Reductive Alkylation of Fluorinated Graphite

Soma Chakraborty, Wenhua Guo, Robert H. Hauge, and W. E. Billups*

Department of Chemistry and The Richard E. Smalley Institute for Nanoscale Science and Technology, Rice University, Houston, Texas 77005

Fluorinated graphite (CF_X) was alkylated reductively to yield functionalized graphite platelets comprised of six to 23 graphene sheets. A free radical mechanism involving a single electron transfer was proposed. The higher level of functionalization that resulted from the fluorinated substrate led to materials that exhibited an enhanced solubility in organic solvents.

Introduction

Graphite occupies a central position among a group of carbon nanomaterials that are poised to occupy a significant role in nanoscience and nanotechnology.[1–5] Soluble derivatives of graphite were prepared recently by the alkylation of oxidized graphite.[6] Potassium graphite (C_8K) was functionalized by dodecyl groups to yield graphite that is soluble in organic solvents.[7] Water soluble PEGylated graphite also was prepared from C_8K.[7] Fluorinated graphite, prepared by direct fluorination,[8] offers another substrate for functionalization. The debundling that results from intercalation of fluorine into the graphene layers and the resulting high fluorine content suggests that a high level of functionalization (and thus solubility) can be expected. The physical appearance of fluorinated graphite can range from black to gray to white depending upon the fluorine content.[9] Haddon and co-workers[10] reported recently that soluble graphene layers were formed when fluorinated graphite was reacted with alkyl lithium reagents. As expected, the products obtained from hexyl lithium were found to be more soluble that those from butyl lithium. Hexyl-CF_1 was found to be the most soluble product. In this paper, we demonstrate that fluorinated graphite can be functionalized by alkyl radicals to yield

Scheme 1
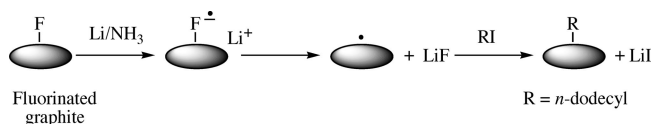
material with a high level of functionalization that exhibits a high solubility in organic solvents.

Experimental Procedures

Materials. Samples of fluorinated graphite were prepared using a previously reported method.[8] Lithium (granules, 99%) and 1-iodododecane were purchased from Aldrich.

General Procedure for the Synthesis of Dodecylated Graphite 1. The fluorinated sample was added under argon to a flame dried three-necked flask. Ammonia was then condensed into the flask followed by the addition of small pieces of lithium metal. The dispersion was then stirred for 30 min followed by the addition of 1-iodododecane. The resulting mixture was stirred overnight at room temperature during which time the ammonia evaporated, leading to a dry residue. The reaction mixture was treated with ethanol, acidified with 10% HCl, extracted into hexane, and washed several times with water. The hexane layer was then filtered through a 0.2 μm PTFE membrane and washed with ethanol followed by a few drops of chloroform. The functionalized graphite was dried overnight in vacuo at 80 °C.

Characterization. The functionalized graphite was characterized by Raman spectroscopy, thermogravimetric analyses (TGA), FT-IR spectroscopy, X-ray photoelectron spectroscopy (XPS), atomic
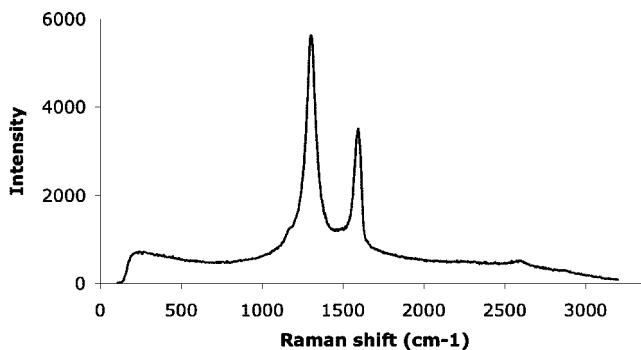

Figure 1. Raman spectrum (780 nm excitation) of dodecylated graphite **1**.

