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Electric Field-Induced Ordering of Reduced Graphene Oxide Particles in Colloid

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We demonstrated that the alignment of reduced graphene oxide (rGO) particles in dimethylformamide dispersions was electrically controlled. The field-induced alignment of the rGO particles imparted an optical anisotropy of both the birefringence and dichroism, simultaneously. The optical transmittance with crossed polarizers is determined by the combination of both birefringence and dichroism, and hence, it is somewhat difficult and inaccurate to calculate the degree of the ordering of rGO particles. On the other hand, by using parallel polarizers in the measurement, the birefringence effect could be eliminated, and we measured the order parameter of the rGO. Interestingly, the order parameter of rGO particles was high and comparable to that in GO dispersion. The saturated *S* order parameter at high electric fields decreased, as the rGO concentration increased. The field-induced rGO ordering will be useful for various applications such as flexible electronics and energy storage devices.

Keywords: Graphene, Reduced Graphene-Oxide, Solution Process.

1. INTRODUCTION

Reduced graphene oxide (rGO) is a conductive 2-dimensional material that is easily obtainable by chemically reducing graphene oxide (GO). Recently, various chemical reduction methods of GO dispersions have been intensively studied in order to take advantage from the remarkable electrical, mechanical, and thermal properties of graphene.[1–5] The solution processability of rGO dispersions is unique and useful for many applications including electronics,[1,3] energy storage,[6,7] and graphene-based field effect transistors for different sensor applications.[8,9] These applications require both the manipulation of individual rGO particles and alignment of many rGO particles; by controlling the rGO flake alignment, the mechanical and electrical properties of rGO fibers and films can be improved.[10,11]

It has been reported that the application of weak electric fields can align GO particles uniformly in diluted GO dispersions.[12–14] Aqueous GO dispersions are known to have a high Kerr coefficient.[12] The high electro-optical sensitivity of GO dispersions derives from the electrical double layer (EDL) of GO particles with extremely high aspect ratio. The thick EDL is related to the large amount of functional groups on the GO basal plane. In contrast, the functional groups are mostly removed in rGO particles, and rGO has very low oxygen content. The field-induced GO alignment can be used to obtain wide uniform areas of aligned GO. In the study, the optical birefringence was used to evaluate the order parameters, that is, the degree of ordering of the GO particles.[15,16] On the other hand, rGO dispersions have a high optical absorption in the visible range, and the optical birefringence measurement is limited, because the anisotropic dichroism is coupled with the optical birefringence.

In this study, we investigate the alignment of rGO flakes dispersed in dimethylformamide (DMF). Since rGO is an opaque material, the light absorption is much higher, even in low concentrations. The optical transmittance of an rGO cell under the crossed polarizer arises from the combination of the birefringence and dichroism effects. Although the measurement using the crossed polarizers can qualitatively approve the field-induced alignment, the quantitative determination of the degree of rGO alignment cannot be made in the method owing to the coupling of the dichroism effect and birefringence. On the other hand, by using parallel polarizers in the optical measurement, in which the birefringence effect is eliminated, the ordering parameter of rGO could be accurately determined. Interestingly, we

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reveal that the rGO particles are well aligned by applying an electric field, and the electrical sensitivity is similar to that of GO dispersions, despite the low density of functional groups. It might be due to the conductivity of rGO particle itself.

2. EXPERIMENTAL DETAILS

Aqueous GO dispersions were prepared using Hummers method, by exfoliating graphite powder.[12, 17] Then, the GO dispersions were reduced using *p*-toluene sulfonic acid (PTSA), following a recently reported method.[18] The PTSA (4 g) was added to 200 mL of a 0.2 wt.% GO dispersion, and the mixture was stirred for 24 h at 90 °C. The brownish GO dispersion gradually changed into a black precipitate. The black precipitate was washed repeatedly with deionized water by centrifugation, and the supernatant liquid was discarded to remove unwanted materials. Then, the rGO was dispersed in DMF. We prepared four rGO-DMF dispersions with rGO concentrations varying from 0.1 to 1 mg/mL. The rGO dispersion was ultra-sonicated to obtain a uniform dispersion. Scanning electron microscopy (SEM) was used to measure the particle size distribution. For SEM, the samples were prepared on a Si substrate by spin coating a much diluted rGO dispersion. The rGO particles were highly poly-dispersed, and the average size was approximately 1.5 μm.

