



A novel method to control atomic defects in graphene sheets, by selective surface reactions

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ABSTRACT

Behaviors of atomic defects in graphene sheets in air at high temperature are studied. Results indicate that the number of defects in graphene sheets decreases after high temperature treatment in air. Mechanism for the behaviors are studied by molecular simulations and interpreted as follows. Charge distributions of atoms in graphene sheets are relatively uniform due to large conjugated π bond, but atomic defects in the graphene sheets change the uniform charge distributions. The change of charge distributions makes these defect-regions have higher chemical activities, thus these defect-regions are easy to be eroded selectively by O_2 in air, which makes the number of them decrease. Thus, high temperature treatment in air can be used as a novel method to control atomic defects in graphene sheets. However, in order to obtain the graphene sheets after reactions, two problems should be dealt with: one is sufficient contact between air and graphene sheets during reaction; the other is transfer and enrichment of graphene sheets after reaction. Our method dealt with the two problems.

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1. Introduction

Recently, atomic defects in graphene sheets have drawn the attention of many researchers [1–6]. These defects include intrinsic zero- or one-dimensional defects (such as vacancies and line defects) and extrinsic defects (such as foreign atoms) [7]. These defects have different effects on the electronic, optical and mechanical properties of graphene sheets; therefore controlling them is very important [8–10]. Many methods have been used to control defects in graphene such as micro-mechanical exfoliation [11], chemical vapor deposition (CVD) [12], carbon segregation [13] and modified Hummers method [14,15], these methods can be used to decrease defects in graphene during preparation of graphene. Recently, a new method has been found to control defects in graphene by defect repair [8], this method can be used to repair defects in graphene after preparation of graphene, which makes it easy to prepare low-defects graphene sheets. In this paper, behaviors of atomic defects in graphene sheets under air at high temperature was studied, we find that high temperature treatment in air can be used as a novel repair way to control atomic defects of graphene sheets.

However, in order to obtain the graphene sheets after sufficient reactions, two problems should be dealt with. One is that air at high temperature will react with graphene sheets violently, so only a few

lightweight graphene sheets after reaction can be left, the airflow may blow these sheets away, which makes us fail to obtain the graphene sheets after reaction; the other is that sufficient contact between air and graphene sheets is needed during reaction. Thus a proper method to deal with the two problems is needed.

In our study, graphene oxide was prepared to introduce extrinsic defects (foreign atoms O) in graphene sheets. To ensure sufficient contact between air and graphene sheets, a sulfonated asphalt hydrosol and a graphene oxide hydrosol were mixed to prepare a carbon membrane with a thickness of about 2.8 μm . The membrane was formed by an assembly process at the liquid/air interface [16]. Sulfonated asphalt is a cheap industrial carbon material. It can be easily produced by oxidizing asphalt with oleum and then treating with NaOH. Sulfonated asphalt has good solubility in water due to the $-\text{SO}_3\text{Na}$ groups and therefore can be mixed uniformly with graphene oxide hydrosols. In addition, sulfonated asphalt decomposes and changes to Na_2SO_4 in air at high temperature. The Na_2SO_4 make the graphene sheets after reaction with air anchored, which makes subsequent steps such as transfer and washing of the graphene sheets easy to perform.

2. Experimental

2.1. Materials and methods

In our study, graphene oxide was prepared to introduce extrinsic defects (foreign atoms O) in graphene sheets by a Hummers method [17]. The obtained graphene oxide (0.8 g) was added to

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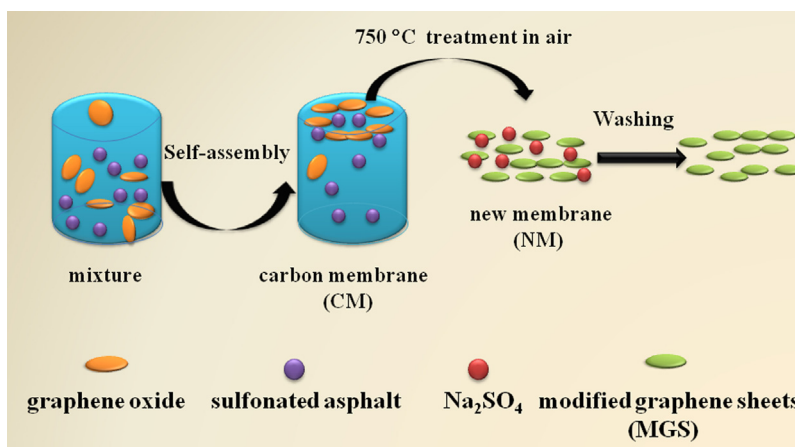


Fig. 1. Diagram for the method to control atomic defects in graphene sheets.

deionized water (200 mL) and treated in an ultrasonic cleaner for 1 h (30 kHz, 200 W). After high-speed centrifugation (3000 rpm) for 30 min to remove impurities, a stable graphene oxide hydrosol with a concentration of 3.5 mg/mL was obtained.

