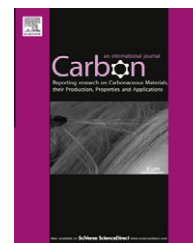


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The effect of concentration of graphene nanoplatelets on mechanical and electrical properties of reduced graphene oxide papers

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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.

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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 H₂O/N,N-dimethylformamide (DMF) solvent mixture was obtained by addition of DMF (volume ratio of DMF:H₂O = 9:1) into the aqueous graphene oxide suspensions. Hydrazine monohydrate (1 μ l 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:H₂O = 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 μ m 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 μ l 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 μ m/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 \sim 3 mm \times 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 AlK α 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

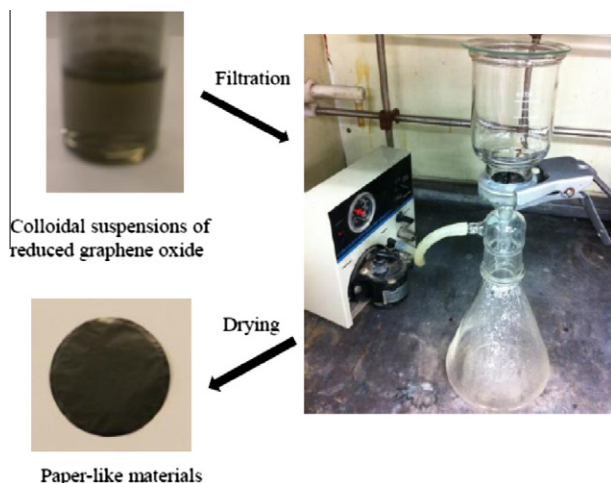


Fig. 1 – A schematic showing production of paper-like materials of reduced graphene oxide.

suspensions using a membrane filter (Fig. 1), and then dried in air for 3 days. All samples had similar thicknesses (approximately 3–5 μm), as determined from SEM images of the cross section.

The C/O atomic ratio of the dried paper samples was about 10, as measured by combustion-based elemental analysis, suggesting significant removal of oxygen functionalities on graphene oxide platelets (C/O atomic ratio of GO = ~ 1.5 ; this value includes contribution from water molecules trapped in GO particles) [20–25]. XPS measurements on the dried paper samples further confirmed successful reduction of graphene oxide (see Supporting information (SI)). The XPS spectrum of the reduced graphene oxide papers in the C1s region showed significant loss of oxygen functional groups relative to that of graphene oxide papers.

The mechanical properties of the paper-like materials were measured by tensile tests on a DMA machine (5–10 paper samples were tested at each concentration). Stress–strain curves of graphene oxide paper samples without hydrazine treatment show a straightening region at small strain followed by a linear region (Fig. 2; see SI for further details) [11,12]. It has been suggested that the straightening region in graphene oxide paper is induced by the significant concentration of water molecules in the interlayer galleries [26]. On the other hand, all paper samples (1–3) of reduced graphene oxide did not show this initial straightening region, as paper materials composed of reduced graphene oxide platelets do not contain water molecules in the interlayer galleries [16]. The samples were brittle and showed high Young's modulus (20–35 GPa), high fracture strength (65–130 MPa), and low fracture strain (0.25–0.69%) [11,13]. Although chemical reduction of graphene oxide with hydrazine significantly improved the electrical properties of paper samples [16], the mechanical properties of both graphene oxide [11,12] and hydrazine-reduced graphene oxide paper samples were similar to each other.

We studied the mechanical properties of paper samples as a function of the concentration of reduced graphene oxide platelets in the homogeneous colloidal suspensions (1–3) used to prepare the papers. As shown in Fig. 2, among the samples tested, the paper sample prepared from the suspension with the lowest concentration (3 mg of GO/40 ml of solvent mixture, 3) exhibited the highest Young's modulus (27 GPa) and fracture strength (132 MPa). The Young's moduli of samples 1 and 2 (~ 20 GPa) were similar to each other; however, both were lower than that of sample 3. Strain at fracture of sample 3 (0.54%) was slightly smaller than those of samples 1 (0.69%) and 2 (0.64%).