X-ray photoelectron spectroscopy (XPS) was used to confirm the quality of the rGO particles. The sample for XPS was prepared on a Si wafer substrate by drop casting the rGO dispersion (1 mg/mL). For the absorption spectrum measurement, we fabricated rGO cells sandwiched between two transparent glass substrates with an optical path length of 1 mm. The absorption spectrum was measured using a UV-Vis spectrometer (SV2100, K-MAC Company, Korea). The field effect on the rGO dispersions was measured using an rGO cell with parallel electrodes. Two parallel electrodes spaced by 2 mm were inserted in the rGO cells. We used a 10 KHz square wave electric field and controlled the amplitude between 0 and 50 V.

3. RESULTS AND DISCUSSION

Figure 1 shows the rGO dispersions in DMF with various concentrations, and a 1 mg/mL GO dispersion in DMF for comparison. Both GO and rGO dispersed well in DMF and formed good dispersions, although GO was better dispersed.[19, 20] As shown in Figure 1, a 1 mg/mL rGO dispersion appears as almost black and opaque, while a GO dispersion with the same concentration appears as brownish and transparent.

XPS analysis is an efficient technique to detect the reduction of GO. The C1s spectra of GO and rGO are shown in Figure 2. Both C1s spectra exhibited three clear peaks, which correspond to the C═C/C–C, C–O/C═O, and O–C═O functionalities. After reduction, the peaks

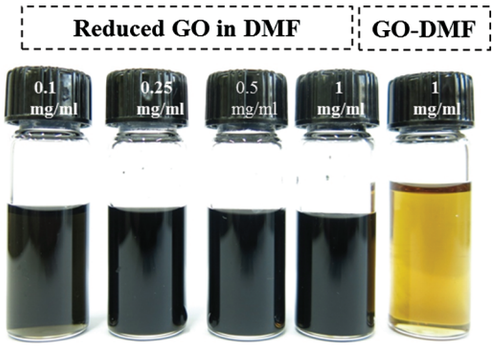

Figure 1. rGO colloidal dispersions in DMF with varying concentrations, and GO dispersion in DMF. The concentrations are indicated on the top of each bottle.

corresponding to the C–O/C═O and O–C═O functionalities (red and blue lines) strongly decreased, indicating the removal of oxygen functionalities. Thus, it is clear that the chemical reduction process was performed correctly, and the GO particles transformed into rGO particles.[1]

As shown in Figure 3, rGO has a high optical absorption in the visible range. Even a single atomic layer of graphene absorbs 2.3% of light.[21] We measured the absorption spectra of the rGO dispersions with different concentrations as shown in Figure 3. At very low concentrations (0.1 mg/mL), the rGO dispersion situated in a 1 mm-thick cell absorbed ~67% of the incident light. As the concentration increased, the absorption increased proportionally.

