



Synthesis of hollow Pt–Ni–graphene nanostructures for nonenzymatic glucose detection



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ABSTRACT

A novel, graphene-supported, and hollow Pt–Ni nanostructure (denoted as hollow Pt–Ni–graphene nanocatalyst) was synthesized using a galvanic replacement approach at ambient temperature. The prepared nanostructures were characterized by transmission electron microscopy (TEM), energy-dispersive spectroscopy (EDS), X-ray powder diffraction (XRD), and X-ray photoelectron spectroscopy (XPS). The electrocatalytic characteristics of the nanostructures pertaining to the oxidation of glucose were evaluated by voltammetry. The results demonstrated that the hollow Pt–Ni–graphene nanocatalysts demonstrate superior electrocatalytic performance in comparison with the solid Pt–Ni–graphene electrocatalysts. A nonenzymatic amperometric glucose sensor was developed using the hollow Pt–Ni–graphene nanostructure as the electrode material. The sensor exhibited good electrocatalytic activity toward the oxidation of glucose and had a rapid response (ca. 2 s), low detection limit (ca. 2 μM), wide linear range (0.5–20 mM), and high sensitivity (ca. 30.3 $\mu\text{A mM}^{-1} \text{cm}^{-2}$), as well as good stability and repeatability. Additionally, the common interfering species, such as ascorbic acid (AA), uric acid (UA), and 3,4-dihydroxyphenylacetic acid (DOPAC) did not cause any interference due to the use of a low detection potential (–0.35 V vs. SCE). Furthermore, the sensor was successfully applied to the determination of glucose concentration in human serum samples.

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1. Introduction

Glucose detection plays an important role in the fields of clinical diagnostics, food and textile industries, environmental monitoring, and others [1–3]. Significant research and effort have been devoted to preparing glucose sensors with high sensitivity, high reliability, fast response, and good selectivity. Many techniques have been used to measure glucose concentration, including infrared spectroscopy [4], Raman spectroscopy [5], fluorescence [6], electrochemiluminescence [7], electrochemical methods [8], and others. Among these various techniques, electrochemical glucose sensors, especially amperometric biosensors, have been widely used because of their high reliability, high sensitivity, low cost, and ease of use [9,10]. Due to their high selectivity and sensitivity, most previous glucose amperometric biosensors are enzymatic and are usually based on glucose dehydrogenase (GDH) or glucose oxidase (GOx) [11–13]. However, the greatest drawback of enzymatic glucose sensors is the lack of stability that originates from their intrinsic dependence on enzyme activity [14,15].

To address this limitation, major research efforts have been devoted to developing nonenzymatic biosensors that rely on the direct current response of glucose oxidation at the electrode surface [16,17]. Many nonenzymatic glucose sensors have been explored, especially Pt-based amperometric glucose sensors [18–20]. However, these pure Pt electrodes often have drawbacks of high cost, low sensitivity, and poor stability caused by surface contamination originating from adsorbed chloride ions and chemisorbed intermediates of glucose oxidation [21]. Additionally, these electrodes often suffer from interference from other electroactive species during electrochemical detection of glucose under physiological conditions [22].

One method that has been demonstrated to improve catalytic activity and to lower cost is the alloying of platinum with other transition metals. Many Pt-based binary catalysts, such Pt–Pd [23,24], Pt–Ru [25], and Pt–Ir [26] have been developed to enhance the amperometric response of glucose oxidation and lower the interference from other electroactive species. It has been reported that alloying Pt with other metals can alter the electronic configuration of Pt and weaken the interaction between the Pt and the intermediate; thereby, enhancing its catalytic performance [27–29].

Moreover, the catalytic activity of these materials is highly dependent on surface areas, surface atomic structures, crystal

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sizes, and shapes [30,31]. By controlling the sizes and shapes of the catalysts, large surface areas and abundant catalytic active sites can be realized, thereby favoring enhanced catalytic performance and improving the Pt utilization efficiency [32,33]. Therefore, many efforts have been devoted to shape- and size-controlled syntheses to develop high performance Pt-based catalysts. Several different morphologies of Pt-based nanostructures, such as mesoporous Pt [21], Pt nanoflowers [34], Pt nanotubules [35], and pinecone-shaped Pt–Pb nanostructures [36], have been successfully synthesized and used for nonenzymatic glucose detection.

Among the various morphologies of nanomaterials, hollow nanostructures have attracted considerable interest due to their high specific surfaces, low densities, and intriguing catalytic activities [37,38]. In our previous study [39], we developed a facile method to prepare graphene-supported hollow Pt–Ni nanospheres (denoted as hollow Pt–Ni–graphene). We found that the novel nanostructures exhibit enhanced electrocatalytic performance toward a methanol oxidation reaction compared to solid Pt–Ni–graphene. In this work, we have found that our hollow Pt–Ni–graphene nanostructures also exhibit high electrocatalytic activities, as well as excellent selectivity and stability for glucose detection compared with a number of electrode materials that have been studied previously [23–26]. It is thought that this results from the synergistic contribution of graphene and the unique hollow structure of the Pt–Ni nanoparticles.

