Facile synthesis and enhanced catalytic performance of reduced graphene oxide decorated with hexagonal structure Ni nanoparticles

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GRAPHICAL ABSTRACT
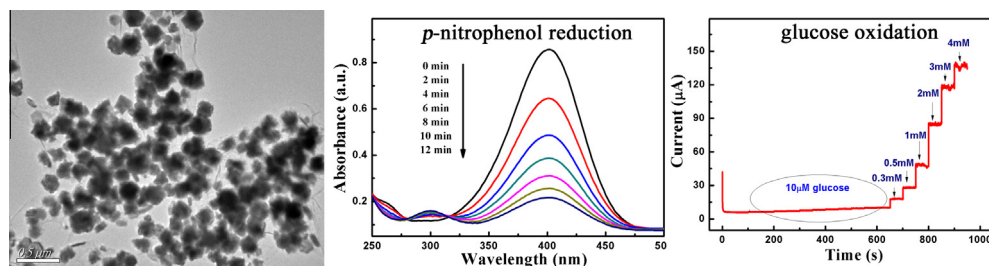
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ABSTRACT

In this study, reduced graphene oxide (RGO) supported Ni nanoparticles were synthesized by a facile in-situ refluxing approach using triethylene glycol as both reductive and dispersing agent. The as-synthesized RGO/Ni nanocomposites were characterized by X-ray diffraction, Raman spectroscopy and transmission electron microscopy, which revealed that Ni nanoparticles with hexagonal close-packed structure were homogeneously dispersed on the surface of RGO sheets. The catalytic activity and electrochemical properties of the RGO/Ni nanocomposites were investigated. It is found that the RGO/Ni nanocomposites exhibit markedly enhanced catalytic activity toward the reduction of p-nitrophenol by $NaBH_4$, which is comparable to noble metal catalyst. The RGO/Ni nanocomposites also exhibited excellent electrocatalytic response to glucose. The linear range, detection limit and sensitivity were estimated to be 0.01–3.0 mM ($R^2 = 0.997$), 2.8 μM and 535.258 μA mM^{-1} cm^{-2}, respectively. It is expected that this facile method presented here could be extended to synthesize other RGO/metal nanocomposites with various functions.

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1. Introduction

In recent years, the research on the catalysis of metal nanoparticles has been developing at an extraordinary pace due to their high density of states near Fermi levels [1,2]. Noble metal nanoparticles are of particular interest in catalysis due to their high chemical stability and catalytic activity [3]. However, high cost and a finite availability of noble metals strongly limit their practical catalytic applications. Thus, in order to avoid the usage of noble metals, non-precious transition metal catalysts become the first choice in many catalytic processes. Among them, nickel metal has received much attention because of its potential applications in hydrogen storage, electrochemical capacitors, magnetic devices, microwave absorption, as well as catalysis in various chemical reactions [4–8]. Notably, to maximize the catalytic activity of nickel metal, loading the nickel nanoparticles on the suitable supporting materials is highly desirable [9].

Over the past two decades, carbon nanomaterials as the solid supports to disperse and stabilize the metal nanoparticles in catalytic process have received a great attention by the researchers. Since its discovery in 2004, graphene has initiated an explosive interest as one of the ideal support among all the carbonaceous materials due to its outstanding properties, such as unique sheet structure, extremely large surface area, high mechanical stiffness, as well as superior chemical stability [10–12]. The synergetic effects between graphene and nanomaterials can enhance the catalytic properties and improve the functionalities of the graphene-based nanocomposites [13–16]. Up to now, some investigations have been done on the synthesis of graphene supported nickel nanoparticles for improving the properties of nickel metal. However, despite the significant efforts, there still exist some challenges and problems in the study of graphene/Ni nanocomposites: (i) many of the synthesis approaches to graphene/Ni nanocomposites suffer from the use of hazardous or toxic reducing agents, and their use should be avoided in the large-scale production. (ii) The nickel nanoparticles supported on graphene are mainly face-centered cubic structure, hexagonal close-packed structure Ni is rarely reported. Specifically, Yang and co-workers established a facile chemical approach to grow hexagonal close-packed Ni nanocrystals on graphene, which exhibit excellent microwave absorbability [17]. However, an organic stabilizer (octadecylamine) is required during the procedure, and the catalytic properties of the as-prepared graphene/Ni nanocomposites are not studied yet. Therefore, it is desirable to develop an environmentally friendly and facile approach to prepare hexagonal close-packed nickel supported on graphene with excellent catalytic properties.

Very recently, we have developed an in-situ reduction approach for the synthesis of RGO-supported and wrapped nickel nanoparticles with face-centered cubic structure, which show enhanced catalytic properties [18]. Continuing with this line of research, in the present manuscript we present a facile refluxing approach for the synthesis of RGO supported hexagonal close-packed Ni nanoparticles using triethylene glycol as both reductive and dispersing agent. In addition, the catalytic properties of the RGO/Ni nanocomposites in the reduction of *p*-nitrophenol by NaBH₄ and electrocatalytic oxidation of glucose are systematically investigated.

