Graphite Functionalization

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Functionalization of Potassium Graphite**

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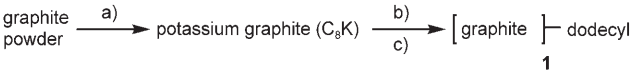
Graphite reacts with potassium to form lamellar compounds by intercalation of potassium atoms between the graphene sheets.[1–6] The most common stoichiometry is C_8K.[7] Although, initially, C_8K was used as a catalyst in polymerization reactions,[8] and in the nuclear and side-chain alkylation of aromatic compounds by ethylene,[9] the use of C_8K as a reducing agent has also been investigated.[10–20] The use of C_8K as a metallation agent in the alkylation of nitriles, esters,[21] and oxazines,[22] and in the reductive cleavage of carbon–sulfur bonds in vinylic and allylic sulfones has been reported.[23,24] Bergbreiter and Killough studied the Lewis basicity and the electron-transfer properties of C_8K.[25,26] Biphenyl is formed in high yield when phenyl halides are treated with C_8K,[27] whereas reactions of C_8K with alkyl halides lead to products ranging from alkanes to typical Wurtz-type coupling products.[26,28] Novel ring-closure reactions leading to the coupling of α-diketones and nitrogen-containing heterocyclic compounds have also been reported.[29,30] Ebert studied reductive alkylations, as well as potassium intercalation, with soot.[31]

In view of the current interest in the synthesis of soluble carbon nanomaterials, it is somewhat surprising that C_8K has not been used as a substrate for the synthesis of soluble derivatives of graphite. Therefore, we decided to use C_8K as a point of departure for the synthesis of soluble, derivatized graphite nanoplatelets with the methodologies that were developed earlier to functionalize coal, fullerenes, and single-walled carbon nanotubes (SWNTs).[32–35]

The synthesis of C_8K, a bronze powder, is achieved readily by melting potassium over graphite (synthetic graphite powder, $<20\,\mu m$, Aldrich) under an atmosphere of argon.[11] Freshly prepared C_8K was treated with 1-iodododecane, as illustrated in Scheme 1, to produce dodecylated graphite (**1**), which is soluble in chloroform, benzene, and 1,2,4-trichlorobenzene.



Scheme 1. Preparation of dodecylated graphite (**1**). Reaction conditions: a) potassium, 200 °C; b) ammonia; c) 1-iodododecane.

The Raman spectra of unfunctionalized and dodecylated graphite (**1**) are presented in Figure 1 a and b, respectively. The appearance of the prominent disorder mode (D band) at

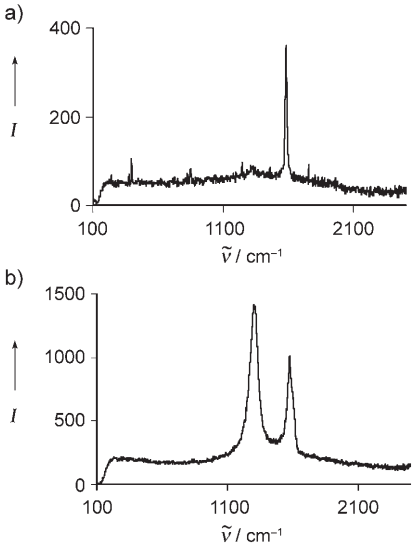


Figure 1. Raman spectra (excitation at 780 nm) of a) commercially available synthetic graphite powder and b) dodecylated graphite (**1**).

1299 cm^{-1} (Figure 1 b) is indicative of the disruption of the sp^2-hybridized carbon atoms in the hexagonal framework of graphite. Thermogravimetric analyses (TGA) of **1** (argon, 10 °C min^{-1} to 800 °C) indicated a weight loss of 15 %, which corresponds to approximately one dodecyl group per 78 graphite carbon atoms. Although protonation has been observed with other systems,[25,36] a control experiment carried out with C_8K and ammonia led to a negligible increase in the intensity of the D band, indicating that the addition of hydrogen to the graphite is not a significant event. The FT-IR spectrum of **1** exhibits C–H stretching bands associated with the dodecyl groups at 2800–3000 cm^{-1}.

