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One-pot preparation of Ni-graphene hybrids with enhanced catalytic performance

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ABSTRACT

A facile *one-pot* method was developed to synthesize magnetic nickel nanoparticles (Ni NPs) decorated on reduced graphene oxide (rGO) with $NaHB_4$ as a reductant under microwave irradiation. The morphologies and structures of the Ni-rGO hybrids were investigated by electron microscopy, thermal gravimetric analysis, X-ray photoelectron spectroscopy, X-ray diffraction, Raman spectroscopy and magnetic measurements. The results showed that Ni-rGO hybrids composed of the well-dispersed Ni NPs with an average diameter of 12 nm were successfully prepared. To demonstrate one potential application, the catalytic ability of Ni-rGO was evaluated and it was found that Ni-rGO showed much enhanced catalytic ability, good recyclability and stability toward the catalytic reduction of *p*-nitrophenol to *p*-aminophenol. The excellent catalytic activity of Ni-rGO hybrids was due possibly to the synergistic effect of Ni NPs and rGO, including the uniform distribution of Ni NPs onto rGO, enhanced electrons separation and transport, as well as the fast *adsorption* of *p*-nitrophenol by rGO.

1. Introduction

Graphene, a monolayer of sp^2-bonded carbon atoms packed into a two-dimensional (2D) honeycomb lattice, has recently attracted tremendous attention owing to its high specific surface area, excellent mobility of charge carriers, high chemical stability, and exceptional thermal, electrical and mechanical properties [1]. In order to further optimize the properties and broaden the applications of graphene, various metal (Ag, Au, Pt, Pd, Ni, Cu) and metal oxide (ZnO, TiO_2, Co_3O_4, Fe_3O_4) nanoparticles (NPs) have been successfully decorated on graphene to form graphene-NPs hybrids [2–7]. It was suggested that these graphene-NPs hybrids can further enhance the overall properties and may introduce new functionalities due to the strong synergistic effect of the two components.

Ni NPs with well-defined and controlled shape have attracted ever increasing attention in metal based nanomaterials [8,9]. When anchoring Ni NPs onto graphene or reduced graphene oxide (rGO), Ni-rGO hybrids further enhance the properties of Ni NPs and show great prospects in biosensor [10], catalysis [11], lithium ion batteries [12], hydrogen production [13], and water remediation [14] owing to their large surface area, high catalytic activity and satisfactory magnetic properties. Currently, their fabrication has become a topic of scientific and technological importance. Various techniques have been developed to synthesize the Ni-rGO hybrids. For instance, Li et al. [15] prepared Ni-rGO hybrids by the simultaneous hydrazine reduction of GO and $NiCl_2$ under the hydrothermal conditions. Ray et al. [16] reported a biomimetic method for synthesizing the Ni-rGO from the petals of lotus and hibiscus flowers by heating the original petals and petals soaked in $NiCl_2$ solution at high temperatures of 800–1600 °C. Guerra et al. [13] employed a deposition–precipitation method to fabricate a thermally rGO-supported Ni NPs with different Ni morphologies. Niu et al. [17] synthesized a series of Ni-rGO hybrids through a simple solvothermal method. Wu et al. [18] fabricated heterostructured Ni-rGO hybrids through a combined electrostatic-induced spread and *in situ*-reduction growth process. However, most of these methods involve unavoidable disadvantages such as sophisticated procedures, long preparation time, and high temperature treatment, which are tedious and low yielding, limiting the practical applications of Ni-rGO on a large scale.

Microwave irradiation (MWI) assisted methods have been used to synthesize a number of nanomaterials, as they offer many advantages, including fast and simple procedure, heating homogeneity, high energy efficiency, and low-cost, as compared with the conventional solvothermal methods [19]. The MWI has been successfully applied in the synthesis of rGO [20–22] and a variety of

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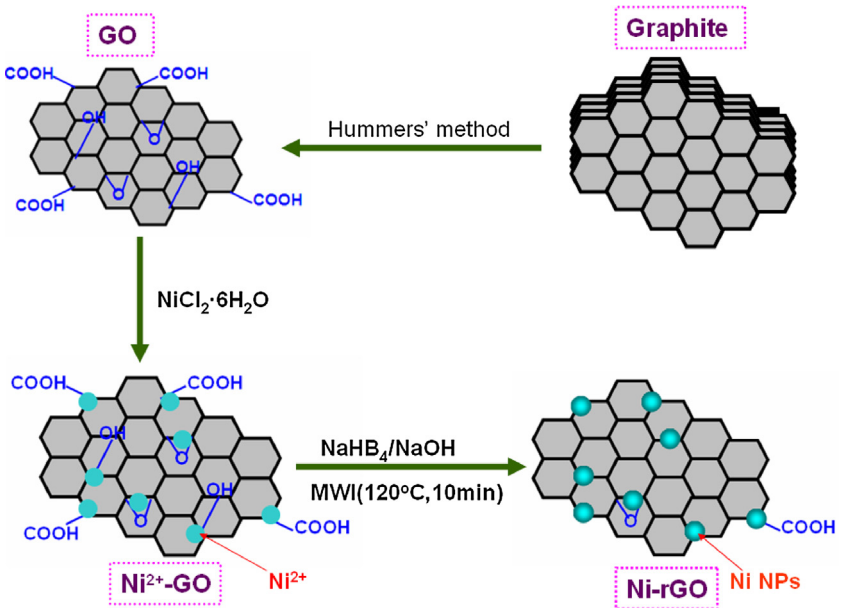