The structural characteristics of the paper samples were observed via SEM study of cross sections (of samples broken

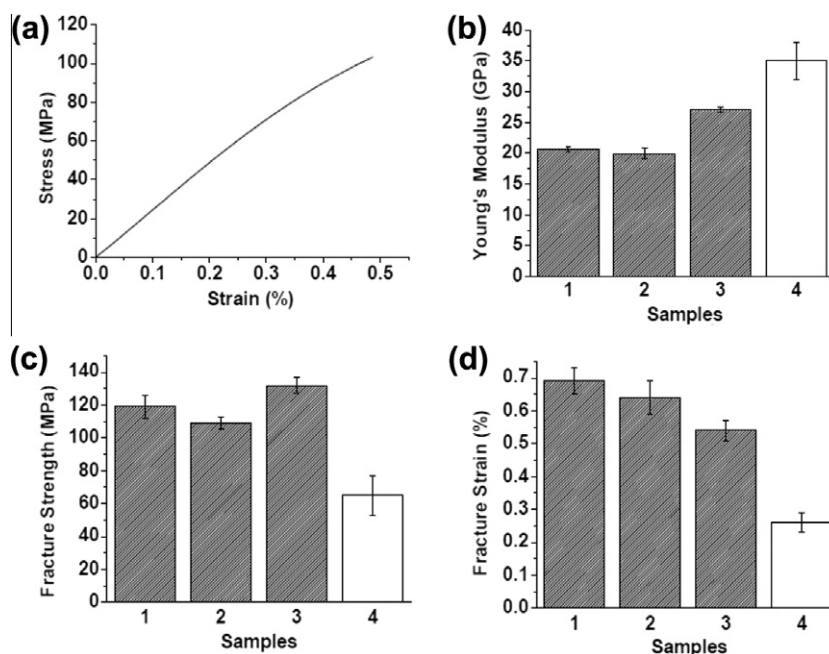


Fig. 2 – Mechanical properties of the paper samples. (a) A stress–strain curve of sample 1. Histograms of (b) Young's modulus, (c) fracture strength, and (d) fracture strain of samples 1–4 (error bars in b, c, and d represent standard deviation).

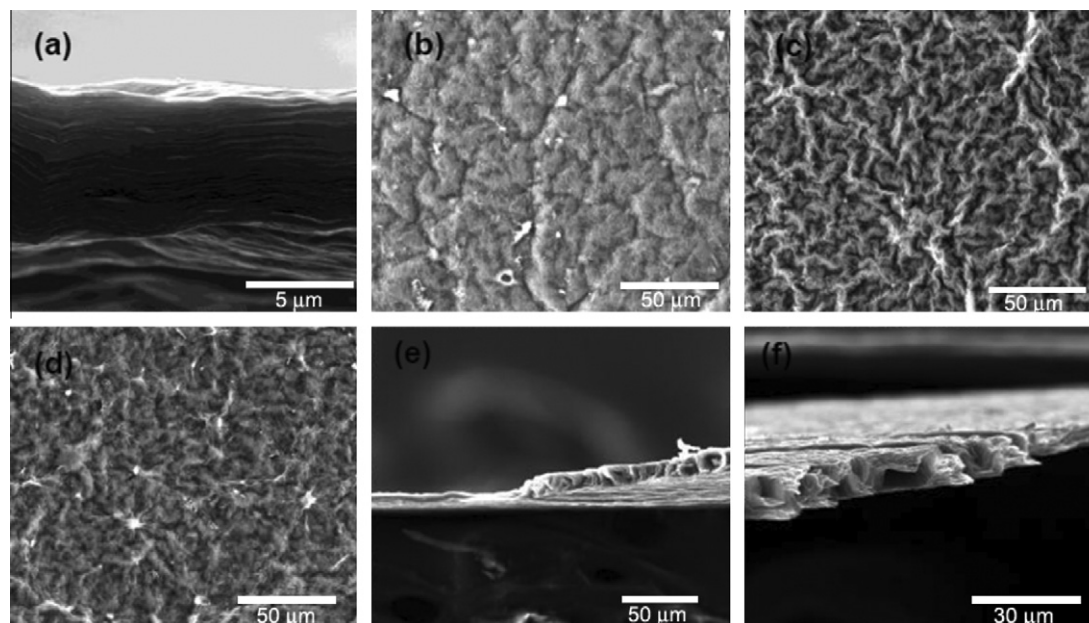


Fig. 3 – SEM images of paper samples. (a) Cross section of sample 1; surface of (b) sample 1, (c) sample 2, and (d) sample 4; (e) and (f) cross sections of sample 4.

