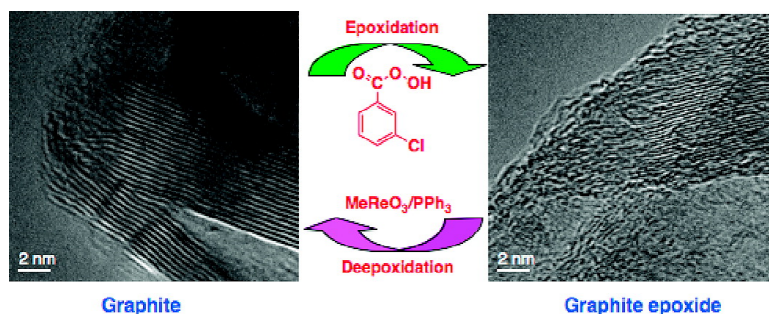


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Graphite Epoxide

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Graphite consists of superimposed lamellae of 2D carbon-carbon covalent networks, referred to as graphene, that form layers as a result of strong van der Waals interactions. Recent results suggest that this venerated material is poised to occupy a significant role in nanoscience and nanotechnology; however, a major impediment for many applications involves debundling of the graphite into graphene nanoplatelets.¹ Although oxidation probably offers the most promising approach, determination of the precise structure of the oxidation product, graphene oxide, has been difficult. Lerf and co-workers have proposed,^{2,3} on the basis of solid-state NMR spectroscopy, that epoxides constitute a major fraction of the material formed when $\text{KMnO}_4/\text{H}_2\text{SO}_4$ is the oxidant. Epoxides have also been considered on the basis of theory as well as from a speculative standpoint.⁴⁻⁶ The formation of cracks (fault lines) that are observed in optical microscopy images of partially oxidized HOPG is proposed to arise from ring opening of epoxides that are formed cooperatively in rows.⁷ In this communication, we report evidence for the discrete existence of graphite epoxides using the epoxidation-deepoxidation method reported earlier for single-walled carbon nanotubes⁸ (Scheme 1).

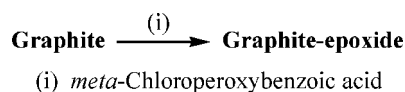
Syntheses of graphite epoxides **1** and **3** were accomplished by dissolving the peracid (77% max, 1.15 g, 6.6 mmol) in CH_2Cl_2 (60 mL). Graphite (40 mg, 3.3 mmol) was then added and the solution stirred overnight at room temperature. The reaction mixture was filtered through a 0.2 μm polytetrafluoroethylene (PTFE) membrane and dried in vacuo at 80 °C.

The Raman spectrum (Figure SI-1) of the oxygenated graphite **1** exhibits a substantial enhancement of the D band at 1335 cm^{-1} because of the chemical disruption of sp^2 -hybridized carbon atoms of the graphite. The ATR FT-IR spectrum shows a band at 1227 cm^{-1} that is assigned to the carbon oxygen stretching frequency of the epoxide moiety (Figure SI-2). Additional evidence for functionalization was evident from thermal gravimetric analysis (TGA) of the oxygenated graphite (argon, 10 °C min^{-1} to 800 °C). The epoxidized graphite **1** shows a 7% weight loss, whereas the weight loss observed when pure graphite was heated to 800 °C in argon was <0.5%.

The salient feature of this study is the removal of the oxygen atoms from the graphite epoxide to a substrate that allows quantification of the epoxide content. The reaction uses the $\text{MeReO}_3/\text{PPh}_3$ catalytic system that is illustrated in Scheme 2.⁹

Deoxygenation occurs by the transfer of an oxygen atom to PPh_3 , and the amount of oxygen transferred is readily quantified by ^{31}P NMR spectroscopy.^{8,9} Thus, from the integration of the peaks in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (Figure SI-3), the percentage of PPh_3 consumed and the total percent mass loss from the sample is obtained and from this the C:O atomic ratio.

Scheme 1. Epoxidation of Graphite



Scheme 2. Deepoxidation of Graphite Epoxide

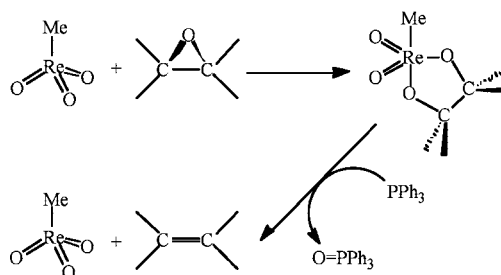


Table 1. Oxygen Content of Various Graphite and Graphite Epoxide Samples as Determined by Catalytic Deoxygenation

sample	molecular formula
synthetic graphite	C_{110}O
synthetic graphite + <i>m</i> -CPBA (1)	C_{12}O
synthetic graphite + $\text{KMnO}_4\text{-H}_2\text{SO}_4$ (2)	C_{78}O
graphite flake	C_{82}O
graphite flake + <i>m</i> -CPBA (3)	C_{57}O

Deoxygenation of graphite epoxides **1-3** was carried out by placing graphite epoxide (250 mg) in a 250 mL Schlenk flask fitted with an addition funnel. After evacuation for 30 min to remove any adsorbed O_2 , a toluene solution (25 mL) of MeReO_3 (50 mg, 0.20 mmol) was added. PPh_3 (57 mg, 0.22 mmol) dissolved in toluene (25 mL) was then added dropwise over 15 min and the mixture stirred overnight at 55 °C. A small portion of the toluene decant was transferred to a NMR tube under N_2 . C_6D_6 (0.2 mL) was added as the locking solvent. The relative integration of PPh_3 (-4.81 ppm) and O=PPh_3 (25.09 ppm) was then determined.