Fig. 1. Schematic diagram of the synthesis procedure of Ni-rGO.

graphene-NPs hybrids [23–26]. On the other hand, hydrazine is the widely used reduction agent for GO and Ni salts [11]. Even though the reductive ability of hydrazine is very effective, it is severe poisonous and potentially explosive. Besides, the side reaction may occur during reduction, which raises electrical resistance in several orders [27]. Sodium borohydride ($NaBH_4$) is a powerful reducing agent to reduce Ni precursor to Ni NPs [28], and it has also been well used to prepare rGO that exhibited a higher electrical conductivity and lower hetero-carbon content compared to hydrazine [29]. Therefore, $NaBH_4$ maybe a good reductant candidate for preparing Ni-rGO hybrids.

Herein, we report a rapid one-step synthesis of Ni-rGO by MWI treatment, with the use of $NaBH_4$ as reducing agent. Scanning electron microscopy (SEM), transmission electron microscopy (TEM), *high-resolution transmission electron microscopy* (*HRTEM*), thermal gravimetric analysis (TGA), X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD) and Raman spectroscopy were used to characterize the morphology and structure of prepared Ni-rGO hybrids. To demonstrate one potential application, the catalytic performance of Ni-rGO hybrids was examined compared to bare rGO and pure Ni NPs toward the catalytic reduction of *p*-nitrophenol to *p*-aminophenol.

2. Experimental

The chemical agents are of analytical grade and were used as received without further purification. GO was prepared from the nature graphite flakes (Qingdao Dongkai Grapite Co., Ltd.) according to the modified Hummers' method [30]. Ni-rGO hybrids were prepared through a *one-pot* way by MWI treatment of Ni^{2+}-GO-$NaHB_4$ mixtures under alkaline condition, as illustrated in Fig. 1. 50 mg of GO powder was dispersed in 100 mL of water by sonication for 1 h to form a stable GO colloid, followed by the addition of 0.2 g of $NiCl_2{\cdot}6H_2O$ with sonication for another 10 min. Then, 3.5 mL of $NaHB_4$ (10 mM) was added into the above solution with adjusting the pH value to 11 by 0.2 M of NaOH solution. After sonication for 30 min, the above suspension was sealed in a quartz tube, and it was treated at 120 °C for 10 min in a microwave oven (800 W maximum power input). After that, the quartz tube was put into the ice water (0 °C) for fast cooling down. Finally, the solid products were separated by centrifugation, washed with ethanol and water, respectively, and dried at 60 °C overnight under vacuum. Bare rGO and Ni NPs were also respectively synthesized with the same method without adding Ni salt or GO.

The morphology of the samples was determined by SEM (JSM-7401F), TEM, and *HRTEM* (*JEM-2100*). The XRD patterns were collected by a Bruker D8 Advance diffractometer using Cu Kα radiation. TGA was conducted using a Q50 TGA Instrument. XPS measurements were carried out on a PHI 5000 C ESCA system. Raman spectra were collected on a Raman spectroscope (Alpha 300R, WITEC). The magnetic properties of the samples were measured with a vibrating sample magnetometer (VSM).

The catalysis of the Ni-rGO, Ni NPs and rGO was evaluated by the reduction of *p*-nitrophenol to *p*-aminophenol with the use of $NaBH_4$ as reaction reductant at room temperature. In brief, 2 mL of *p*-nitrophenol solution (3 mM) was dispersed in 100 mL water, followed by addition of 1.5 mL of $NaBH_4$ (1 M). Then, 30 μL of catalyst (1 mg/mL) was added to the above solution to start the reaction under slow stirring. The yellow color of the solution became less intense, and the reaction process was monitored at a regular time interval of 30 min by UV–vis spectrophotometer through its absorption peak at 400 nm. The recyclability of the Ni-rGO was also evaluated. In each cycle, the catalyst was collected by a magnet after the reaction.

3. Results and discussion

The general formation mechanism of Ni-rGO hybrids by our method is as follows, as illustrated in Fig. 1. It is known that the abundant negatively charged functional groups on the basal plane and edges of the GO provide multiple sites for binding Ni^{2+} ions to form Ni^{2+}-GO complex through electrostatic force [31–33]. After introducing $NaHB_4$ under MWI treatment in alkaline medium, the strong reducing ability of $NaHB_4$ ensures simultaneous reduction of GO and Ni^{2+} ions according to the following reaction.

$$4Ni^{2+} + GO + BH_4^- + 8OH^- \xrightarrow{120\,^{\circ}C} 4Ni + rGO + BO_2^- + 6H_2O \quad (1)$$

Consequently, Ni^{2+} ions are *in situ* reduced to Ni NPs, while GO is reduced to rGO at the same time to form Ni-rGO.

The morphologies and structures of as-prepared GO and Ni-rGO were investigated by SEM/TEM/HRTEM, as shown in Fig. 2. SEM