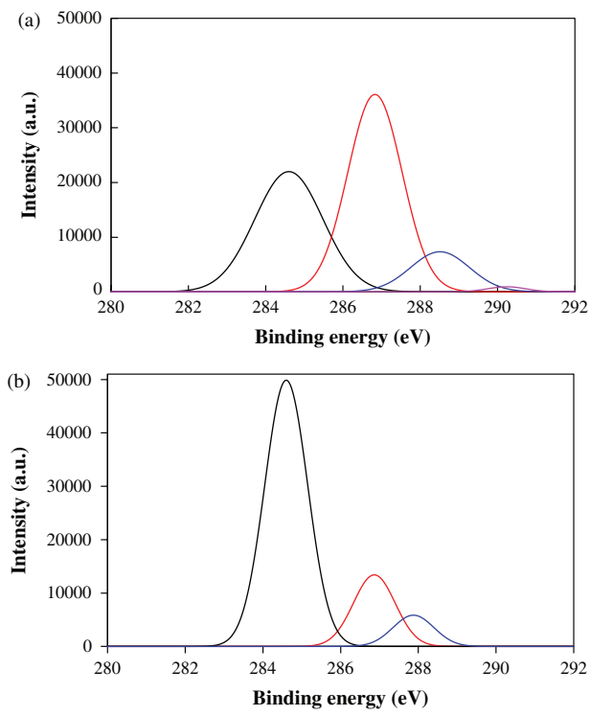

Figure 2. XPS: C1s spectra of the (a) GO and (b) rGO films deposited on the Si wafer by drop casting.

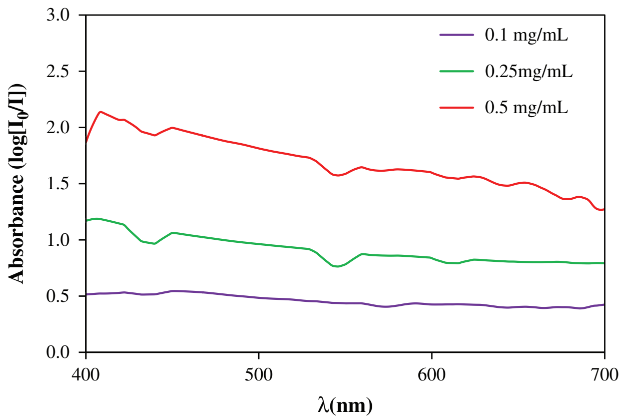

Figure 3. Absorption spectra of the rGO dispersions with varying concentrations.

For the 1 mg/mL rGO dispersion, the cell appeared very dark and the transmittance was lower than ~0.1%.

We performed an electro-optical measurement to determine the effect of the field on the rGO-DMF dispersions. In the first experiment, we measured the optical transmittance as a function of applied voltage under the crossed polarizers, using the experimental set-up illustrated in Figure 4(a).[12,22] The angle between the crossed polarizer and the electric field was 45°. The cells were dark at 0 V, indicating the absence of birefringence due to the isotropic ordering of the rGO particles (left image in Fig. 4(b)). When the electric voltage was applied across the parallel electrodes, the area between the two parallel electrodes was brightened as shown in the right side image in Figure 4(b), indicating that the rGO particles were aligned by the electric fields. When the field was switched off, the cell returned to a dark state after a few seconds. Figure 4(c) shows the optical transmittance as a function of applied voltage. The transmittance increased with increasing voltage and saturated at different levels depending on the concentration of rGO particles in dispersion. The dispersion with 0.25 mg/mL concentration of rGO showed the maximum field induced transmittance. The overall transmittance decreased with a further increase of the rGO concentration. The optical birefringence clearly shows that rGO particles are aligned well by applying electric field. The transmittance in the optical measurement can be expressed as[12]

$$I = I_0 \exp\left(\frac{4\pi d k_{avg}}{\lambda}\right)\left\{\sin^2\frac{\pi d\Delta n}{\lambda} + \frac{1}{4}\left(\frac{2\pi d\Delta k}{\lambda}\right)^2 + \cdots\right\} \quad (1)$$

Here, $k_{avg} = (k_0 + k_{90})/2$, $\Delta k = (k_0 - k_{90})$, Δn, d, and λ denote birefringence, optical path length, and wavelength, respectively. In case of GO dispersion, the absorption is low and ignorable, but this is not the case for rGO dispersion. Hence, it is difficult to obtain the quantitative order parameter using the optical measurement shown in Figure 4(c).

