



The effect of the thermal reduction temperature on the structure and sorption capacity of reduced graphene oxide materials



Alexandr V. Dolbin^{a,*}, Maria V. Khlistyuck^a, Valentin B. Esel'son^a, Viktor G. Gavrillo^a, Nikolay A. Vinnikov^a, Razet M. Basnukaeva^a, Irene Maluenda^b, Wolfgang K. Maser^b, Ana M. Benito^b

^a B. Verkin Institute for Low Temperature Physics and Engineering of the National Academy of Sciences of Ukraine, 47 Lenin Ave., Kharkov 61103, Ukraine

^b Instituto de Carboquímica, ICB-CSIC, Miguel Luesma Castán, 4, E-50018 Zaragoza, Spain

ARTICLE INFO

Article history:

Received 15 July 2015

Received in revised form 26 October 2015

Accepted 16 November 2015

Available online 21 November 2015

Keywords:

Graphene oxide
Thermal reduction
Gas adsorption

ABSTRACT

The influence of reduction temperatures on the structure and the sorption capacity of thermally reduced graphene (TRGO) has been investigated systematically. A set of TRGO materials were prepared by thermal treatment of parent graphene oxide (GO) at five temperatures ($T = 200, 300, 500, 700, \text{ and } 900^\circ\text{C}$). Investigations of these materials by X-ray diffraction, Raman spectroscopy and X-ray photoemission spectroscopy methods have shown that both the structure and the residual oxygen functional groups on the TRGO surface can be controlled by varying the temperature of the thermal treatment. The data on the sorption and desorption of ^4He , H_2 , N_2 , Ne and Kr gases in the temperature interval $T = 2\text{--}290\text{ K}$ clearly demonstrate that the sorption capacity of TRGO is closely related to the structural changes induced by the treatment temperatures. It is important that the sorption capacities of TRGOs treated at 300°C and at 900°C significantly increase for all the gases used. The prominent increase in the sorption capacity at 300°C is attributed to the structural disorder and liberation of the pores caused by the removal of intercalated water and labile oxygen functional groups (oFGs) favored at this temperature. At 900°C the sorption capacity increases due to the generation of new defects on the TRGO surface, which provide additional access to the internal space between the folds and sheets of the TRGO structure. By tailoring the structural properties we emphasize the potential of TRGO as a highly efficient sorbent.

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

Graphene is a highly attractive two-dimensional nanobuilding block [1]. Its unique properties, such as high specific surface area, carrier mobility, electrical and thermal conductivity and well-defined optical absorption make it attractive for applications in photovoltaics, fuel-cells, and supercapacitors among others [2–6]. The well-ordered honeycomb lattice of sp^2 hybridized carbon atoms forms the base for the exceptional properties and application potential of graphene. The lattice defects and oxygen functionalities present on the graphene basal plane have generally been considered detrimental to most technological applications. However, these imperfections can be highly beneficial in gas-adsorption technologies. If such imperfections are of a suitable type and size, they can act as specific sites in systems of gas storage, separation or cleaning. Therefore, controlling the graphene structure in the

course of its synthesis or post-synthesis treatments is of critical importance in preparing materials for gas adsorption applications.

Although there exist a large variety of synthetic methods, the chemical oxidation-based approaches [7–9] for obtaining graphite oxide (GtO) and its posterior chemical or thermal reduction remain more advantageous for gas adsorption applications. This is due to a larger number of imperfections as compared to the graphene materials prepared by other methods, such as CVD or mechanical exfoliation methods [10,11]. Prior to chemical reduction, the GtO material is exfoliated, usually by ultrasonic techniques, and the resulting graphene oxide (GO) is then chemically reduced to remove oxygen functional groups (oFGs). However, this approach is less efficient in restoring the sp^2 network and usually requires a posterior thermal treatment [12,13], which hampers the control of defects in the basal plane. Exfoliation of graphite oxide [14–16] through thermal treatment is a promising strategy that yields more ordered graphene and additionally allows simultaneous exfoliation and reduction through sudden expansion of CO or CO_2 gases evolving from the graphene sheets during the fast thermal heating of GtO [17]. This rapid thermal process, the removal of oFGs and the

