Carbon 105 (2016) 291–296

Contents lists available at ScienceDirect

Carbon

journal homepage: www.elsevier.com/locate/carbon

Engineering nano-porous graphene oxide by hydroxyl radicals

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ARTICLE INFO

Article history:
Received 14 December 2015
Received in revised form
15 April 2016
Accepted 20 April 2016
Available online 22 April 2016

ABSTRACT

Graphene oxide (GO) has recently been identified as an excellent candidate for membrane science, but the relatively small number of channels for species to transport across the laminated GO membranes is one of the major limitations for the membrane permeability. Thus, engineering porous structures on GO sheets, such as pores and notched edges, is a promising solution to increase channels across the laminate when GO sheets are stacked into membranes. However, a controllable approach for constructing porous GO sheets requires further development. Here, we demonstrated that nano-porous GO sheets with well-controlled nano-pores and 'lacelike' edges were generated after 'etching' GO sheets by hydroxyl radicals (OH•), which were generated from water radiolysis by γ-irradiation. Furthermore, the average diameter of nano-pores can be easily tuned from 3.7 to 13.6 nm by varying the 'etching' time. Carbon atoms in GO sheets where oxygen-containing groups were bonded to could be oxidized and removed by OH• radicals, leaving the defects in GO sheets. Then, the formation mechanism for the porous structures and the oxidation behavior of GO sheets are systematically investigated. These results should provide a new approach for engineering fluidic channels in GO membranes for future applications in nanofiltration and molecular separation.

1. Introduction

As a functionalized graphene derivative, graphene oxide (GO) has attracted tremendous attention for its potential use in membrane science because of its two-dimensional structure and high mechanical strength [1–5]. More recently, it is reported that the interlayer galleries between the laminated GO sheets possess an atomic-scaled interlayer distance ($d \approx 9 \pm 1$ Å), which solely allow unimpeded permeation of H_2O through the interlayer galleries, but in the absence of H_2O are completely impermeable to other liquids, vapors, and gases [1]. Furthermore, increasing d to approximately 13 ± 1 Å by swelling the GO membranes in water, some small ions with hydrated radii of less than 4.5 Å can also be permeated through the GO membranes [2]. This superior performance endows GO membranes with excellent potential for nanofiltration and molecular separation applications [3–5].

Thus far, despite many promising applications, the permeability of GO membranes remains limited especially compared with that of commercial ultrafiltration membranes, and the relatively small number of fluidic channels for species to transport across the membranes is one of the major limiting factors [6–9]. Considering the laminated microstructure, the interlayer galleries are the transverse fluidic channels in GO membranes. Interedge spaces between neighboring GO sheets and pores within GO sheets are the channels which allow the species to transport across the laminated GO sheets [6,7]. Some earlier experiments have already suggested that increasing the edge-to-area and porosity of GO sheets can improve the permeability of the prepared GO membranes [8,9]. For example, GO sheets with different mean sizes were synthesized by different oxidation methods (*Hummer's* method or *Marcano's* method), and their transport characteristics were also determined. The results indicate that increasing edge-to-area ratio by decreasing the mean size of GO sheets, the permeability of the prepared GO laminates increases linearly [8]. Other work indicates that defects in GO sheets, such as pores, produced during *Hummer's* method can also obviously enhance the water permeance of GO membranes, and the effect is especially significant for ultrathin membranes [9]. Nevertheless, the formation of defects within GO

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http://dx.doi.org/10.1016/j.carbon.2016.04.050

sheets during the synthesis processes is hardly controlled. Therefore, a controllable approach to construct porous structures within GO sheets, such as notched edges and nano-pores is urgently required. By far, many advanced methods for porous graphene synthesis have already been developed [10–15]; however, inadequate effort has been dedicated to the preparation of porous GO.

The OH• radical is one of the most powerful oxidants in nature, which can oxidize the majority of organics into CO_2 and H_2O. Thus, OH• radicals are used to oxidize and mineralize the substituted aromatic compounds [16,17], which have similar structures to the segments within GO sheets where the oxygen-containing groups are bonded [18,19]. On the other hand, chemical radiation methods has demonstrated its unique advantages in the synthesis of graphene-based materials [20–22]. Taking advantage of the high-energy, the covalent bonds of graphene sheets or substances can be broken and generate reactive species such as radicals and electrons. Then, the subsequent reactions of these species carry out immediately under ambient conditions and without ‘synthetic’ steps. Under γ-irradiation, OH• radical and e^-_{aq} are the dominant oxidative and reductive species for water radiolysis, respectively [20,22]. However, when water is previously saturated by N_2O, e^-_{aq} can be immediately transformed into OH• radicals during irradiation, and create a oxidizing medium [23,24].

In the present work, using GO as a precursor and OH• radicals as oxidizing agents generated directly from water radiolysis via γ-irradiation, we expect to develop a novel method for ‘etching’ GO sheets and engineering porous structures on GO sheets. The oxidation behavior of GO is intensively investigated by ultraviolet−visible (UV−Vis), Fourier transform infrared spectroscopy (FTIR), X-ray photoelectron spectroscopy (XPS) and Raman spectroscopy. The formation mechanism for the porous structures is also discussed using transmission electron microscopy (TEM) and atomic force microscope (AFM).

