



Lateral diffusion of graphene oxides in water and the size effect on the orientation of dispersions and electrical conductivity



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ABSTRACT

We have measured the translational and rotational diffusion coefficients of graphene oxide (GO) sheets in water by using dynamic light scattering (DLS) and depolarized DLS. We show that the GO sheets in dilute regime translate laterally in such a way that rigid-rods move perpendicularly to their axis direction. This discovery renders a facile method for the determination of the average lateral size of GO sheets by using DLS with the simple rod-model. The lateral size (L) determined by DLS is 20.15, 3.65, 1.79, and 1.09 μm for samples with ultra-sonication exposure times of 0, 3, 12, and 60 min, respectively. The L is correlated with the critical LC concentration and the electrical percolation threshold. The size dependency of the critical LC concentration follows the scaling of the Onsager model if and only if $L \leq 3.65 \mu\text{m}$. In the reduced GO (rGO) coated films, the electrically conductive networks are two dimension in percolation scaling law when $L \geq 3.65 \mu\text{m}$, but the higher fractal dimension when $L \leq 1.79 \mu\text{m}$. In the films having 85% light transmittance, the surface resistivity is 6.2 $\text{k}\Omega/\text{sq}$ when $L \geq 3.65 \mu\text{m}$, and 60 $\text{k}\Omega/\text{sq}$ when $L \leq 1.79 \mu\text{m}$.

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1. Introduction

Graphene, a one-atom thick carbonic material, has been of great interest due to its excellent electrical, optical, mechanical, and thermal properties [1]. The chemical exfoliation method is an economic and scalable way to obtain graphene oxide (GO) sheets from natural graphite flakes [2–4]. GO has at least four kinds of oxygen functionalities. Epoxide and hydroxyl are located on the basal plane of GO, while carboxyl and carbonyl are located at the edge [5–7]. In order to make the properties of GO sheets close to those of graphene sheets, many reduction methods have been suggested [8–17]. In addition, GO dispersions, reduced GOs (rGOs), and graphene sheets in various organic solvents have been widely investigated [18–24]. In turn, characterizing GO sheets dispersed in a solvent has gained interest for potential applications utilizing the excellent properties of graphene [25–35]. The lateral dimension of graphene sheets is one of the most important characteristics of GO

sheets because it affects various properties such as the electrical conductivity [25] and thermal conductivity [26,27]. For GO sheets, size-controlled synthesis [28–30] and size fractionation methods [31–35] have also been reported. In general, determining the shape and size of nanoparticles can be important in a variety of studies on various nanostructure composites [36–49]. Because electron microscope images represent the size of objects only in a local area, developing a method to determine the size distribution of GO sheets dispersed in a solvent is one of the important research issues in graphene-related technologies. Recently, flow cytometry [50] and ultracentrifugation [51] have been proposed to determine lateral size of GO sheets and its distribution.

Dynamic light scattering (DLS) is a well-established method for the measurement of diffusion coefficients of particles with any shape [52–54]. However, adequate mathematical models are required for the correlation of the measured diffusion coefficients with the shape and size of the particles. For spherical particles, the Stokes-Einstein equation is used for the determination of particle size by using DLS. The hydrodynamic equivalent diameter of non-spherical particle such as GO sheets can be estimated by using the Stokes-Einstein equation [55]. For a single-walled carbon nanotube (with the length shorter than 32 μm), a rigid rod model

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can be used for the determination of the lengths of CNTs from the measured diffusion coefficients [52,56]. For multi-walled carbon nanotubes, a worm-like chain model with static bending was used for the determination of the shape and size of them [52,57]. However, there has yet to be a method established to determine the lateral size of GO using DLS and depolarized DLS.

In this work, we show that the GO sheets translate mainly in the lateral direction. From this discovery, we present a facile method to determine the lateral size distribution of GO sheets with DLS and depolarized DLS by using the simple rod-model. The proposed method is promising for the measurement of the lateral size of GO sheets ranging in size from submicron to tens of microns. This method is highly reproducible (within 18% error) as a useful method for measuring the average lateral size when GO sheets (prepared by a modified Hummers method [3,4]) are dispersed in neutral water (pH = 6.0–7.0). In the case of GO sheets prepared by a Brodie method [2,58], the reproducibility is also good (within 18% error) when pH is 8.0–9.0. We also demonstrate that the average lateral size determined via DLS is well-correlated with either the critical LC concentration or the percolation threshold of electrical conductivity in GO-coated film. We show that the size dependency of the critical LC concentration follows the scaling of the Onsager model if and only if the average lateral size equals or less than 3.65 μm . In the case of GO coated films, the electrically conductive networks are two dimension in percolation scaling law when the average lateral size is 3.65 μm or more, but the higher fractal dimension when the average lateral size is 1.79 μm or less.

2. Experimental

2.1. Graphene oxide dispersions

GO dispersion was prepared from flake graphite (19 μm nominal particle size, Asbury Co., LTD.) using a modified Hummers method [3,4] as reported in our previous work [4]. The synthesized GO was washed with distilled water repeatedly reaching until pH 6–7 [4]. In a 20 ml vial, a GO dispersion of 0.0028 wt% was exposed for 0–60 min to a bath sonicator (WUC-A06H, Daihan Scientific, 40 KHz, 150 W).

