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# Supercritical fluid conversion of graphene oxides

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ABSTRACT

In the preparation of graphene sheets for various studies and applications, the indirect route through the reduction of graphene oxides (GOs) has been widely pursued. Exfoliated GOs are shown to be mostly single-layer sheets in aqueous solution, and they are also demonstrated for conversion to recover some of the properties intrinsic to graphene. Beyond the commonly used thermal annealing and chemical reduction methods, several environmentally friendly conversion strategies have been explored in the literature. Reported here is a method of annealing GOs in supercritical fluids (SCFs, including carbon dioxide and ethanol) at relatively lower temperatures (up to only 300 °C) for their conversion to reduced GOs (rGOs). The characteristic properties of SCFs include low densities (thus low viscosity/high diffusivity) and diminished surface tension, which have found successful applications in extraction and the cleaning of fragile electronic devices, and also found to enable lower-temperature crystallization of amorphous nanomaterials in a fluid-assisted calcination process. In this study the same principles for lower-temperature calcination in SCFs were applied to the conversion of GOs. The rGOs thus obtained were characterized, with their electrical and thermal conductive properties evaluated and correlated with the different processing conditions. The benefits and shortcomings of the SCF processing method are discussed.

## 1. Introduction

In recent extensive investigations on graphene and related nanomaterials, single-layer graphene sheets have been emphasized for good reasons [1–6]. For a general lack of efficient methods to directly produce significant quantities of single-layer graphene sheets, the indirect route through the recovery from graphene oxides (GOs) has been widely pursued [6]. Exfoliated GOs are shown to be mostly single-layer sheets in aqueous solution [6,7], and they are also demonstrated for conversion to recover some of the properties intrinsic to graphene [6–10]. Among popular conversion strategies are thermal annealing and chemical reduction pathways or their combination [6–8,11–23]. The former has been effective in producing graphene-like films with a high carbon-to-oxygen ratio and a minimal amount of defects [11,12], but usually requires a high temperature (above 1000 °C), so the applicability is limited to the type of substrates compatible with the high-temperature condition. Films from the thermal annealing are generally difficult to be re-dispersed in a liquid medium, representing further limitations. The chemical reduction has been performed at relatively lower temperatures (less than 100 °C), with the use of reducing agents such as hydrazines and hydrides [13–29]. Disadvantages of the method include slow reduction reactions and the fact that many of the reducing agents are highly toxic and/or dangerously unstable or explosive. The chemically reduced GO films also tend to exhibit low flexibility and/or integrity and low electrical conductivity due to impurities introduced in the reduction process [19,20,30]. Other methods such as electrochemical reduction [31], photocatalytic reduction [32], and flash conversion [33] have also been explored for the conversion of GOs.

For environmentally more friendly conversion, several relatively benign reducing agents such as vitamin C, sugar, and protein were used under various reaction conditions [34–38]. GOs were also processed in a suspension under strongly alkaline conditions at moderate temperatures (50–90 °C) [18], or through a hydrothermal dehydration (180 °C) route for the targeted conversion [39]. Reported here is a method of annealing GOs in supercritical fluids (SCFs), including carbon dioxide ($CO_2$, $T_C = 31.1\,^\circ C$ and $P_C = 7.38$ MPa) and ethanol ($T_C = 240.1\,^\circ C$ and $P_C = 6.14$ MPa), at relatively lower temperatures (up to only 300 °C) for their conversion

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to reduced GOs (rGOs). $CO_2$ serves as a benchmark among environmentally friendly SCFs, while ethanol is also relatively benign and polar, thus more compatible with highly hydrophilic GOs. As known in the literature [40,41], SCFs are characterized by low densities (thus low viscosity/high diffusivity) and diminished surface tension, famous for their successful applications in chromatography and extraction, including the cleaning of fragile electronic devices [41]. These characteristic properties of SCFs were also found to enable lower-temperature crystallization of amorphous nanomaterials in a fluid-assisted calcination process [42–44]. In this study the same principles for lower-temperature calcination in SCFs were applied to the conversion of GOs (for which ethanol might also have some weak reductive effect). The rGOs thus obtained were characterized, with their electrical and thermal conductive properties evaluated and correlated with the different processing conditions. The benefits and shortcomings of the SCF processing method are discussed.

## 2. Experimental

### 2.1. Materials

The expanded graphite (surface-enhanced flake graphite, grade 3805) sample was provided by Asbury Carbons. $CO_2$ (high purity SCF grade) was purchased from Air Products. Sulfuric acid (93%), nitric acid (73%), hydrochloric acid (36%), hydrogen peroxide (35%), and phosphorus pentoxide ($P_2O_5$) were obtained from Acros, ammonium persulfate ($(NH_4)_2S_2O_8$) from Aldrich, and potassium permanganate ($KMnO_4$) and ethanol (>99%) from Fisher Scientific. PVDF membrane filters (0.2 μm pore size) were supplied by Fisher Scientific, the dialysis membrane tubing (MWCO ~ 3500) by Spectrum Laboratories, and carbon-coated copper grids for electron microscopy by SPI Supplies. Water was deionized and purified by being passed through a Labconco WaterPros water purification system.

