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Low-temperature thermal reduction of graphene oxide films in ambient atmosphere: Infra-red spectroscopic studies and gas sensing applications

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ABSTRACT

Low-temperature (≤300 °C) thermal treatment of graphene oxide (GO) films in ambient air is examined. In particular, the role of low to moderate heating temperatures, to the evolution of the original functional groups anchored on the GO skeleton, is closely investigated by Fourier transform infra red (FT-IR) spectroscopy. The study shows that, contrary to vacuum or inert ambient heating, heating under ambient atmosphere triggers concomitant reduction and oxidation reactions. Hydroxyl and epoxy groups are progressively eliminated, but at the same time newly formed carbonyls appear due to oxidation. Electrical measurements indicate that despite the presence of oxygen containing groups in the restored graphene sp^2 network, the conductivity enhances. The process, therefore, lends itself to the production of conductive reduced GO with increased functionalities suitable for application in gas sensor fabrication. The concept is evaluated with a humidity sensor where thermally reduced GO is prepared at different reduction temperatures. The evaluation unveils that a critical reduction temperature exists where sensor sensitivity is optimized.

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1. Introduction

Graphene is a two-dimensional monolayer of carbon atoms tightly packed into a flat hexagonal structure, similar to a honeycomb lattice possessing innovative mechanical, electrical, thermal, and optical properties [1]. Current research on graphene materials is an exciting field that interfaces chemistry, physics, materials science and engineering. As graphene materials and their derivatives, maintain the unique graphene's properties in bulk, they have a wide range of applications in various fields such as batteries [2,3], organic photovoltaics [4–10], transistors [11,12], biology [13], hydrogen storage [14], as field-emission cathodes [15], as well as for the mass production of solution processable chemically exfoliated graphene oxide [16,17]. In particular, graphene's two-dimensional nature and high electron mobility translate into high sensitivity to surface chemical interactions thereby making it an ideal platform for gas sensors [18]. Nevertheless, graphene is difficult to produce and process on a large scale. Among other approaches, one of the promising mass production routes of graphene is through reduction of graphene oxide (GO) [19]. GO [20,21], prepared by the oxidation of graphite and the exfoliation of the generated graphite oxide, can be viewed as a graphene layer asymmetrically decorated with oxygen-containing functional groups on the basal plane and the edges. Despite extensive research, GO remains an elusive material with hardly obtainable direct structure information [22]. According to the widely accepted Lerf-Klinowski model [23], GO contains two kinds

of regions: aromatic regions with flat unoxidized benzene rings and wrinkled regions with alicyclic six-membered rings bearing C=C, hydroxyl, and ether groups, while GO sheets terminate with hydroxyl and carboxyl groups. In other words, GO is an insulating and disordered analogue of the highly conducting crystalline graphene.

GO reduction can be effected by various external stimuli such as heating [24], chemical treatment [25], and laser [26] or gamma ray irradiation [27]. It yields reduced GO (rGO) that resembles pristine graphene structure and is electrically conductive (due to restoration of graphene sp^2 network). Depending on reduction extent, a partly restored sp^2 lattice may be generated while also retaining some oxygen-bearing groups. In this way, rGO can find applications as a graphene alternative and provide *ad hoc* functionalized forms of graphene, for instance in order to optimize rGO response to gas vapors.

Graphene-based gas sensors can detect vapor adsorption down to the single-molecule level [28], with the mechanism stated to be charge transfer induced by adsorption/desorption of molecules (which act as electron donors or acceptors) on the graphene surface, leading to changes in graphene conductance. In recent years, research has aimed to identify and optimize the factors affecting the analytical performance of rGO gas sensors, namely, sensitivity, selectivity and stability. Such factors include voltage activation [29], film thickness [30], e-beam radiation [31,32], chemical functionalization [33,34], nanoparticle doping [35–37], the type of chemical reduction [38], and the extent of reduction [39–40].

In this work, aided by Fourier-transform infra red (FT-IR) spectroscopy, we investigate in a systematic way the extent of GO thermal reduction at low to moderate heating temperatures (90 °C–300 °C), for

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gas sensing applications. The reduction is conducted under ambient air conditions, *i.e.* without high vacuum or any special atmosphere involved. Our findings prove that both oxidation and reduction take place concurrently: hydroxyl and epoxy groups are progressively eliminated, but at the same time newly formed oxidation groups appear. The final product is a partly restored graphene sp^2 network bearing oxygen containing groups and it is electrically conductive. Furthermore, a humidity sensor based on a mildly thermally treated rGO is fabricated and evaluated for different reduction temperatures.

2. Experimental

2.1. Material

A commercial "Single Layer Graphene Oxide Ethanol Dispersion" was purchased from ACS Material® and used as is.

2.2. Characterization of rGO

GO dispersion was spin-coated on 4″ silicon wafer substrates to create uniform films of approx. 500 nm thickness. Then the films were heated on a hot plate at 90 °C, 120 °C, 150 °C, 180 °C, 200 °C, and 300 °C, for 1 h. Film thickness was measured before and after each heating step by a profilometer (XP-2, Ambios Technology). The morphology of thermally treated GO films was characterized by field emission scanning electron microscopy (FESEM, JSM -7401f, JEOL). Thermal gravimetric analysis (TGA) was performed on a Mettler Toledo TGA/SDTA851e thermogravimetric/differential thermal analyzer. GO thermal behavior was examined at 1 °C/min heating rate and 50 mL/min air flow.

