 6 h to form a layer of the AuNPs on its surface. The resulting electrode was activated between −1.0 and 1.0 V in 0.5 M H_2SO_4. The PAN was then deposited by cycling in a potential range between −0.2 and 1.3 V in a 0.5 M H_2SO_4 solution containing 0.02 M aniline. For comparison, a PAN/ITO electrode was also prepared on a bare ITO electrode under the same conditions.

3. Results and discussion

Polyaniline modification on the AuNP/ITO and ITO electrodes was carried out by potentiodynamic deposition. A series of successive cyclic voltammograms (CVs) of the AuNP/ITO and ITO electrodes was measured in a 0.5 M H_2SO_4 solution containing 0.02 M aniline between −0.2 and 1.3 V, the results are presented in Fig. 1. The distinguishable difference between the behaviors of aniline polymerization on the bare ITO electrode and the AuNP-modified ITO electrode was observed during the initial cycle. The oxidation of aniline started at 1.1 V on the bare ITO electrode, whereas the oxidation on the AuNP/ITO electrode occurred at 0.8 V, along with an anodic peak at 1.133 V. This result indicates that the oxidation of aniline is much easier in the presence of AuNPs, probably due to the strong adsorption of aniline monomers and the catalytic activity of gold cations toward the oxidation of aniline [25,26]. Thus, the AuNPs could be oxidized to form gold cations as the electrode potential is greater than 1.0 V. The resulting gold cations further catalyze the oxidation of aniline to form an oligomer. In the consequent cycles, the electrochemical behavior on both electrodes was quite similar, with the exception of the current on the AuNP-modified electrode being larger than that on the bare ITO electrode (Fig. 1b). Three pairs of well-defined redox peaks with oxidation peaks located at 0.20, 0.47, and 0.66 V can be distinguished. The oxidation peaks at 0.20 V and 0.66 V can be attributed to the oxidation of the leucoemeraldine state to the emeraldine state, and the further oxidation of the emeraldine state to the pernigraniline state, respectively [27]. The intermediate redox pair at 0.47 V has been assigned to the defects in the linear structure of the polymer [28]. The current of these peaks increased with repeated potential cycling, suggesting that the conducting PAN was continually growing at the electrode and the polymer film was in the emeraldine salt state.

The thickness of the PAN film can be well controlled by the growth cycle number. Two electrodes with different thickness of PAN (thin and thick AuNP/PAN electrodes) were obtained after 5 and 20 continuous polymerization growth cycles, respectively. The electrodes were removed from the solution and completely washed with water. Then, the CVs of both electrodes were measured in a solution containing 0.1 M H_2SO_4; the results are shown in Fig. 1d. Three characteristic pairs of redox peaks of PAN can be clearly observed with oxidation potentials at ca. 0.2, 0.45, and 0.6 V, respectively, corresponding to the interconversion among various oxidation states such as leucoemeraldine (fully-reduced form), emeraldine (half-reduced form), and pernigraniline base (fully-oxidized form) [29]. The larger current for AuNP-modified ITO electrode corresponds with a larger amount of PAN. In addition,