Improved mechanical and functional properties of elastomer/graphite nanocomposites prepared by latex compounding

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Abstract

The facile latex approach has been adopted to finely incorporate graphite nanosheets into elastomeric polymer matrix to obtain high-performance elastomeric nanocomposites with improved mechanical properties and functional properties. Scanning electron microscopy, transmission electron microscopy and X-ray diffraction experiments show that the nanostructures of the final nanocomposites exhibit a high degree of exfoliation and intercalation of graphite in the nitrile-butadiene rubber (NBR) matrix. Mechanical and dynamic-mechanical tests demonstrate that the NBR/graphite nanocomposites possess greatly increased elastic modulus and tensile strength, and desirably strong interfaces. The unexpected self-crosslinking of elastomer/graphite nanocomposites was discovered and then verified by oscillating disc rheometry and equilibrium swelling experiments. After critically examining various polymer types by X-ray photoelectron spectroscopy, electron spin resonance and Fourier transform infrared spectroscopy, a radical initiation mechanism was proposed to explain the self-crosslinking reaction. These NBR/graphite nanocomposites possess significantly improved wear resistance and gas barrier properties, and superior electrical/thermal conductivity. Such versatile functional properties make NBR nanocomposites a promising new class of advanced materials.

Keywords: Nanocomposites; Elastomers; Graphite; Nanostructure; Latex compounding

1. Introduction

Nanocomposites have been shown to afford remarkable property enhancements compared to conventional microcomposites [1–3]. Polymer nanocomposites with layered silicates [4–9] and carbon nanotubes [10–12] have attracted great interest for the improvement of structural properties and the development of new materials with different functional properties. Graphite is a layered material with a high aspect ratio in its exfoliated state; it is also one of the strongest materials per unit weight and has unique functional properties (e.g. good electrical and thermal conductivities, and good lubricating properties) compared to layered silicates [13]. In addition, graphite is cheap compared to carbon nanotubes. Recently, polymer/graphite nanosheet composites have made a great impact in nanocomposite research [14–27].

To date, some polymer/expanded graphite (EG) nanocomposites with good electrical conductivity have been prepared (e.g. via in situ polymerization) [14–22]. But EG does not significantly enhance the mechanical properties of the polymers due to poor dispersion of the graphite, voids trapped in the composites and weak interfacial adhesion [19–26]. Indeed, the functional performance of the
Intercalation and Stitching of Graphite Oxide with Diaminoalkanes

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The intercalation reaction of graphite oxide with diaminoalkanes, with the general formula H2N(CH2)nNH2 (n = 4–10), was studied as a method for synthesizing pillared graphite with tailored interlayer spacing. Interlayer spacings from 0.8 to 1.0 nm were tailored by varying the size of the intercalant from (CH2)4 to (CH2)10. X-ray diffraction and infrared spectroscopy were used to confirm intercalation, and the frequency of the CH2 stretch confirmed that the intercalants are in a disordered state, with an important contribution from the gauche conformer. Sequential intercalation of diaminoalkanes followed by dodecylamine demonstrated the inability of these “stitched” systems to undergo expansion along the c-direction, indicative of cross-linking. Finally, the reaction of graphite oxide with diaminoalkanes under reflux and for extended periods (>72 h) resulted in the chemical reduction of the graphite oxide to a disordered graphic structure.

Introduction

Intercalation of organic molecules in the gallery spacing of layered materials is a common modification technique since the simplicity of these reactions allows facile control over the chemical and physicochemical characteristics of the derivatives. An example of the applicability of this method is in the fabrication of polymer/clay nanocomposites, where dispersability of the inorganic platelets within the polymer matrix has a profound influence on the mechanical, thermal, and barrier properties of the resulting composite. Organicophilization of inherently hydrophilic aluminosilicates through ion-exchange reactions with alkylammonium quaternary salts results in surfaces that exhibit enhanced compatibility with hydrophobic polymers, therefore improving their dispersability. Recently much attention has been focused on intercalation of difunctional reagents since they can lead to bridged or pillared nanostructures with potential applications as catalytic supports, selective adsorbents, and molecular vessels.

