



Assembly of graphene and nickel nanoparticles on anion exchange resin microspheres for the amperometric detection of carbohydrates in combination with capillary electrophoresis



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ABSTRACT

Graphene and nickel nanoparticles (NiNPs) were assembled on anion exchange resin (AER) microspheres based on the electrostatic interaction between graphene oxide sheets and AER and the subsequent chemical reduction. The prepared AER@graphene–NiNP composite core–shell microspheres were characterized by scanning electron microscopy, energy dispersive spectroscopy, X-ray diffraction, and Fourier transform infrared spectroscopy. Moreover, they were embedded in the bores of pipette tips to fabricate electrodes. The performance of the novel electrodes was demonstrated by measuring sucrose, glucose and fructose in combination with capillary electrophoresis. The three analytes were well separated within 8 min in a 40 cm long capillary at a separation voltage of 12 kV. The graphene–NiNP composite microsphere electrodes exhibited higher sensitivity ($213.578\text{--}317.064\text{ nA mM}^{-1}$), lower detection limits ($0.75\text{--}1.05\text{ }\mu\text{M}$) and enhanced separation efficiency in the detection of these carbohydrates. The advantages of the electrodes include ease of fabrication, low cost and pronounced electrocatalytic activity toward carbohydrates, indicating great promise for a wide range of applications.

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1. Introduction

Since Novoselov and Geim successfully isolated and characterized graphene in 2004, it became a rising star in the carbon family owing to its unique structure and excellent chemical and physical properties [1,2]. It has been employed to fabricate electrochemical sensors and biosensors because of its high electric conductivity and electrocatalytic activity [3,4]. The existing fabrication methods of the graphene-based electrodes include surface modification [5,6], electrochemical deposition [7], in situ polymerization [8,9], magnetic loading [10], paraffin oil mixing [11], etc.

Ion-exchange resins can be classified into cation exchange resins and anion exchange resins (AERs) [12]. Graphene oxide (GO) is basically a single atomic layer of carbon covered with carboxyl, carbonyl, epoxy, and hydroxyl groups [13]. AER microspheres contain positive charged groups that can capture negatively charged GO sheets on their surface based on electrostatic interaction. In a previous report, we assembled graphene on AER microspheres to fabricate electrodes for sensing some bioactive substances [14]. However, the electrodes cannot be employed in the direct detec-

tion of carbohydrates. Because carbohydrates can be oxidized on nickel-base electrodes in alkaline solution, it is of high interest to coat AER microspheres with graphene–nickel nanoparticle (NiNP) composite to fabricate microsphere electrodes for the sensitive measurement of carbohydrates.

In 2011, Escarpa et al. prepared nickel nanowires by electrodeposition [15]. The magnetic nanowires were loaded on screen-printed carbon electrodes with the aid of magnets for the determination of several carbohydrates. Moreover, NiO nanoparticles [16] were also employed to modify electrodes for sensing carbohydrates. In 2012, Qiao and Zheng modified the nanocomposite of $\text{Ni}(\text{OH})_2$ and graphene on glassy carbon electrodes to prepare a nonenzymatic glucose sensors [17]. Recently, Qu et al. loaded graphene–nickel nanoparticle (NiNP) hybrid on the surface of a magnetic electrode for measuring carbohydrates [10]. In 2014, Escarpa et al. modified carbon electrodes with copper nanowires for the sensitive determination of carbohydrates in honeys in combination with microchip electrophoresis [18]. All the detection electrodes were prepared by surface modification.

In this work, graphene and NiNPs were assembled on AER microspheres based on the electrostatic interaction and the following chemical reduction. The prepared AER@graphene–NiNP composite microspheres were embedded in the bores of pipette tips to fabricate the detection electrodes of capillary electrophoresis (CE). The

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NiNPs assembled on the AER microspheres exhibited higher electrocatalytic activity toward the oxidation of carbohydrates while graphene improved the electron transduction so that their current responses were significantly enhanced.

2. Experimental

2.1. Reagent and solutions

Nickel(II) sulfate hexahydrate ($\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$), graphite powder (granularity, $\leq 30 \mu\text{m}$), sodium nitrate, potassium permanganate, hydrogen peroxide solution (30 wt.%), hydrazine hydrate (85% w/w), strongly basic quaternary ammonium-type polystyrene AER in chloride form (717; granularity, 0.3–1.2 mm), glucose, fructose, sucrose and paraffin oil were all purchased by SinoPharm (Shanghai, China). The separation medium of CE was 75 mM NaOH aqueous solution.

2.2. Preparation of NiNPs

NiNPs were prepared by the reaction between an aqueous solution (20 mL) of $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ (2.62 g, 10 mmol) and a mixture solution of 4 mL of hydrazine hydrate (85% w/w) and 25 mL of 1 M NaOH aqueous solution at 80 °C for 30 min. The black gray NiNPs were separated and dried under vacuum.

