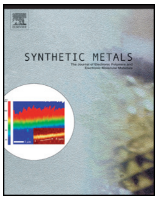
Synthetic Metals 204 (2015) 90–94

Contents lists available at ScienceDirect

Synthetic Metals

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



Transition of graphene oxide-coated fiber bundles from insulator to conductor by chemical reduction

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ARTICLE INFO

Article history:
Received 25 February 2015
Accepted 19 March 2015
Available online 28 March 2015

Keywords:
Graphene oxide
Polymer
Chemical reduction
Raman spectroscopy
Electrical conductance

ABSTRACT

We fabricate graphene oxide (GO)-coated fiber bundles *via* electrostatic deposition of GO sheets on polyester/cotton fiber bundles and investigate the changes in their properties by chemical reduction in a hydroiodic acid solution. The structural properties of GO sheets change rapidly upon exposure to reduction agents but remain under a high defect density regime after the reduction. The electrical resistance of the fiber bundles decreases logarithmically for the first minute of the reduction. In contrast to the structural property, a longer chemical reduction over tens of minutes deteriorates the electrical property. The effect of chemical reduction on the electrical conductance of GO-coated fiber bundles is discussed based on the competition of various factors, such as the number of conducting pathways and the carrier density, among others.

1. Introduction

Graphene oxide (GO) has attracted significant attention as an intermediate material for the mass production of graphene because it can be easily converted into conducting reduced graphene oxide (RGO) through the post-reduction process. Chemically exfoliated mono- or few-layered GO sheets are derived by treating bulk graphite with strong oxidizing agents in aqueous solutions [1–4]. New types of textiles fabricated by coating natural or synthetic textiles with GO sheets and post-treating are expected to advance the development of flexible and stretchable smart materials for wearable electronic devices and healthcare fabrics with antibacterial activity at a low cost and on a large scale [5–11].

GO is electrically insulating because of the significant number of attached oxygenated functional groups (hydroxyl and epoxy groups, among others), which induces a highly disordered lattice structure. During the post-reduction process, which converts insulating GO into conducting p-type RGO, the structural and electrical properties of GO change [4,12–16]. Boer et al. have reported a correlation between the apparent surface roughness and the level of deoxygenation of GO sheets by employing scanning tunneling microscopy [17]. However, the detailed transition behavior of GO from insulator to conductor remains unknown. To date, many researchers have continued the reduction process over an extended period (>30 min) to prepare RGO with high electrical conductivity [2–6,16–19]. A longer reduction time might be an obstacle to developing a continuous and rapid manufacturing process for the mass production of RGO-based materials. It is believed that the RGO sheet is composed of nanometer-sized conducting crystalline sp^2 domains interspersed with insulating oxidized regions on which oxygenated functional groups are densely attached [14,15,19], and that the charge transport mechanism through the RGO sheet generally follows the variable range hopping (VRH) model [19–21].

A detailed understanding of the structural and electrical properties of RGO-coated textiles is required to develop flexible and stretchable smart materials suitable for individual requirements. In this study, we fabricate RGO-coated fiber bundles, and analyze their as-fabricated structural and electrical property changes as a function of post-chemical reduction time using micro-Raman spectroscopy and electrical transport measurements. Our measurements show that the property changes occur rapidly upon exposure to the reduction agents (hydroiodic acid). However, the electrical characteristic shows different behaviors from those in the Raman spectroscopy studies upon reduction

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http://dx.doi.org/10.1016/j.synthmet.2015.03.018
0379-6779/

because the resistance further increases, even after the structural variation becomes saturated.

2. Experimental

We wrap commercially available polyester fiber bundles (Hana Spinning Co., polyester, 100%) with negatively charged GO sheets *via* electrostatic deposition using positively charged bovine serum albumin (BSA) molecules as adhesive agents in aqueous solutions [22,23]. Polyester is a flexible synthetic polymer that is extensively employed in daily life (apparel and home furnishings) and in industry (safety belts, bottles, and insulating tapes). We also obtained GO-coated cotton fiber bundles (Fujix Ltd., cotton, 100%) using the same method.

The GO sheets are prepared from natural graphite by using a modified Hummers and Offeman method [1,8]. The deposition of the GO sheets on the fibers continues until the attractive forces between the GO sheets and the BSA molecules become too weak to attract additional GO sheets; thus, a few layers of GO might be deposited (Fig. 1). The charges on the GO sheets and BSA molecules depend on the preparation conditions, especially the pH value. Our samples are prepared in aqueous solutions with a pH value from 3 to 4. The GO layers are post-reduced by immersing the GO-coated fiber bundles in a solution of 2.0 ml of hydroiodic acid (57 wt% in H_2O) and 5.0 ml of acetic acid (>99.7%) at 40 °C. Subsequently, the samples are rinsed with a saturated sodium bicarbonate ($NaHCO_3$) solution and then with distilled water and, finally, dried at room temperature. The reduction changes the color of the GO-coated fibers from light brown to black. Details on the fabrication of the RGO-coated fiber bundles are described elsewhere [8].