Depending on the nature of the host and the intercalant, pillaring and stitching can be accomplished by three methods: (i) ion exchange between a difunctional ionic intercalant and the native ions of the host; (ii) exfoliation of the host followed by reaction with the difunctional reagent and reassembly; and (iii) intercalation of a difunctional molecule chemically anchored at one end and capable of undergoing a different reaction on the other end. Noteworthy examples of bridged systems include γ-zirconium phosphate bridged with n-alkanediphosphonic acids or polyethylene oxide, montmorillonite (MMT) clay bridged by diaminoalkanes, and graphite oxide (GO) pillared with (3-aminopropyl)trimethoxysilane or iron oxide. Intercalation of a difunctional reagent, however, does not ensure bridging, since the intercalant can also adopt a single-tail tethered conformation, where only one end of the difunctional molecule reacts, or a loop conformation, where each end interacts with the same layer.

GO, an oxygen-rich derivative of graphite, is a layered material capable of undergoing intercalation by one-dimensional expansion along its c-axis. Since its first synthesis by Brodie in the 1850s, GO has been characterized by a combination of spectroscopic techniques in order to establish a structural model that explains its chemical composition and reactivity. Although its stoichiometry depends on the method used for its preparation, it is commonly accepted that it consists of randomly distributed regions of unoxidized (aromatic) graphite and regions of aliphatic six-membered rings, rich in oxygen-containing functional groups, including epoxys and hydroxyls. It is believed that the epoxy and hydroxyl functionalities lie above and below each layer, while carboxylic acid groups decorate the edges. Oxidation, therefore, provides the otherwise unreactive graphite with functional groups that can be used as reactive handles to tailor its properties. The hydroxyl groups possess acidic protons, allowing GO to undergo intercalation through ion exchange, analogous to MMT clays. However, unlike MMT, its rich surface chemistry also allows covalent bonding of the intercalant directly to the layers. Chemistries targeted at the hydroxy and epoxy functionalites have been studied previously, with the objective of assessing the reactivity of these functional groups in the intercalated structure, as well as controlling the interlayer spacing and hydrophobicity by careful consideration of the size and molecular structure of the intercalants.

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(9) Brodie, B. C. Philos. Trans. R. Soc. London 1859, 149, 249.
An interesting and potentially important application of pillared graphitic materials is in the area of hydrogen storage. Recent theoretical calculations indicate that confinement effects should have a major impact on hydrogen storage between graphite sheets.20 Simulations show that there exists an optimal combination of pressure and pore geometry (interlayer distance) that maximizes the storage capacity.20 Furthermore, chemical substitution disrupts the planarity of the graphene sheets and creates a distorted surface, which has been referred to as “puckered”21 or “roughened”.22 The combination of altered aromaticity, bond distortion, and local coordination changes arising from the distortion, cause an increase in the polarizability of distortion, and local coordination changes arising from the distorted surface, has been referred to as “puckered”21 or “roughened”.22 This reaction results in an increase in the polarizability of the distorted surface, which has been referred to as “puckered”21 or “roughened”.22 The combination of altered aromaticity, bond distortion, and local coordination changes arising from the distorted surface, cause an increase in the polarizability of graphene. Binding energies for hydrogen range from 52 meV in a distorted surface, which has been referred to as “puckered”21 or “roughened”.22 The combination of altered aromaticity, bond distortion, and local coordination changes arising from the distorted surface, has been referred to as “puckered”21 or “roughened”.22 The combination of altered aromaticity, bond distortion, and local coordination changes arising from the distorted surface, which has been referred to as “puckered”21 or “roughened”.22 This reaction results in an increase in the polarizability of the distorted surface, has been referred to as “puckered”21 or “roughened”.22 The combination of altered aromaticity, bond distortion, and local coordination changes arising from the distorted surface, cause an increase in the polarizability of distortion, and local coordination changes arising from the distortion, which has been referred to as “puckered”21 or “roughened”.22 The combination of altered aromaticity, bond distortion, and local coordination changes arising from the distorted surface, has been referred to as “puckered”21 or “roughened”.22 This reaction results in an increase in the polarizability of distortion, which has been referred to as “puckered”21 or “roughened”.22 The combination of altered aromaticity, bond distortion, and local coordination changes arising from the distorted surface, which has been referred to as “puckered”21 or “roughened”.22 This reaction results in an increase in the polarizability of distortion, which has been referred to as “puckered”21 or “roughened”.22 The combination of altered aromaticity, bond distortion, and local coordination changes arising from the distorted surface, cause an increase in the polarizability of distortion, and local coordination changes arising from the distortion, which has been referred to as “puckered”21 or “roughened”.22

