01 Sep 2005

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Recommended Citation

A. D. Lueking et al., "Exfoliated Graphite Nanofibers for Hydrogen Storage," *Proceedings of the 230th American Chemical Society, Division of Fuel Chemistry National Meeting (2005, Washington, DC)*, vol. 50, no. 2, pp. 457-459, American Chemical Society (ACS), Division of Fuel Chemistry, Sep 2005.

EXFOLIATED GRAPHITE NANOFIBERS FOR HYDROGEN STORAGE

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Abstract

Exfoliation of graphite nanofibers (GNF) expands the interplanar spacing of the GNF which leads to increased hydrogen storage. The exfoliation technique plays a large role in the resulting GNF microstructure, surface area, and hydrogen storage properties. Variations in preparation conditions expand the GNF lattice from 3.4 Å to over 500 Å. The BET surface area of the exfoliated GNF increases as much as 10-fold to 555 m^2/g. Increased surface area correlates with low temperature physisorption of hydrogen at 77K with an observed uptake of 1.2% at 77K and 20 bar. Conversely, observed dislocations in the graphitic structure correlate with a fourteen-fold increased ambient temperature adsorption at 20 bar. These results suggest that selective exfoliation of a nanocarbon is a means by which to control the relative binding energy of the hydrogen interaction with the carbon structure and thus vary the operative adsorption temperature.

Introduction

Despite early hydrogen storage claims in carbon materials that were largely irreproducible, reports continue to emerge showing hydrogen uptake ranging from 3-17%. An explanation emerging from these reports is that post-synthesis treatments modify the carbon structure and enhance hydrogen adsorption. Nuclear diffraction has shown that hydrogen may become chemically bound to graphitic carbon during certain preparations [1], terminal carbons have been suggested to act as catalytic entities to dissociate hydrogen [2], and electron micrographs have suggested that simple exposure to hydrogen may expand the graphite lattice of certain carbon nanostructures [3].

In an effort to test the emerging hypothesis that defects, dislocations, and/or terminal carbons lead to increased hydrogen storage via hydrogen intercalation into the graphite lattice, we have worked to develop methods that expand the graphite lattice a priori in nano-carbonaceous materials. Unlike exfoliation of single-wall nanotubes, intended to separate bundles into individual tubes, our exfoliation method targets intra-particle spacings. Our method is derived from well-established techniques to exfoliate graphite, in which intercalation of graphite is followed by a thermal shock to expand the graphitic layers.

Herringbone GNF provide an interesting candidate for carbon exfoliation, with their slit-pore geometry, nano-scale dimensions, high aspect ratio, and graphitic layers that terminate along the fiber axis. Herringbone graphite nanofibers (GNF) provide an interesting candidate for carbon exfoliation, with their slit-pore geometry, nano-scale dimensions, high aspect ratio, and graphitic layers that terminate along the fiber axis. It was previously thought that the high aspect ratio and nanoscale dimensions of the GNF would preclude exfoliation. However, our preliminary data shows that we have successfully exfoliated herringbone GNF, with a resulting nanoscale structure that is previously unreported.

Experimental

Highly ordered, herring-bone graphite nanofibers were purchased from Catalytic Materials, Ltd; with a metal content of less than 1% as reported by the manufacturer; these GNF had a low baseline hydrogen uptake and were not activated prior to us. Based on preliminary studies with graphite exfoliation, the primary exfoliation method used in this study was a 50/50 mixture of nitric and sulfuric acids followed by thermal shocking at 700 °C (EGNF-700). A portion of this sample was subjected to an additional high temperature treatment by heating the sample under flowing Argon at 1000 ºC for 36 hours (EGNF-1000).

Characterization. Materials were characterized using standard BET methods with nitrogen at 77K (Quantachrome Autosorb I) and helium densitometry measurements (Hiden IGA-003). Scanning electron microscopy (SEM) (Philips XL20) and TEM (JEOL 2010 and JEOL 2010F) were used to characterize the microstructure of the material. Total ash content was determined by temperature programmed oxidation on a low-pressure Perkin Elmer Thermogravimetric analyzer 7 (TGA).

Hydrogen Uptake. A high-pressure thermo-gravimetric analyzer (Hiden Isochema IGA-003) was used to evaluate hydrogen uptake at pressures up to 20 bar. The IGA provided a highly sensitive (+1 µg) measurement with precise temperature and pressure control for automated measurements of adsorption and desorption isotherms. All samples were subjected to an in situ degas at 150 °C, unless otherwise stated. Hydrogen uptake measurements were normalized to sample mass after pretreatment, with buoyancy corrections determined from density measurements with helium. With a typical sample size of 50 mg, the error in the hydrogen due to instrumental limitations is +0.02 wt% absolute. Select samples were chosen for quality checks to ensure the reproducibility of the measurements.

