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Short communication

In-situ preparation of three-dimensional Ni@graphene-Cu composites for ultrafast reduction of Cr(VI) at room temperature

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ABSTRACT

Novel three-dimensional Ni@graphene-Cu composites were synthesized by a facile calcination method for the first time. The *in-situ* generated graphene played an important role in the successful fabrication of Ni@graphene-Cu that it acted both as an effective reductant to achieve the conversion of CuO to Cu nanoparticles (NPs) and as an ideal support to prevent the agglomeration of Cu NPs. The as-prepared Ni@graphene-Cu showed excellent catalytic activity for Cr(VI) reduction to Cr(III) at room temperature with formic acid as reductants.

1. Introduction

Hexavalent chromium (Cr(VI)) is a carcinogenic and mutagenic pollutant, which is frequently found in wastewater, possibly stemming from pigment production, metal plating, and leather tanning, etc. [1–3]. However, Cr(III) is relatively inert, nontoxic, and convinced to be an essential element to human metabolism [4]. Thus, the conversion of Cr(VI) to Cr(III) is an important subject in the field of inorganic pollutants elimination. Recent studies showed that Cr(VI) can be reduced to Cr(III) using various reductive agents, such as Fe(0), organic compounds, HCOOH and so on [5]. At the same time, metal nanoparticles (NPs) based materials were developed as effective catalysts for Cr(VI) reduction. For example, Omole et al. [6] first reported the reduction of Cr(VI) to Cr(III) using colloidal Pd as a catalyst and HCOOH as a reductant at 45 °C. Dandapatet et al. [1] demonstrated that Pd-γ-Al_2O_3 can work as a catalyst for the reduction of Cr(VI) with the reaction rate constant of 0.085 min^{-1} at 50 °C. And Ni-RGO can also be utilized as a catalyst for Cr(VI) reduction at 25 °C according to Bhowmik et al. [7]. Nevertheless, the search for advanced catalysts for Cr(VI) reduction with relatively simple fabrication process and high activity is still underway.

Cu-based catalysts have attracted great attention due to their relatively low price, non-toxicity as well as high catalytic activity [8,9]. However, Cu NPs is unstable and prone to be oxidized and agglomerate in air, which limits its practical application. In recent years, graphene has attracted considerable interest owing to its high conductivity, fast mass and electron transport kinetics, and large specific surface area [10–12]. Our previous studies have already demonstrated that the combination of graphene with metal NPs such as Cu [13] and Pt [14] not only solved the metal NPs agglomeration problem, but also showed high catalytic activity. Herein, based on the good properties of Cu NPs and graphene, a novel high-efficient and magnetically separable Ni@graphene-Cu (Ni@GE-Cu) catalyst was fabricated and applied in the reduction of Cr(VI) to Cr(III). First, the three-dimensional (3D) Ni@GE composites were synthesized by the Ni-catalyzed glucose-blowing method we previously reported [15]. Then, the growth of the outer Cu NPs was accomplished by one-step calcination process. The introduction of graphene membrane in Ni@GE composite was aimed to act as a reductant for the conversion of CuO to Cu NPs as well as a support for Cu NPs to prevent the agglomeration. The results demonstrated that the as-prepared Ni@GE-Cu was an effective catalyst for Cr(VI) reduction, and the catalytic efficiency is much better than that of other reported CuNi nanoalloy [16] and Copper-organic cationic ring catalysts [17].

2. Experimental

2.1. Preparation of Ni@GE-Cu

The synthetic route of Ni@GE-Cu was illustrated in Fig. 1. A series of Ni@GE-Cu composites with a different Cu content (55, 65, 75, 85 and 95 wt.%) were synthesized *via* a facile calcination method and denoted as Ni@GE-Cu_x (x = 0.55, 0.65, 0.75, 0.85 and 0.95, respectively). A typical procedure was as follows: 0.02 g of Ni@GE composites [15] was dispersed into 60 mL of ethanol with sonication for 5 min while 0.24 g

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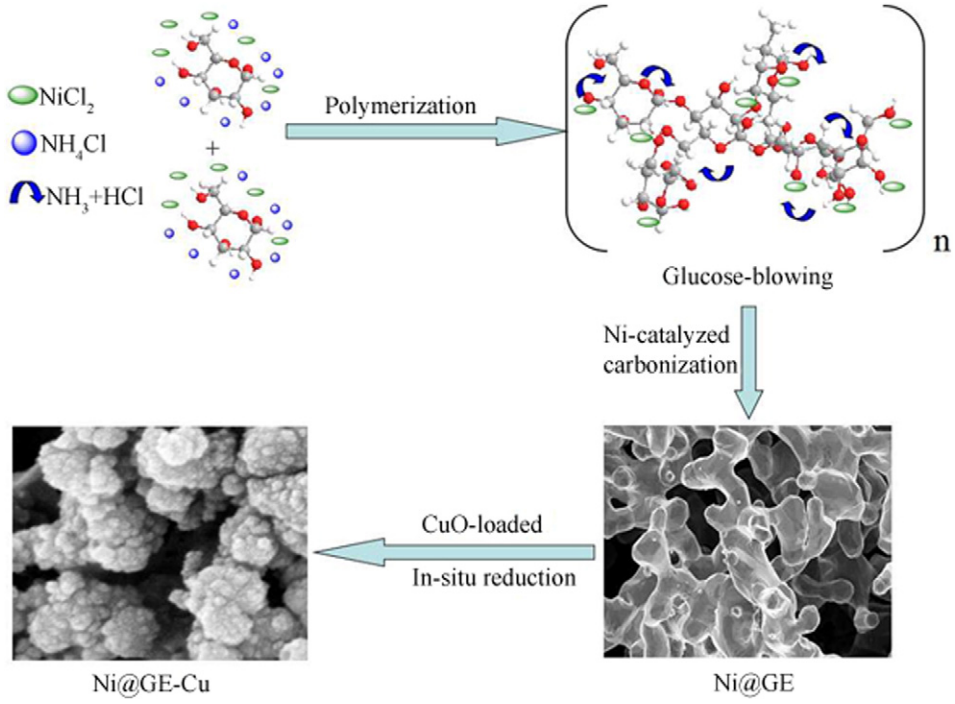