The present work describes a detailed study of the intercalation reaction of α,ω-diaminoalkanes with GO to produce chemically bridged derivatives. The size of the intercalant was systematically varied to determine its effect on the interlayer spacing, and the transformation of the intercalant in the layered structure was assessed by swelling experiments.

Experimental Section

Materials. All materials were used as received. Graphite particles (40 μm particle size) were provided by Asbury Carbon, New Jersey. Sulfuric acid (98%), hydrochloric acid (37%), and nitric acid (fuming, 90%) were purchased from Fisher. Potassium chloride, ethanol (reagent grade), diaminoalkanes, and alkylamines were obtained from Aldrich.

Graphite Oxide. GO was synthesized from natural flake graphite (40 μm particle size) by the Staudenmaier method.23 Sulfuric acid (160 mL) and nitric acid (90 mL) were added to a round-bottom flask, containing a stir bar, and cooled with an ice bath for 1 h. Graphite particles (10 g) were added to the acids mixture under vigorous stirring, and the suspension was cooled for 20 min. Potassium chloride (110 g) was slowly added over 15 min, while keeping the reaction vessel inside an ice bath, making sure that the temperature did not exceed 35 °C. Caution! This reaction results in the formation of chlorine dioxide gas, which is explosive at high concentrations.24 To minimize the risk of explosion it is recommended that the addition of potassium chloride be done slowly while monitoring the temperature. Oxidation was allowed to proceed for 96 h. The suspension was washed with an aqueous hydrochloric acid solution (10 vol %) to remove the sulfate ions and then washed repeatedly with deionized (DI) water until neutral pH. The final concentration of GO in the suspension was approximately 6 mg GO/mL.

Intercalation of Graphite Oxide with Mono- and Disfunctional Amines. In a typical experiment, 1,8-diaminooctane (600 mg) was dissolved in ethanol (35 mL) and added dropwise to a suspension of GO (200 mg GO, 33 mL) under vigorous stirring. The reaction continued for 24 h at room temperature or under reflux (78 °C). Intercalated GO was isolated by centrifugation and thoroughly washed with 1:1 ethanol/water (45 mL, 4×), filtered, and dried at 80 °C under vacuum for a minimum of 12 h prior to characterization. Reactions with alkylamines CH3(CH2)nNH2 (n = 4–12) or diaminoalkanes H2N(CH2)nNH2 (n = 4–10) were conducted following the same procedure.

Characterization. X-ray diffraction (XRD) patterns were acquired on a Rigaku MiniFlex diffractometer with Cu Kα radiation. Simultaneous thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) experiments were conducted with a Neetzst STA 449C thermal analyzer. Analyses were done under a nitrogen atmosphere (50 mL/min flow rate) at a heating rate of 1 °C/min. Fourier transform infrared spectroscopy (FTIR) was performed on a ThermoNicolet 6700 FT-IR spectrometer. GO and its derivatives were then dried on a hot plate ground, mixed with potassium bromide to a final concentration of approximately 0.15 wt %, and pressed into pellets. Elemental analysis was performed by Atlantic Microlab Inc., Norcross GA.