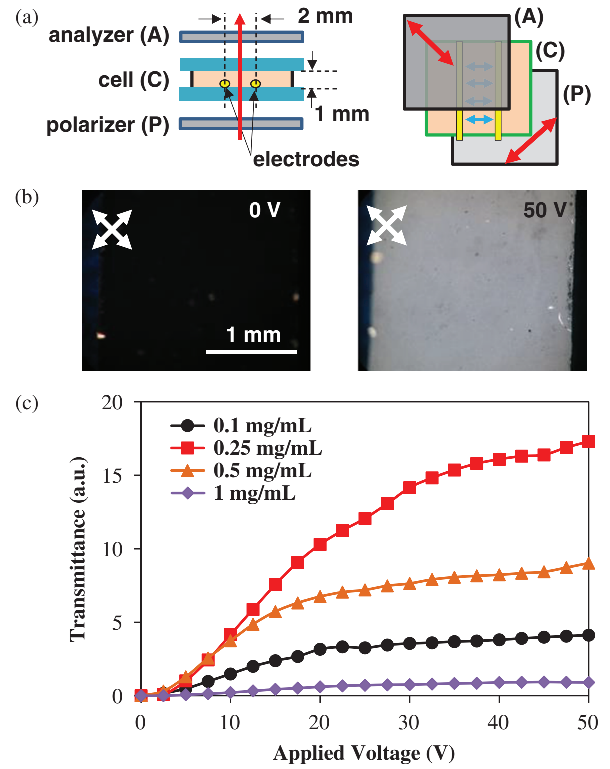

Figure 4. (a) Experimental setup used for field induced ordering and direction of polarizer and analyzer with respect to electric field for crossed polarizer case (b) microscopic images for 0.25 mg/ml rGO dispersion under crossed polarizers; under the applications of 0 V and 50 V, respectively and (c) optical transmittance as a function of applied voltage.

Then, we measured the absorption anisotropy in order to calculate the field-induced ordering of the rGO. During this measurement, the polarizer and analyzer of the polarized optical microscope were set parallel to each other. By setting the direction of the polarizers parallel or perpendicular to the direction of the electric field (see the illustrations in Fig. 5), the birefringence effect can be excluded.[23] We measured the intensity of the transmitted light as a function of the applied voltage. The directions of the polarizer and analyzer were set as parallel to the electric field in the first experiment and as perpendicular in the second experiment. The intensity of the transmitted light can be expressed using absorption coefficients (k parameters) as:

$$T_0 = \exp\left(-\frac{4\pi k_0 d}{\lambda}\right) \quad (2)$$

and,

$$T_{90} = \exp\left(-\frac{4\pi k_{90} d}{\lambda}\right) \quad (3)$$

Here, T_0 and T_{90} are the light intensities parallel and perpendicular to the applied electric field direction, and k_0 and k_{90} are the corresponding absorption coefficients; d and λ are the optical path length and wavelength of the light, respectively.

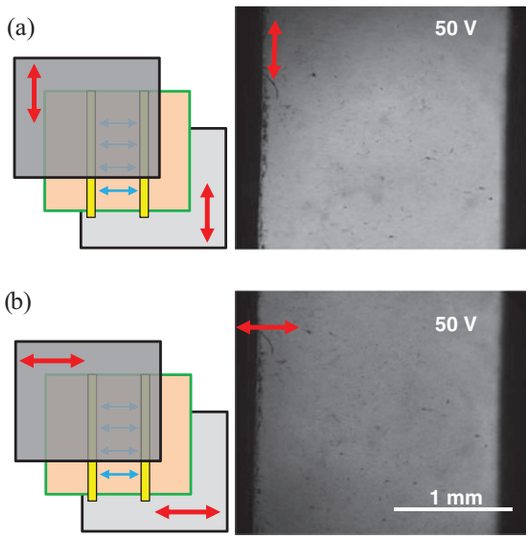

Figure 5. (a–b) Microscopic images for 0.25 mg/ml rGO dispersion cell under polarizers perpendicular and parallel to electric field, respectively, at 50 V. Left side illustrations show the direction of polarizers for the measurements.

