



Preparation of graphene nanosheets through repeated supercritical carbon dioxide process

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ABSTRACT

In this study, we reported that the supercritical carbon dioxide (scCO₂) process is potentially useful for exfoliation of graphite to provide less-damaged graphene nanosheets (GNs). Also, the repeated scCO₂ process was found to further reduce the thickness of the exfoliated GNs, which shows the possibility of producing thickness-controlled GNs by varying numbers of scCO₂ process.

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1. Introduction

Graphene nanosheets (GNs) are carbon nano-fillers which consist of mono- to few-layer graphene sheets. GNs have two-dimensional (2D) structures composed of hexagonally ordered sp²-hybridized carbon atoms. Because of these unique structures, GNs have many fascinating properties such as high thermal and electrical conductivity, superior mechanical strength, and barrier properties [1–5].

Several exfoliation techniques for graphite have been developed to produce GNs. Micromechanical cleavage of graphite, also known as the ‘Scotch-tape’ method is the first to isolate graphene from graphite [6]. This technique makes it possible to fabricate pure and best quality of GNs, which are useful for various applications. However, the large quantity production of GNs still remains a great challenge and this method is limited to a laboratory level. Also, exfoliation of graphite by chemical route like modified Hummer’s method is considered as promising candidate for large-scale production of GNs [7–9]. These methods involve oxidation and sonication process of graphite, followed by reduction process using reducing agent like hydrazine. But, the oxidation and reduction processes are too complicated and time-consuming. Moreover, strong acids and toxic material, especially hydrazine used in this method can cause serious environmental contamination. Therefore, it is highly required to explore the eco-friendly method to fabricate GNs.

Recently, various approaches have been developed for the mass production of pure and high-quality GNs without oxidation and reduction stages, including exfoliation of graphite using sonication [10,11], wet ball milling [12–14], and supercritical fluids (SCFs)

process [15,16], etc. Especially, in 2009, Pu et al. reported the exfoliation method of graphite which produced few-layer GNs with supercritical carbon dioxide (scCO₂) process [15]. Carbon dioxide (CO₂) has an easily accessible critical point at temperature and pressure conditions ($T_c=31.1\text{ }^\circ\text{C}$ and $P_c=73.8\text{ bar}$). Because of the scCO₂’s low viscosity, small molecule size, high diffusivity and permeability, the scCO₂ was diffused and intercalated between tightly-stacked natural graphite layers. Then, quick depressurization caused to expand the scCO₂ and exfoliate the CO₂-intercalated graphite. As a result, GNs were well separated and the minimum thickness of the obtained sheets was about 3.8 nm. In 2010, Rangappa et al. developed direct one-pot delamination method of graphite crystals by using SCFs, such as ethanol, N-methylpyrrolidone (NMP), and N,N-dimethylformamide (DMF) [16].

Herein, we reported the exfoliation method of graphite for preparing GNs via scCO₂ process. Under various supercritical and subcritical CO₂ conditions, the exfoliation process of graphite was done and the resulting GNs were characterized to establish the optimum reaction condition. Also, the effect of repeated scCO₂ process on the thickness and lateral size of GNs was investigated. These results demonstrate that the exfoliation of graphite into GNs using repeated scCO₂ process is potentially one of eco-friendly methods for obtaining high-quality GNs.

2. Experimental

2.1. Materials

The graphite used in this study was expanded graphite (EG) supplied by JEIO Co., Ltd. (Incheon, South Korea). The EG was

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intercalated with acid and then pre-exfoliated by rapid heating. The graphite flake was used as our starting material and the average particle size is about 5–10 μm with a densely stacked layer structure of parallel sheets. Sodium dodecylbenzenesulfonate (SDBS) was purchased from Sigma-Aldrich. Sulfuric acid (H_2SO_4 , 95%) and

hydrogen peroxide (H_2O_2 , 30%) were purchased from Junsei Chemical Co., Ltd. High-purity carbon dioxide (99.999%) was obtained from Shin Yang Gas Co. (Seoul, Korea). All chemicals were used without any further purification.

2.2. Supercritical CO_2 (scCO_2) process

EG was placed into a high-pressure batch reactor. The reactor has a mechanical stirrer, a temperature-controller, a thermometer, and a window cell. The reactor was then filled with CO_2 using a high-pressure pump and heated until it reached to the supercritical state. The pressure and temperature were controlled with the amount of CO_2 and the temperature controller, respectively. At the desired condition, the EG was immersed in the scCO_2 with stirring for predetermined time. During the immersion state in scCO_2 , CO_2 molecules are diffused and intercalated into the space between EG layers. The depressurization of the reactor was conducted by rapidly opening a vent valve and the sudden expansion of CO_2 molecules intercalated between EG layers caused the exfoliation of the EG into GNs. Fig. 1 illustrates exfoliation mechanism of graphite during scCO_2 process. The exfoliated GNs were collected directly into SDBS solution to prevent re-stacking. The GNs-dispersed solution was then subjected to centrifuge to remove unexfoliated graphite.