2.2. Characterization

The sonicated GO dispersion was cast onto a silicon wafer for scanning electron microscopy. The morphology of the graphene oxide flake was observed with a field-emission scanning electron microscopy (FE-SEM, JSM-6700F, JEOL, Japan) and high-resolution transmission electron microscopy (TEM, JEM-2010, JEOL, Japan). The sonicated GO dispersion was cast onto a mica surface for atomic force microscopy. The thickness of the GO flake was estimated with a tapping mode atomic force microscope (AFM, MMAFM-2, Digital Instruments). X-ray diffraction (XRD) analyses of graphite, GO and rGO were performed using a Rigaku (Japan) - Ultima with CuK_α radiation. The changes in the carbon-to-oxygen (C/O) atomic ratio of GO sheets were observed with X-ray photoelectron spectroscopy (XPS, MultiLab 2000, Thermo Scientific, UK) using Mg K_α radiation ($h\nu = 1253.68 \text{ eV}$, 300 W). The carbon structure of GO and rGO sheets was analyzed with Raman spectroscopy (NTEGRA SPECTRA, NT-MDT, Spectrum Instruments) using 532 nm wavelength laser.

2.3. Dynamic light scattering

The diffusion coefficients were measured by dynamic light scattering apparatus (Multiscope, Korea). A diode-pumped solid state laser (DPSSL) supplied approximately 100 mW of energy at

$\lambda_0 = 532 \text{ nm}$. A 256-channel digital autocorrelator was used to compute the scattered photons' time autocorrelation function, with a 480 ns minimum delay time. Measurements were made at several scattering angles, from 30 to 90°. Both the polarizer and detector had a 1:100,000 extinction ratio. The detector was rotated at a 1-degree resolution by a motor control unit. The concentration of the GO dispersion in all measurements was 0.0028 wt%. The GO dispersions were neutral pH at all measurements. All measurements were performed at room temperature.

2.4. Preparation of rGO/PET films

Isopropyl alcohol (IPA, 99.9%, Honeywell) was added to an aqueous sonicated GO dispersion (volume ratio = 1:1). The GO/IPA/water dispersions of various GO concentrations (0.01, 0.02, 0.04 and 0.08 wt%) were casted onto a PET film (thickness 125 μm , Kolon industries). The thickness of each dispersion layer was set at 12.5, 25, 50, and 100 μm , respectively, in order to vary the number of GO sheets on the PET film after drying. The liquid-cast film was dried at 323.15 K for 10 min. The film was exposed to a hydroiodic acid (HI acid, 55%, Sigma Aldrich) atmosphere at 353.15 K for 1 h. The reduction was performed by placing the GO films in a HI acid atmosphere. rGO films were rinsed with ethanol (94%, SK Chemicals) for 10 min to remove residual HI acid, then dried in a vacuum oven for 30 min at 323.15K. Surface resistivities were measured by a Keithley 2400 electrometer, using the four-point probe technique.

3. Results and discussion

3.1. Characterization of GO and rGO

GO dispersions were prepared by using a modified Hummers method [3,4]. FE-SEM image of the edge of the dried GOs (in powder form) are presented in Fig. 1a, showing a layered structure. TEM image of the sonicated GO sheets showed the electron transparency of the typical image of graphene oxide as seen in Fig. 1b. XRD patterns of graphite, GO and reduced GO (rGO) by HI acid are presented in Fig. 1c. Graphite powder peak was observed at $2\theta = 26.4^\circ$, which corresponds to the interlayer spacing of 0.34 nm (Fig. 1c) [4]. The peak of dried GO and rGO powder was seen at $2\theta = 9.4^\circ$ and 24.2° , respectively (Fig. 1c). The interlayer spacing of the rGO was decreased to 0.37 nm from 0.94 nm because of the removal of the oxygen functional groups on the surface of GO sheet [4,59]. Fig. 1d and e shows the C1s peaks of GO before and after HI acid reduction, respectively. The C1s peak of GO was contributed by two main components arising from C–C/C=C (284.87 eV) and C–O (286.89 eV) groups, and by two minor components from C=O (288.77 eV) and O=C–O (290.61 eV) groups (Fig. 1d) [12,59]. Most of oxygen functional groups in GO were hydroxyl and epoxy groups [12,59]. After reduction of GO, C–O (286.21 eV) bonds of main oxygen functional group were almost removed as seen in Fig. 1e. From the XPS analysis, we calculated the surface C/O atomic ratio of GO and rGO. The C/O atomic ratio of GO was 1.93. After reduction, the C/O atomic ratio increased to 4.37. The intensity ratio of D peak (1344 cm^{-1}) to G peak (1588 cm^{-1}) (I_D/I_G) in the Raman spectrum was increased after HI acid reduction as seen in Fig. 1f [59]. The increase of I_D/I_G was owing to the increase of sp^2 sites of carbon in rGO after reduction [59,60].

3.2. Lateral size and thickness of GO sheets

FE-SEM images of GO sheets (on a silicon wafer) corresponding to ultra-sonication exposure times of 0, 3, 12, and 60 min are presented in Fig. 2a. The lateral size of the GO sheets was reduced by

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