Chemical structure characterization of the films was performed by a FT-IR spectrophotometer (Spectrum One, Perkin Elmer). All spectra were recorded from 4000 to 400 cm^{-1} in transmittance mode with a resolution of 4 cm^{-1} at 128 scans. Clean silicon wafers were used as background because of their transparency at the mid-IR range. In order to quantify the spectroscopic observations, the transmission measurements were converted into corresponding absorbance data and a polynomial baseline was subtracted from all raw spectra. By dividing by the film thickness of each sample, the spectra were normalized. Finally, peak areas were calculated between relative baseline points.

For the electrical characterization of GO, the dispersion was dropcasted using a micropipette between two gold electrodes, patterned on insulating silicon oxide over silicon substrate with standard lithographic techniques. Then, the samples were heated. Electrical transport measurements of thermally treated GO drops were carried out at room temperature using a two-point probe technique (Prober Karl-Suss Micromanipulator 7000 LTE equipped with HP4140B pAmeter/DC voltage source). GO electrical resistance was calculated from the slope of the I–V curves, and then converted to conductivity (σ).

2.3. Sensor fabrication

For the evaluation of sensor efficiency, GO was drop-casted between electrodes and heated at 120 °C, 150 °C, 180 °C, 200 °C, and 300 °C, for 1 h. Different concentrations of analyte vapors were introduced in a small volume (~7 cm^3) chamber where relative humidity and temperature were controlled to within 0.1% and 0.1 °C, respectively. The device response was investigated by measuring electrical resistance changes, when the analyte molecules were adsorbed on the sensing element surface.

3. Results and discussion

3.1. rGO characterization

For all samples heated up to 200 °C, a rough wrinkled sheet-like surface with no obvious morphology change was observed (Fig. 1), while at 300 °C surface morphology appeared less wrinkled but "blistered". During thermal treatment, volatile products (*e.g.* residual H_2O, CO_2, CO or other small gas molecules) were formed and trapped within GO layers due to the limited nature of diffusion; therefore they created the observed "blisters". We noticed that upon heating at higher temperatures (500 °C) these molecules were released by tearing the surface.

TGA diagram gave additional information about the thermal stability of oxygen-containing groups attached to GO. The thickness of GO films remaining after each thermal step was also compared to the TGA results. Both curves presented in Fig. 1(c), displayed three discrete stages. Firstly, a slight mass loss (~6%) occurred up to 120 °C, primarily attributed to the elimination of physisorbed and interlamellar water molecules. Secondly, the thermal decomposition of covalently bonded oxygen caused an additional significant mass loss (~31%), occurring up to 200 °C. Finally, a 12% mass loss observed up to 300 °C was probably due to the removal of more stable oxygen containing functional groups. These results are in good agreement to previous thermograms published in literature [41,42]. Furthermore, 50% film shrinkage has also been reported as a result of reduction of GO films by hydroiodic acid [43].

To probe the course of reactions occurring upon heating in ambient air, we employed FT-IR spectroscopy as a monitoring tool of the evolution of GO functional groups. Fig. 2a depicts all FT-IR spectra as heating temperature increases. We observe that a critical transition temperature
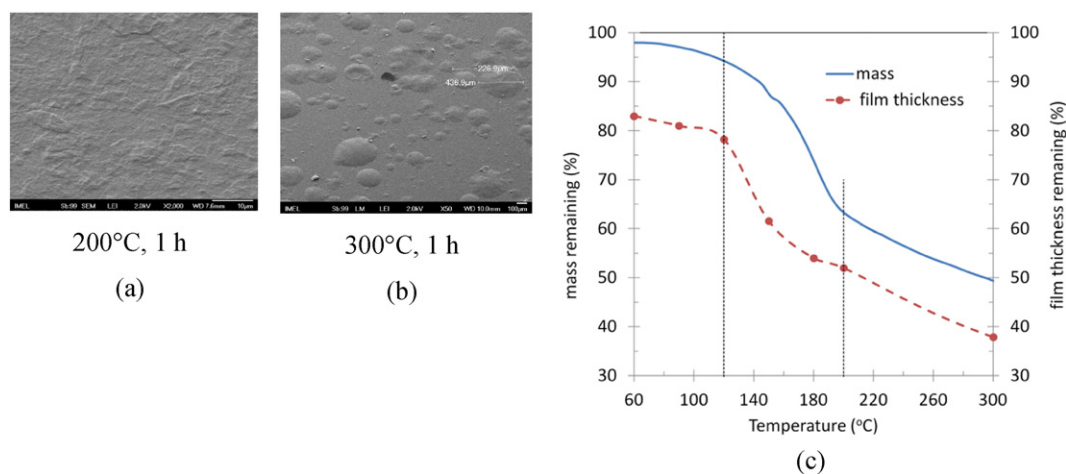
Fig. 1. (a) and (b) FESEM pictures of rGO films heated at 200 °C and 300 °C for 1 h. At 200 °C a rough wrinkled sheet-like morphology is observed while at 300 °C the surface is less wrinkled but "blistered". (c) A typical TGA thermogram of GO showing a significant mass loss due to the removal of oxygen containing groups from the basal plane. Remaining film thickness of GO after each thermal step is also presented in the same plot.