2. Experimental section

2.1. Chemicals

Graphene oxide (GO, Nanjing XFNANO Materials Tech Co., Ltd.), K_2PtCl_6 (Sinopharm Chemical Reagent Co. Ltd.), $NiCl_2 \cdot 6H_2O$ (Shanghai Chemical Reagent Co. Ltd., Shanghai, China), $NaBH_4$ (Shanghai Chemical Reagent Co. Ltd.), poly(vinyl pyrrolidone) (PVP, $M_w \approx 10,000$, Aldrich), and β -D-glucose (Aldrich–Sigma) were used as received. The stock glucose solution was allowed to mutarotate for at least 24 h before use. All other chemicals were of analytical grade or better. All solutions were prepared with double-distilled water. A phosphate buffer solution (PBS, 0.1 M, pH 7.4) was made from Na_2HPO_4 and NaH_2PO_4 .

2.2. Preparation of the hollow Pt–Ni/graphene nanostructures

The hollow Pt–Ni–graphene nanostructures were synthesized via the reduction of GO and metal salt precursors [39]. In a typical preparation, $NiCl_2 \cdot 6H_2O$ (7.1 mg) and PVP (200 mg) were dissolved in 40 mL of a GO suspension (0.5 mg/mL, suspended in water) and were stirred vigorously at ambient temperature. Then, 30 mL of freshly prepared $NaBH_4$ solution (1 mg/mL) was added drop-wise into the mixture. After a few minutes, 30 mL of K_2PtCl_6 solution (3 mM) was slowly added into the system (the molar ratio of the $PtCl_6^{2-}/Ni^{2+}$ was 3:1). To avoid oxidation of the newly formed Ni nanosheets, high-purity N_2 was bubbled into the solution during the reaction. The mixed solution was stirred for 1 h at ambient temperature. The products were collected by centrifugation, washed sequentially at least three times with double-distilled water, and dried in vacuum at ambient temperature.

For comparison, the graphene-supported solid Pt–Ni nanocatalysts (denoted as solid Pt–Ni–graphene) were also synthesized using previously published procedures [28]. Their electrocatalytic characteristics toward glucose oxidation were measured and compared with those of the hollow Pt–Ni–graphene nanocatalysts.

2.3. Apparatus and procedures

The morphology of the nanostructures was confirmed by transmission electron microscopy (TEM), which were carried out on a JEOL-2100F transmission electron microscope operating with an accelerating voltage of 120 kV. The samples were prepared by dispersing the nanostructures in ethanol and evaporating one drop of the suspension onto a carbon-coated film supported by a copper grid for TEM measurements. The composition of the prepared hollow Pt–Ni–graphene was analyzed using energy-dispersive spectroscopy (EDS). The EDS data were measured with an Oxford Link ISIS energy-dispersive spectrometer on the microscope. The crystalline structures of the prepared nanostructures were examined by X-ray diffraction (XRD, Rigaku/Max-3A X-ray diffractometer) with $Cu K\alpha$ radiation ($\lambda = 0.15418$ nm). The surface characteristics of the nanocatalysts were examined by X-ray photoelectron spectroscopy (XPS), which were measured on an ESCALAB 250 XPS spectrometer (VG Scientific) using the monochromatic $Al K\alpha$ line at 1486.6 eV. The binding energies were calibrated with respect to the C 1s peak at 284.6 eV. The peak fit analysis was performed using the XPS PEAK program (version 4.0).

The electrochemical measurements were performed with a CHI 660B electrochemical workstation (CH Instruments). A conventional three-electrode system was used with a glassy carbon (GC) electrode (3 mm in diameter) as the working electrode. A coiled Pt wire and a saturated calomel electrode (SCE) were used as the counter electrode and the reference electrode, respectively. Prior to use, the GC electrode was polished sequentially with alumina grain sizes of 0.3 μm and 0.05 μm to create a mirror finish. The electrode was then sonicated with absolute ethanol and double-distilled water for approximately 1 min, rinsed thoroughly with double-distilled water and dried under ambient temperature. A 6 μL suspension of hollow Pt–Ni–graphene nanocatalysts (2 mg mL^{-1}), which was prepared by sonicating the nanocatalysts in water for 30 s, was cast onto the surface of the GC electrode with a microsyringe, and the solvent was allowed to evaporate at ambient temperature before use. The buffer was purged with high-purity nitrogen for at least 30 min prior to each electrochemical measurement, and the nitrogen environment was then kept over the solution to protect the solution from oxygen. Amperometric detection was performed under an applied potential of -0.35 V. The solution was continuously stirred using a magnetic bar at a speed of 250 rpm. All electrochemical measurements were performed at ambient temperature (22 ± 1 °C).

3. Results and discussion

3.1. Synthesis of characterization of the hollow Pt–Ni–graphene nanostructures

Graphene-supported Pt–Ni nanocatalysts can be synthesized with GO, Ni^{2+} , and $PtCl_6^{2-}$ as precursors. When $NaBH_4$ is introduced into the mixture, the GO is reduced to graphene and the Ni^{2+} ions to Ni nanosheets. The Ni nanosheets deposit on the graphene surface. With the addition of $PtCl_6^{2-}$, the hollow Pt–Ni nanostructures are formed due to a displacement reaction between the Ni nanosheets and $PtCl_6^{2-}$ ions. The morphology of the hollow Pt–Ni–graphene nanocatalysts were characterized by TEM. The image recorded at lower-magnification indicates that the products are well-dispersed on the graphene surface (Fig. 1A), and the diameter of the nanospheres is approximately 30 nm (Fig. 1B). The hollow architecture is clearly revealed by the contrast between the shells and hollow interiors. It can be seen from Fig. 1B that the shell seems to be rough, incomplete, and porous. This feature endows the nanocatalysts with a large surface area and high accessibility to guest species.

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