

A comparative study of graphene oxide reduction in vapor and liquid phases

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Abstract: Graphene oxide (GO) was reduced by formaldehyde or formic acid in vapor or liquid phases below 200 °C. The influence of the concentrations of reducing agents, reaction temperature and time on the electrical conductivity of the reduced graphene oxide (rGO) was investigated. The rGOs were characterized by XRD, XPS and Raman spectroscopy. Results show that the optimum reaction temperatures are 150 and 175 °C in the vapor phase and the liquid phase, respectively, based on the electrical conductivities of the rGOs. The ratio of the areas of the C1s peaks related to the C-C and C-O (R_{cc/co}) from XPS decreases with reaction time from 9 to 24 h in the vapor phase, and increases from 2 to 24 h in the liquid phase, which are in agreement with the electrical conductivities and Raman results. Gasification of carbon atoms in GO sheets may be responsible for the decrease of R_{cc/co} with prolonged reaction time in the vapor phase.

Key Words: Graphene oxide; Graphene; Formaldehyde; Formic acid

1 Introduction

Graphene, as a two-dimensional hexagonal lattice carbon material, constructed by a single layer of sp² bonded carbon, possesses outstanding properties^[1-4]. With the rapid growth of graphene-based materials in various applications^[5,6], a facile, efficient, inexpensive and eco-friendly method for a large-scale production of graphene is needed. In recent years, both physical and chemical methods have been developed to produce graphene. The micromechanical exfoliation^[4], epitaxial growth^[7] and chemical vapor deposition^[8] can produce high-quality graphene, but the production efficiency is very low. Chemical reduction of graphene oxide (rGO) is another mean to produce graphene in large-scale. The conjugated structures of graphene are partially restored by deoxygenation of graphene oxide (GO) during the chemical reduction^[10] or thermal treatment at high temperature^[9]. Compared with the method of thermal anneal, chemical reduction is usually carried out below 200 °C, which is beneficial for practical applications and considered as the most promising route.

So far, various reducing agents such as hydrazine monohydrate^[10], sodium borohydride^[11], hydroiodic acid^[12], hydroquinone^[13], hydrazine vapor^[12,14] and strong alkali^[15,16] have been explored to prepare rGO, but these reducers will give rise to serious environmental or safety problems because of their strong corrosive, toxic or explosive properties. At present, considerable efforts are being devoted to seeking relatively safe and effective reducing reagents for mass

production of rGO to meet the requirement of various applications. For example, sodium citrate^[17], urea^[18], mitochondrial polypeptide^[19] and sodium ascorbate^[20] have been used as reducing agents to prepare rGO. Compared with the commonly used reducing agent such as hydrazine monohydrate and sodium borohydride, formaldehyde and formic acid as one carbon-containing organic reagents have been used as an effective and relatively mild reductant to prepare metal particles because of their relatively low toxicity and nonexplosive properties^[21,22].

It is well known that physical and chemical properties of rGO are significantly influenced by the reduction degree of GO. Hence, we choose formaldehyde and formic acid as reductants to prepare rGO through the reaction in liquid and vapor phase. The different rGOs prepared at different conditions have also been investigated through X-ray photoelectron spectroscopy (XPS) and Raman spectroscopy. This study may be helpful to choose reaction conditions for adjusting the rGO's properties.

2 Experimental

2.1 Reduction of GO by reducing agents in vapor

The GO was prepared from natural graphite powder (325 mesh) according to the method reported in the literature^[14] (see supporting information). Fig. 1 illustrates preparation of rGO through reduction in vapor. Briefly, 2.0 mg freeze-dried GO on a small Buchner funnel was put into a 20 mL teflon-

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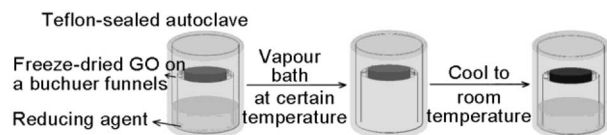


Fig. 1 A schematic illustration of the process in preparation of rGOs in vapor phase.

sealed autoclave, which had been filled with 1.5 mL reducing agents with different concentrations (formaldehyde: 3.5, 6.9, 13.4 mol L⁻¹ and formic acid: 7.6, 13.55, 18.11, 21.5, 23 mol L⁻¹). Commercial formic acid (88%) has a concentration of 23 mol L⁻¹, but commercial formaldehyde solution (38%) is only about 13.4 mol L⁻¹. Then the autoclave was heated at 100-200 °C for 1-24 h in an oven. After the autoclave was cooled to room temperature, the resulting rGOs were washed with ethanol and dried at 50 °C. The obtained rGOs reduced by formaldehyde vapor (rGO-FV) and formic acid vapor (rGO-FaV) at the optimum concentrations of reductants and optimum reaction temperature were defined as rGO-FVn and rGO-FaVn, respectively, where n represents the reduction time in hour. The samples were pressed into thin tablets for electrical conductivity measurement (Fig. S1) and other characterizations.

