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Preparation of large-area graphene oxide sheets with a high density of carboxyl groups using O_2/H_2 low-damage plasma

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ABSTRACT

We have used low-damage O_2 plasma treatment (O_2-LDPT), with chemically reactive radicals generated in an inductively coupled plasma system equipped with a complementary filter, to prepare large-area graphene oxide (GO) sheets. Raman spectroscopy and X-ray photoelectron spectroscopy demonstrated that oxidative functionalities were formed on the graphene surfaces. However, the carboxyl group, which is the most important functional group for biological applications, only occupied about 6.1% of the GO sheets formed using O_2-LDPT. By adding H_2 during O_2-LDPT, the compositional ratio of carboxyl group could be greatly increased to 10.8%. Optical emission spectroscopy revealed that this enhancement was achieved because of the presence of hydroxyl radicals in O_2/H_2-LDPT.

1. Introduction

Since graphene was first reported in 2004 [1], it has attracted great attention and research interest because of its fundamental physical properties and potential applications resulting from its exceptionally high electronic conductivity, thermal conductivity, and mechanical strength [1–3]. Although the bulk properties of graphene are very promising for various applications, the development of graphene-based devices requires precise control over the covalent functionalization of its surface, because the surface of the material is the main factor influencing its compatibility with an environment. Graphene oxide (GO) is one branch of graphene functionalization. GO sheets are typically covalently functionalized with hydroxyl, epoxy, carbonyl, and carboxyl groups [4]. Among these functional groups, carboxyl groups play an important role because they can be used to graft functional molecules by reacting with proteins, DNA, cells, and other biopolymers via amide or ester linkages [5–8]. Therefore, GO sheets as a sensing membrane are highly suitable for the development of electrochemical biosensors, which are analytical devices that convert biological responses into electrical signals via electrochemical strategies. The modified Hummer's method is one of the most widely used approaches for preparing GO sheets [9]. Using strongly acidic oxidants, graphite is converted to GO [10,11], and the oxidation degree of GO is subsequently controlled by various reductants such as hydrazine, sodium borohydride, hydroiodic acid, and L-ascorbic acid [12–15]. More recently, Chong et al. used natural reducing agent, such as lemon juice and vinegar, instead of environmentally harmful chemicals to control the oxidation degree of GO [16]. However, the reproducible preparation of GO sheets with well-defined chemical structures, i.e. layer numbers, composition, and film morphology, is still a major challenge. In addition, Hummer's method utilizes harsh chemicals and requires a significantly long time for completion. Plasma treatment is an alternative method for oxidizing a large area for the preparation of GO sheets. It can generate, even at room temperature, a large amount of species, including electrons, ions, and radicals that can chemically react to functionalize graphene within a short time. Therefore, O_2 plasma treatment allows the ready oxidation of graphene to alter its intrinsic properties for various applications [17–20]. However, it has been reported that even multiple sheets of graphene are readily etched away within a few seconds in a conventional plasma environment because of the presence of ions and vacuum ultraviolet (VUV) radiation [21–24]. Both ions and VUV radiation in plasma can break the graphene lattice and destroy the honeycomb-like C nanostructure with ease, because their energies are higher than the bond energy of the C–C bonds of sp^2-hybridized C atoms in graphene. As a result, the etching rate is generally too fast to allow precise control over the degree and type of oxidation. To overcome this narrow process window, Childres et al. exposed graphene to a series of

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Abbreviations: LDPT, low-damage plasma treatment; GO, graphene oxide; VUV, vacuum ultraviolet; CVD, chemical vapor deposition; PMMA, poly(methyl methacrylate); SLG, single-layer graphene; OES, optical emission spectroscopy; XPS, X-ray photoelectron spectroscopy.

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short pulses of O_2 plasma and used the resulting material to prepare a field-effect transistor [20]. Although downstream plasma treatment can be performed to functionalize a graphene surface without ion bombardment, the resulting material will still be sensitive to VUV radiation [19]. The high-intensity VUV radiation generated in a plasma system can greatly enhance the rate of etching [25].

In this study, we proposed a low-damage plasma treatment (LDPT) to oxidize graphene sheets without ions or VUV radiation using which oxidization can be carried out in a highly controllable manner. As displayed schematically in Fig. 1, shielding against ions and VUV radiation with high energy, which cause the maximum damage to graphene, can be efficiently achieved by inserting a complementary filter into the inductively coupled plasma system. This allows only radicals, which have the highest reactivity among plasma-generated species, to diffuse through the filter with extremely low kinetic energy (ca. 0.03 eV) [26] and reach the nanomaterials to gently functionalize them. Generally, O_2 gas is introduced into the plasma chamber when using plasma treatment for the preparation of GO sheets. In this study, in order to obtain GO sheets with more carboxyl groups, we also investigated the effect of H_2 gas addition.

