Carbon 95 (2015) 338–346

Contents lists available at ScienceDirect

Carbon

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

Reducing and multiple-element doping of graphene oxide using active screen plasma treatments

Jian Chen [a, *, 1], Xiangru Shi [a], Shaojun Qi [b], Miklós Mohai [c], Imre Bertóti [c, 1], Ying Gao [a], Hanshan Dong [b, 1]

[a] Jiangsu Key Laboratory of Advanced Metallic Materials, School of Materials Science and Engineering, Southeast University, Nanjing 211189, China
[b] School of Metallurgy and Materials, The University of Birmingham, Birmingham B15 2TT, UK
[c] Institute of Materials and Environmental Chemistry, Research Centre for Natural Sciences, Hungarian Academy of Sciences, Budapest H-1519, Hungary

ARTICLE INFO

Article history:
Received 29 March 2015
Received in revised form
25 July 2015
Accepted 15 August 2015
Available online 20 August 2015

ABSTRACT

A transparent graphene oxide layer on a non-conductive poly(ethylene terephthalate) film was treated by a new active screen plasma technology at temperatures ranging from 100 °C to 200 °C in pure hydrogen and in a gas mixture of hydrogen and nitrogen. To study the thermal reducing effects of the active screen plasma, parallel thermal annealing treatments were also carried out at the same temperatures. UV–visible absorption spectra, X-ray diffraction, Raman spectroscopy, X-ray photoelectron spectroscopy (XPS) and electrical properties confirmed that the graphene oxide can be effectively reduced by the active screen plasma treatments. Detailed XPS quantitative analyses have revealed that the carboxylic groups are not stable, and their amount can be decreased effectively by the active screen plasma treatments. Only about one third of the carbonyl type C=O can be reduced at the same time. In addition to the reduction, simultaneous multi-element doping of GO with nitrogen from the gas supply and with Fe, Cr and Mo from the stainless steel active screen was also detected by XPS.

1. Introduction

Graphene has received significant attentions in the past years due to its excellent charge carrier mobility, thermal conductivity, optical transparency and mechanical properties [1,2]. Various synthesis methods [3–5] have been proposed to obtain high-quality graphene with large-size and/or large quantity. Among these methods, the chemical solution route through the precursor graphene oxide (GO) gained great successes as it enables the massive production and the chemical functionalization of graphene.

GO has a similar sheet-like structure as graphene and each GO nano-sheet can be considered as a multifunctional network [6,7]. It contains several oxygen functionalities including hydroxyls, epoxides, diols, ketones and carboxyls, which are attached to the carbon backbone. The reduced GO (rGO) can then be obtained by removing the oxygen functionalities to recover the physical properties of graphene. A diversity of reducing methods [8] have been developed such as chemical agent reaction [9], thermal annealing [10], microwave irradiation [11], photocatalysis [12], electrochemical reaction [13], and solvothermal reduction [14]. The most widely used methods are the chemical agent reaction and the thermal annealing.

Chemical reagent reduction, involving hydrazine [9,15–17], metal hydrides [18], alkaline (NaOH) [19], ascorbic acid (Vitamin C) [20,21] and hydroiodic acid (HI) [22], etc., is based on their chemical reactions with GO. Although large quantities of rGO can be obtained due to the facile solution-based reduction, these chemical agents are usually hazardous and sometimes harmful to the support for the graphene and the environment. On the other hand, thermal annealing is effective in reducing GO [10,15,17,23–26], and the reduction extent can be improved with the increase of the temperature. But its drawbacks are also obvious as heating requires large energy consumption and critical conditions [8]. Moreover, GO on the substrates with low-melting points, such as polymers for flexible electronic devices, cannot be effectively reduced without substrate degradation.

Plasma treatments provide one promising option to circumvent these problems, as an eco-friendly and energy-saving alternative to existing processes. Gomez-Navarro et al. [6] successfully reduced

---

* Corresponding author.
E-mail address: j.chen@seu.edu.cn (J. Chen).
[1] These authors contributed equally to this work.

http://dx.doi.org/10.1016/j.carbon.2015.08.046
0008-6223/

GO by hydrogen (H_2) plasma, further investigated its atomic scale features. The plasma reduced GO layers were found to comprise of defect-free graphene areas with sizes of a few nanometres interspersed with defective areas dominated by clustered pentagons and heptagons. Wang et al. [27] realized reducing and nitrogen doping (N-doping) of GO by a plasma treatment. In another study, GO powders were simultaneously reduced and N-doped at near room temperature by employing a plasma-assisted microwave technology [28].

It is known that doping is a common strategy in tuning the properties of carbon-based nanomaterial. The doping methods for this two-dimension material are different from the conventional methods for bulk materials. Doping of graphene is a key issue to its future applications [29], e.g., in field effect transistors, supercapacitors, and lithium batteries because it can confer new chemistry and physics to graphene. For example, N-doping can tune the chemically derived functionalized graphene from being a p-type to n-type semiconductor. Plasma treatments have proven its feasibility in doping graphene. Bertóti et al. [30] reported that 15 at.% nitrogen (N_2) was implanted into the graphene surface using a radio frequency activated low pressure N_2 plasma. N-doped graphene was also obtained by exposing thermally reduced GO/glassy carbon to N_2 plasma by Shao et al. [31] It was found that N-doped graphene exhibited a much higher electrocatalytic activity toward H_2O_2 reduction than graphene, and a much higher durability and selectivity than the widely-used expensive Pt. Wang et al. [27] also obtained N-doped graphene with different percentage (from 0.11 to 1.35 at.%) of N in N_2 plasma by controlling the exposure time.

