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A nonenzymatic electrochemical nitrite sensor based on Pt nanoparticles loaded $Ni(OH)_2$/multi-walled carbon nanotubes nanocomposites

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ABSTRACT

In this paper, a sensitive novel non-enzymatic nitrite electrochemical sensor based on Pt nanoparticles loaded $Ni(OH)_2$/Multi-Walled Carbon Nanotubes nanocomposites (Pt/$Ni(OH)_2$/MWCNTs) was described. The composition and morphology of the Pt/$Ni(OH)_2$/MWCNTs were characterized by transmission electron microscope and investigated energy dispersive X-ray spectra respectively. Results showed that the Pt nanoparticles could be anchored on the surface of the $Ni(OH)_2$/MWCNTs uniformly through a simple reduction process. The electrochemical investigation of the sensor revealed that the Pt/$Ni(OH)_2$/MWCNTs exhibited remarkable electrocatalytic performance toward nitrite oxidation, with a sensitivity of 145 μA mM^{-1} cm^{-2} and a low detection limit of 0.13 mM. Moreover, the obtained Pt/$Ni(OH)_2$/MWCNTs modified GCE with excellent reproducibility and selectivity also allows for practical application. It is expected that the combination of noble metal with $Ni(OH)_2$/MWCNTs could be expanded to enhance the catalytic performances of nanocomposites and used for the construction of high-sensitive electrochemical sensors.

1. Introduction

Nitrite is extensively present in food, fertilizers and corrosion inhibitors, and many other fields. However, nitrite is an inorganic pollutant to the environment and human health [1]. Specially, the concentration level of nitrite is a very significant parameter for environmental and biological safety. For one thing, excessive nitrite in the human body can lead to hemoglobin irreversible oxidation, and reduce the blood capacity. For another, nitrite interacts with amines to convert into carcinogenic nitrosamines, resulting in serious hazards to human and animal health, such as cancer and hypertension [2–4]. Therefore, it is of great importance to develop an efficient method for the detection of nitrite level with high sensitivity and simple operating procedures to overcome the traditional complex pre-treatments. Nonenzymatic electrochemical sensors based on the direct oxidation or reduction of analytes have recently been advocated due to its simple operation, fast responses, variable sensitivity, good selectivity, and excellent reliability [5–7]. However, the detection of nitrite is easily influenced by other electroactive species that could be more easily oxidized, because of the electrochemical oxidation of nitrite usually involves a relatively high overpotential. To improve the electrocatalytic properties of nitrite sensor, various nanomaterials-based modified electrodes, such as metals, metal oxides, and carbon materials, have been developed for sensitive and selective nonenzymatic nitrite sensing [8–11].

Nanostructured carbon materials as one of the promising active materials for sensors and biosensors have been widely investigated, such as activated carbon, carbon nanotubes (CNTs), and graphene. Among various nanostructured carbon materials, the Multi-Walled Carbon Nanotubes (MWCNTs) has been widely recognized that the conductive supports due to the specific surface area, high electrical conductivity, good chemical stability and easy availability, which can greatly improve the electrochemical performance of catalysts [12–15]. Recently, transition metallic NPs, including gold (Au) [16], silver (Ag) [17], palladium (Pd) [18], and platinum (Pt) [19], have been applied widely to improve the performances of non-enzymatic electrochemical sensors due to the special electrochemical catalytic activities. Yang et al. made a novel three dimensional (3D) ternary Pt nanodendrite/reduced graphene oxide/MnO_2 nanoflower (Pt/RGO/MnO_2) nanomaterials for the determination of dopamine (DA) in the presence of ascorbic acid (AA) and uric acid (UA). The modified electrode shows excellent selectivity and sensitivity [20]. Unnikrishnan et al. fabricated the polydiphenylamine-Pt (PDPA-Pt) composite by electrochemical method on glassy carbon electrode. The composite film showed excellent electrocatalytic activity toward the oxidation of nitrite. In addition, the PDPA-Pt film modified GCE is used for nitrite determination in various water samples [21]. Xiao et al. developed a novel nonenzymatic glucose sensor based on PtM (M = Ru, Pd and Au) nanoparticles on the composite surface of multi-walled carbon nano-

