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Evolution, structure, and electrical performance of voltage-reduced graphene oxide

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Voltage-induced graphene oxide (GO) reduction is a facile and environmentally benign procedure for removing oxygen-containing functional groups from GO and recovering electrical conductivity. In this work, we perform a comprehensive investigation of the reduction process, structure, and electrical properties associated with voltage-reduced graphene oxide (V-rGO), obtained by applying a voltage between lateral electrode pairs. *In situ* optical microscopy during reduction reveals the growth of dendritic filaments of V-rGO that advance from the negative to positive terminal, eventually bridging and filling the entire electrode gap region. The growth rate of V-rGO filaments is found to sharply increase with humidity and film thickness. Through the use of varied electrode geometries, we demonstrate that V-rGO growth proceeds along electric field lines, opposite the field's direction. Following reduction, significant recovery of sp^2 carbon bonding and removal of oxygen-containing functional groups leads to electrical performance that is competitive with standard reduction schemes. Variable temperature resistance measurements identify Efros-Shklovskii variable-range hopping as the dominant transport mechanism, a result that is consistent with V-rGO acting as a polydisperse quantum dot array. Overall, this work suggests that voltage-induced reduction can be used in place of more cumbersome and hazardous reduction methods.

Introduction

Graphene oxide (GO) is a promising material for electronic applications both as a potential precursor for graphene [1] and in its own right as a versatile two-dimensional material with tunable electrical properties [2,3]. Unlike pristine graphene, GO is decorated with oxidation-induced lattice defects and oxygen-containing functional groups: predominantly hydroxyl and epoxide along the basal plane, and carbonyl and carboxyl along sheet edges [4]. These defects and oxygen groups disrupt the sp^2 conjugated carbon network and render GO electrically insulating [4,5].

The development of schemes for removing oxygen-containing groups and restoring the sp^2 carbon network, through reduction, is an active field of research with the primary goal of recovering charge transport [3,6,7]. The electrical performance of reduced graphene oxide (rGO) is, however, highly dependent on the degree of reduction and the method used [1,7,8]. Standard GO reduction approaches involve high temperatures in inert atmospheres (incompatible with flexible plastic substrates) or hazardous chemicals [7]. Although far less studied, there has been significant progress in producing highly-reduced rGO films with green reduction processes, the most notable of these being chemical reduction with ascorbic acid (Vitamin C) [6,9], electrochemical reduction [10], and photo-reduction [11].

In this work, we focus on a simple green method of GO reduction using an electric bias applied across electrode pairs under ambient or humid conditions [12–15]. This method is distinct from electrochemical [7,10,16,17] and electrophoretic reduction [18,19] in that the sample does not need to be immersed in a liquid. The voltage-induced reduction process exploits the hydrophilic nature of GO, whereby water adsorbed from the surrounding environment provides an electrochemical medium for reduction [15]. We have previously explored the capabilities of voltage-induced reduction using a conductive atomic force microscope (C-AFM) probe, demonstrating sub-10 nm to micrometer-scale patterning of conducting pathways in insulating GO [12,15]. Voltage-induced reduction between electrode pairs in patterned electrode arrays has also been shown [14]. Other researchers have investigated the use of voltage-induced reduction for resistive memory [20] and opto-electronic [21,22] applications. To date, however, very little is

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known about the voltage-induced reduction process or the material properties of voltage-reduced GO (V-rGO), including the chemical composition, degree of lattice disorder, charge transport performance, or charge transport mechanisms.

This work provides much-needed spectroscopic and electrical characterization of V-rGO. The chemical and structural makeup of V-rGO are thoroughly characterized using Raman spectroscopy, Fourier transform infrared spectroscopy (FTIR), and X-ray photoelectron spectroscopy (XPS), providing benchmarks to compare against established reduction methods. In addition, key mechanisms and properties of the voltage-induced reduction process are identified through simultaneous *in-situ* electrical characterization and optical microscopy. We demonstrate that voltage-induced reduction in a lateral electrode configuration is a quick process (V-rGO front growth rates up to 6.6 μm/s) that is adaptable to length scales ranging from micrometers to millimeters. By using different electrode geometries, we show that the V-rGO growth direction is dictated by the local electric field. Most importantly, voltage-induced reduction produces rGO with an electrical performance that is competitive with that found in rGO produced with standard reduction methods; furthermore, voltage-induced reduction is achieved with a simple and easily adopted procedure, without additional chemicals, high temperatures, or inert conditions.

