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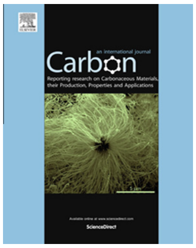

Ultra-low-damage radical treatment for the highly controllable oxidation of large-scale graphene sheets

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ABSTRACT

We have used low-damage oxygen radical treatment (O-LDRT)—with chemically reactive radicals generated in a plasma system equipped with a complementary filter—to prepare large-scale graphene oxide sheets with highly controllable levels of oxidation. Raman spectroscopy and X-ray photoelectron spectroscopy revealed that oxidative functionalities were formed on the graphene surfaces in a highly controllable manner and with a wide process window. Contact angle measurements revealed the high hydrophilicity of the large-scale graphene after O-LDRT. We measured the current–voltage characteristics of oxidized double-layer graphene (DLG) sheets to confirm the low degree of damage after using O-LDRT for the oxidation process. For treatment times of up to 5 min, the current passing through the DLG sheets remained almost identical to that passing through the corresponding sample that had not been subjected to O-LDRT, indicating that the bottom layer of the graphene sheet remained almost unmodified, whereas a massive number of oxidative functionalities had been formed on the top layer of the graphene sheet; in addition, the adhesion energy increased to approximately twice that of the untreated graphene sheet.

1. Introduction

Since it was first reported in 2004 [1], graphene—a two-dimensional, single layer of sp^2-hybridized C atoms—has received tremendous attention and research interest for its fundamental physical properties and potential applications resulting from its exceptionally high electronic conductivity, thermal conductivity, and mechanical strength [1–3]. In particular, graphene is a very promising material for use in future nanoelectronic devices [4–6]. The growth of graphene through chemical vapor deposition (CVD) [7], a process compatible with very-large-scale integration (VLSI), has increased its

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applicability in, for example, field-effect transistors, biosensors, and optoelectronics [8–10]. Although the bulk properties of graphene are very promising for a variety of applications, the development of graphene-based devices will require greater control over its surface functionalization and modification, because the surface of a material is the primary factor influencing its compatibility with an environment. Several methods have been proposed for tuning and controlling the chemical functionality and quality of graphene [11]. Plasma treatment is a major tool in VLSI processes; it can generate a large amount of species—including electrons, ions and radicals, even at room temperature—that can react chemically with various substrates. Therefore, plasma treatment allows the ready modification or functionalization of materials to alter their intrinsic properties for various applications. A number of groups have employed plasma treatment to functionalize graphene surfaces. Gokus et al. exposed mechanically exfoliated graphene sheets to O_2 plasma and then investigated their photoluminescence [12]. Choi et al. investigated the terahertz and optical characteristics of graphene oxide sheets produced using O_2 plasma [13]. Shen et al. reported few-layer graphene sheets that underwent structural changes induced by CF_4 plasma [14]. Notably, however, even multiple sheets of graphene can be etched away readily within a few seconds in a conventional plasma environment, due to the presence of ions and vacuum ultraviolet (VUV) irradiation [15,16]. Both species of ions and VUV in plasma have energy higher than that of the C–C bonds of sp^2-hybridized C atoms in graphene, thereby breaking the lattice of graphene with ease and destroying the honeycomb-like C nanostructure. As a result, the etching rate is generally too fast to allow precise control over the degree and type of functionalization. To overcome the narrow process window, Childres et al. exposed graphene to a series of short pulses of O_2 plasma and used the resulting material to prepare a field-effect transistor [17]. Although downstream plasma treatment can be performed to functionalize a graphene surface without ion bombardment, the resulting material will still inevitably be sensitive to the VUV [18]. A high-density VUV generated in a plasma system will greatly enhance the rate of etching [19]. In previous studies, we developed a method—low-damage radical treatment (LDRT)—based on Samukawa's damage-free neutral beam [20,21], for the functionalization of nanocrystalline and thin film materials for applications in flash memories and ion sensors, respectively [22,23]. As displayed schematically in Fig. 1, by inserting a complementary filter into a parallel plate plasma system, the ions and VUV with higher energy (i.e., the sources of most damage to the nanomaterials), can be efficiently shielded by the filter, allowing 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) [24] and reach the nanomaterials to gently functionalize them (i.e., with ultra-low damage). In this study, we used low-damage oxygen radical treatment (O-LDRT) to oxidize graphene sheets without ions or VUV, allowing oxidization to be conducted in a highly controllable manner. When using O-LDRT, even a treatment time of greater than 5 min provided products with Raman spectra featuring peaks representing graphene. This method enabled us to investigate the detailed evolution of large-scale graphene sheets with respect to changes in the radical treatment time.

2. Experimental

2.1. Sample preparation

Sample preparation began with growth of a large-scale single-layer graphene (SLG) film on copper foil, using CVD in a tubular quartz furnace [25]. The Cu foil was placed at the center of the quartz tube and then the system was flushed under a constant flow of H_2 (50 sccm) at 1 torr for 50 min. The Cu foil was annealed at 1000 °C for 40 min to remove organic matter and oxides from the surface. A gas mixture of CH_4 (60 sccm) and H_2 (15 sccm) was introduced into the system at 1000 °C and then the pressure was kept at 1 torr for growth of the 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 thermally grown SiO_2 substrate (thickness: 300 nm) atop a Si substrate (SiO_2/Si) 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 the SLG/SiO_2/Si. Double-layer graphene (DLG) was also prepared by repeating the transfer procedure with the SLG/SiO_2/Si substrate to obtain DLG/SiO_2/Si samples.

The oxidation process was performed using O-LDRT to form graphene oxide sheets. The samples were loaded onto lower electrode underneath the complementary filter with distance of 2 cm. The complementary filter made of quartz was placed on an insulating supporter, as shown in Fig. 1(b). It consists of upper and lower plates separated by a quartz spacer. Both plates contain many stripes and slits of the same width. One side of the upper plate is coated with a thin metal film to maintain the energetic electrons and ions to be confined to the plasma area between the upper electrode and the filter. In addition, the slits of the upper plate are aligned with the stripes of the lower plate, which can block the collimated ions with high energy and prevent UV irradiation to samples directly. In our previous study [22,23], we confirmed that more than 95% of UV intensity can be reduced. Therefore, the filter can efficiently shield the samples from plasma damage caused by energetic ions and UV irradiation. It only permits only neutral and reactive oxygen radicals to diffuse through the filter and reach the heated substrate, thus realizing a low damage treatment process. Processing conditions involved a 200-W radio frequency for plasma generation, a substrate temperature of 200 °C, and a pressure of 0.5 torr. The treatment time was varied to investigate the ability to control of the degree of oxidation of the graphene oxide sheets.