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Graphene sheets/cobalt nanocomposites as low-cost/high-performance catalysts for hydrogen generation

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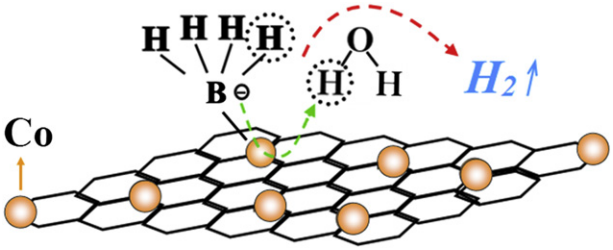
HIGHLIGHTS

- Graphene sheets/cobalt nanocomposites were prepared by a one-step solvothermal method.
- The maximum saturation magnetization value of the composites reached 80.8 emu g^{-1}.
- The graphene support greatly increased the catalytic activity of cobalt.
- An easily removed, recycled and controlled functional filter was obtained.

GRAPHICAL ABSTRACT



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ABSTRACT

The production of clean and renewable hydrogen through the hydrolysis of sodium borohydride has received much attention owing to increasing global energy demands. Graphene sheets/cobalt (GRs/Co) nanocomposites, which are highly efficient catalysts, have been prepared using a one-step solvothermal method in ethylene glycol. Co^{2+} salts were converted to Co nanoparticles, which were simultaneously inserted into the graphene layers with the reduction of graphite oxide sheets to GRs. The as-synthesized samples were characterized by X-ray diffraction, Fourier transform infrared spectra, Raman spectroscopy, field emission scanning electron microscopy, transmission electron microscopy, high-resolution transmission electron microscopy and vibrating sample magnetometer. The maximum saturation magnetization value reached 80.8 emu g^{-1}, meaning they are more suitable for magnet-controlled generation of H_2 than noble metal catalysts. The catalytic activity of the composite was investigated by the hydrolysis of sodium borohydride in aqueous solution both with and without a GRs support. It was found that the high electronic conductive GRs support increased the hydrogen generation rate (about two times) compared with pure cobalt. The improved hydrogen generation rate, low cost and uncomplicated recycling makes the GRs/Co nanocomposites promising candidates as catalysts for hydrogen generation.

1. Introduction

Hydrogen has been considered as a clean and environmental benign fuel and received much concern for a long period. It is expected to be widely used in heating, electricity generation, mechanical power and transportation [1,2]. There are many ways to obtain hydrogen, such as water electrolysis [3], ethanol steam reforming [4], hydrolysis of hydrazine borane [5] and sodium borohydride ($NaBH_4$) [6], etc. In particular, the hydrolysis of $NaBH_4$

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is regarded as an efficient way to generate hydrogen owing to its high hydrogen storage capacity (10.8 wt%), acceptable hydrogen generation rate even at low temperature, and the good stability under ordinary conditions in solid state and solution [6]. During the hydrolysis of $NaBH_4$, the hydrogen generation rate can be controlled by supported catalysts such as platinum [7], gold [8], ruthenium [9] and rhodium [10]. However, the use of the above catalysts is limited due to the high cost. On the other hand, the low cost catalyst (e.g., cobalt) is also widely used in the hydrolysis of $NaBH_4$ [11], but its catalyst activity is much lower than that of noble metal catalysts. To improve the catalyst activity, catalyst support materials with high electric conductivity could be introduced to the catalyst systems.

Graphene, which is a planar monolayer of sp^2-bonded carbon atoms tightly packed into a two-dimensional honeycomb lattice, has drawn tremendous attention since it was isolated in 2004 [12]. Owing to the unique two-dimensional (2D) structure and excellent physical and chemical properties, researchers have made intensive efforts in investigating graphene and its functionalized derivatives in recent years [13,14].

The dispersion of inorganic nanomaterials on graphene, thus forming novel hybrid materials, could lead to a myriad of potential applications [15]. Many graphene-based metal nanocomposites have been synthesized recently. Hu et al. [16] discussed the electrocatalytic activity toward the oxygen reduction and glucose oxidation of a graphene/Au composite that had a higher catalytic activity than Au nanoparticles or graphene alone. Kim et al. [17] investigated the incorporation of Ag-doped graphene into polypyrrole (PPy) and the effect on its electrochemical properties. They found that the Ag nanoparticles deposited onto the graphene improved the electrochemical performance of the catalyst by increasing of the charge transfer between graphene and PPy by the bridge effect. Liu et al. [18] reported that the expandable graphene nanocomposites containing platinum nanoparticles that were synthesized via electrochemical reduction exhibited high catalytic activity and good stability for the oxidation of methanol, which was attributed to the improved electrical conductivity and the high specific surface area of the graphene catalyst support.

In this paper, graphene nanosheets/Co (GRs/Co) hybrids with different proportions of GO and $Co(NO_3)_2{\cdot}6H_2O$ were prepared by a one-step solvothermal method. The catalytic activities of the composites were investigated by the hydrolysis of $NaBH_4$ in aqueous solution. The magnetic properties of the hybrids were also evaluated.