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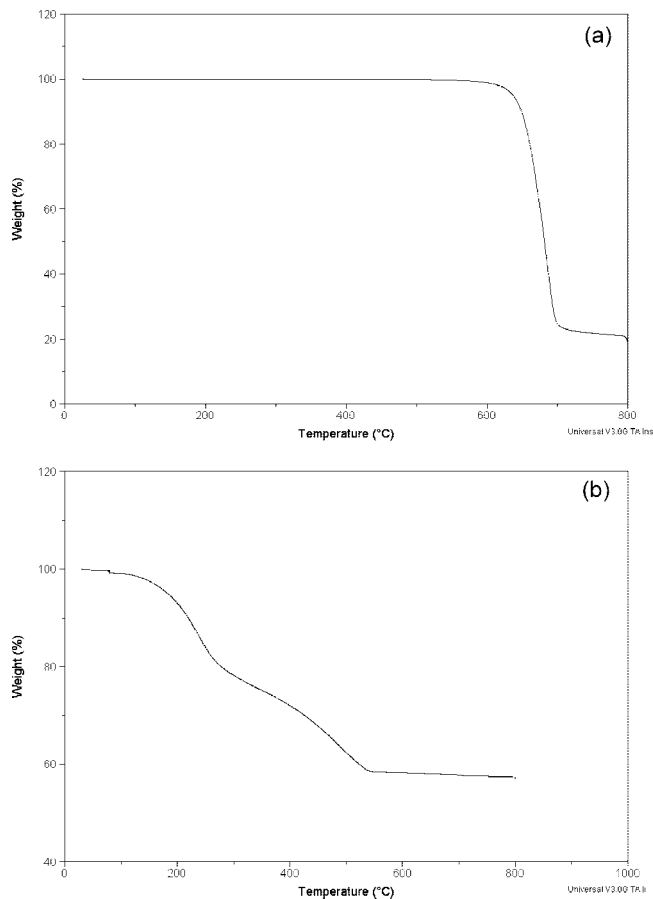
Reductive Alkylation of Fluorinated Graphite

Chem. Mater., Vol. 20, No. 9, 2008 **3135**

Figure 2. Weight loss of (a) fluorinated graphite and (b) dodecylated graphite determined by TGA analyses in argon from 80 to 800 °C.
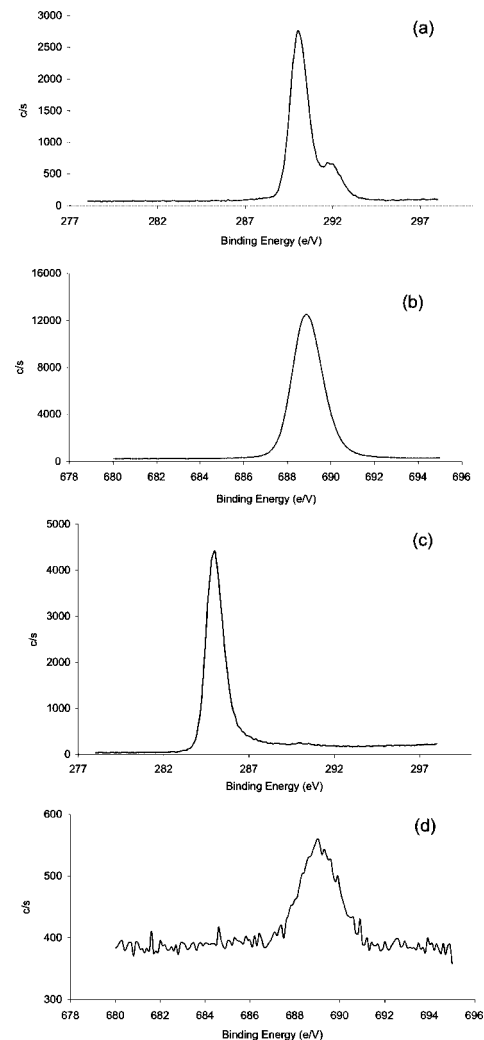

Figure 3. XPS images of fluorinated graphite: (a) carbon 1s region, 39.6% and (b) fluorine 1s region, 60.4%. XPS images of dodecylated graphite **1**: (c) carbon 1s region, 97.6% and (d) fluorine 1s region, 2.4%.