Notwithstanding the fact that these plasma treatments demonstrated their successes in doping and reducing, they required a conductive electrode such as glassy carbon [27,31], or pre-reducing to recover the conductivity [32], which has eliminated or at least retarded the applications of graphene on non-conductive substrates such as for transparent and flexible graphene-based electronic devices; in addition, all these plasma treatments can, to date, dope graphene only by nitrogen but multi-element doping is desirable for multi-functionalizing graphene.

A new type of plasma activation, active screen (AS) plasma technology, has been developed in the past few years to overcome the drawbacks of traditional direct current (DC) glow discharge plasma treatments, such as arcing, hollow cathode and edge effects [33–36]. In an AS treatment, the worktable (or the sample) is not the cathode as used in DC treatments but a metallic mesh surrounding the samples and the worktable is serving as cathode. Glow discharge, therefore, does not take place on the surface of the samples and the worktable but on the metal mesh cylinder called as the active screen. The drawbacks of tradition DC plasma can be overcome, furthermore nonconductive materials, such as polymers [33], biomaterials [37], can be treated in the AS plasma. Currently, there is still argument on the mechanisms on the AS plasma due to various plasma surface interactions. It has been generally accepted that a mechanism of sputtering and redeposition is of fundamental importance [38]. This could allow for tailoring the surface chemical compositions and physical properties of carbon-based materials by changing two facile parameters, the plasma gas composition and the screen material.

Therefore, it might be feasible to combine the reducing, N-doping and possibly the metallic atoms-doping (from the metallic mesh) of GO on a transparent nonconductive polymeric substrate in one process. In this study, the feasibility of reducing and multi-element doping the GO on a non-conductive poly(ethylene terephthalate) (PET) substrate has been investigated for the first time using the advanced active screen plasma technology. Parallel heat treatments were also carried out to differentiate the plasma effects from the thermal effects. Detailed chemical analysis was carried out using XPS and Raman to study the mechanisms involved in reducing and multi-element doping of graphene.

2. Experimental

2.1. Preparation of GO and GO/PET films

The graphene oxide was prepared at Southeast University using the modified Hummer's method [39]. Natural graphite powder with an average size of 30 μm (1 g), $NaNO_3$ (1 g) and KMnO4 (6 g) were slowly added to H_2SO_4 (230 ml) at 0 °C (ice bath). Then the mixture was stirred at 0 °C for 2 h and then at 36 °C for 2 h. The solution was then slowly dropped into icy distilled water (230 ml) to obtain a graphite oxide suspension. It was further treated with H_2O_2 to reduce the residual permanganate and manganese dioxide, washed with deionized water and centrifuged to completely remove residual salts and acids. The dispersion was ultrasonically treated for 15 min to exfoliate the GO nanosheets. Finally, the GO/PET film samples were prepared by drop casting the dispersion (600 μl) with a GO concentration of 0.25 mg/ml on a rectangle PET substrate (Lumirror T60, Toray Industries, Inc., Japan) with a size of 20 × 20 mm, and a thickness of 188 μm. These film samples were then dried at 60 °C. The thickness of the GO layer is measured to be about 20 μm.

2.2. Active screen plasma treatment

Active screen plasma treatments were carried out at University of Birmingham using a lab scale active-screen plasma device within a traditional plasma nitriding unit (40 kW Klöckner DC plasma unit). The plasma is formed on the screen made from a stainless steel mesh with the size of holes about 8 mm that acts as cathode and the wall of the chamber is the anode. As the table is isolated from the chamber, the GO/PET samples remain in a floating potential as shown in Fig. 1. The sample-mesh distance (from the top of mesh to the table) is about 2.5 cm.

As listed in Table 1, two types of active screen plasma treatments were carried out: (i) in pure H_2 (the ASP series) and (ii) in a gas mixture of 75%H_2 and 25% N_2 (the ASPN series). To differentiate plasma effects from temperature effects, some samples were also heat-treated in pure H_2 using a vacuum furnace (the HT series). The treatments were carried out at temperatures ranging from 100 °C to 200 °C (which is below the melting point of the PET substrate) for 1 h at a pressure of 400 Pa (4 mbar). In the following text, these treated samples were named according to their code (Table 1).

2.3. Characterisation

The prepared GO dispersion was characterized using optical microscope (OM, MV5000, Jiangnan Noval Optical Co., China) and transmission electron microscope (Tecnai G2-T20, FEI Co., USA). The OM and TEM samples were prepared by dissolving a small amount of dispersion in ethanol, and then one droplet was spread over a silicon wafer and copper mesh with carbon film. After dried in the ambient condition, the samples were investigated.

The transparency of as-cast and treated GO/PET samples was characterized using ultraviolet–visible spectroscopy (UV–vis, UV-6000, Shanghai metash instruments Co., China). X-ray diffraction (XRD) was conducted using a D8-Discover X-ray spectrometer (Bruker Co., German), with a Cu Kα radiation. Raman analysis was also carried out (LabRAM HR800, Horiba Jobin Yvon, Japan) using an excitation wavelength of 514.5 nm. Two edges of the graphene/PET samples were coated with silver with a distance about 13 mm, and the electrical conductivity was measured.

Detailed chemical analysis was performed by X-ray