



X-ray absorption spectroscopy study on the thermal and hydrazine reduction of graphene oxide



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ABSTRACT

X-ray absorption spectroscopy (XAS) was applied to systemically investigate the deoxygenation of graphene oxide (GO) via annealing and hydrazine treatment. Detailed evolution of the electronic structures and chemical bonding of GO was presented. The enhanced intensity of π^* resonance and the appearance of splitting σ^* resonance in C K-edge XAS spectra suggest high extents of recoveries of π -conjugation upon reduction using thermal annealing or hydrazine. Experimental results revealed that the carboxyl as well as epoxide and hydroxyl groups on the surface of GO were thermally reduced first, followed by the more difficult removal of carbonyl and cyclic ether groups at higher temperatures. The hydrazine reduction could remove epoxide, hydroxyl and carboxyl groups effectively, whereas the carbonyl groups were partially reduced with the incorporation of nitrogen species simultaneously. The residual oxygen functional groups on hydrazine-reduced GO could be further removed after modest thermal annealing. It was proposed that a combination of both types of reductions would give the best deoxygenation efficiency for the production of graphene.

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1. Introduction

Graphene—a single planar layer of sp^2 -hybridized carbon atoms found in graphite—is now well known for its intriguing mechanical, electrical and thermal properties [1–3]. It has promising potential applications in electronics, sensors, and energy-storage capacitors [4–7]. Graphene has emerged as a “shining star” in materials science. However, several of these applications are still not feasible because the large-scale production of high-quality graphene remains as a challenge. Several laboratory methods have been proposed, each with its own advantages and shortcomings [3,7,8]. Among them, one promising method toward large-scale synthesis of graphene is the chemical oxidation of graphite, which introduces oxygen functional groups to exfoliate pristine graphite into individual sheets, called graphene oxide (GO) [9,10].

GO is electrically insulating, but some degree of conductivity can be restored through the use of chemical or thermal reduction [11]. Recently, restoration of graphene's electronic structure is still a major of interest in graphene research, and consequently considerable efforts have been spent to investigate various deoxygenation

routes [12–14]. The clear need for deoxygenation routes arises from the requirements of processing GO thin films deposited onto plastic and glass substrates as well as in situ within GO-embodied polymer matrices. However, the structure of GO is still unclear to this day, the detailed electronic structure and its evolution of GO during the chemical or thermal reduction remains largely ambiguous, hindering the potential applications of graphene [10]. To make further progress on optimizing and designing reduction procedures, which is the key to numerous applications, GO needs to be well characterized and its deoxygenation should be well understood. The X-ray absorption spectroscopy (XAS) is sensitive to local electronic structure and is one of the promising methods to study carbon-based systems [15].

XAS spectroscopy is an effective tool to investigate both structural changes and surface chemical functionalization [16]. XAS is a technique that involves the excitation of electrons from a core level to local and partial empty states [17,18]. It is an important, element-specific characterization tool capable to obtain electronic, structural and bond information in carbon-based systems. Recently, XAS has been used to investigate structural changes, electronic structure and surface chemical functionalities of graphene [19–22]. Here, we have applied XAS to study the evolution of electronic structure and the surface chemistries of the reduced GO derivatives obtained by treating GO with thermal annealing and hydrazine. Investigation of such evolution will help to develop the

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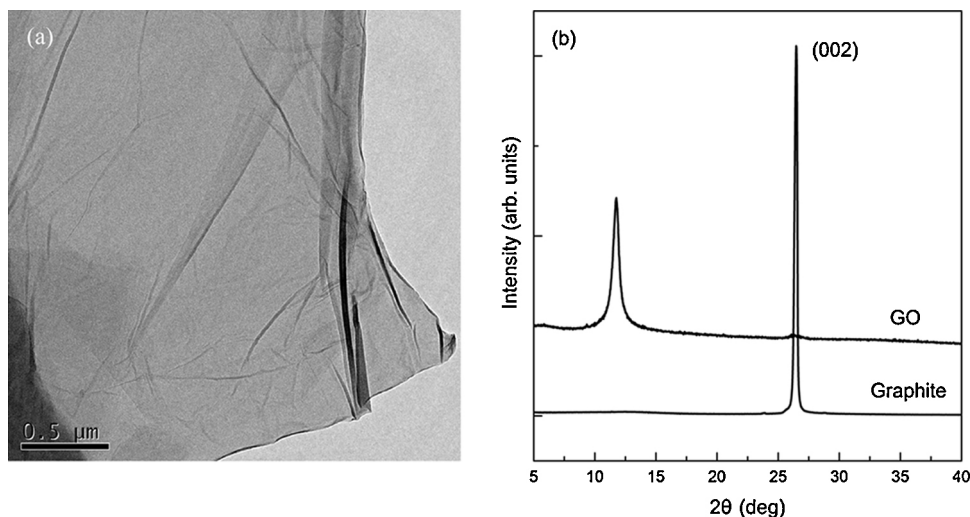


Fig. 1. (a) TEM image of GO and (b) XRD spectra of graphite and GO.

comprehensive view and improved performance on the reduction of GO for applications.