2.3. Characterization

The average particle size and morphology of the starting graphite materials and GNs were observed by field emission scanning electron microscopy (FE-SEM, JSM-6701F, JEOL). For SEM analysis of the EG and GNs, the graphite powders were scattered onto carbon tape and the GNs-dispersed solution was drop-casted onto a 0.02 μm anodized aluminum oxide (AAO) membrane and dried. Atomic force microscopy (AFM, Asylum Research MFP3D) was used to examine the lateral size and thickness of the exfoliated GNs. Samples for AFM were prepared via spin coating of the GNs dispersions on a Si wafer cleaned with piranha solution (7/3 v/v of 95% H_2SO_4 and 30% H_2O_2) and dried. Electrical conductivity was measured by a four-point-probe measurement system (CRESBOX, Napson).

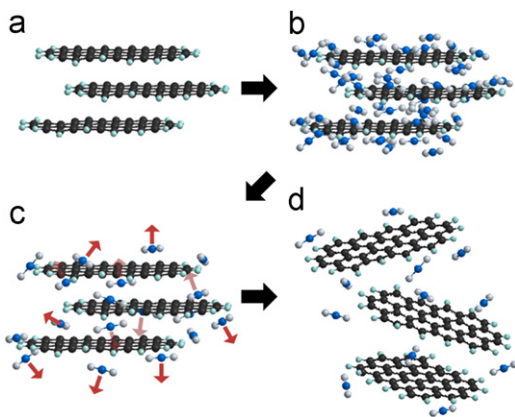


Fig. 1. Exfoliation mechanism of graphite through the scCO_2 process.

Table 1

The thickness and lateral size of GNs prepared under various processing condition.

Supercritical condition	Stirring time		
	10 min	30 min	60 min
150 bar (45 °C)	–	T: 1.0–6.0 nm L/S: 0.2–1.0 μm	T: 1.0–6.0 nm L/S: 0.2–1.0 μm
100 bar (45 °C)	–	T: 4.5–10.0 nm L/S: 0.4–1.0 μm	T: 3.0–6.0 nm L/S: 0.4–1.0 μm
85 bar (45 °C)	–	–	T: 6.0–10.0 nm L/S: 0.6–1.2 μm
Subcritical condition (65 bar/30 °C)	–	–	–

(T: thickness and L/S: lateral size).

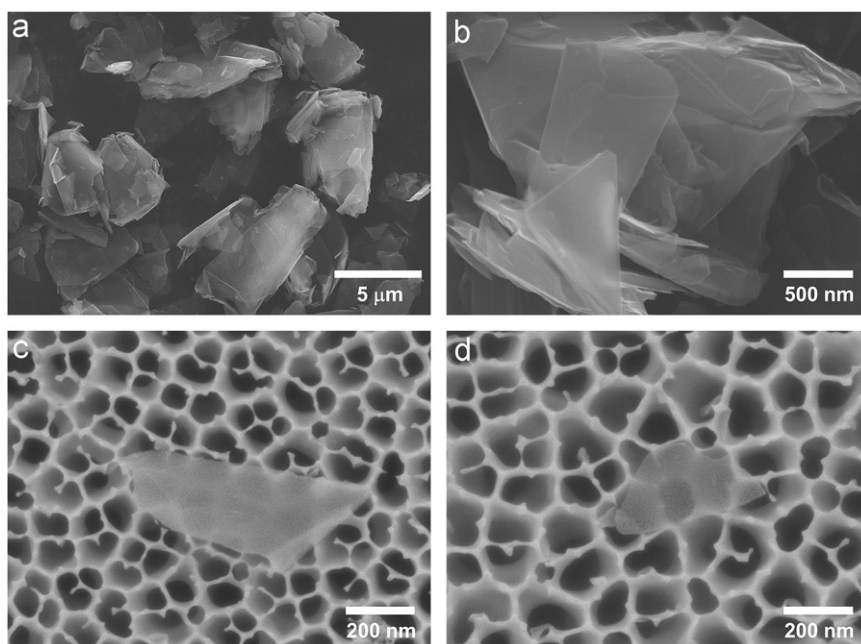


Fig. 2. (a) SEM images of starting graphite material, (b) enlarged view of (a), (c) and (d) SEM images of the exfoliated GNs.

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