Fig. 1. Schematic illustration of Ni@GE-Cu fabrication.

of $Cu(NO_3)_2 \cdot 3H_2O$ was dissolved in 10 mL of ethanol. After the above two systems were mixed and stirred for 2 h, the pH of the reaction mixture was adjusted to 10 by NaOH (6 M) then stirred for another 2 h at 40 °C. The obtained precursor was washed with deionized water and ethanol, then vacuum dried at 60 °C. The sample, denoted as Ni@GE-$CuO_{0.75}$, was heated to 560 °C with a heating rate of 4 °C/min under N_2 atmosphere and maintained for 1 h to yield the *in-situ* growth of Cu NPs-embedded Ni@GE sample, which was denoted as Ni@GE-$Cu_{0.75}$. Additionally, the synthesis methods of bare Ni and Cu NPs, Cu-GE and Ni@GE composites have been provided in Supplementary material (S1–S3). For comparison, the obtained Ni@GE samples were etched by 3 M HCl and denoted as E-Ni@GE.

2.2. Characterization

The structure of the samples was analyzed by powder X-ray diffraction (XRD, Bruker D/max 2500 PC), Raman spectroscopy (Raman, Renishaw RM1000-Invia), field emission scanning electron microscopy (FESEM, SAPPHIRE SUPRA55) and transmission electron microscopy (TEM, JEOL JEM-2100). The content of Nickel and Copper in Ni@GE-Cu composites was indirectly determined by an inductively coupled plasma-atomic emission spectrometer (ICP, Analytik Jena AG novAA 300). The reduction of Cr(VI) ions was monitored by measuring the absorbance values at various intervals of time using a UV–visible spectrometer (UV–Vis, DDR UV2700) at room temperature (25 °C).

2.3. Catalytic activity measurement

Typically, 50 mL of reaction solution was prepared by mixing 49 mL of $K_2Cr_2O_7$ solution (100 mg/L) with 1 mL of HCOOH (88 wt.%). The concentrations of $K_2Cr_2O_7$ and HCOOH are 0.34 mM and 500 mM, respectively. The pH of the reaction mixture was adjusted by NaOH solution to be 2, 4 and 6, respectively, and almost no changes of pH was detected during each reaction process. The absorption spectrum of the as-prepared solution was recorded and regarded as 0 min data. Subsequently, 4 mg of catalyst powder was added to the mixture, and the absorption spectra were recorded at 1, 3, 6, 9, 12, 15 min, respectively.

The turnover frequency (TOF), defined as the number of Cr(VI) that per mole of the catalyst active sites can reduce per minute [18], can be calculated by Eq. (1), where $n(Cr(VI))$ is the mole of Cr(VI) (mol) reduced; $n(CAS)$ is the mole of the catalyst active sites (mol); t is the reaction time (min).

$$TOF = \frac{n(Cr(VI))}{n(CAS) \times t} \quad (1)$$

3. Results and discussion

The morphology of Ni@GE was observed through TEM and FESEM. As shown in Fig. 2a, after calcination process, Ni^{2+} was reduced to nickel skeleton with irregular morphology. The skeleton was enfolded with few-layered graphene converted from glucose-derived polymers [15]. From the HRTEM image of Ni@GE (Fig. 2b), the lattice fringes of Ni with the *d*-spacing of 0.21 nm and few-layered graphene were observed [19]. Moreover, the TEM image of the E-Ni@GE (Fig. 2c) displays the silk veil-like graphene layers in collapsed state due to its low mechanical stability [15,20]. From TEM image of Ni@GE-$Cu_{0.75}$ (Fig. 2d), it could be observed that Cu NPs were uniformly loaded on the outer surfaces of Ni@GE, which could provide active sites for catalytic reaction. Besides, the FESEM image of Ni@GE-$Cu_{0.75}$ (Fig. 2e) also shows that Cu NPs were successfully loaded on the surface of Ni@GE, which is consistent with the TEM result. In addition, the EDS measurement of Ni@GE-$Cu_{0.75}$ showed that the composites contain Ni, Cu, C and O elements (Fig. 2f), which were 14.21%, 74.72%, 9.16%, and 1.91%, respectively. This result provided further evidence for the successful preparation of Ni@GE-$Cu_{0.75}$ composites. In addition, the size distribution histogram of Cu NPs (Fig. S1) showed that the average size of Cu NPs is about 10 nm.

The XRD patterns of Ni@GE, Ni@GE-$CuO_{0.75}$ and Ni@GE-$Cu_{0.75}$ composites are shown in Fig. 3a. The XRD pattern of Ni@GE depicts diffraction peaks at $2\theta = 44.5$, 51.8, and 76.4°, which could be indexed to the (111), (200) and (220) planes of cubic Ni (JCPDS: 04–0850), indicating that Ni^{2+} ion was converted into metallic Ni after calcination [15]. In addition, the presence of diffraction peaks at $2\theta = 32.5$, 35.6, 38.8, 48.8, 53.5, 58.4, 61.6, 65.8, 68.1, and 75.3° corresponds to the