2. Experimental

GO was prepared from natural graphite flake by a modified Hummers method [23]. Typically, 3 g of graphite and 1.5 g NaNO_3 were added into 70 mL concentrated H_2SO_4 at room temperature. This reaction was carried out for 16 h, after which 9 g of KMnO_4 was gradually added in an ice bath with vigorous stirring for 2 h. The ice bath was then removed, and the mixture was maintained at room temperature for 3 h. Then, 400 mL ice water was added into the mixture slowly and the temperature was raised to 98°C . After 15 min, 10 mL of 30% H_2O_2 aqueous solution were added into the brown mixture with stirring overnight. After reaction, the suspension was filtered with micropore filters and the resulting solid was washed with dilute HCl aqueous solution and H_2O several times. Finally, the resulting solid sample was dried at 60°C under vacuum overnight.

The thermal treatment was performed by placing the GO samples into a tube furnace, which was heated to the different temperatures (300°C , 600°C and 900°C) for 2 h under the protection of Ar atmosphere. For chemical treatment, GO was dispersed into 200 mL water under mild ultrasound yielding a transparent yellow-brown suspension, then 4 mL hydrazine hydrate (80 wt%) was added and the solution was heated in an oil bath maintaining at 100°C under a water-cooled condenser for 24 h. After the reaction, the product was collected by vacuum filtration and dried in a vacuum desiccator overnight. Some product powder was further annealed at 300°C under Ar atmosphere.

The XAS measurements were performed at the Soft X-ray Magnetic Circular Dichroism (SXMCD) station of the National Synchrotron Radiation Lab (NSRL). Samples were loaded in an UHV chamber maintained at a pressure of $\sim 5 \times 10^{-7}$ Pa during data acquisition. The angle of incident X-ray beam was fixed at 55° from the sample surface. All spectra were recorded at room temperature with an experimental resolution of 0.2 eV at the C, N and O K-edge, using the total electron yield (TEY) mode. All the spectra were normalized to the incident photo flux.

3. Results and discussion

Fig. 1(a) shows the typical TEM images of the as-prepared GO. It can be seen that the material is transparent with a crumpled

sheet like morphology. The crumpled structures in GO may originate from the heteroatoms or defects created in the plane of graphene. The structure of GO was further characterized by XRD. As Fig. 1(b) shown, the XRD pattern of original graphite appeared a basal reflection (002) with a strong and sharp peak at $2\theta = 26.46^\circ$, corresponding to $d = 0.34$ nm spacing between atomic planes. Upon oxidation of the original graphite, the (002) peak shifted to a lower angle ($2\theta = 11.76^\circ$) and the interlayer distance of GO increased to $d = 0.75$ nm. The larger interlayer spacing of GO compared to the original graphite could be attributed to the formation of oxygen functional groups between the layers of graphite.

XAS is demonstrated to be an effective technique for simultaneously probing the surface chemistry, electronic and local structural information of graphitic materials. Fig. 2(a) shows the C K-edge XAS spectra of as-prepared GO and GO annealed in Ar atmosphere at different temperatures. The spectrum of GO is characterized by three main features: the edge, the atomic contribution of C–C π^* transition at ~ 285 eV, a resonance of C–C σ^* transition centered at ~ 292.4 eV and a structure in the range of 286–290.4 eV, which are labeled as A, C (C2) and B in all spectra, respectively. Actually, the structure of between 286 eV and 290.4 eV is characterized by two features (B1 and B2) at ~ 286.4 eV and 288.6 eV along with a shoulder (B2) at ~ 287.4 eV. According to the previous reports, feature B1 can be assigned to the π^* states of C–O bonds derived from hydroxyl groups, feature B3 to the π^* states of C=O bonds originating from carboxyl and carbonyl groups, while feature B2 to epoxide groups on the basal plane of GO [20,24,25].

When GO has been thermally treated under Ar atmosphere, a number of important changes can be identified in the XAS spectra. After thermal annealing at 300°C , a less pronounced feature B2 can be observed with a sharp reduction of feature B3, indicating the removal of epoxide and carboxylic groups from the GO sheets. Instead, a new spectral feature between feature B2 and B3 occurs at ~ 288 eV, which may originate from the contributions of C=O and/or C–O groups [24,25]. In addition, the feature B1 disappears at 300°C and the FWHM of feature A becomes broader. These changes can be attributed to the elimination of hydroxyl groups and the defunctionalization-induced creation of larger π -conjugated domains from alkene fragment to a few fused polyaromatic rings [25]. With the increase of annealing temperature, the feature at ~ 288 eV decreases and disappears at 900°C , indicating that carbonyl moieties are more thermally stable than COOH moieties and removed at higher temperatures. Upon thermal treatment, there is a curious splitting of the C–C σ^* peak into two peaks, with the

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