Results and Discussion

The exfoliated GNF retains the overall nanosized dimensions of the original GNF, with the exfoliation temperature determining the degree of induced defects, lattice expansion, and resulting microstructure. Transmission electron microscopy (TEM) confirmed the herringbone structure of the lattice spacing and a 3.4 Å lattice spacing (Figure 1). The EGNF-700 fibers had dislocations in the graphitic structure and a 4% increase in graphitic lattice spacing to 3.5 Å (Figure 2). The EGNF-1000 fibers were significantly expanded along the fiber axis, with regular intervals of graphitic and amorphous regions ranging from 0.5 to >50 nm in width (Figure 3). The surface area of the starting material was increased from 47 m^2/g to 67 m^2/g for EGNF-700 and to 555 m^2/g for the ENGF-1000 (Table 1).

Table 1. Characterization of GNF before and after Exfoliation

	GNF	EGNF-700	ENGF-1000
Treatment	None	Acid intercalation; 700 °C 2 minutes	+ 1000 °C for 36 hours in Argon
BET Surface Area (m^2/g)	47	67	555
Helium Density (g/cm^3)	1.38	1.04	1.36
H_2 Uptake (77K, 20 bar)	0.34%	0.39%	0.39%
H_2 Uptake (300K, 20 bar)	0.02%	0.29%	0.03%
Ash Content (wt%)	1.5%	*	1.1%

*in progress

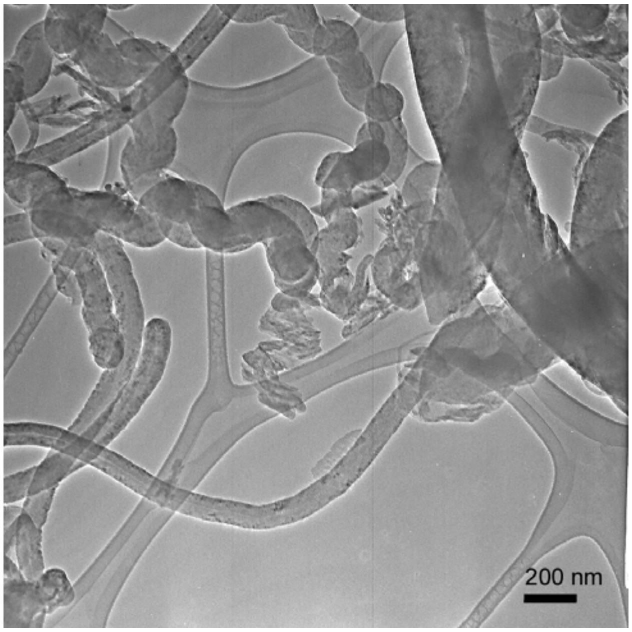

Figure 1. Transmission electron micrographs of untreated GNF.

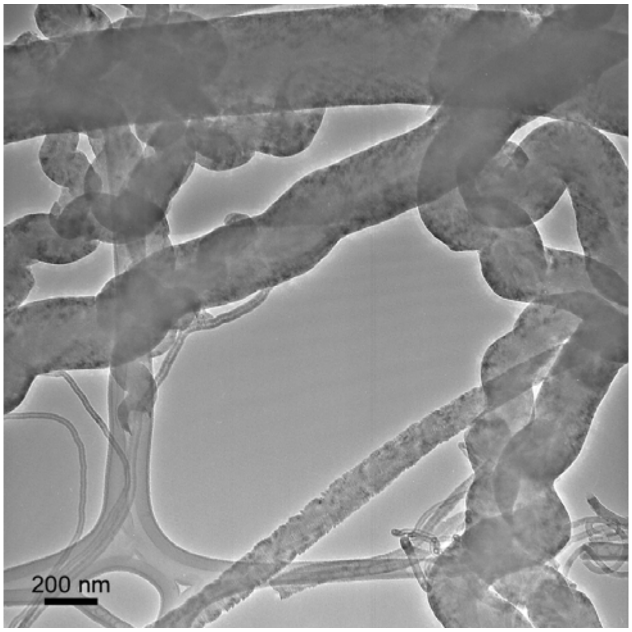

Figure 2. Transmission electron micrographs of exfoliated GNF after a 700 °C thermal treatment (EGNF-700)

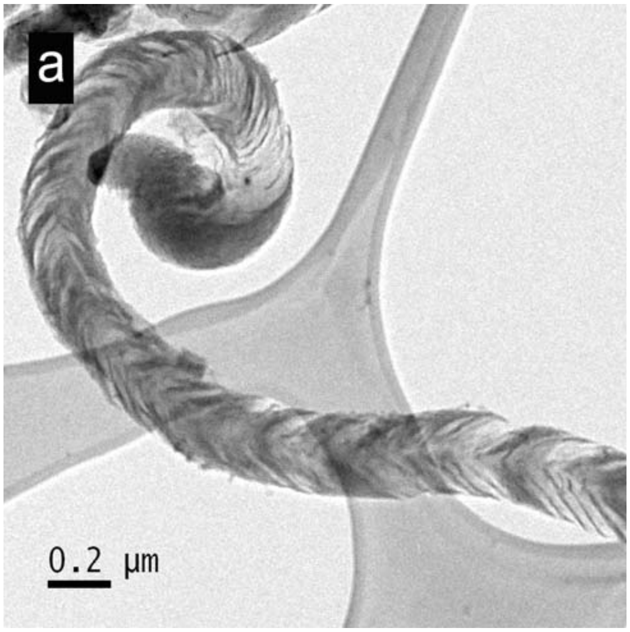

Figure 3. Transmission electron micrographs of exfoliated GNF after an extended 1000 ° thermal treatment.

