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Superior dispersion of highly reduced graphene oxide in N,N-dimethylformamide

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ABSTRACT

Here, we report the effect of temperature on the extent of hydrazine reduction of graphene oxide in N,N-dimethylformamide (DMF)/water (80/20 v/v) and the dispersibility of the resultant graphene in DMF. The highly reduced graphene oxide (HRG) had a high C/O ratio and good dispersibility in DMF. The good dispersibility of HRGs is due to the solvation effect of DMF on graphene sheets during the hydrazine reduction, which diminishes the formation of irreversible graphene sheet aggregates. The dispersibility of the HRGs was varied from 1.66 to 0.38 mg/mL when the reduction temperature increased from 25 °C to 80 °C. The dispersibility of the HRGs was inversely proportional to the electrical conductivity of the HRGs, which varied from 17,400 to 25,500 S/m. The relationships between the C/O ratio, electrical conductivity, and dispersibility of the HRGs were determined and these properties were found to be easily controlled by manipulating the reduction temperature.

1. Introduction

Graphene has been studied since its discovery in 2004 by Geim and co-workers due to its excellent mechanical, electrical, thermal, and optical properties, and high specific surface area [1,2]. Several approaches have been developed for producing graphene, such as micromechanical exfoliation [1], epitaxial growth [3,4], chemical vapor deposition [5,6], and chemical methods [7–10]. Unlike other approaches, the chemical method is scalable for producing chemically converted graphene (from graphite and derivatives of graphite) in large quantities and at low cost [11,12]. Graphene oxide is prepared by exfoliation of graphite oxide obtained from graphite oxidation in the presence of strong acids and oxidants. Chemical reduction of graphene oxide is the most widely applied technique for preparing reduced graphene oxide (RGO), one of the most popular chemically converted graphenes (CCGs) [11,12]. RGO is a very promising candidate for many applications such as electronic devices [13,14], polymer composites [15–18], energy conversion, storage materials [19,20], and sensors [21]. To date, the chemical reduction of a colloidal dispersion of graphene oxide is the most popular method used to prepare RGO [11,12]. Several reducing agents have been used to reduce graphene oxide, such as hydrazine [7,8,22–25], sodium borohydride [26], hydroiodic acid [27,28], sulfur-containing compounds [29], ascorbic acid [30], and vitamin C [31]. Among them, hydrazine is widely used because it is an effective reducing agent and well suited to the reduction of graphene oxide in various media, including the aqueous phase [7,8,22], gas phase [23], and especially in organic solvents [24,25].

The hydrazine reduction of a colloidal suspension of graphene oxide in organic solvents could create a colloidal suspension of RGO that provides a solution-phase, low-cost approach to fabricating RGO-based materials [24,25]. These organic solvents must have appropriate Hansen solubility parameters (the sum of the polarity cohesion parameter (δ_p) and the hydrogen bonding cohesion parameter (δ_h) in the range of 13–29 [24]), such as N,N-dimethylformamide (DMF) and N-methyl-2-pyrrolidone (NMP). Unfortunately, the concentration of RGO colloidal suspensions prepared by directly reducing graphene oxide in organic solvents is quite low, less than 0.1 mg/mL. The low dispersion of RGO is not appropriate for some applications, such as polymer-graphene nanocomposites or conductive inks. A common strategy used to increase the dispersibility of RGO in organic solvents is functionalization [32–35]. Lomeda et al. [32] reported that RGO functionalized by an aryl diazonium salt was dispersed in DMF at concentrations up to 0.5 mg/mL. However, the presence of functionalized groups on the surface of RGO sheets is undesirable because they may deteriorate the electrical properties of RGO [25].

Recently, we attempted a new strategy to improve the dispersibility of RGO in organic solvent by controlling the conditions of the hydrazine reduction [36]. Instead of reducing the graphene oxide using hydrazine at high temperature (80–100 °C) as previously reported [7,8,24,25,32], excess amounts of hydrazine were used. The hydrazine reduction was performed at ambient temperature, and the resulting RGO filter cake was redispersed in organic solvents. A two-step procedure achieved extensive reduction with a C/O

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ratio of approximately 9.5, which is comparable to previous reports, while the RGO dispersibility in NMP was as high as 0.71 mg/mL. The key to achieving highly dispersed RGO is performing the hydrazine reduction of graphene oxide at low temperature, which minimizes the formation of irreversible RGO aggregates.

To this end, we investigated the effect of the hydrazine reduction of graphene in organic solvents at different temperatures on the extent of reduction and RGO dispersibility in organic solvent. As expected, the dispersibility of the RGO prepared via the hydrazine reduction of a colloidal suspension of graphene oxide in DMF was significantly improved in comparison with that of RGO prepared via the hydrazine reduction of an aqueous suspension of graphene oxide. The results indicate that DMF plays an important role in preventing the irreversible formation of RGO aggregates during reduction.

2. Experimental

2.1. Materials

Expandable graphite (Grade 1721) was kindly provided by Asbury Carbon. Concentrated sulfuric acid (H_2SO_4), potassium permanganate ($KMnO_4$), hydrochloric acid (HCl), hydrogen peroxide (H_2O_2), and N,N-dimethylformamide (DMF) were purchased from Samchun Chemicals (Korea). Hydrazine monohydrate was purchased from Sigma Aldrich. All chemicals were used as received without further purification.