* Corresponding author. Tel.: +380 573410979; fax: +380 573403370.
E-mail address: dolbin@ilt.kharkov.ua (A.V. Dolbin).

de-intercalation of water lead to an increase of pressure between the stacked layers facilitating the exfoliation of the material. The temperature of reduction influences the final oxygen contents and the structural damage produced by removing water and oFGs from the surface [15]. The gas atmosphere during thermal treatment is also an important factor. Therefore, thermal expansion-reduction is usually carried out in vacuum or an inert environment [18]. Furthermore, this approach does not involve reducing agents and thus avoids the corresponding chemical impurities on the graphenic surfaces [13,19]. The thermal expansion of GtO is then a valuable approach to producing bulk quantities of graphene with controllable structures for gas adsorption.

The adsorption-desorption properties are of key importance in assessing the applicability of materials for specific uses and in further refining our understanding of the mechanisms involved. Moreover, the adsorption of some gas impurities can be used to develop materials with new properties. The sorption and the subsequent desorption of ^4He , H_2 , N_2 , Ne and Kr impurities by graphene oxide, two chemically reduced graphene oxide (RGO) materials, glucose-reduced GO and hydrazine-reduced GO were earlier investigated in [20]. It was found that for GO in the temperature interval $T=2\text{--}290\text{ K}$, the temperature dependences of the diffusion coefficients of light impurities (hydrogen and helium) were determined by a competition between two diffusion mechanisms, namely, the thermally activated and tunnel processes. The contribution of the tunnel process was dominant at low temperatures, which made the diffusion coefficients largely temperature independent. However, the tunneling effects were less pronounced when heavier impurities (N_2 , CH_4 , Kr) were used. Tunnel diffusion of light impurities at low temperatures was also observed in other carbon nanostructures, such as carbon nanotubes [21,22] and fullerene C_{60} [23–25]. We can thus assume that the kinetics of gas sorption by carbon nanostructures is significantly influenced by the surface structure. Besides, it was found that oFGs and defects also had a considerable effect on the sorption properties of graphene oxide [20]. The sorption capacity of graphene oxide increased three- to six-fold after the oFGs were removed through hydrazine reduction. It is evident that the removal of oFGs unblocks and/or generates new defects that allow penetration of the gas impurities through the graphene surface to the interlayer space.

Consequently, the final sorption properties of the graphenic materials greatly depend on the type, quantity and distribution of the oxygen functional groups on the graphene surface, as well as on the number and the type of defects generated on oFG removal. In turn, these factors are dependent on the applied reduction technique. Therefore, investigation of the reduction effect on the sorption characteristics of graphenic materials allows us to trace the structural evolution during the GO reduction and opens the way of tailoring the properties of reduced graphene oxide materials. Here we have investigated the sorption characteristics of five thermally reduced graphene oxide (TRGO) materials using gas impurities of various masses and effective sizes (^4He , H_2 , Ne , N_2 , Kr). The influence of the structure and the chemical surface of the TRGO materials on the final sorption properties has also been examined.

2. Experimental

The starting graphite oxide (GtO) was prepared from graphite powder (Sigma–Aldrich) in an ice bath using the modified Hummers method and vigorous oxidating agents NaNO_3 , H_2SO_4 , KMnO_4 (see [7,13]). 170 mL of concentrated H_2SO_4 was added to a mixture of graphite flakes (5.0 g) and NaNO_3 (3.75 g). The mixture was cooled in an ice bath and stirred for thirty minutes. KMnO_4 (25 g) was then slowly added and the mixture was stirred for another

thirty minutes. The resulting product was warmed-up to $35\text{ }^\circ\text{C}$ and stirred for two more hours. Water (250 mL) was then slowly added and followed by 30% H_2O_2 (20 mL). The mixture was stirred for an hour and filtered. The obtained powder was repeatedly washed with 400 mL of $\text{HCl}:\text{H}_2\text{O}$ (1:10) and dried.