2. Experimental

2.1. Materials

Natural flake graphite (45 μm, 99.95%) was obtained from Aladdin Industrial Corporation (Shanghai, China). All of the other reagents employed in this study are commercially available analytical-grade and used as received without further purification. Graphite oxide was synthesized by the oxidative treatment of natural flake graphite using a modified Hummers method reported previously [19,20].

2.2. Preparation of RGO/Ni nanocomposites

In a typical procedure to synthesize the RGO/Ni nanocomposites, 25 mg of graphite oxide was dispersed in 50 mL of triethylene glycol by ultrasonication to form a homogeneous dispersion. Subsequently, 0.3 g of nickel acetylacetonate was added to the above system. After stirring for about 15 min, the resulting mixture was then transferred into a 100 mL round-bottomed flask and heated at 270 °C under magnetic stirring for 1 h. The solid products were separated by centrifugation, washed thoroughly with water and ethanol to remove any impurities, and then dried in a vacuum oven at 45 °C for 12 h. RGO/Ni nanocomposites with different Ni loadings were prepared by simply varying the feed amount of

nickel acetylacetonate with other experimental conditions unchanged. The obtained samples were denoted as RGO/Ni-0.2 and RGO/Ni-0.35 for feeding 0.2 and 0.35 g of nickel acetylacetonate, respectively. Pure RGO and Ni were also obtained through a similar procedure in the absence of nickel acetylacetonate and graphite oxide, respectively.

2.3. Instrumentation and measurements

Powder X-ray diffraction (XRD) measurements were carried out on an X-ray diffractometer (Shimadzu XRD-6100 Lab) with Cu Kα radiation (λ = 1.5406 Å) at a scanning rate of 5° min⁻¹. The morphology and size of the products were examined by transmission electron microscopy (TEM) and high resolution TEM (HRTEM, JEOL JEM-2100). The loading amounts of Ni in the RGO/Ni nanocomposites were evaluated by an inductively coupled plasma-optical emission spectrometer (ICP-OES, Vista-MXP, Varian). Raman scattering was collected at room temperature using a DXR Raman spectrometer with 532 nm laser source from an Ar⁺ laser. The X-ray photoelectron spectroscopy (XPS) measurements were performed by using a Thermo ESCALAB 250XI spectrometer. Ultraviolet–visible (UV–vis) spectroscopy measurements were recorded with a UV-1800PC UV–vis spectrophotometer.

2.4. Catalytic reduction of p-nitrophenol

In a typical procedure, the aqueous solutions of *p*-nitrophenol (10 mM) and NaBH₄ (1.0 M) were freshly prepared. Then, 5 mg of catalysts and 2 mL of NaBH₄ solution were added to 100 mL of distilled water under magnetic stirring. After stirring for about 15 min, 0.5 mL of 4-NP solution was then added to start the reaction. The reaction was carried out at room temperature with continuous stirring until the deep yellow color of the solution became colorless. During the reaction process, a small portion of the reaction mixture was quickly withdrawn from the reaction system, followed by measuring UV–vis absorption spectra of the solution to monitor the concentration of *p*-nitrophenol through its absorption peak at 400 nm.

2.5. Electrocatalytic experiments

The electrocatalytic properties of the RGO/Ni nanocomposites toward glucose were carried out on a beaker-type three-electrode setup using a CHI 760D electrochemical analyzer (Chen Hua Instruments, Shanghai, China) at room temperature. Platinum wire, saturated calomel electrode (SCE) and glassy carbon (3 mm in diameter) coated with nanocomposites were used as counter electrode, reference electrode and working electrode, respectively. Before surface modification, the glassy carbon electrode was polished with 1.0, 0.3, and 0.05 μm alumina powders sequentially, followed by sonication in ethanol and distilled water successively. Then the washed glassy carbon electrode was dried at room temperature and ready for modification. To obtain the RGO/Ni nanocomposites modified glassy carbon electrode, 5.0 mg of RGO/Ni powder and 20 μL of Nafion solution (5 wt%, Alfa Aesar) were dispersed in 1.0 mL of ethanol and ultrasonicated for 30 min to form a homogeneous catalyst ink. A total of 6 μL of the RGO/Ni dispersion was dropped on the clean surface of glassy carbon electrode and was allowed to dry in ambient air. Using the modified RGO/Ni working electrode, cyclic voltammetry was conducted in an aqueous solution with an electrolyte of 0.1 M NaOH at room temperature. The cyclic voltammetry measurements required operation of the electrode in a range of potential of 0.1–0.6 V versus SCE. Amperometric measurements were performed by successive injection of a certain concentration of