by tensile testing) and the surfaces of the papers. A highly-layered structure, which is typically observed in the graphene-based paper samples [11–13], was observed in all SEM images of the cross sections (Fig. 3a). Interestingly, SEM images of the surface of sample 3 showed a smoother morphology relative to those of sample 1 and 2 (Fig. 3). This suggests that the concentration of graphene platelets in colloidal suspensions has a significant effect on the surface morphology of the paper samples, at least for this method of preparing samples. The better mechanical properties of sample 3 might be the result of the lower concentration of the suspension, relative to samples 1 and 2. XRD patterns (see SI) of three paper samples (1–3) showed two broad peaks at $2\theta = 22.8^\circ$ and 13.8° , corresponding to an interlayer distance (d -spacing) of 3.9 and 6.4 Å, respectively. Those distances are smaller than that of graphene oxide paper [11], suggesting successful removal of oxygen functional groups and water molecules trapped in the interlayer galleries of graphene oxide paper. However, no major differences were observed between the XRD patterns of the paper samples 1–3.

While suspensions 1–3 were homogeneous colloidal dispersions of reduced graphene oxide, hydrazine reduction of the suspension of graphene oxide with the highest concentration (3 mg of GO/5 ml of solvent mixture, 4) resulted in agglomeration of reduced graphene oxide platelets. Interestingly, filtration of agglomerated platelets (4) also produced free-standing paper samples, meaning that homogeneous colloidal suspensions are not necessarily required to make paper samples. Surface morphology of the paper sample (4) in a SEM image was rougher than that of sample 1. SEM images of the cross section of the paper show a crumpled morphology in localized regions (Fig. 3e and f). To observe agglomerated particles by SEM, the suspensions that were used for the production of sample 4 were dropped on a glass slide and dried. As compared to the thin nano-platelets that

were typically observed from homogeneous suspensions of reduced graphene oxide, agglomerated particles with lateral dimensions of approximately 400–800 nm and various shapes were observed in the SEM images of dried down suspensions used to make sample 4 (see SI). SEM images of the fracture sections of the paper sample 4 (which was torn by hand) showed that the inside surface is considerably rougher than the paper sample 3 (see SFig. 6 in SI). Agglomeration of the platelets in the batch could lead to the formation of such a crumpled cross-sectional morphology and rough surface morphology observed in paper sample 4. However, the paper sample 4 was significantly stiffer than samples 1–3, despite being produced from a reduced graphene oxide mixture containing agglomerated particles. The modulus (~ 35 GPa) of sample 4 was 30–75% higher than that of other samples. Although the mechanisms are unknown, we speculate that physical interlocking between agglomerated platelets might lead to such a high stiffness.

The electrical conductivity is another important property of reduced graphene oxide systems. Additionally, the conductivity of the paper samples has been often used to assess the degree of reduction of graphene oxide platelets in colloidal suspensions [13,14,16,17,20]. We measured the conductivity of paper samples (1–4) by a four-probe measurement. Interestingly, as the concentration increased, the conductivity increased as shown in Table 1. Contrarily, the mechanical properties of the paper samples improved as the concentration decreased (see above). The paper sample 4, which was produced from the mixture primarily composed of agglomerated particles, showed the highest conductivity. This could be due to the presence of crumpled particles, which may be advantageous for promoting formation of out-of-plane conductive networks between reduced graphene oxide platelets relative to highly-oriented and layered platelets, leading to a higher electrical conductivity of the paper sample.

Table 1 – Electrical conductivity of a set of paper samples (1–4).

Sample (conc.)	1 (3 mg/10 ml)	2 (3 mg/20 ml)	3 (3 mg/30 ml)	4 (3 mg/5 ml)
Conductivity (S/m)	152	108	86	253

4. Conclusion

We prepared a set of homogeneous colloidal suspensions of hydrazine-reduced graphene oxide in a DMF/H₂O mixture with different concentrations of platelets. Paper-like materials composed of reduced graphene oxide platelets were prepared by simple filtration of such suspensions. Young's modulus, fracture strength, and fracture strain of such paper samples were measured by tensile tests on a DMA machine. The paper samples prepared from the lowest concentration colloidal suspension had the highest modulus and fracture strength and showed the smoothest surface morphology observed in SEM images. The electrical conductivity measured by four-probe measurement increased as the concentration increased. Reduction of graphene oxide in a concentrated suspension resulted in the agglomeration of reduced graphene oxide platelets. The paper sample produced by filtration of such agglomerated mixture showed a significantly higher modulus and electrical conductivity than those generated from homogeneous colloidal suspensions. This study could be useful to control the mechanical and electrical properties of graphene-based paper materials which are a good candidate for various applications.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.carbon.2012.05.042>.

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