Thermal exfoliation of the GO powder (300 mg per batch) was carried out at several temperatures (200, 300, 500, 700 and $900\text{ }^\circ\text{C}$) for 15 min in the Ar atmosphere. The obtained graphene-like materials are labeled as TRGO-200, TRGO-300, TRGO-500, TRGO-700 and TRGO-900.

The GtO and TRGO materials were fully characterized by transmission electron microscopy (TEM) employing a JEOL-2000 FXII. X-ray diffraction (XRD) studies were performed with a Bruker AXS D8 Advance diffractometer using $\text{CuK}\alpha$ radiation. Micro Raman spectroscopy was performed in a HORIBA Jobin Yvon spectrometer (model HR 800 UV) employing a laser excitation wavelength of 532 nm. Three to four representative spectra of different sample zones were considered for each material. XPS was performed in an ESCA Plus Omicron spectrometer equipped with a Mg anode (1253.6 eV) 150 W, (15 mA, 10 kV). When required, the binding energy positions were corrected by setting the aromatic carbon band at 284.5 eV. Thermogravimetry (TGA) was carried out using a Setaram balance, model Setsys Evolution in the inert N_2 atmosphere with a heating ramp of $10\text{ }^\circ\text{C min}^{-1}$.

The sorption properties of the thermally reduced GO materials were investigated using a laboratory test bench (its design and operation are detailed elsewhere [23,26]). The temperature interval ranged from $T=2\text{--}290\text{ K}$. Prior to testing, the powder samples were evacuated at room temperature for five days in the measuring cell of the test bench.

3. Results and discussion

3.1. Thermally reduced graphite oxide (TRGO)

The XRD patterns in Fig. 1 show that oxidation of graphite by the Hummers method causes a significant disorder and a loss of the crystalline structure of graphite. This is evident as considerable broadening and a decreased intensity of the (002) diffraction peak at $2\theta=26.7^\circ$. Furthermore, the shift of the (002) peak to $2\theta=25.6^\circ$ and the (001) peak appearing at $2\theta=10.3^\circ$ suggest that the interlayer distance changes from 3.4 Å in the parent graphite to 8.6 Å in the graphite oxide. The change is caused by intercalation of water that penetrates into the space between the graphite layers, and by incorporation of oxygen functional groups in the graphenic network during rough oxidation [27,28].

As shown in Fig. 1b, during the thermal process the (001) peak disappears while the (002) peak shifts to the position typical for graphite ($2\theta=26.7^\circ$). This can be attributed to water deintercalation, oFGs removal and to a partial restoration of the sp^2 network [28–30]. The (002) peak does not regain its original intensity and width, which points to a good degree of GtO exfoliation during the thermal treatment. Above $500\text{ }^\circ\text{C}$ the (002) peak does not exhibit significant changes, either in position or in width, which suggests that the graphene layers in the treated materials have comparable interlayer spacings and similar stacking thicknesses. However, the (002) peaks of the samples obtained at 200 and $300\text{ }^\circ\text{C}$ are somewhat broader and appear at slightly lower 2θ values (26.4 and 26.5 , respectively), indicating that some intercalation is still present and less water and/or oFGs have been removed.

The TEM analysis proves that thermal treatment causes exfoliation of graphite oxide. TRGO materials consist of flakes of graphene with a low number of layers (1–10) whose lateral sizes range up to a few micrometers (Fig. 2). The basal planes of all the materials treated at $T<700\text{ }^\circ\text{C}$ are not perfectly ordered and exhibit no

Download English Version:

<https://daneshyari.com/en/article/5353479>

Download Persian Version:

<https://daneshyari.com/article/5353479>

[Daneshyari.com](https://daneshyari.com)