2.2. Preparation of the colloidal suspension of RGO in DMF

The aqueous suspension of graphene oxide was prepared by the modified Hummers method with initial expanded graphite, which was prepared by the microwave-assisted thermal expansion of expandable graphite [22,36]. The aqueous suspension of graphene oxide (10 mg/mL) was diluted with DMF to a concentration of 2 mg/mL and sonicated in an ultrasonic bath (Jeiotech UC-10, 200W) for 1 h to create a homogenous suspension of graphene oxide in DMF/water (80:20 v/v). The hydrazine reduction was performed by adding 5 mL of hydrazine monohydrate (98%) to 100 mL of the graphene suspension, which was stirred at a desired temperature (25, 40, 60, or 80 °C) in an oil bath for 24 h. The resulting reduced graphene oxide samples were denoted as HRG25, HRG40, HRG60, and HRG80 based on the reaction temperature at 25, 40, 60, and 80 °C, respectively. The HRG suspensions were filtered and washed with copious amounts of DMF to remove excess hydrazine. The HRG filter cakes were redispersed in DMF by sonication for 2 h (the temperature of the sonication bath was kept less than 30 °C).

To determine the dispersibility of HRGs in DMF, 50 mL of HRG suspensions was centrifuged at 3000 rpm for 15 min, after which 20 mL of the upper supernatant was carefully taken, coagulated by adding a few drops of HCl (1 M) and filtered. The filter cakes were washed with methanol, dried in a vacuum at 100 °C, and weighed to calculate the dispersibility of the HRGs [36].

2.3. Characterizations

To analyze the elemental composition of the HRGs, the HRG filter cakes were washed with copious amounts of methanol and dried at 100 °C for 24 h. The elemental compositions of the HRGs were analyzed using an elemental analyzer (Flash 2000, Thermo Scientific). The UV–Vis absorption spectra of the HRGs spray-coated on the quartz substrate were recorded using a double-beam UV–Vis spectrophotometer (AnalytikJena, Specord 210 Plus). X-ray photoelectron spectroscopy (XPS) analysis was performed on a K-alpha spectrometer (Thermal Scientific) with monochromatic Al K_a radiation ($h\nu = 1486.6$ eV). Raman spectra were characterized using a confocal Raman microscope (Thermo Scientific) with a 532 nm wavelength incident laser light. Thermogravimetric analysis (TGA) was analyzed under a nitrogen atmosphere at a heating rate of 10 °C/min (Q50, TA Instrument). Atomic force microscopy (AFM) images were taken using a Veeco Dimension 3100 SPM with a silicon cantilever operated in tapping mode. X-ray diffraction (XRD) patterns were recorded on a high-power X-ray diffractometer (D/MAZX 2500 V/PC, Rigaku) at 40 kV and 30 mA with a scan rate of 2°/min. The electrical resistances of free-standing HRG papers were measured by the four-point probe method (CMT-10 MP, Advanced Instrument Technology). The thickness of the free-standing HRG papers was determined from cross-sectional images obtained by scanning electron microscopy (SEM, JEOL, JSM-6500 FE).

3. Results and discussion

3.1. Reduction of graphene oxide in DMF

Graphene oxide is highly hydrophilic and easily dispersed in water and several polar organic solvents due to the presence of several oxygenated functional groups [37]. During reduction, the oxygenated functional groups are gradually removed and the graphene sheets become hydrophobic, readily agglomerating in hydrophilic solvents [7]. DMF is one of the most powerful solvents for dispersing different kinds of graphene, including graphene oxide [37], RGO [24], and pristine graphene [38]. Furthermore, DMF solvent is considered a good candidate for the prevention of irreversible graphene sheet aggregation during the hydrazine reduction of graphene oxide. Hydrazine reduction at low temperature yielded HRG that is easily redispersed in organic solvents such as DMF or NMP.

3.2. The effect of temperature on the extent of hydrazine reduction in a DMF/water system

The elemental composition and dispersibility of HRGs compared to CCGs obtained from the hydrazine reduction of graphene oxide in water are shown in Table 1. While the C/O atomic ratio of the HRGs gradually increased as the reduction temperature increased, the dispersibility in organic solvent decreased sharply. Increasing the reduction temperature from 25 °C to 40 °C, 60 °C and 80 °C increased the C/O ratio of HRG from 7.92 to 10.73, 12.66, and 13.76, while the dispersibility in DMF decreased from 1.66 to 0.97, 0.52, and 0.38 mg/mL, respectively. However, the HRG dispersibility was much higher than that of CCG at a similar C/O ratio. Although the C/O ratio of HRG40 (10.7) was higher than that of CCG-30 (9.58), its dispersibility (0.97 mg/mL) in DMF was significantly greater than that of CCG-30 (0.64 mg/mL). The high dispersibility of the HRGs indicates that DMF played an important role in preventing the irreversible aggregation of the graphene sheets during hydrazine reduction. This can be explained by the solvation effect of DMF on the HRG sheets. DMF is polar enough to disperse graphene oxide [37], and its cohesive energies ($\delta_p + \delta_h$: ~25) are sufficient to solvate the HRG sheets [24]. The agglomerates of solvated HRG sheets can be redispersed in polar organic solvents such as DMF, NMP, or dimethylacetamide with mild sonication. Furthermore, the C/O ratio of the HRGs was significantly higher than that of the CCGs obtained from the hydrazine reduction of graphene oxide in water at the same reduction temperature, especially at a high temperature. As shown in Table 1, the C/O ratio of HRG80 was 13.76, which was significantly greater than that of CCG-80 (11.13). The higher extent of HRG reduction