2.3. Preparation of AER@graphene–NiNP composite core–shell microspheres

In this work, a previously reported method was employed to prepare oxidized graphite [11]. To prepare GO solution, 200 mg oxidized graphite was dispersed in 100 mL doubly distilled water and sonicated in an ultrasonic cleaner (SKQ-2200, frequency 56 kHz, 100 W) for 1 h to exfoliate it to GO sheets. And then, AER microspheres (2.0 g) were dispersed in 40 mL of 1 mg mL⁻¹ GO solution containing 200 mg NiNPs in a glass beaker with the aid of ultrasonication. After 0.8 mL of hydrazine hydrate (85 wt.%) was added, the beaker was put on a hot plate while the solution was gently shaken. The surface temperature of the hot plate was adjusted to be ~300 °C. About 10 min later, the AER microspheres coated by graphene–NiNP composite were collected and washed with doubly distilled water. Finally, they were dried under an infrared lamp. For comparison, graphene-coated AFR microspheres were also prepared following the same procedures except no NiNP was added in the reaction mixture. Standard sieves were employed to separate the prepared microspheres with the diameter of ~800 μm for fabricating electrodes. Graphene was also prepared by reducing GO sheets with hydrazine [19].

2.4. Fabrication of graphene–NiNP composite microsphere electrode

The fabrication procedures of graphene–NiNP composite microsphere electrode are illustrated in Fig. S1 (Supplementary Information). A piece of AER@graphene–NiNP composite core–shell microsphere was pressed into a polypropylene pipette tip (1 mL, bore diameter, ~700 μm) until half of the microsphere protruded outside. And then, a piece of 0.5 mm diameter tin-coated copper wire was employed to connect the conductive microsphere to the electrochemical instrument with the aid of a piece of trapezoidal silicon rubber holder. For comparison, NiNP paste electrode was also fabricated. NiNP powder was mixed with paraffin oil at a weight ratio of 3:1 on a glass plate. And then, the paste was filled in to the suction nozzles of a polypropylene pipette tip (1 mL, bore diameter, ~700 μm) to a height of 5 mm. And then, a piece of 0.5 mm diameter copper wire was inserted into the pipette tip

until its end touched the packed NiNP paste for electrical contact. Finally, the paste electrode was smoothed on a piece of weighing paper to get a flat surface.

2.5. Apparatus

The CE system with an amperometric detector used in this work has been described in our previous reports [11]. A ± 30 kV high-voltage DC power supply (Shanghai Institute of Nuclear Research, China) provided a separation voltage between the two ends of the capillary. The inlet of the capillary was held at a positive potential while the outlet of capillary was maintained at ground. The separations were carried out in a piece of 40 cm long fused silica capillary (25 μm I.D., 360 μm O.D., Polymicro Technologies, USA). A three-electrode electrochemical cell consisting of a detection electrode, a platinum auxiliary electrode, and a saturated calomel electrode (SCE) as the reference electrode, was used in combination with a BAS LC-4C amperometric detector (Bioanalytical Systems Inc., West Lafayette, IN, USA). The detection electrode was positioned carefully opposite the outlet of the capillary with the aid of a micromanipulator (CORRECT, Tokyo, Japan) and arranged in a wall-jet configuration. The distance between the tip of the working electrode and the capillary outlet was adjusted to ~50 μm . Cyclic voltammetry (CV) was performed using a CHI 660D electrochemical analyzer (CH Instruments, Austin, USA) in combination with the three-electrode electrochemical cell mentioned above.

The surface morphologies and energy dispersive spectroscopy (EDS) spectra of the prepared materials were measured by using a scanning electron microscope (PHILIPS XL 30, Eindhoven, The Netherlands). X-ray diffraction (XRD) measurements were carried out using a Rigaku D/max-rB diffractometer (Rigaku, Tokyo, Japan) with CuK-1 radiation (40 kV, 60 mA). The Fourier transform infrared (FT-IR) spectra of GO, graphene, NiNPs, and graphene–NiNP composite were obtained using a FT-IR spectrometer (NEXUS470, NICOLET).

2.6. Sample preparation

After the stones of red dates (purchased from a local supermarket) were removed, they were pulverized using a motor-driven blade grinder. About 3.0 g of the sample was weighed accurately and homogenized in 100 mL of doubly distilled water with the aid of a bar-type ultrasonic processor (FS-600N, frequency 20 kHz, 600 W). The homogenate was diluted to 250 mL and filtered through a filter paper. The filtrate was further diluted with 75 mM NaOH aqueous solution at a ratio of 40 (1–40) for subsequent CE analysis.

2.7. CE Procedures

Before use, the separation capillary was rinsed with 75 mM NaOH aqueous solution for at least 10 min. Subsequently, the capillary was conditioned at a voltage of 12 kV between its two ends for 10 min. Both the separation and injection voltages were 12 kV for convenience. The potential applied to the working electrode was 0.65 V (vs. SCE). Samples were injected electrokinetically at 12 kV for 6 s.

3. Results and discussion

In this work, AER microspheres were employed for the assembly of graphene sheets and NiNPs. They comprise divinylbenzene-cross-linked polystyrene bearing strongly basic quaternary ammonium groups (Fig. S2 Supplementary Information). When AER microspheres were dispersed in NiNP-containing GO solution,

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