

Intercalation and Exfoliation of Herringbone Graphite Nanofibers

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Abstract:

We investigated how to control the expansion of the structure of graphite nanofibers (GNF). Lueking et. al. [1] have reported that this goal can be accomplished via intercalation followed by exfoliation. We studied the various factors that affect the exfoliation of GNF. We found that the conditions of both the intercalation and exfoliation influence the final structure of GNF.

Temperature controlled desorption (TPD) data was used to show that the exfoliated GNF (EGNF) structure is unstable and changes with time. High-Resolution Transmission Electron Microscopy (HRTEM) was used to monitor changes in structure after exfoliation. B.E.T. surface area measurements helped determine the degree of exfoliation or change in surface area.

Introduction:

GNF are interesting because their properties can be manipulated using various intercalation compounds and exfoliation techniques. Lueking et. al. [1] have reported that by varying the exfoliation process, the GNF lattice spacing can be expanded from 5% to 20-fold and the surface area can be expanded up to 10-fold. We hope to characterize the exfoliation process thus making the surface area and pore-size tunable. This versatile process can be used to make GNF useful in a variety of industries textiles to Micro-Electro-Mechanical systems (MEMS) devices.

Experimental Method

Intercalation and Exfoliation:

Ultra-high purity Herringbone graphite nanofibers with high order (Figure 1) were obtained from Catalytic Materials LLC. This material was intercalated using a 1:1 mixture of concentrated sulfuric acid and nitric acid. Starting materials were mixed in a plastic beaker and stirred with a magnetic stirrer for 2 hours. The GNF were exfoliated using a flat-bed oven in ultra-high purity (UHP) nitrogen atmosphere flown in at 100 cc. Exfoliation was also done in a volatile matter furnace at room temperature and pressure (250°C and 1 atm).

Characterization:

Temperature programmed desorption data was obtained using a Perkin Elmer Thermo Gravimetric Analyzer (TGA) 7 (c) in an UHP argon atmosphere. The sample was first degassed *in situ* at 1500°C for 4 hours. For analysis and degassing, the heating rate was 100°C/min and argon (UHP) gas was flown in at 100 cc.

Surface area data was obtained using nitrogen as the adsorbent at 77 K. The sample was first degassed at 1100°C (heating rate 100°C/minute) for 2 hours. The surface area was determined using the B.E.T. equation. All measurements and calculations were done using Micromeritics 2020(c).

High-resolution transmission electron microscope (HRTEM) images were obtained with a JEOL 2010F (200 kV). These pictures were taken by Dr. Humberto Rodriguez Gutierrez of Pennsylvania State University.

Data

Temperature Programmed Desorption:

The temperature programmed desorption data allowed us to study the rate of mass loss at different temperatures (Figure 1). The longer the sample was stored, the narrower the dips of the derivative became. The red graph was created from data collected

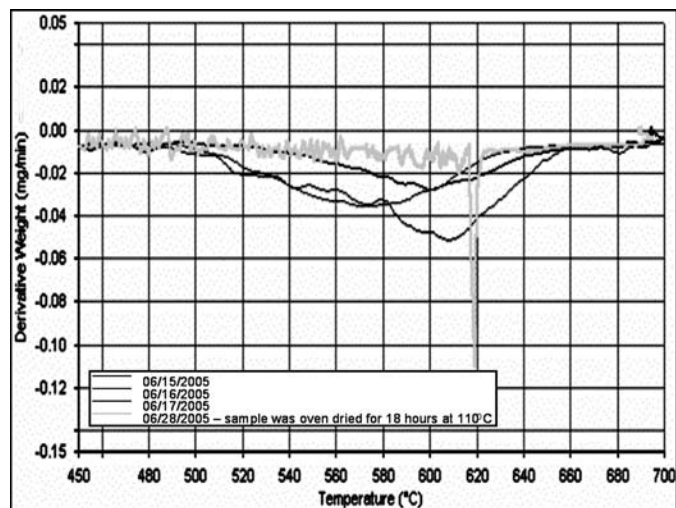


Figure 1: Phase change temperature of sample changes.

immediately after exfoliation. This graph has the broadest peak half-width area (500°C). The blue sample was characterized one day after exfoliation and had a peak half-width area of 37.50°C. The green sample was studied two days after exfoliation and has a peak half-width area of 350°C. The samples contain approximately 5 wt% of GNF and so, as the sample ages, more volatile intercalates leave the sample. This leads to a more stable compound. The sharpest dip is for the sample that was oven dried at 1100°C for 18 hours and was studied 13 days after exfoliation (cyan). We currently believe the heating led to better intercalation, such that the intercalant was driven inside the GNF to form a very stable compound. Future mass spectroscopy data will help investigate our hypothesis.

