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The effect of concentration of graphene nanoplatelets on mechanical and electrical properties of reduced graphene oxide papers

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ABSTRACT

Macroscopic, freestanding graphene-based paper-like materials are of interest for use as mechanically strong, stiff, and flexible and electrically conductive materials. Chemically reduced graphene oxide paper shows promise for such applications. In this work, we studied the mechanical and electrical properties of a set of paper materials prepared by filtration of homogeneous colloidal suspensions of hydrazine-reduced graphene oxide with different concentrations. Young's modulus, fracture strength, and fracture strain of each type of sample was determined by tensile tests. The paper sample prepared from the colloidal suspension with the lowest concentration of reduced graphene oxide platelets had the highest modulus and fracture strength and showed the smoothest surface morphology. The electrical conductivity measured by the four-probe measurement method increased as the concentration was increased.

1. Introduction

Graphene, a two dimensional one atom thick sp^2 carbon network, is of interest in part due to its excellent mechanical, electrical, and thermal properties [1–9]. The physical and chemical properties of graphene-based materials can be tuned by chemical modification [1,10]. A macroscopic, freestanding graphene-based paper-like material can be produced by filtration of homogeneous colloidal suspensions of chemically modified graphene (CMG) platelets using membrane filters [11–17]. Such paper-like materials may be a good candidate for use as flexible substrates with high thermal and chemical stability, gaskets, sealants, actuators, and biocompatible substrates due to their good mechanical and electrical properties [18,19]. Herein we describe an approach to tune the mechanical and electrical properties of paper-like materials by controlling the concentration of reduced graphene oxide platelets in the colloidal suspensions.

The mechanical and electrical properties of graphene-based paper materials have been controlled by chemical modification of graphene oxide platelets in the suspensions or by post-modification of paper samples [11,13–16,20]. Chemical reduction of electrically insulating graphene oxide papers can also produce conductive reduced graphene oxide papers [13,14,16,17]. Recently, we developed a new route to make homogeneous colloidal suspensions of reduced graphene

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oxide in a wide variety of organic solvents and reported on the good electrical properties of paper-like materials produced by filtration of such suspensions [16]. Here, we have studied the mechanical and electrical properties of reduced graphene oxide paper samples as a function of the platelet concentration of the initial colloidal suspensions used to prepare the papers. We found that suspensions with a relatively low concentration of CMG platelets produced paper samples with a smooth surface morphology and superior mechanical properties relative to paper samples obtained from concentrated suspensions. The electrical conductivity measured by a four-probe method increased as the concentration was increased. A degree of control of the mechanical and electrical properties of graphene-based paper materials is thus obtained by varying the concentration of CMG platelets in the suspension.

2. Experimental

2.1. Sample preparation

2.1.1. Preparation of a batch of a colloidal suspension of reduced graphene oxide [16]

Graphite oxide (GO) was synthesized from natural graphite (SP-1, Bay Carbon, MI) by the modified Hummers method [20].

A colloidal suspension of graphene oxide platelets in purified water (50 mg of GO, 3 mg/ml) was prepared in a 250 ml flask with 2 h of bath ultrasound (VWR B2500A-MT). A suspension of graphene oxide in the H_2O/*N*,*N*-dimethylformamide (DMF) solvent mixture was obtained by addition of DMF (volume ratio of DMF:H_2O = 9:1) into the aqueous graphene oxide suspensions. Hydrazine monohydrate (1 μl per 3 mg of GO) (98%, Aldrich) was subsequently added to the suspension. Additional stirring with a Teflon-coated stirring bar at 80 °C for 12 h yielded a black suspension of reduced graphene oxide platelets.

2.1.2. Preparation of a set of reduced graphene oxide paper samples (samples 1–3)

The suspension produced as above was diluted to produce three suspensions with different concentrations in the DMF/water mixture (DMF:H_2O = 9:1) by further addition of the DMF/water mixture (total amount of GO = 12 mg, concentration (GO/solvent mixture) = 3 mg/10 ml (1), 3 mg/20 ml (2), and 3 mg/40 ml (3), respectively). Paper samples were produced by filtration (Anodisc® membrane filter, 47 mm in diameter, 0.2 μm pore size, Whatman, Middlesex, UK) of each batch, separately. The paper samples (**1**–**3**) were dried in air and peeled off the membrane, and then were further dried in air for 3 days.

2.1.3. Preparation of reduced graphene oxide paper samples with agglomerated platelets (sample 4)

An aqueous suspension (GO/solvent mixture = 3 mg/5 ml, total amount of GO = 12 mg) of graphene oxide was produced as described above. Hydrazine monohydrate (1 μl per 3 mg of GO) was subsequently added to the suspension. Additional stirring with a Teflon-coated stirring bar at 80 °C for 12 h yielded agglomerated particles of reduced graphene oxide platelets. Paper samples were produced by filtration of the mixture with a membrane filter. The paper sample (**4**) was dried in air and peeled off the membrane, and then was further dried in air for 3 days.

2.2. Measurement of mechanical and electrical properties of the paper samples

In order to characterize the stress–strain behavior of the materials, static uniaxial tensile tests were conducted with a dynamic mechanical analyzer (DMA Q800, TA Instruments). The samples were cut into a rectangular shape and clamped using film tension clamps with a clamp compliance of about 0.2 μm/N. A preload force of 0.01 N was applied to the samples at 35 °C for 4 h to reach thermal equilibrium. Tensile tests were conducted in controlled-force mode with a force ramp rate of 0.05 N/min. The sample width was measured using standard calipers. The length between the clamps was measured by the DMA instrument. The sample thickness was determined by averaging thicknesses measured at five or more places on each scanning electron microscopy (SEM) image of the fractured cross section.

The electrical conductivity (σ) of reduced graphene oxide films was obtained using the simple relation $\sigma = 1/Rt$, where R is the surface resistivity and t is the film thickness. The surface resistivity was measured by the four-point probe method (CRESBOX, Napson) and the thickness was measured from SEM images of the cross-section of broken paper samples.

2.3. Instruments

SEM images of the paper samples were taken with an FEI Quanta-600 FEG Environmental SEM. X-ray Diffraction (XRD) of the paper samples was performed for two theta values from 10° to 50° in order to characterize the interlayer spacing. The characterization was done in a Phillips powder X-ray diffractometer at 40 keV and 30 mA with a step size of 0.02° and a dwell time of 2.0 s. Samples with a size of ~3 mm × 3 mm were sectioned and mounted using a low melting temperature wax onto a special Quartz substrate (cut 6° from (0001)) designed to minimize the background signal. X-ray photoelectron spectroscopy (XPS) measurements of paper samples were performed with an Omicron ESCA Probe (Omicron Nanotechnology, Taunusstein, Germany) using monochromatic AlKα radiation ($h\nu$ = 1486.6 eV).

3. Results and discussion

Homogeneous colloidal suspensions of reduced graphene oxide platelets were produced by hydrazine treatment of suspensions of graphene oxide in the DMF/water mixture at 80 °C (DMF:water = 9:1 by volume; see the Section 2) [16]. A set of suspensions with three different concentrations were prepared as described in the Experimental section (concentration of GO/solvent mixture: 3 mg/10 ml (**1**), 3 mg/20 ml (**2**), and 3 mg/40 ml (**3**)). Suspension **1** was used to make other suspensions with lower concentrations (suspensions **2** and **3**) by adding more amounts of the DMF/water mixture into suspension **1**. The paper samples were prepared by filtering such