Materials and methods

Sample preparation

GO powder (Graphene Supermarket) was dispersed in deionized water at concentrations of 0.5 mg/ml, 1.0 mg/ml, and 2.0 mg/ml, and stirred for at least 30 days. For removal of multilayer GO, GO suspensions were centrifuged for one hour and the supernatant was employed for casting films. Bottom-contact electrodes with gap sizes of 100 μm, 200 μm, 500 μm and 1.2 mm were prepared by depositing 5 nm of chromium and 50 nm of gold by thermal evaporation through shadow-masks onto substrates. Field-effect mobility measurements were performed using commercially-available patterned electrode substrates (Fraunhofer OFET Gen. 4) with channel lengths of 2.5 μm, 5 μm, 10 μm, and 20 μm, and a channel width of 10 mm. Samples for spectroscopic characterization were prepared on glass (for XPS) or silicon (for FTIR) with 500 μm electrode gaps. Substrates were cleaned by sonication in acetone, 2-propanol, and distilled water for 5 minutes each. Prior to GO deposition, samples were treated with UV/Ozone for 60 minutes to assist with film wetting. Thin GO samples ($\sim$7 nm film thickness) were spin-coated three times in succession, with the supernatant of the 0.5 mg/ml GO suspension at 1500 RPM for 30 s. Intermediate thickness GO films ($\sim$45 nm) were drop cast using the supernatant of the 1.0 mg/ml GO suspension. Thicker films ($\sim$175 nm) were drop cast from the supernatant of the 2.0 mg/ml GO suspension. For drop cast films, the volume of GO solution was adjusted to the sample area with a proportion of 20 μL/cm^2. The GO solution was dropped onto the center area of the substrates, was allowed to spread until it covered the majority of the surface, and was left to dry under ambient conditions. Film thickness was verified by atomic force microscopy.

Voltage-induced reduction

Voltage-induced reduction was performed using a bias voltage of 5 V applied between electrode pairs while continuously measuring the current level with a Keithley 2425 SourceMeter. All reduction experiments were done in a humidity-controlled glovebox with the relative humidity (RH) fixed at 70%, unless otherwise noted. GO samples were stored in the humidity-controlled glovebox for a minimum of 24 h to ensure the adsorption and intercalation of water from the surrounding environment.

Structural characterization

Raman spectroscopy was carried out using an inVia Renishaw confocal Raman microscope. Raman spectra were acquired under a 532 nm laser with a spot size of 1 μm. The spectrometer was calibrated using an internal silicon reference source prior to measurement. FTIR on GO and V-rGO was done with a Nicolet 8700 FT-IR spectrometer operated in reflective-IR mode. XPS characterization of GO and V-rGO was performed in ultrahigh vacuum (10^{-7} Pa) using a PHI 5000 VersaProbe instrument. A 100 W monochromatic Al Kα (1486.7 eV) X-ray source was used to obtain spectra from 100 μm × 100 μm areas on the GO and V-rGO. XPS spectra were calibrated to the location of the sp^2 carbon peak (284.5 eV).

Electrical characterization

Field-effect charge carrier mobility and conductivity measurements were performed in a nitrogen environment using a Keithley 2636A SourceMeter. Low temperature electrical resistance measurements were performed in a variable temperature cryostat at 10–250 K using a Keithley 4200-SCS. Prior to electrical characterization, the samples were annealed at a low temperature (100 °C) for 60 min in a nitrogen-filled glovebox to ensure removal of intercalated water, but at the same time avoid thermal reduction [18]. Conductive atomic force microscopy (C-AFM) [23] was implemented with an AIST-NT Combiscope 1000 AFM. Platinum-coated silicon cantilevers (Budget Sensors ContE-g with nominal spring constant $k = 0.2$ N/m, resonance frequency $f_0 = 13$ kHz, and probe radius <25 nm) were used for C-AFM current mapping with an applied force of 15 nN and a sample bias of 100 mV.

Results and discussion

Reduction mechanisms and time evolution of voltage-induced reduction

The process of voltage-induced reduction is highly dependent on water absorbed on, and intercalated between, the hydrophilic GO sheets under ambient or humid conditions [12,15]. Our proposed mechanisms for reduction [15], adapted to the lateral electrode geometry used here, are illustrated in Fig. 1a. The overall reaction scheme can be described as:

$$2H_2O \rightarrow 4H^+ + O_2 + 4e^- \quad (1)$$

$$aH^+ + be^- + GO \rightarrow rGO + cH_2O \quad (2)$$

A DC electrical bias applied between Au electrode pairs induces water oxidation at the positive electrode, generating hydrogen ions (H^+), electrons (e^-), and oxygen gas, per reaction (1). The H^+ ions are then driven by the electric field to percolate through the GO film towards the negative electrode. At the negative electrode, the H^+, along with e^- injected from the electrode, react with GO's oxygen-containing groups, such as hydroxyls, carbonyls, and epoxides, resulting in oxygen removal from the GO. Water is formed as a by-product. It is known that GO has an intrinsic negative charge [19], so it is also possible that GO can compensate for an electron to proceed with reaction (2). Once reduced, the conductive V-rGO serves as an extension of the negative electrode and provides electrons for continued reduction at the GO/V-rGO interface. In this way, voltage-induced reduction propagates across the electrode gap in a direction opposite the electric field.