The properties of the as-fabricated RGO-coated fiber bundles are investigated using micro-Raman spectroscopy and electrical measurements. A confocal micro-Raman experiment is performed under ambient conditions in backscattering geometry. A laser line of 514.5 nm (2.41 eV) is focused on the RGO sheets attached to the fibers using a 50× objective lens, and the scattered light is analyzed using a Horiba Jobin Yvon spectrometer (LabRAM HR) equipped with a cooled charge-coupled device. The electrical conductance is analyzed by measuring the current *versus* voltage (I–V) relationships in the low bias-voltage regime in a vacuum using a probe station (LakeShore, CRX-4K).

3. Results and discussion

RGO-coated fiber bundles are composed of hundreds of individual microfibers with diameters of approximately 10 μm. The optical microscope and scanning electron microscope (SEM) images show that the GO coating on the fibers is inhomogeneous (Fig. 1). We collect Raman signals from the RGO sheets that are partially detached from the fibers to exclude the strong Raman signals from the underlying fibers. In cases of arbitrary points of RGO-coated polyester/cotton fibers, the Raman signals from the underlying polyester/cotton are too strong to overshadow the subtle changes in the Raman spectra of RGO. Raman spectra from the underlying fibers show a polarization dependence on the fiber direction. However, the Raman spectra of the RGO sheets show no polarization dependence. (Fig. A.1, Supplementary material).

Fig. 2 shows a series of Raman spectra of RGO as a function of reduction time. The G peak at approximately 1580 cm^{-1} is the stretching mode of the C—C bond of the sp^2 structure in the rings and chains, while the D peak at approximately 1350 cm^{-1}, related to the breathing of the sp^2 carbon rings, is only Raman active in the presence of point defects. In addition, the D′ peak, shown as a shoulder of the G peak at approximately 1620 cm^{-1}, is also related to defects [24–26]. A strong D peak and broad G peak compared with those of pristine graphene imply that there are many structural disorders, such as vacancies and corrugations, on the RGO sheets. Note that the intensity ratio of the D peak to the G peak (I(D)/I(G)) increases by reduction, indicating that our samples are in a highly defective state, even after the chemical reduction in a hydroiodic acid solution is completed, as explained in later.

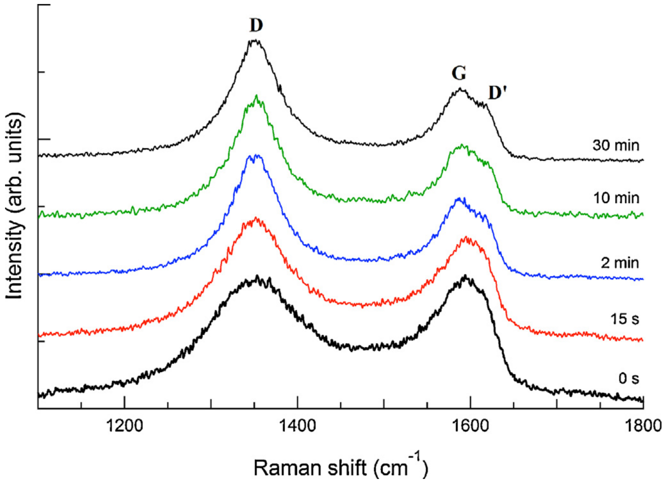

Fig. 2. Change of the Raman spectrum of the RGO sheets deposited on polyester fibers as a function of chemical reduction time. All of the Raman spectra are normalized to have the same D peak intensity. The incident laser line is 514.5 nm.

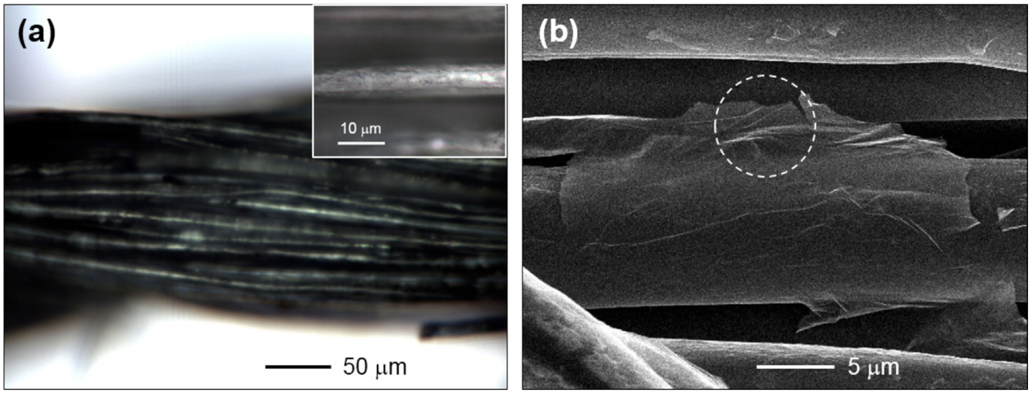

Fig. 1. (a) An optical microscope image of the RGO-coated polyester fiber bundle. The inset shows an enlarged image of an individual polyester fiber. (b) SEM image showing the RGO sheet incompletely wrapping a fiber. The dotted circle indicates the part of the RGO sheet from which the as-fabricated Raman spectrum is obtained, selected to exclude the strong effects of the underlying fiber.