GOs were prepared by the Hummers method [45] with minor modification. In the preparation, concentrated $H_2SO_4$ (10 mL) in a 500 mL flask was heated to 80 °C, to which $(NH_4)_2S_2O_8$ (0.9 g) and $P_2O_5$ (0.9 g) were added. The mixture was stirred until the reagents were completely dissolved. The graphite sample (1 g) was added, and the resulting mixture was heated at 80 °C for 4.5 h. Upon being cooled to room temperature, the reaction mixture was diluted with water (250 mL) and kept for ~12 h. It was then filtrated and washed repeatedly with water, followed by drying in a vacuum oven. The solid sample was added to concentrated $H_2SO_4$ (40 mL) in a 500 mL flask cooled in an ice bath. To the mixture was added slowly $KMnO_4$ (5 g over 40 min), during which the temperature was kept at <10 °C. The reaction mixture, with a change in color from black to greenish brown, was heated at 35 °C for 2 h, followed by dilution with water (85 mL – caution: the temperature must be kept at <35 °C throughout to avoid the strongly acidic and oxidative materials being violently spilled) and further stirring for 2 h. The reaction mixture was poured into a large beaker, to which water (250 mL) and then aqueous $H_2O_2$ (30%, 10 mL) were added. Bubbles from the aqueous mixture along with a color change to brilliant yellow were observed. After the mixture was allowed to settle for ~12 h, the clear supernatant was decanted, and the sediment was washed repeatedly with aqueous $H_2SO_4$ (5 wt%)–$H_2O_2$ (0.5 wt%) and HCl solution (10 wt%), followed by washing repeatedly with water until no layer separation observed after centrifuging. The sample was then dialyzed (MWCO ~ 3500) against water for 7 days to yield a clean aqueous dispersion of GOs. The aqueous GOs thus obtained (acid form) were titrated by aqueous NaOH (0.1 M) till pH reaches 9. The resulting GOs (sodium form) were again dialyzed (MWCO ~ 3500) to reach neutral pH. Finally, the aqueous suspension of GOs was diluted (~0.2 wt%) and sonicated for 30 min to achieve complete exfoliation.

### 2.2. Measurements

Optical absorption spectra were recorded on a Shimadzu UV-3600 UV/vis/near-IR spectrophotometer. Raman spectra were measured on a Jobin Yvon T64000 Raman spectrometer equipped with a Melles-Griot 35 mW He–Ne laser source for 633 nm excitation, a triple monochromator, an Olympus BX-41 microscope, and a cooled Symphony detector. X-ray powder diffraction measurements were carried out on a Rigaku Ultima IV powder diffraction system. Atomic force microscopy (AFM) images were obtained in the acoustic AC mode on a Molecular Imaging PicoPlus system equipped with a multipurpose scanner for a maximum imaging area of 10 μm × 10 μm and a NanoWorld Pointprobe NCH sensor (125 μm in length). The height profile analysis was assisted by using the SPIP software distributed by Image Metrology. Transmission electron microscopy (TEM) imaging was performed on a Hitachi HD-2000 S-TEM system.

The electrical conductivity in thin films was measured in terms of the traditional four-probe method by using a Keithley 2400 multimeter controlled by Lab Tracer 2.0 software (Keithley Instruments, Inc.) and a probe station (Multiheight probe, Jandel). The conductivity values were calculated from the $I/V$ data according to the equation $\sigma = [(\ln 2/\pi)^*(I/V)]/t$, where $t$ is the thickness of the specimen. The in-plane thermal diffusivity in the thin films (30 mm × 4 mm in dimension) was determined on an Ulvac Laser-PIT thermal diffusivity/conductivity meter operated in a vacuum of 0.01 Pa at room temperature. At least three frequencies were used in the measurement of each film sample, and the readings were averaged for the specific specimen.

### 2.3. SCF processing

The treatment of GO films was carried out in a stainless steel high-pressure vessel (25 mL volume), for which the system pressure was generated by a syringe pump and monitored by a pressure gauge (Heise 901A), and the system temperature was controlled and monitored by an RTD temperature controller (Omega 4200A) coupled with a pair of cartridge heaters (Gaumer 150 W) inserted into the body of the stainless-steel vessel. The system pressure (such as 10 MPa in most experiments) was maintained at each given temperature.

## 3. Results and discussion

GOs of mostly single-layer sheets were prepared from a commercially supplied sample of expanded graphite by using the Hummers method with minor modification [45], coupled with the subsequent exfoliation procedure already established in the literature [23]. The as-prepared aqueous GOs were highly acidic, due to the oxidation of carbons at graphene sheet edges and defects into carboxylic acids, so they were converted to the salt form in base treatment to make the resulting aqueous dispersion more stable [23,46]. Raman spectroscopy results suggested no meaningful difference between the acid and salt forms of GOs, with the G-band and D-band features for both samples similar to those already reported in the literature [47]. The aqueous dispersion was diluted for the preparation of specimens for transmission electron microscopy (TEM) and atomic force microscopy (AFM) characterizations. The images shown in Fig. 1 suggest that the GOs were indeed single sheets. In the X-ray diffraction characterization of the GOs, no graphitic peaks were found in the results (Fig. 2), as expected.