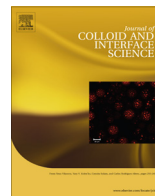




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## Facile reduction of graphene oxide at room temperature by ammonia borane via salting out effect



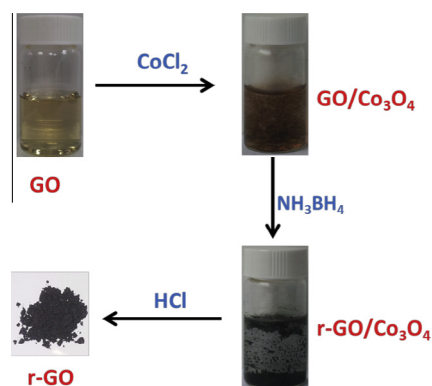
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### GRAPHICAL ABSTRACT

We report an approach to synthesize graphene used  $\text{Co}_3\text{O}_4$  nanoparticles as the catalyst for the hydrolysis reaction of  $\text{NH}_3\text{BH}_3$  to reduce the GO at room temperature.



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### ABSTRACT

Nascent hydrogen as a strong reducing and environmentally benign agent can be used as the efficient reductant of graphene oxide. The common method is to dissolve metal in acid graphene oxide (GO) solution to generate nascent hydrogen and reduce graphene oxide. However, hydrophobic metal particles cannot contact well with hydrophilic GO. Lots of nascent hydrogen atoms generated surrounding metal particles would quickly form hydrogen instead of reducing GO, which results in low reduction efficiency. In this work, based on the salting effect of GO, we report a facile approach to synthesize graphene by mild reducing of GO using  $\text{NH}_3\text{BH}_3$  as the reducing agent and  $\text{Co}_3\text{O}_4$  as the catalyst at room temperature. This method exhibited higher nascent hydrogen reduction efficiency and higher C/O atomic ratio of reduced graphene oxide than using Fe, Zn, and Al among others. Also the reaction is conducted under mild conditions (room temperature), resulting in fewer defects.

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## 1. Introduction

Graphene has attracted much attention due to its unique electronic structure and extraordinary properties for potential applications in nanoelectronics [1–3], sensors [4,5], capacitors [6–9], and hybrid [10,11]. So far, graphene has been prepared by a variety of techniques, such as micromechanical exfoliation of graphite [12], chemical vapor deposition [13,14], chemical reduction of GO [15–20], and epitaxial growth [21]. Compared to other methods, chemical reduction of GO is one of the most efficient approaches to prepare graphene (also called reduced graphene oxide (r-GO)) due to its high production and low cost. To date, GO can be synthesized at large scale from inexpensive graphite powders by Hummers [22] method. GO has abundant functional groups such as epoxide, carbonyl, hydroxyl and carboxy at the edges and in the plane which make it hydrophilic [15]. Due to its solubility and electrostatic repulsion of negative-charged carboxylate groups, GO colloids would form stable liquid crystal in water and a large number of polar organic solvent. However, the contribution is not strong enough to resist the increase of ion strength, because of the screen effect of ions to the electrostatic field [23]. Salting out is an extremely simple method in which a salt is added to an aqueous solution containing a heterogeneous mixture of molecules. As the salt concentration increases, molecules with low solubility precipitate first, due to the lack of available water molecules for dissolution. Like many proteins, GO also has salting out [24,25]. For example, 50 mM NaCl would make GO sheets aggregate [26].

So far, a large number of chemical reductants have been developed for chemical reduction of GO. For example, hydrazine [15] or HI/CH<sub>3</sub>COOH [27] as strong reducing agent were used for the reduction of GO. However, these reductants are either highly toxic or strong corrosive thus limiting their usage. In addition, some other reductants could be used for reduction of GO, such as NaBH<sub>4</sub> [17,28], and sugar [29] L-ascorbic acid [30]. But most of these reaction process should be conducted at a relative high temperature which will result in the increase of the defects in graphene as examined by Raman spectroscopy [30]. In recent years, many works focus on reducing graphene oxide at room temperature by green reductants, especially nascent hydrogen [17,31–33]. Nascent hydrogen is a strong reducing agent and environmentally benign. For instance, Fan et al. used Fe and acid to generate nascent hydrogen to reduce GO [31]. Huang et al. developed similar reduced GO by Zn and HCl [32]. However, hydrophobic metal particles cannot contact well with hydrophilic GO. Much nascent hydrogen atoms generated surrounding metal particles would quickly form hydrogen instead of reducing GO.