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tubes-ionic liquid by using ultrasonic-electrodeposition method. The results showed that the PtRu(1:1)-MWNT-IL modified electrode had larger active surface and higher electrocatalytic activity toward glucose oxidation in neutral solutions [22]. Through a microwave irradiation polyol method, Kivrak et al. prepared carbon supported Pt-MnO_x and Pt catalysts for the oxidation of hydrogen peroxide (H_2O_2) [23]. Liu et al. have presented a simple approach to synthesize the Fe_3O_4@Pt core-shell nanocomposites for oxidation of nitrite. For the materials, Pt shell could provide more electro-catalytic activity based on larger surface area of the magnetic Fe_3O_4 core [24]. Among the reported in the literature, Pt is an attractive inorganic material for electrode materials because of its easy preparation and high catalytic ability.

Herein, to enhance the loading of Pt nanoparticles, we firstly deposited the $Ni(OH)_2$ on conductive Multi-Walled Carbon Nanotubes (MWCNTs), then the Pt nanoparticles loaded on the surface of $Ni(OH)_2$/MWCNTs nanocomposites through a mild reduction reaction. Nickel hydroxide is an attractive catalyst and supporting materials due to its well-defined electrochemical redox activity, low cost and various morphologies. It is expected that the $Ni(OH)_2$ works as catalyst support can enhance the electrocatalytic activity of nanocomposites [25–27]. However, the low conductivity of these metal compounds will constrain electrolyte ion and electron transfer and further affect their electrochemical performances. So, the MWCNTs were directly coupled with $Ni(OH)_2$ to configure carbon nanohybrids. The coating of $Ni(OH)_2$ onto MWCNTs facilitates improve the specific surface area of the nanohybrids and the number of active sites for metals nanoparticles generation, meanwhile, the CNT as a conductive networks enhances electron transfer and increases the conductivity of electrode material [28,29]. The electrocatalytic performances of the synthesized catalysts were evaluated by nitrite oxidation. As an active catalyst, the Pt/$Ni(OH)_2$/MWCNTs nanocomposites exhibits admirable catalytic activity to the electrochemical detection of nitrite with excellent sensitivity, selectivity and desirable detection limits. In addition, it was also applied in milk samples effectively.

2. Experimental section

2.1. Materials

Carboxylic multiwall carbon nanotubes (MWCNTs, purity > 95%) and Sodium hexachloroplatinate (IV) hexahydrate ($Na_2PtCl_6{\cdot}6H_2O$) was from Aladdin Industrial Corporation (Shanghai, China). Nickel(II) nitrate hexahydrate ($Ni(NO_3)_2{\cdot}6H_2O$), urea (CH_4N_2O), ethylene glycol ($C_2H_6O_2$), sodium hydroxide (NaOH) and sodium nitrite ($NaNO_2$) were all obtained from were purchased from Xi'an Chemical Reagent (Xi'an, China). Chitosan (CS, MW 5–6 × 10^5, > 90% deacetylation) was purchased from Shanghai Yuanju Biotechnology Co., Ltd. (Shanghai, China). And other reagents and chemicals were also all of analytical grade and used without further purification. A fresh solution of $NaNO_2$ was prepared daily. The 0.1 M phosphate buffer solution (PBS, pH 7.4) was employed as a supporting electrolyte in electrochemical experiments.

2.2. Apparatus

Transmission Electron Microscope (TEM) analysis was performed by Tecnai G2 F20 S-TWIN (FEI, USA). Energy Dispersive X-ray (EDX) spectra were obtained with a Field Emission Scanning Electron Microscopy (FESEM; Carl Zeiss SIGMA). X-ray Photoelectron Spectroscopy (XPS) analysis was measured on an ESCALAB MK II X-ray photoelectron spectrometer using Mg as the exciting source.

Electrochemical experiments were carried out with a CHI 660 electrochemical workstation (Shanghai CH Instrument Co. Ltd., China) in a conventional three-electrode system. A conventional three-electrode cell was used, including a modified glassy carbon electrode (GCE) as the working electrode, the saturated calomel electrode (SCE) as the reference, and a platinum wire as the auxiliary electrode. In this work, all potentials were referred to the saturated calomel electrode. All electrochemical experiments were conducted at room temperature.