The oxygen content determined for several samples is shown in Table 1.¹⁰ Since the $\text{MeReO}_3/\text{PPh}_3$ system has been shown to be selective for removal of epoxide oxygen, we propose that epoxides account for nearly all of the oxygen that is added via the epoxidation reactions. Unfunctionalized synthetic graphite powder appears to contain a low oxygen content (C_{110}O). As shown in Table 1, epoxidation of graphite flake (Aldrich, 75+ mesh) proved to be more difficult. Material prepared (known as graphite oxide; GO)¹¹⁻¹³ by oxidation of synthetic graphite using $\text{KMnO}_4\text{-H}_2\text{SO}_4$ has 1 epoxide per 78 carbon atoms (C_{78}O). This result supports the work of Lerf and co-workers who proposed that epoxides are formed when $\text{KMnO}_4\text{-H}_2\text{SO}_4$

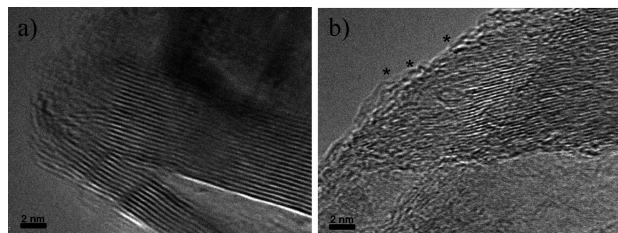


Figure 1. HRTEM images of (a) unfunctionalized synthetic graphite; (b) graphite epoxide **1**. The scale bar is 2 nm; * indicates functionalization areas.

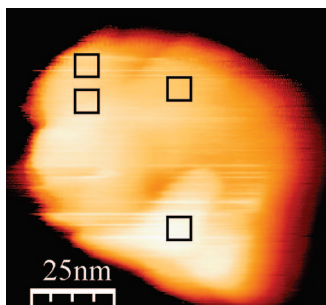


Figure 2. STM image of graphite epoxide **1** on Au(111) substrate. Tunneling current and bias voltage are 0.3 nA and 100 mV. Roughness of the boxed areas was compared to the similar sized regions of pristine nanoparticles of the synthetic graphite powder surface.

is the oxidant.² As expected, the graphite contains a higher oxygen content when the peracid is used as the oxidant.

Additional evidence for epoxidization is provided by inspection of the high-resolution transmission electron microscopy (HRTEM) images presented in Figure 1. Unfunctionalized synthetic graphite shows (Figure 1a) smooth edges and sidewalls with visible graphite lattice fringes. The HRTEM image of graphite epoxide **1** exhibits (Figure 1b) characteristic roughness of the graphite edges, indicating edge functionalization.^{14,15}

To investigate the location of epoxide defect sites on the graphite, scanning tunneling microscopy (STM) was performed on both unfunctionalized and functionalized synthetic graphite samples.¹⁶ Since it was difficult to obtain a detailed atomic resolution of the epoxide samples,¹⁷ surface texture analysis was utilized as a means to quantify any changes. Root mean square roughness was measured on the chosen areas of the sample shown in Figure 2. If epoxidation occurred on the basal plane, the graphite epoxide would be much rougher when compared with the unmodified synthetic graphite material. However, after imaging several flat areas as judged by a minimum of step edges, no significant difference in roughness was observed between the unfunctionalized and the chemically epoxidized synthetic graphite samples.¹⁸ Thus, it is reasonable to assume that the functionalization occurs at the edges rather than on the basal plane of the graphite and that bulk graphite oxide is not formed.

As a further control, the same chemical epoxidation procedure was carried out with macroscopic crystalline samples of highly ordered pyrolytic graphite (HOPG) at varying concentrations. However, tunneling microscopy of the functionalized HOPG did not yield any differences when compared to pristine samples. In addition, atomic resolution was readily obtained on many terraces of the epoxidized HOPG, strongly suggesting that any chemical reaction was carried out at the step edges.

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Supporting Information Available: Raman spectra of pure graphite powder and graphite epoxide (**1**), FT-IR spectra of graphite epoxide (**1**), and ³¹P{¹H} NMR spectrum of MTO/PPh₃/graphite epoxide (**1**) solution after 17 h. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (16) Scanning tunneling microscopy was carried out in an Omicron variable temperature UHV system using mechanically cut Pt/Rh (80/20) tips. The graphite nanoparticles were spun cast onto Au(111) on mica substrate purchased from Molecular Imaging.
- (17) Due to the radius of the AFM tip, which is comparable or bigger than the individual graphene domains, a more detailed structure was not possible.
- (18) By inspecting the STM image of graphite epoxide **1** and its cross-sectional area, the height of the material was determined to be ~20 nm with an average particle size of the order of a few hundred nanometers. In addition, to determine the bulk property of the functionalized material, powder X-ray diffraction (PXRD) was used. The crystallite size of unfunctionalized synthetic graphite was found to be ~58 and ~20(±1) nm for the graphite epoxide **1**, consistent with the STM result. These results suggest that few layers of graphite can be obtained after epoxidation.

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