force microscopy (AFM), and transmission electron microscopy (TEM). Raman spectra of solid samples were recorded using a Renishaw 1000 microRaman system equipped with a 780 nm excitation laser source. Multiple spectra (three to five) were obtained, normalized to the G band, and averaged to give a comprehensive snapshot of the material. TGA experiments were carried out under argon using a SDT 2960 TA instrument. Samples were degassed at 80 °C and then heated for 10 °C/min to 800 °C and held there for 30 min. FT-IR spectra were obtained using a Nicolet spectrometer with the ATR accessory. XPS data were obtained using a physical electronics (PHI QUANTERA) XPS/ ESCA system. The base pressure was at 5×10^{-9} Torr. A monochromatic Al X-ray source at 100 W was used with a pass energy of 26 eV and with a 45° takeoff angle. The beam diameter was 100.0 μm. Low-resolution survey scans and higher resolution scans of C and F were taken. At least two separate locations were analyzed for each sample. AFM images were taken of a chloroform solution, spin-coated onto mica, using a Digital Instrument Nanoscope IIIa in tapping mode with a 3045 JVW piezo tube scanner. The tapping frequency was between 270 and 310 kHz. TEM images were obtained from JEOL 2010 at 100 kV with a FasTEM operating system.

Results and Discussion

Highly functionalized graphite was prepared by treating fluorinated graphite as illustrated in Scheme 1. The functionalized material was found to be soluble in CHCl$_3$, CH$_2$Cl$_2$, DMF, DMSO, and benzene. The solubility in CHCl$_3$ was determined to be 1.2 g/L.

During the functionalization process, the white fluorinated graphite turned black, indicating that dodecyl radicals replaced the fluorine groups. Electron transfer from lithium to the fluorinated graphite yielded a transient radical anion that decomposes rapidly to give a carbon centered free radical and lithium fluoride. A similar electron transfer process formed the radical anion of dodecyl iodide. The dodecyl radicals that formed by decomposition of this transient species combined with radical sites on the graphite surface to yield the functionalized material. A radical transfer mechanism also was observed previously in the case of carbon nanotube chemistry.[11]

Evidence for functionalization can be determined by inspection of the Raman spectrum that is illustrated in Figure 1. The dodecylated graphite exhibits a tangential mode (G band) at 1590 cm^{-1} and a prominent disorder mode (D band) at 1290 cm^{-1} that arises from covalent attachment of the dodecyl groups. The D/G ratio is 2:1, indicating a high level of functionalization. Similar results were reported by Haddon and co-workers for the material obtained from the reaction

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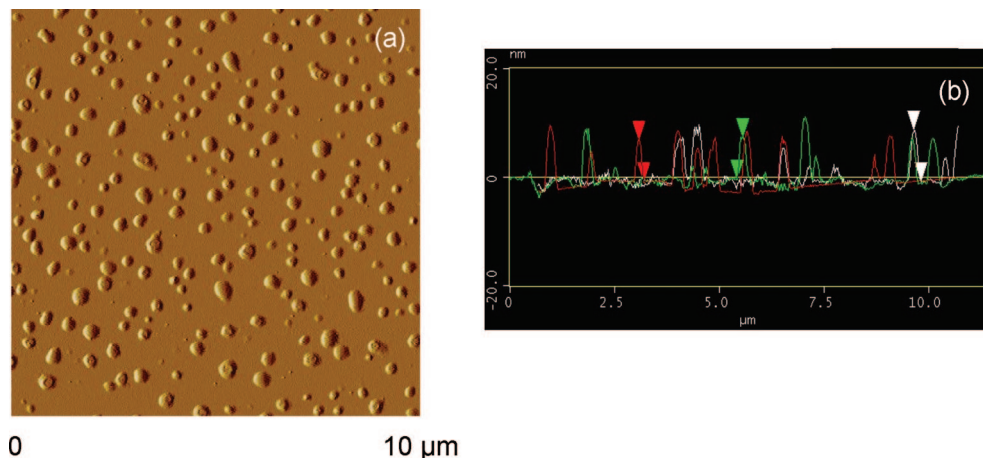
Figure 4. (a) AFM (10 μm $\times$ 10 μm) amplitude image of dodecylated graphite (**1**) spin coated onto freshly cleaved mica from chloroform and (b) AFM section analysis of **1** (*x*-axis in μm and *y*-axis in nm).
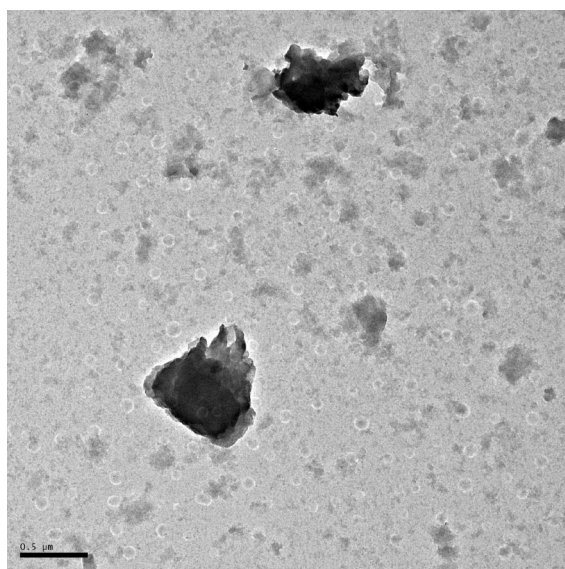