Results and Discussion

Graphite Oxide Characterization. GO was characterized by elemental analysis, 13C NMR, XPS, and FTIR. Results from XPS and elemental analysis were discussed in a previous publication.25 Briefly, the chemical composition of GO determined by elemental analysis was C6O3.3H4.6, while the C/O ratio calculated from XPS was 2.6. High-resolution C1s XPS (Figure 1, Supporting Information) showed signals characteristic of graphitic carbon (C=C, 284.6 eV) and carbon singly bound to oxygen (C=O, 286.6 eV), either as epoxide or hydroxyl.12,26 The broad O1s spectrum is also indicative of the presence of more than one oxygen-containing species: oxygen in carboxyls (531.3 eV), Csp2,sp2=O (532.6 eV), and C aromatic–O (531.1 eV).22 Solid-state 13C NMR results (Figure 2, Supporting Information) are in agreement with the XPS data. The spectrum contains two distinguishable peaks at chemical shifts (δ) of 60–70 and 133 ppm. The signal between 60 and 70 ppm is composed of two peaks, which have been assigned to hydroxyl (70 ppm) and 1,2-epoxy groups (60 ppm). The peak at 133 ppm corresponds to sp2-hybridized carbon. The third signal, observed at lower fields (210–220 ppm), has been assigned to spinning side bands of the unsaturated carbons.11 The NMR spectrum is in qualitative agreement with the model proposed by Lerf et al.10 FTIR analysis of GO is discussed in more detail further in the text.

Intercalation of Graphite Oxide with α,ω-Diaminoalkanes. The rich surface chemistry of GO allows for covalent modification by reactions at hydroxy and epoxy groups. An example is the intercalation reaction of GO with monofunctional amines, which proceeds by nucleophilic substitution on the epoxy groups, provided that the amines are in neutral form.7,10 It is possible then, that intercalation of a difunctional amine could produce a pillared structure, as shown in Figure 1.

For this, GO was reacted with a series of α,ω-diaminoalkanes that differ in the number of methylene units (n) separating the terminal amine groups. XRD patterns of GO and the intercalated derivatives are shown in Figure 2. A gradual increase in the basal spacing of GO is observed as the hydrocarbon chain length of the diamine increases from n = 4 to n = 10, suggesting that intercalation takes place and that the interlayer spacing is sensitive to the size of the intercalant.
Coupled quantum mechanical/molecular mechanical modeling of the fracture of defective carbon nanotubes and graphene sheets

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Coupled quantum mechanical/molecular mechanical (QM/MM) calculations were used to study the effects of large defects and cracks on the mechanical properties of carbon nanotubes and graphene sheets. The semi-empirical method PM3 was used to treat the QM subdomains and a Tersoff-Brenner potential was used for the molecular mechanics; some of the QM calculations were also done using density functional theory (DFT). Scaling of the Tersoff-Brenner potential so that the modulus and overall stress-strain behavior of the QM and MM models matched quite closely was essential for obtaining meaningful coupled calculations of the mechanical properties. The numerical results show that at the nanoscale, the weakening effects of holes, slits, and cracks vary only moderately with the shape of the defect, and instead depend primarily on the cross section of the defect perpendicular to the loading direction and the structure near the fracture initiation point. The fracture stresses for defective graphene sheets are in surprisingly good agreement with the Griffith formula for defects as small as 10 Å, which calls into question the notion of nanoscale flaw tolerance. The energy release rate at the point of crack extension in graphene was calculated by the J-integral method and exceeds twice the surface energy density by 10% for the QM(DFT)/MM results, which indicates a modest lattice trapping effect.

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I. INTRODUCTION

Due to their favorable mechanical properties, carbon nanotubes (CNTs) and exfoliated graphene sheets have attracted considerable interest as nanoreinforcements for polymer composites. Electronic structure calculations1–7 of the mechanical behavior of pristine CNTs predict fracture strengths in the range of 75–135 GPa and ultimate strains of as much as 30%. However, manufacture of mass-quantities of perfect CNTs or graphene sheets may prove challenging; in practice, mechanical properties will often be limited by the presence of defects—in many cases of substantial size. Oxidative purification treatments8–10 are commonly used in the production of CNTs and we have suggested6,11 that these can result in pitting, which provides a plausible explanation for the deviations between the CNT strength measurements of Yu et al.12 and theoretical predictions. One route for the exfoliation of graphene sheets involves thermal exfoliation of graphite oxide.13 During this process approximately 30% of the carbon atoms are lost as CO2; thus, the resulting sheets are expected to be highly defected. A detailed understanding of the consequences of such defects may be crucial to the effective utilization of these materials.