2. Experimental

2.1. Materials

Graphite powder (CP), N_2O and other chemical reagents (AR) were purchased from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China). All chemicals are used as received without further purification. Milli-Q water is used for all experiments unless otherwise stated.

2.2. Preparation of nano-porous GO

GO was firstly prepared from commercial graphite powder according to a modified *Hummer's* method [25], and the details are presented in the Supporting Information. The ‘etching’ of GO sheets was carried out at room temperature. GO was synthesized and dispersed in water to obtain a uniform dispersion with a content of 0.1 mg mL^{-1}. Then, the GO aqueous solution was sealed in a glass vial after being saturated with N_2O by bubbling for 30 min, and exposed to γ-ray irradiation using a ^{60}Co source at Shanghai Institute of Applied Physics, Chinese Academy of Sciences. As mentioned before, when water is previously saturated by N_2O, e^-_{aq} can be immediately transformed into OH• radicals during irradiation, and the details are presented in the Supporting Information. All of the GO aqueous solution were irradiated at a dose rate of 0.6 or 0.9 kGy h^{-1}, and used as they were prepared after irradiation.

2.3. Characterization

UV−Vis absorption spectra were recorded with a HITACHI U-3010 spectrophotometer, and the water was used as the solvent. Raman spectra were obtained on a RENISHAW inVia plus laser Raman spectrometer by using excitation wavelength of 532 nm. FTIR spectra were collected by scanning the sample on the transmission module of Thermo Nicolet Avatar 370 FTIR spectrometer at 4 cm^{-1} resolution and 32 scans. XPS spectra were recorded by using a SHIMADZU Kratos AXIS Ultra DLD XPS instrument equipped with a monochromated Al Kα X-ray source. TEM images were obtained using a Tecnai F20 transmission electron microscope with an acceleration voltage of 200 kV. Samples for observation were prepared by drying a drop of the irradiated GO aqueous solution on copper grids coated by a carbon support film, and the pore size statistics were carried out using Digital Micrograph.

3. Results and discussion

As mentioned earlier, when GO aqueous solution previously saturated by N_2O is irradiated by γ-ray, the generated OH• radicals immediately attack the GO sheets (Fig. 1a). The oxidation of GO was easily observed by visual inspection, and photographs of the N_2O-saturated GO aqueous solution after various irradiation times revealed different degrees of color changes (Fig. 1b). With increasing irradiation time, the color of the GO solution gradually lightened, which indicated that the GO content in solution decreased. Considering the chemical inertness of graphene when encountered OH• radicals [15], this result proved that the presence of the oxygen-containing groups in GO sheets was crucial to the oxidation process, which may be attributed to the defected π-conjugated network. Besides, the ‘no-N_2O’ control experiments were also carried out, and the details were presented in the supporting information (Table S1 and Fig. S1). The results indicated that when both e^-_{aq} and OH• radicals were produced as the major products of water radiolysis during γ-irradiation, GO might react with e^-_{aq} priorly and be partly reduced. Therefore, using N_2O to transform e^-_{aq} into OH• radicals during irradiation is essential for the oxidation of GO.

Then, the relationship between the GO oxidation and irradiation conditions was further determined using UV−Vis spectroscopy (Fig. 1c). As observed, a higher dose rate and longer irradiation time led to higher OH· yield in aqueous solution, which greatly accelerated the oxidation. However, for irradiation times longer than 40 h, a similar termination of the oxidation appeared to occur regardless of the dose rate, and the GO content was reduced to approximate 20%. It suggests that the OH• radicals were almost consumed for the irradiation times longer than 40 h under all of the conditions. Thus, for irradiation times less than 40 h, the oxidation behavior of GO can be easily tuned by varying either the irradiation time or dose rate. In addition, the UV−Vis results (Fig. 1d) reveal the gradual blue-shift of the sharp absorption peak around 230 nm, which represents $\pi \rightarrow \pi^*$ transition of aromatic C−C bonds of GO, to 210 nm after irradiation [22,26]. This result indicates that the π-conjugated network of GO was further broken after oxidation, which is also consistent with that of Raman spectra (Fig. 1e). After being irradiated for 6 h, the G-band of GO originally observed at 1585 cm^{-1} shifted to 1592 cm^{-1}, and the intensity ratio of the D band and G band (I_D/I_G) slightly increased from 0.96 to 0.98. These results indicate that more defects, such as pores, may emerge in the π-conjugated network of GO after oxidation. Thus, the morphology of GO after oxidation was investigated using AFM (Fig. 2) and TEM (Fig. 3).

According to the AFM results (Fig. 2a and b), after irradiation for 6 h (0.6 kGy h^{-1}), the surface roughness of GO sheets (Rq) clearly increased from 0.260 nm to 0.398 nm after irradiation for 6 h, which indicates that defects did emerge inside the GO sheets after oxidation. Further TEM results presented that, compared with pristine GO (Fig. S2a), nano-pores with an average particle size (d_{av})