Sulfonated asphalt was purchased from Taizhou Fine Chemical Factory in China. The sulfonated asphalt (200 g) was first added to deionized water and stirred for 2 h to give a black suspension. Then the suspension was allowed to stand at room temperature for 3 days. After filtering-out the sediments, black sulfonated asphalt hydrosol with a concentration of 0.1 g/mL was obtained.

The graphene oxide hydrosol (66 g) was then mixed with the sulfonated asphalt hydrosol (2 g) and stirred for 1 h. The mixture was then heated at 75 °C in a water bath for 1.5 h to prepare a carbon membrane (CM) by an assembly process at the liquid/air interface [16].

The CM membrane was kept in air at 750 °C for 1 h and a new membrane (NM) was obtained. After the NM was washed with deionized water and dried at 80 °C for 12 h, graphene sheets after reaction were obtained, these sheets were named as modified graphene sheets (MGS). Fig. 1 shows the diagram for our method to control atomic defects in graphene sheets.

Some graphene oxide prepared in this study was kept in N₂ at 750 °C for 1 h to prepare normal graphene sheets, which is used to make a comparison on the different behaviors of defects in the graphene sheets under air or N₂ atmosphere.

Mechanism for the behaviors of defects in graphene sheets in air at high temperature was studied by molecular simulations. The natural bond orbital (NBO) method [18] was used for studying charge distributions using Gaussian09 software [19] with a B3LYP/3-21G* basis set.

2.2. Characterization of materials

Scanning electron microscopy (SEM) was done with a Philips XL30 instrument and transmission electron microscopy (TEM) was performed on a JEOL JEM-2100F instrument. X-ray diffraction (XRD) was performed on a RigakuD/Max2500 X-ray diffractometer using CuK α radiation (40 kV, 200 mA, $\lambda = 1.54056 \text{ \AA}$) and X-ray photoelectron spectroscopy (XPS) was performed on a PHI-1600 ESCA electron system (America PE company) with AlK α (1486.6 eV) radiation. Raman spectroscopy was carried out using a Thermo Electron Raman microscopy ($\lambda = 532 \text{ nm}$). Atomic force microscopy (AFM) and conductive atomic force microscopy (C-AFM) were done with a Bruker (Veeco) DIMENSION icon instrument with highly ordered pyrolytic graphite (HOPG) substrate at a bias voltage of 0.1 V.

3. Results and discussion

The insert of Fig. 2a shows that the thickness of the CM was only about 2.8 μm , which is thin enough to offer sufficient contact between the CM and air. Fig. 2a and b shows the optical photos of the CM and NM, respectively, and Fig. 2d and e shows the SEM images of the CM and NM surfaces, respectively. As shown in Fig. 2b, although the edges of the membrane curled after the reactions, the shape of the membrane was well maintained. This makes subsequent steps such as transfer and washing easy to perform. The surface of the CM (Fig. 2d) is not smooth due to the many white sulfonated asphalt crystals in the CM (see region in the red square). The XRD analysis (presented in Fig. S1 in the Supplementary materials) confirmed that these crystals changed to Na₂SO₄ (the white crystals shown in Fig. 2e) in the NM after the CM was treated at 750 °C in air for 1 h. In the NM (Fig. 2e), there are many smooth sheets with sizes of 5–30 μm (see sheet in the red square). These sheets can be easily isolated by washing the NM with deionized water to remove the Na₂SO₄. These sheets are MGS, which can be confirmed by XPS and Raman analysis (presented later). Due to the high mechanical strength of the MGS and the formation of Na₂SO₄ in the NM, the shape of the CM membrane was maintained when it changed to the NM. Fig. 2c and f show the TEM images of the MGS. The surfaces of the MGS (Fig. 2c) are smooth and the edges of the MGS curl. As shown in Fig. 2f, there are 4–9 layers of stacked graphene in the MGS and ordered crystalline lattices of graphene can be clearly seen. This indicates that the MGS have a characteristic graphene sheet structure.

Fig. 3a–c show the XPS spectra of graphene oxide, normal graphene sheets and the MGS, respectively. The C1s XPS spectra of graphene oxide (Fig. 3a) have a C–C/C=C (284.5 eV) peak and two peaks for two kinds of oxygen functional groups (C–O and C(O)O). Comparing with the C–O (286.5 eV) peak in graphene oxide (Fig. 3a), in the normal graphene sheets spectra (Fig. 3b), the C–O (286.5 eV) peak decreased largely. Interestingly, in the MGS spectra, the C–O (286.5 eV) peak disappeared. It is well known that extrinsic defects (O atoms) in the graphene sheets can be eliminated due to decomposition at high temperature [20–23], but as shown in Fig. 3b, 750 °C treatment in N₂ cannot eliminate the C–O in graphene sheets absolutely. Thus, it means that these extrinsic defects in graphene sheets can be accelerated to eliminate with the assistance of air at high temperature. Fig. 3d–f show the Raman spectra of graphene oxide, normal graphene sheets and the MGS, respectively. Value I_D/I_G of graphene in Raman spectra can be used to show relative number of defects in graphene, the higher I_D/I_G

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