From these absorption coefficients, the nematic scalar order parameter (S) can be calculated as[23, 24]

$$S = \frac{N-1}{N+2}, \quad \text{where } N = k_0/k_{90} \tag{4}$$

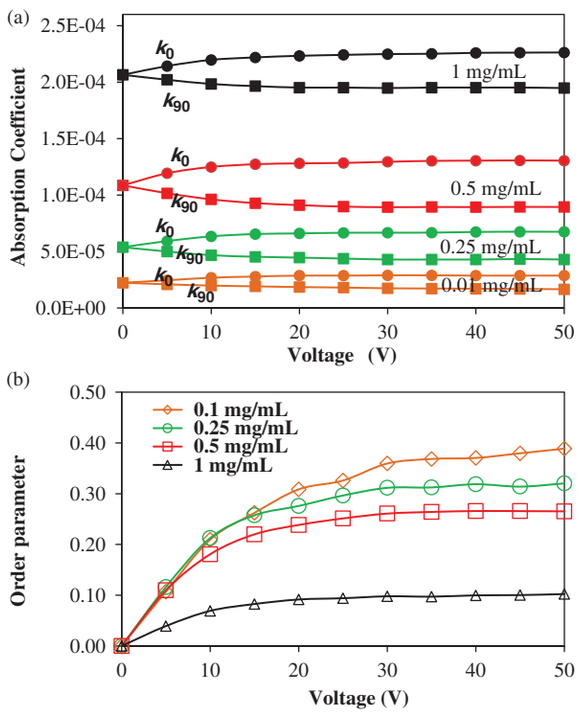

Figure 6. (a) Absorption coefficient and (b) S order parameter as a function of applied voltage for various rGO dispersions.

The microscopic images shown in Figures 5(a and b) were taken when the polarizers were perpendicular and parallel to the electric field, respectively. The contrast between two images is less than that under the crossed polarizers, but the transmittance difference can be used to determine the rGO order parameter. Figures 6(a and b) show the absorption coefficients and order parameter for the rGO dispersions as a function of the applied voltage. As the applied voltage increased, the difference between the absorption coefficients parallel and perpendicular to the field increased, indicating a field-induced alignment of the rGO particles. The intensity is quadrupolar as the polarizer rotates, and we can determine the direction of the rGO alignment. Since $k_0 > k_{90}$, the rGO particles are parallel to the electric field, as expected. From these absorption coefficients, we calculated the S order parameter that determines the degree of rGO ordering. The maximum order parameter was obtained with a 0.1 mg/mL rGO dispersion, in which S increased up to 0.39. The order parameter decreased with increase of the rGO concentration, and a 1 mg/mL rGO dispersion had an order parameter of ~0.1. As the rGO concentration increases, the interparticle interaction may disturb the particle ordering and the order parameter may decrease.

4. CONCLUSION

We investigated the alignment of rGO dispersions under the application of an external electric field by optical microscopy. Unlike the characterization of GO dispersions, rGO has a high optical absorption in the visible range. As a result, the transmittance with crossed polarizers is determined by the combined effect from the dichroism and birefringence. This hinders the calculation of the order parameter for the rGO particles using the transmitted light with crossed polarizers. On the other hand, the dichroism, that is, the absorption anisotropy, allows a better analysis of the ordering effect of the rGO particles, and we could measure the order parameters of the field-induced rGO particles for 0.1 to 1 mg/mL rGO dispersions. It was revealed that the rGO particles align well under the application of an electric field. The best alignment was obtained for the dispersion with low rGO concentration, and the order parameter decreased with increasing concentration.

The controlled assembly of colloidal particles is crucial in the potential applications of nano and micro structured materials in many fields; for example, photonic crystals, birefringent optics, fabrication of fibers and papers, and energy storage applications.[1, 12] In these applications, the measurement and manipulation of particle ordering are essential; hence, the method we suggested in the study can be useful for the potential applications using rGO colloids.

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