Figure 5. TEM image of **1**. The scale bar is 0.5 μm.

of fluorinated graphite with alkyl lithium reagents.[10] In fluorinated carbon nanofibers, a D/G ratio of 1:1 was reported.[12]

TGA analysis of the starting fluorinated graphite showed a 77% weight loss above 600 °C (Figure 2a). As reported previously, the loss of CF_4 and C_2F_4 probably accounts for this unusually large weight loss. The TGA weight loss of degassed dodecylated graphite was 40% (Figure 2b), indicating that the functionalized graphite has one dodecyl group per 21 graphitic carbon atoms. Since all of the weight loss is between 150 and 540 °C, the weight loss is predominantly from the dodecyl functionalities. A similar TGA profile was observed with single-walled carbon nanotubes functionalized by dodecyl groups.[11] The results of these experiments are in agreement with the Raman spectra (Figure 1) as well as XPS data (see later), confirming a high level of functionalization. TGA of dodecylated graphite prepared from potassium graphite provided a weight loss of 15%, corresponding to approximately one dodecyl group per 78 graphite carbon atoms.[7]

In accordance with earlier studies,[8] the fluorinated graphite exhibited strong IR stretching absorptions between 1072 and 1342 cm^{-1}. In addition to the absence of the C$-$F stretching absorptions, the functionalized material shows C$-$H stretching bands associated with the dodecyl groups at 2800–3000 cm^{-1}.

XPS provides direct evidence for the replacement of fluorine atoms by dodecyl groups. XPS spectra corresponding to the region between 0 and 1100 eV are presented in Figure 3. A survey scan (Figure 3a) of the starting fluorinated graphite shows only the presence of carbon and fluorine. The percentage of fluorine obtained from XPS compares favorably to that obtained from the TGA measurements. The stoichiometric ratio from these data is (CF)$_1$. On reacting with the dodecyl groups, nearly all of the fluorine atoms were displaced by the dodecyl functionalities.

As expected, the functionalized material is remarkably soluble in organic solvents including $CHCl_3$, CH_2Cl_2, DMF, DMSO, benzene, and 1,2,4-trichlorobenzene. The AFM image of the dodecylated graphite (Figure 4) shows irregular graphite nanoplatelets.[7,13] The horizontal distance varied between ~0.1 and 0.5 μm. The average height varied between ~2 and 12 nm with 50% of the functionalized platelets having a thickness of 8 nm, indicative of ~23 graphene sheets per nanoplatelet.

Additional evidence for the size distribution of functionalized graphite nanoplatelets was provided from the TEM studies. The functionalized material has particles with horizontal distances varying between ~0.1 and 0.5 μm (Figure 5). This result is in agreement with the size variation obtained from the AFM data.

Studies on the uses of these materials in composites are underway.

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