Ammonia borane (NH<sub>3</sub>BH<sub>3</sub>) is a stable chemical hydride that has been extensively investigated as a potential hydrogen storage material due to its high hydrogen content (19.6%). The release of hydrogen from NH<sub>3</sub>BH<sub>3</sub> can be obtained through thermal dehydrogenation in solid state [34], and methanolysis [35,36] or hydrolysis [37,38] in solution. Generally speaking, thermal dehydrogenation process requires high temperature and power consumption. In contrast, NH<sub>3</sub>BH<sub>3</sub> can release hydrogen via hydrolysis reaction in the presence of a suitable catalyst (Ru [39], Pd [40], Co [41]) at room temperature.

Herein, based on the salting out effect of GO, we developed a simple method to reduce GO in aqueous solution using NH<sub>3</sub>BH<sub>3</sub> as the reducing agent and Co<sub>3</sub>O<sub>4</sub> as the catalyst. Compared to other existing methods, the merits of this method are: (i) the reducing agent system, NH<sub>3</sub>BH<sub>3</sub> with Co<sub>3</sub>O<sub>4</sub> nanoparticles (NPs), is not explosive, poisonous or corrosive, which is environmentally friendly; (ii) this method exhibits high nascent hydrogen reduction rate; (iii) the reaction is proceeded at room temperature, which brings in few defects during the process of reducing GO.

## 2. Experimental

### 2.1. Materials

GO was prepared from graphite powder by the modified Hummers method [22]. NH<sub>3</sub>BH<sub>3</sub> were purchased from Alfa Aesar. CoCl<sub>2</sub> and hydrochloric acid were obtained from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China).

### 2.2. Reduction of GO

In a typical experiment, firstly, 10 mg of the as-prepared GO were dispersed into 100 mL DI water under mild ultrasonic treatment to obtain a uniform GO aqueous solution (0.1 mg/mL). Then, 10 mL GO solution (1 mg GO) was transferred to a 20 mL vial, and 1 mL of 100 mM CoCl<sub>2</sub> and 10 mg NH<sub>3</sub>BH<sub>3</sub> were added into the solution, respectively. After 1 h reaction, a suspension solution was obtained. The product was harvested by centrifugation and washed by 3% HCl and DI water for 3 times, respectively. Afterwards, the product was put into a plastic centrifuge tube and frozen in a freezer for 24 h, and then it was placed in a vacuum freeze dryer to remove moisture for 72 h to form r-GO powder.

### 2.3. Characterization

UV–Vis detection was carried out on a LAMBDA 750 spectrometer (PerkinElmer). Raman spectra were obtained on a Renishaw Raman spectrometer with 532 nm wavelength incident laser. The morphology of r-GO/Co<sub>3</sub>O<sub>4</sub> and r-GO was characterized by transmission electron microscopy (TEM) (FEI Tecnai G2 F20 S-TIWN) with an accelerating voltage of 200 kV. The composition of the samples was analyzed in an X-ray photoelectron spectrometer (XPS) measurement (Kratos AXIS UltraDLD ultrahigh vacuum (UHV) surface analysis system), with a pass energy of 10 eV, a power of 130 W and the non-monochromatized Al K $\alpha$  radiation (1486 eV). All the samples were analyzed on the central part of the sample, i.e., over a 2 × 3 mm<sup>2</sup> spot area. Binding energies (BE) were corrected by using C1s BE lowest energy to 284.6 eV corresponding to a mixture of sp<sup>2</sup> and sp<sup>3</sup>. For quantification purposes, sensitivity factors were 0.66 for O1s, 0.25 for C1s as supplied by Kratos. In order to measure the reduction efficiency of different methods, an instrument to measure the hydrogen content was designed (Fig. 1) [42]. Firstly, a measured curb full of water is inverted in a basin and one end of a rubber pipe is inserted. After adding CoCl<sub>2</sub> and NH<sub>3</sub>BH<sub>3</sub> into the GO solution, the vial is sealed by a plug connecting another side of rubber pipe. With the reaction

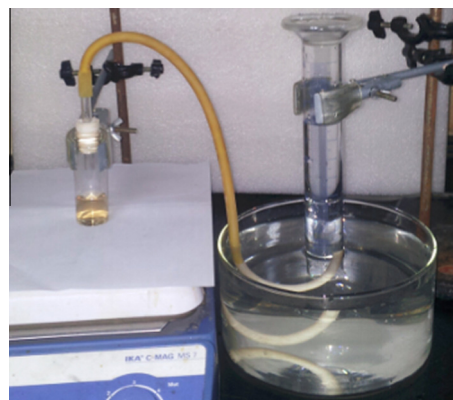


Fig. 1. The instrument to measure the hydrogen contents.

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