2. Experimental

2.1. Synthesis of GO

All reagents were analytical grade and used as obtained without further purification. GO was prepared using the Hummers' method [19]. In a typical reaction, 4 g of natural flake graphite powder was added to 92 ml of cold (0 °C) concentrated H_2SO_4. $KMnO_4$ (12 g) was then added gradually with stirring and cooling in an ice bath. Then the mixture was stirred at 35 °C for 2 h. Distilled water (184 ml) was slowly added to the mixture and the temperature of the mixture was maintained below 100 °C for 15 min. After that, 560 ml of 30% H_2O_2 solution was added to the mixture. The product was collected by filtration and washed with 1000 ml of 10% HCl aqueous solution to remove metal ions, before a final wash with distilled water. The brown yellow powder of GO thus obtained was dried for hybrid preparation.

2.2. Solvothermal synthesis of GRs/Co hybrids

Various GRs/Co hybrids with different initial $Co(NO_3)_2{\cdot}6H_2O$/GO weight ratios (1:1, 2:1, 3:1, 4:1 and 5:1) were prepared using the solvothermal method. A typical preparation of the GRs/Co hybrid (3:1 $Co(NO_3)_2{\cdot}6H_2O$/GO) was as follows: 55 mg of GO sheets dispersed in 55 ml of ethylene glycol (EG) was sonicated for 30 min. Then, 165 mg of $Co(NO_3)_2{\cdot}6H_2O$, 1.80 g of anhydrous sodium acetate and 0.3 ml of polyethylene glycol (PEG, $M_w = 200$) were added to the suspension, and stirred for 1 h. Subsequently, the slurry was sealed in a Teflon-lined stainless steel bomb (70 ml capacity) and held at 200 °C for 12 h. On cooling to ambient temperature, the product was collected by centrifugation and washed with distilled water and anhydrous ethanol several times. The final product was dried in vacuum at 60 °C for 18 h.

2.3. Hydrolysis of sodium borohydride

The catalytic hydrolysis of $NaBH_4$ was performed at 20 ± 0.5 °C. The 3:1 GRs/Co hybrid (100 mg) was filtered onto filter paper to form a catalytic filter. $NaBH_4$ (568 mg) was dissolved in 100 ml of distilled water. The solution was then flowed through the filter at a rate of 10 ml min^{-1}. The hydrogen gas generated was collected in the water column [20], which was immersed into a measuring cylinder. The amount of hydrogen was recorded with respect to time. As a control group, GRs and Co powders were used in the hydrolysis experiment following the same procedure.

2.4. Characterization techniques

GRs/Co hybrids were analyzed using a laser Raman microscope (InVia-Reflex, Renishaw) with a Raman shift from 1000 to 2000 cm^{-1} using an excitation wavelength of 785 nm. Fourier transform infrared (FTIR) spectra were recorded on a Nicolet NEXUS-670 spectrometer in KBr pellets from 4000 to 700 cm^{-1}. Powder X-ray diffraction (XRD) was carried out on a Rigaku D/max 2550 V X-ray diffractometer using Cu K_α irradiation ($k = 1.5406$ Å). The operating voltage and current were kept at 40 kV and 300 mA, respectively. The particle size and morphology of the as-prepared products were determined at 20 kV by a JSM-6700F field emission scanning electron microscopy (FESEM). Transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) images were collected using a JEOL-2100F electron microscope to determine further details of the as-prepared samples. Magnetic characterization was conducted on a vibrating sample magnetometer (VSM, PPMS Model 6000) in fields from −10 kOe to +10 kOe at 298 K. The cobalt content in the samples was obtained by inductively coupled plasma-atomic emission spectrometer (ICP-AES, Leeman Prodigy).

3. Results and discussion

Fig. 1 shows the XRD patterns of GO and the GRs/Co hybrid with the initial weight ratio of cobalt precursor to GO of 3:1 (3:1 GRs/Co). As shown in line a, the sharp peak at around $2\theta = 10.8°$ (pattern of GO) corresponds to the (001) reflection of GO, indicating that GO forms a well-ordered layered structure [15,21]. In line b, a new peak observed at 24.3° could be attributed to the graphite structure (002) plane of the graphene nanosheets, while the other three peaks match well with the (111), (200) and (220) planes of cubic cobalt (JCPDS card No. 15-0806). The size of the cobalt crystals was calculated to have an average size of 14.91 nm by Scherrer's equation. Furthermore, the (001) reflection peak of layered GO disappeared, which indicates that the layers of GO were exfoliated and the restacking of the GRs produced in the reduction was effectively prevented [22,23]. During the exfoliation of GO sheets, metal ions intercalated into the layered GO sheets and absorbed onto them, and then the GRs/Co hybrids were formed by the