Previous electronic structure calculations of defected CNTs were limited to small defects because of the high computational cost of QM calculations. Therefore, the studies6,14 of larger defects were restricted to MM calculations. However, the modified15,16 second generation17 Tersoff-Brenner (MTB-G2) potential employed in those calculations tends to systematically underestimate the strength of both pristine and defected CNTs as compared to QM calculations, and has been shown3 to predict qualitatively different mechanisms for the fracture of defected CNTs. Thus, a better understand-
nanoscale (5–20 nm) defects: for any defect, the strength is below the theoretical strength, as would be expected.

Crack-like defects, which we called slits, were constructed by removing four rows of carbon atoms in the zigzag CNTs and by removing three rows of carbon atoms in the armchair CNTs. The resulting dangling bonds were capped with hydrogen atoms. This is to be contrasted with crack models based on omitting bonds between adjacent atoms in MM calculations, which are pervasive in the literature. Such defects cannot exist in electronic structure models because interactions between nearby atom pairs cannot simply be neglected at moderate distances. Thus, the ability of such schemes to accurately model crack behavior is questionable. Crack-like defects can be formed by displacing a lattice according to the asymptotic near-field of elastic fracture mechanics, as we reported in Sec. IV. However, such cracks will not exist in a solid in a stress-free state.

To ascertain the magnitude of lattice trapping in graphene, we computed the energy release rate using a discrete J-integral and compared it to twice the surface energy density, 2γ. These results indicate a modest amount of lattice trapping; the energy release rate calculated by DFT for a graphene sheet at fracture exceeds 2γ by 10%.

The coupled QM/MM calculations were performed with the ONIOM methodology. We checked the accuracy of the method by performing a series of calculations for small defects with QM fragments of increasing size. The resulting stress-strain curves agreed closely over most of the range even for relatively small QM fragments. The fracture stresses and strains also appear to converge, but are more sensitive to the QM fragment size and even for the largest two fragments studied, the fracture stresses and strains differed from the pure QM results by 4% and 8%, respectively, for a [10,0] CNT with a two-atom vacancy defect. Thus, the absolute accuracy of the coupled QM/MM calculations for the failure stress is probably only a few percent and the results are more useful for comparing defects of various sizes than in obtaining quantitative values of failure stresses.

We introduced a simple scaling scheme to improve the compatibility of the MM and QM models. If the MM interaction potential is used unscaled, mismatches between the stiffness and strength of the MM and QM subdomains result in highly spurious behavior. Comparisons of the QM/MM calculations with MM calculations using the scaled potential show good agreement for the failure stresses and stress-strain curves. In most cases, the differences were less than 15%, and the qualitative pattern of dependence on defect size agreed well. It should be noted that this good agreement is only achieved for the scaled MM potential. The details of the fracture processes predicted by the QM/MM method and the MM method differ significantly. For example, QM/MM calculations show significantly more elongation of the bond at the crack tip.

The results provide further credence to the hypothesis that large defects such as holes are the reason behind the low CNT fracture strengths observed in some experiments. Although the QM/MM models predict failure stresses that are about 40% higher than unscaled MM results modeled previously, they are still in the range observed in the Yu et al. experiments.

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Oxygen-Driven Unzipping of Graphitic Materials

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Optical microscope images of graphite oxide (GO) reveal the occurrence of fault lines resulting from the oxidative processes. The fault lines and cracks of GO are also responsible for their much smaller size compared with the starting graphite materials. We propose an unzipping mechanism to explain the formation of cracks on GO and cutting of carbon nanotubes in an oxidizing acid. GO unzipping is initiated by the strain generated by the cooperative alignment of epoxy groups on a carbon lattice. We employ two small GO platelets to show that through the binding of a new epoxy group or the hopping of a nearby existing epoxy group, the unzipping process can be continued during the oxidative process of graphite. The same epoxy group binding pattern is also likely to be present in an oxidized carbon nanotube and cause its breakup.