Solubility in water was achieved by initial functionalization of the graphite surface using 5-bromovaleric acid and subsequent reaction with amine-terminated poly(ethylene glycol) (PEG) chains, as illustrated in Scheme 2. As expected, the Raman spectrum of the acid-functionalized graphite (**2**) exhibits a strong D band (Figure S1 in the Supporting Information), and the TGA trace of **2** reveals a weight loss of 12 %, corresponding to one $C_4H_8CO_2H$ group per 61 graph-

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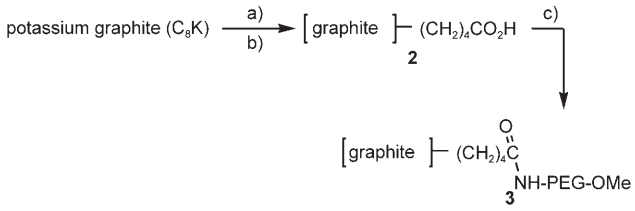

Scheme 2. Preparation of acid-derivatized graphite (**2**) and PEGylated graphite (**3**). Reaction conditions: a) ammonia; b) 5-bromovaleric acid; c) H_2N-PEG-OMe (M_r = 5000 Da), DCC, DMAP, DMSO/DMF.

ite carbon atoms. The FT-IR spectrum of the carboxylic acid functionalized material shows a broad hydroxy absorption at 3400 cm^{-1} and a sharp carbonyl absorption at 1678 cm^{-1}. The carbonyl absorption in the spectrum of the PEGylated graphite (**3**) is shifted to 1624 cm^{-1}, and the N–H stretch is found at 3738 cm^{-1}, in accordance with amide-bond formation.

X-ray photoelectron spectroscopy (XPS) provides direct evidence for the linkage of nitrogen to the carboxylate group during the PEGylation reaction. XPS spectra of the region between 0–1100 eV indicate the presence of carbon, nitrogen, and oxygen in the PEGylated graphite. The C 1s, O 1s, and N 1s XPS spectra (Figure S2) show distinct peaks at 284.6, 533, and 400.2 eV, respectively. The presence of the distinct N 1s peak is indicative of the amide bond in **3**.

Additional evidence for functionalization is provided by the high-resolution transmission electron microscopy (HRTEM) study of **3** (Figure 2a). The PEGylated graphite shows a morphology expected for functionalized graphite. TEM images of unfunctionalized graphite are generally known to have smooth sidewalls.[37] Analogous to SWNTs,[38,39] the "bumps" along the sidewalls of the graphite structure are indicative of surface functionalization. The HRTEM image of **3** shows that the fringes are long and that 6–20 fringes are formed in tangled ribbons in a network-like structure. Cryogenic TEM (Cryo-TEM) study of **3** (Figure 2b) shows that, in the aqueous phase, the PEGylated-graphite particles have an average size of the order of 0.1 μm.

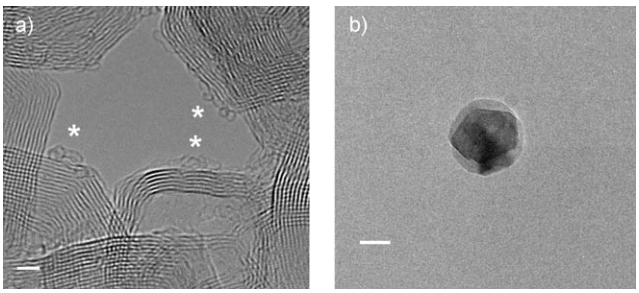

Figure 2. a) HRTEM image of PEGylated graphite (**3**); the scale bar is 2 nm; * indicates functionalization on the graphite surface. b) Cryo-TEM image of **3** (in water); the scale bar is 50 nm.

The average height distribution of the functionalized material determined by atomic force microscopy (AFM) is in good agreement with that detected in TEM images of **3**. AFM images of the three types of functionalized graphite (**1**–**3**) reveal irregular graphite nanoplatelets (Figure 3a,c and Figure S3a). The statistical distributions, from 50 nanoplatelets each of **1**–**3**, show that 70% of each of the functionalized materials has an average height of 7–9 nm, whereas 30% has an average height of 2–4 nm (Figure 3b,d and Figure S3b). The horizontal distances across the nanoplatelets of these functionalized materials vary between 0.1–1.4 μm.