Hydrogen uptake measurements at 20 bar indicate that the overall hydrogen uptake and operative adsorption temperature are sensitive to the structural variations and graphitic spacing. The increased surface area of the ENGF-1000 led to a 1.2% hydrogen uptake at 77K and 20 bar, a three-fold increase in hydrogen physisorption of the starting material (Figure 4). The uptake of the 700 °C treated material had a 0.29% uptake at 300K and 20 bar (figure 5); although low, this was a fourteen-fold uptake over the starting material and higher than other commonly used pretreatment methods. These results suggest that selective exfoliation of a nanofiber is a means by which to control the relative binding energy of the hydrogen interaction with the carbon structure and thus vary the operative adsorption temperature.

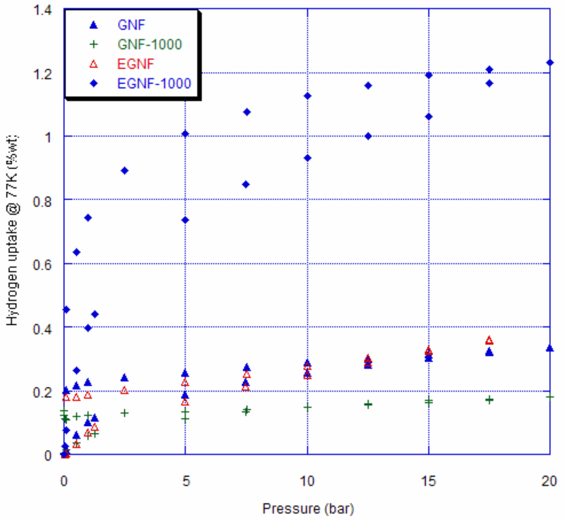

Figure 4. Hydrogen Isotherms for various fibers at 77K.

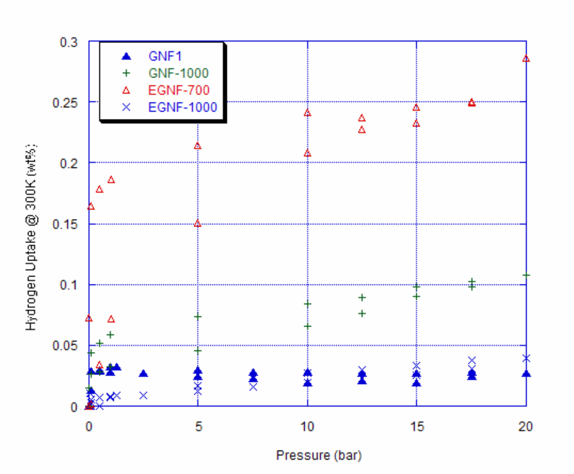

Figure 5. Hydrogen Isotherms for various fibers at 300K.

The overall hydrogen uptake for the EGNF-700 and EGNF-1000 is not close to the DOE hydrogen storage targets. We are, however, encouraged by the data that suggests that exfoliation is a means by which to control the carbon-hydrogen binding energy. At 77K, the hydrogen uptake for EGNF-1000 is comparable to recent reports of 2.7 wt% uptake in a spherical nanoporous carbon with surface areas between 946 and 1646 m^2/g at 77K and 50 bar[4] and 2 wt% for commercially available activated carbon fibers at 77K and 20 bar.[5]

Conclusions

A new exfoliated carbon fiber with nanodimensions was synthesized by graphite exfoliation followed by high temperature treatment. The exfoliated carbon nanofiber had a unique microstructure, with repeating units of high-density graphitic regions separated by low density regions that were amorphous in nature. An expansion along the fiber axis was accompanied by a ten-fold increase in BET surface area. At the other end of the preparation spectrum, GNF were prepared with mild dislocations within the graphitic structure and a 4% increased latticed spacing. Overall hydrogen uptake and operative adsorption temperature was drastically different for these two exfoliated materials, suggesting a means by which to control the carbon-hydrogen binding energy through variation of exfoliation conditions. Future work will include systematic variations on exfoliation conditions in an attempt to synthesize materials with an array of slit pore dimensions, and include subsequent chemical treatments to control the resulting surface chemistry on the exfoliated carbon structures.

Acknowledgement. The authors would like to thank E. Dickey for her feedback on the TEM presented in this work. This work was funded through start-up funds proved by PSU’s Institute for the Environment, The Energy Institute, and the College of Earth & Mineral Sciences. Funding for exfoliation of carbon for hydrogen storage was provided, in part, by the H2E Center at Penn State University.

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