2. Materials and methods

2.1. Sample preparation

Large-area single-layer graphene (SLG) films were prepared on copper foil by chemical vapor deposition (CVD) in a tubular quartz furnace. The Cu foil was placed at the center of the quartz tube and then the system was heated to 1050 °C under a constant flow of H_2 (20 sccm) at 2.8×10^{-1} Torr for 50 min. Then, oxygen gas (3 sccm) was introduced into the furnace at 7.4×10^{-2} Torr for 3 min to grow a thin copper oxide layer. After that, a mixture of CH_4 (50 sccm) and H_2 (20 sccm) gases was introduced into the system at 1050 °C and the pressure was kept at 6.5×10^{-1} Torr for growing monolayer graphene; the graphene and Cu foil were then cooled to 25 °C. The as-grown graphene was transferred from the Cu foil to a 300 nm-SiO_2/Si substrate using the following transfer procedure: (i) a poly(methyl methacrylate) (PMMA) film was spin-coated onto the surface of the graphene on the Cu foil; (ii) the PMMA/graphene layer was separated from the Cu foil through chemical etching of the Cu in a $FeCl_3$ solution; (iii) the suspended PMMA/graphene layer was placed on the surface of deionized water overnight to remove any residual Cu etchant; (iv) the PMMA/graphene layer was transferred to the SiO_2/Si substrate; (v) after drying on a hotplate at 120 °C, the PMMA was dissolved and washed away by soaking the substrate in hot acetone to leave only the SLG sheet on the SiO_2/Si substrate; (vi) finally, the sample was rinsed with isopropyl alcohol and deionized water to obtain SLG/SiO_2/Si. The oxidation process was performed using LDPT to form graphene oxide sheets. The samples were loaded onto a stage 3 cm beneath the complementary filter. The filter consists of upper and lower plates separated by a ceramic spacer. Both plates contain many stripes and slits of the same width. The slits on the upper plate are aligned with the stripes on the lower plate, which can block high-energy collimated ions and prevent direct exposure of the samples to UV radiation. In our previous study [27,28], we confirmed that the UV intensity can be reduced by more than 95%. Therefore, the filter can efficiently shield the samples from plasma damage caused by energetic ions and UV radiation. The filter only permits neutral and reactive radicals to diffuse through and reach the heated substrate, thus realizing a low-damage treatment process. A 13.56 MHz radio frequency at a power of 200 W was applied to the coil to generate high-density plasma. The chamber pressure was maintained at 0.2 Torr. O_2 or a gas mixture of O_2 and H_2 (O_2/H_2) was introduced during LDPT to oxidize SLG at room temperature. The treatment time was varied to investigate the ability to control the degree of oxidation of the GO sheets. Owing to the addition of H_2 during LDPT, optical emission spectroscopy (OES) was used to monitor the plasma composition.

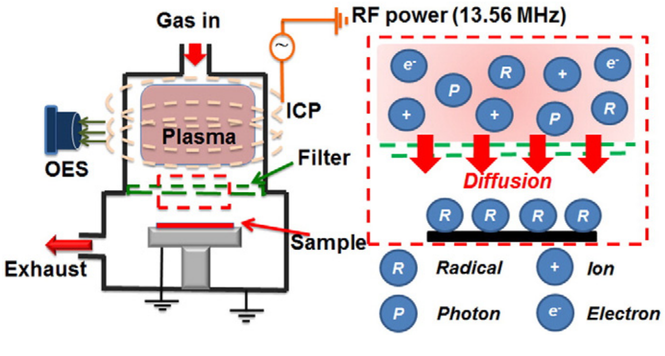

Fig. 1. Schematic of the LDPT system and the enlarged view of the dashed red rectangle.

2.2. Characterization of GO sheets

After the preparation of GO sheets using LDPT, the chemical compositions of the GO sheets were examined using X-ray photoelectron spectroscopy (XPS, VG ESCA Scientific Theta Probe) with a monochromated Al Kα source. Raman spectra were collected using a Horiba Raman system, iHR-550. The Si peak at 520 cm^{-1} was used as the reference for wavenumber calibration prior to each measurement.

3. Results and discussion

Raman spectroscopy is a fast, non-destructive, and powerful instrument for characterizing graphene. The spectrum of pristine graphene showed two featured peaks: a G band (ca. 1575 cm^{-1}) and a 2D band (ca. 2680 cm^{-1}), which are characteristic of the C–C bonds of sp^2-hybridized C atoms. In addition, a D band (ca. 1335 cm^{-1}) represents bonds involving non-sp^2-hybridized C atoms, derived from atomic-scale defects or lattice disorders. In this study, we observed that the Raman spectrum of untreated pristine graphene [Fig. 2(a)] exhibited a 2D to G band intensity ratio [$I(2D)/I(G)$] of ca. 3.1 and a narrow full width at half maximum for the 2D band (ca. 30 cm^{-1}), which is consistent with SLG [29]. In addition, the D band was almost invisible in the spectrum, suggesting that the SLG used in our experiment was of high quality. After subjecting the SLG samples to LDPT with O_2 (O_2-LDPT) for obtaining the GO sheets, new featured peaks corresponding to defect-activated bands appeared in the Raman spectra. Fig. 2(a) displays representative Raman spectra for the SLG samples after O_2-LDPT for 0 to 7 min. The intensity of the D band near 1615 cm^{-1} was enhanced remarkably after O_2-LDPT, suggesting the formation of defects in the SLG. The G band became broadened and a pronounced shoulder, denoted as the D′ band, appeared near 1615 cm^{-1} because of the intra-valley resonance of Raman scattering [30]. As the exposure time increased, the intensities of the D and D′ bands were enhanced, while the 2D band was suppressed and broadened. These features can be related to the nature of the graphene nanostructure. To quantify the defect density in sp^2-bonded carbons, the D to G band intensity ratio from the Raman spectral evolution of SLG after O_2-LDPT as a function of exposure time is plotted in Fig. 2(b). In this study, we found that the I(D)/I(G) ratio increased upon increasing the treatment time until 1 min. This can be considered the time at which the introduction of defects into the sp^2 lattice occurs. The intensity ratio decreases after long treatment times, which is attributed to the amorphization of graphene because of the high density of defects. This result is consistent with previous reports [20,30]. XPS was performed to quantify the oxidative compositions and bonding states of GO sheets after subjecting graphene to O_2-LDPT, because the chemical functionalization of graphene sheets induces strong chemical shifts in the C 1s bonding energy. Fig. 3(a) shows XPS C 1s spectra of