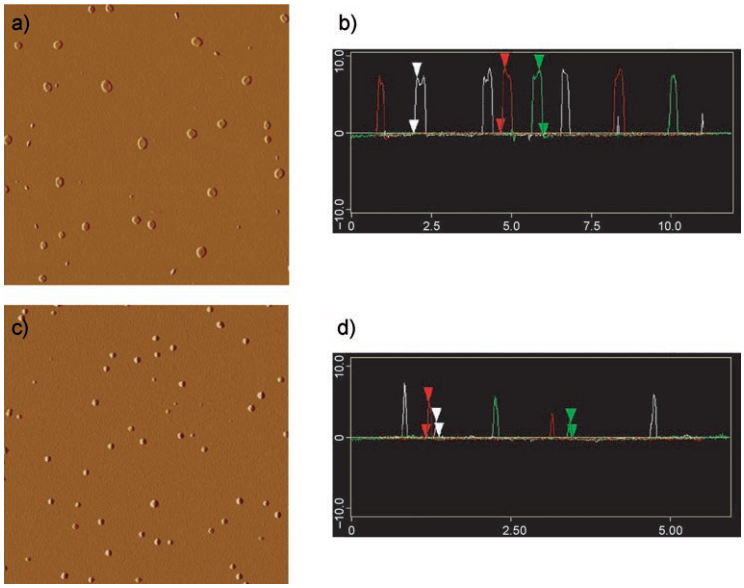

Figure 3. a) AFM amplitude image (10×10 μm^2) of dodecylated graphite (**1**) spin-coated onto freshly cleaved mica from chloroform. b) AFM section analysis of **1**; *x* axis in μm and *y* axis in nm. c) AFM amplitude image (10×10 μm^2) of PEGylated graphite (**3**) spin-coated onto freshly cleaved mica from water. d) AFM section analysis of **3**; *x* axis in μm and *y* axis in nm. The colored triangles indicate the section analysis for different points of functionalized graphite samples.

In summary, we have developed a new route to functionalized graphite nanoplatelets that are soluble in either organic solvents or water. Future work will include studies on the use of these materials in composites.

Experimental Section

Dodecylated graphite (**1**): In a typical reaction, graphite powder (2.5 mmol) and a stir bar were added to a three-necked flask that was previously flushed with argon. The graphite powder was heated to 200°C, and then small pieces of potassium (0.32 mmol) were added. The mixture was stirred and heated at 200°C for 30 min. The resulting bronze-colored C_8K mixture was then cooled to room temperature. Dry ammonia (60 mL) was then condensed into the reaction vessel, and the mixture was stirred for 30 min in a dry-ice–acetone bath. 1-Iodododecane (10 mmol) was then added slowly, and the suspension was stirred overnight at room temperature, leading to slow evaporation of ammonia. The flask was then cooled in an ice bath, and the reaction mixture was quenched by slow addition of ethanol and water. The mixture was acidified with HCl (10%), and the product was extracted into hexanes and washed several times with water. The

hexane layer was then filtered through a 0.2-μm polytetrafluoroethylene (PTFE) membrane. The precipitate was washed with ethanol, as well as chloroform, and dried overnight in vacuo at 80 °C.

Acid-functionalized graphite (**2**): Graphite was also functionalized using 5-bromovaleric acid to generate **2**, in a manner similar to that mentioned above.

PEGylated graphite (**3**): The acid-functionalized graphite (**2**) (2.5 mmol) was then taken in dimethylformamide (DMF; 14 mL) and sonicated for approximately 15 min to achieve a homogeneous dispersion. 4-Dimethylaminopyridine (DMAP; 2.5 mmol) in DMF (3.5 mL) and H_2N-PEG-OMe (4×10^{-5} mmol) in DMF (7.5 mL) were added slowly to this dispersion as the mixture was stirred. *N*,*N*′-Dicyclohexylcarbodiimide (DCC; 2.7 mmol) dissolved in a mixture of DMF (7.5 mL) and dimethyl sulfoxide (DMSO; 10 mL) was added dropwise over 1 h, and the resulting mixture was stirred at room temperature for 72 h. The solution was filtered through a 0.2-μm PTFE membrane and washed several times with DMF followed by chloroform. The product was then dried overnight in vacuo at 50 °C. An aqueous solution of the PEGylated graphite (**3**) was dialyzed (SnakeSkinT Dialysis Tubing, 10000-Da molecular-weight cut-off) at room temperature in Nanopure water (Barnstead International). The dialyzed solution was used for further studies.

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