2.2 Reduction of GO by solvothermal treatment

Typically, 0.17 mL GO suspension (5.8 mg mL⁻¹) was dispersed in 3.82 mL solution of reductants with different concentrations (formaldehyde: 0.26, 2.57, 7.8, 13.4 mol L⁻¹ and formic acid: 0.17, 1.7, 5.15, 8.8, 23 mol L⁻¹) in a small bottle. After ultrasonic for 5 min, the small bottle containing

the reactants were put into a teflon-sealed autoclave and then heated at 100-200 °C for about 1-24 h in an oven. After the autoclave was cooled to room temperature, the obtained rGOs were filtered, washed with distilled water and ethanol, and then dried. All the samples were pressed into thin tablets for conductivity measurement and other characterizations. The obtained rGOs reduced by formaldehyde (rGO-FL) and formic acid (rGO-FaL) solutions at the optimum concentrations of reductants and optimum reaction temperature were defined as rGO-FLn and rGO-FaLn, respectively, where n represents the reduction time in hour.

As-prepared GO and the obtained representative rGOs were analyzed by XPS and Raman spectroscopy, and the detailed characterizations of samples were shown in the supporting information.

3 Results and discussion

Fig. 2 shows the relationships between the electrical conductivities of the rGOs reduced by the vapor reductants and the reaction conditions. As shown in Fig. 2A, the conductivities of rGO-FV prepared at 150 °C increase with the formaldehyde concentrations to 1.1 S/cm in all concentrations investigated. However, the conductivities of rGO-FaV reach to a maximum of 0.72 S/cm at 13.5 mol L⁻¹ with the formic acid concentration. Fig. 2B reveals that the optimum reaction temperature for rGO-FV and rGO-FaV is about 150 °C when GO is reduced for 3 h at the optimum concentrations of formic acid or formaldehyde. It is interesting to find that the conductivities of rGO-FV and rGO-FaV exhibit a maximum of 1.8 and 1.6 S/cm at 12 and 9 h, respectively, (Fig. 2C) with the reaction time.

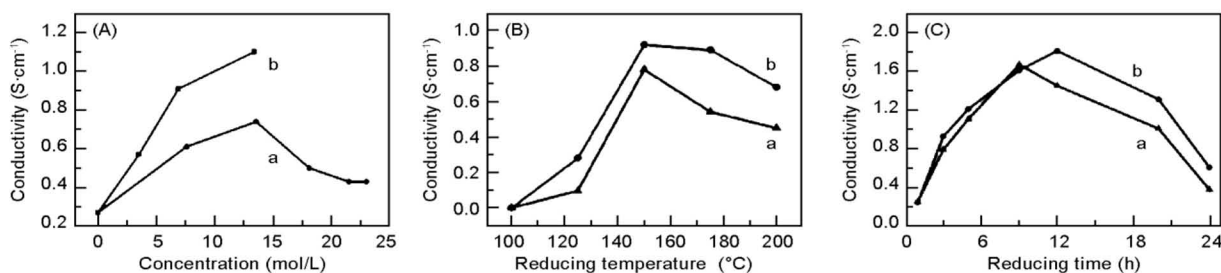


Fig. 2 The plots of electrical conductivity of rGOs prepared in vapor reducing agents versus (A) the concentration of the reducing agents, (B) the temperature and (C) the reaction time. (a) rGO-FaV and (b) rGO-FV.

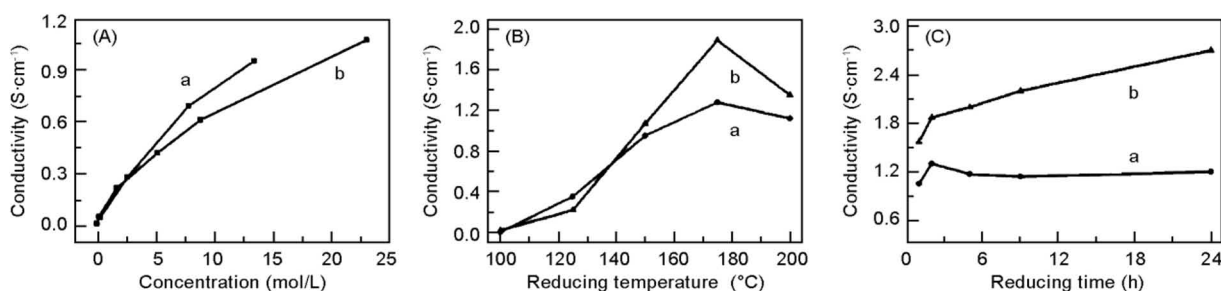


Fig. 3 The plots of electrical conductivity of the rGOs reduced by solvothermal reaction versus (A) the concentration of the reducing agents, (B) the temperature and (C) the reaction time: (a) rGO-FL and (b) rGO-FaL.

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