Surface Area:

The surface area data indicates that changing the exfoliation temperature changes the surface area of the sample (Table 1).

Sample	B.E.T. Surface Area (m ² /g)
Original GNF	75.7
GNF after heating at 225°C for 37 hours	102.3
GNF after heating at 700°C for 2 minutes	24.8
GNF after further heating at 1000°C for 6 hours	190.8
GNF after further heating at 1000°C for 36 hours	361.7

Table 1: Summary surface area varying with exfoliation treatment.

Exfoliation of GNF at higher temperatures causes the surface area to increase. The anomaly seems to be for the 700°C for 2 minutes treatment. This is probably because the sample contains intercalates and since the surface area is reported in m²/g, the number is artificially small. In the future we can verify this by studying the weight % of GNF.

HR-TEM:

The HR-TEMs revealed that the lattice spacing of GNF becomes more distorted after exfoliation (Figure 2). Our HR-TEMs indicate the cross-section of the GNF to be circular (Figure 3c). Catalytic Materials LLC reported their material has a rectangular cross-section. This discrepancy could be due to a lack of information when the stacked-card model was proposed or because the samples are different.

Conclusion:

From our studies, we can conclude that despite their high aspect ratio, GNF can be exfoliated using acid intercalates. The surface area was shown to be a function of exfoliation temperature and time of treatment. TPD data shows the intercalant desorbs from the GNF with time. The intercalated structure can be stabilized by heat treatment which causes intercalants to be more ordered [2]. HR-TEM shows that the structure of the GNF resembles stacked cones with a circular cross-section rather than the previously proposed stacked card model with a rectangular cross-section.

In the future, we wish to conduct XRD studies to research changes in lattice spacing and structure. Mass spectroscopy needs to be studied to understand the phase changes indicated by our TPD data. We want to test the applicability of GNF.

Acknowledgements:

The author wishes to thank Dr. Lueking, Deepa, Puja, and Humberto for their assistance. Also, thanks to Penn State, NNIN and NSF for this REU program.

References:

- [1] Lueking, A. D., J. Phys. Chem. B., 2005 109: 12710.
- [2] Inagaki, M., F. Kang and M. Toyoda, Exfoliation of Graphite via Intercalation compounds, L.R. Radovic, Editor. 2004, Marcel Dekker: New York. p. 1.
- [3] Dresselhaus, M.S. and G. Dresselhaus, Adv. Phys, 2002. 51: 1.
- [4] Rodriguez, et. al., Langmuir, Vol. 11, No. 10, 1995.

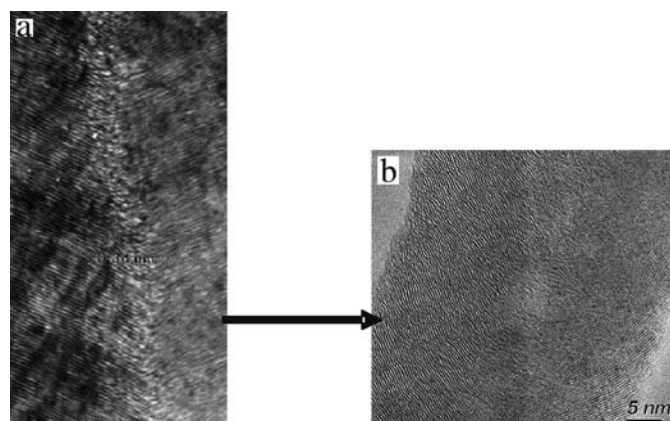


Figure 2, above: HR-TEM of (a) Original GNF4; (b) GNF at 700°C for 2 minutes. Figure 3, below: (a) Stacked card model4; (b) HRTEM of GNF after being treated at 700°C for 2 minutes; (c) stacked cone model.