2.3. Formation of the Pt/$Ni(OH)_2$/MWCNTs nanocomposites

For the typical synthesis of the $Ni(OH)_2$/MWCNTs nanocomposites, 20 mg of MWCNTs was dispersed in 10 mL of distilled water and ultrasonicated for 1 h. Then 0.7269 g $Ni(NO_3)_2{\cdot}6H_2O$ and 3 g urea were added in the above carbon dispersion solution under violently magnetic stirring, respectively. After which, the mixed solution was transferred to a round-bottomed flask, heated to 80 °C in an oil bath and held for 2 h under continuous stirring. Afterwards the obtained solution was cooled naturally to room temperature and aged overnight. The synthesized nanocomposites was separated by centrifugation, washed with excess deionized water and ethanol, and dried in an oven at 60 °C for 12 h.

The Pt nanoparticles were synthesized through a mild reduction reaction with ethylene glycol as a reducing agent. Typically, 10 mg $Ni(OH)_2$/MWCNTs nanocomposites can be well dispersed in 20 mL ethylene glycol (EG) by ultrasonic treatment for 1 h. 0.5 mL $Na_2PtCl_6{\cdot}6H_2O$ was added the above solution drop by drop under stirring. The pH value of this mixture was then adjusted to 12.5 with NaOH aqueous solution. Subsequently, the above mixture was transferred into a round-bottomed flask and refluxed at 140 °C. After the mixture was stirred for 3 h, the resulting precipitates were collected via centrifugation and washed with deionized water and ethanol several times. The product was dried in an oven at 60 °C for 12 h.

2.4. Preparation of Pt/$Ni(OH)_2$/MWCNTs nanocomposites modified electrode

A glassy carbon electrode (GCE) was cleaned by polishing with alumina powder followed by ultrasonic treatment in deionized water and ethanol. An amount of 1 mg of the catalyst was dispersed in 1 mL of 0.5% chitosan solution ultrasonically. After that, 10 μL of the above suspension was dropping on the glassy carbon electrode surface and drying at room temperature. The prepared electrode was denoted as Pt/$Ni(OH)_2$/MWCNTs/GCE. The electrochemical active surface area was calculated as 0.126 cm^2 based on the Randles–Sevčik equation.

3. Results and discussion

3.1. Synthetic route and characterization of Pt/$Ni(OH)_2$/MWCNTs nanocomposites

The Pt/$Ni(OH)_2$/MWCNTs nanocomposites were prepared by using a two-step method. The scheme for the Pt/$Ni(OH)_2$/MWCNTs preparation is shown in Fig. 1. At first, Ni^{2+} ions are preferentially anchored on the surface of carboxylic MWCNTs. After the addition of urea solutions, ammonia is released and OH^- ions are generated. Then, the OH^- ions precipitate Ni^{2+} to form $Ni(OH)_2$ on the surface of MWCNTs. Finally, the Pt NPs were further decorated on the $Ni(OH)_2$/MWCNTs by using Na_2PtCl_6 as a Pt source in an ethylene glycol reduction.

The structure and morphology of MWCNTs, $Ni(OH)_2$/MWCNTs and Pt/$Ni(OH)_2$/MWCNTs were examined by transmission electron microscopy (TEM). These CNTs have hollow tubular morphological features and smooth walls with outer diameters of about 10–20 nm (Fig. 2A). Fig. 2B and C display the TEM images of $Ni(OH)_2$/MWCNTs nanocomposites. It can be observed that the CNTs show a rough surface and the tube structures become not very clear. The diameter of $Ni(OH)_2$/MWCNTs nanocomposites increases obviously. These indicated that the thin layer of $Ni(OH)_2$ was successfully coated on the nanotube structure. The small sized Pt nanoparticles are dispersed uniformly on the $Ni(OH)_2$/MWCNTs surface as shown in Fig. 2D, and the Pt nanoparticles possess an average size of around 6 nm. Fig. 2E shows