Carbon based materials play a significant role in nanoscience and nanotechnology applications. Fullerenes, nanotubes, and 2D graphite platelets are the building blocks for nanoelectronic devices [1], chemical and biosensors [2,3], drug delivery applications [4], hydrogen-storage systems [5], quantum wires [6], and nanocomposites [7,8]. Fabrication and manipulation of these building blocks involves both new physics and new technology. Oxidation is one of the basic processes used to manipulate carbon materials as in the case of carbon nanotube cutting [9]. Similarly, graphite oxide (GO) is an important intermediate in the process of graphite exfoliation to produce very thin graphitic flakes that in some cases consist of a single atomic layer [10]. It is relatively well known how oxygen can be incorporated into a graphene layer: oxidation results in functionalization by epoxy and hydroxyl groups. The extensive literature on the chemistry of graphite oxidation has provided information on average substitution levels, the varieties of oxygen species, and reaction conditions [11–13]. Yet, surprisingly little has been done to connect oxidation chemistry to the morphology of the graphene sheets, except for the layer spacing during intercalation and curved graphitic structure caused by topological or vacancy defects in the carbon lattice. Intriguingly, we have observed cracks in GO that are directly related to the oxidation process. However, the processes that lead to crack formation in GO and carbon nanotube cutting are not known at the atomistic level. Here we find that cracks are the result of a cooperative effect that leads to unzipping. Using first-principles quantum mechanical calculations we elucidate the origin of the reaction mechanism that causes ordered oxidation and subsequent unzipping and cracking. This result was unanticipated by the previous purely “mean field” chemical understanding of graphite oxidation.

Under a well-controlled oxidation process, we examined the dark field optical microscope images of GO produced by the Staudenmaier method [14] which reveals the occurrence of fault lines not observed in the starting graphite material (Fig. 1). It is also known that oxidation of single-wall carbon nanotubes is an effective method to chemically cut and shorten their lengths [9]. A basic question thus arises: how can such a fracture occur upon oxidation? By utilizing a density-functional theory (DFT) approach, we aim to investigate the low level oxidation processes occurring on a graphene sheet and identify those reactions that could lead to cracks. This is of importance to the molecular control of distribution and location of the oxygenated functional groups [15]. In addition, understanding the energetics that drives the unzipping process is indispensable for finely tuned fabrication and engineering of the graphite composites at the nanolength scale. In this Letter we propose a model of GO unzipping initiated by the formation of epoxy groups on the graphite surface. During the oxidative process on a graphene sheet,

FIG. 1 (color online). During oxidization of graphite, a marked decrease in size is observed. An optical microscope image of partially oxidized highly oriented pyrolytic graphite (HOPG) shows line defects (fault lines). The same defects are not observed on freshly cleaved HOPG.
FIG. 8 (color online). Two epoxy groups create a small crack on a SWCNT. Inset: a single epoxy group does not break the attached C-C bond.

to the inner graphitic layers [21]. The unzipping process described above results in linearly serial breaking of C-C bonds, so the mechanism can be easily realized for the circumferential direction of a carbon nanotube and account for its breaking.

Figure 8 shows a [10, 0] SWCNT with one or two epoxy groups attached to it. When an epoxy group binds to the SWCNT, the underlying C-C bond is stretched from 1.4 to 1.5 Å, similar to the case of graphene sheets. When two epoxy groups bind to the opposite ends of a hexagonal carbon ring, the underlying C-C bonds cannot sustain the concerted stretch and break. Note that this is in striking contrast with fluorinated nanotubes where even a high density of attached fluorines leaves the carbon network mostly intact [22, 23]. The binding energy profile of epoxy groups on a SWCNT is similar to that on graphite: when two epoxy groups are well separated, their binding energies are additive; on the other hand, if two epoxy groups bind cooperatively, the system gains an additional energy \( \sim 1 \) eV from the released strain energy in C-C bonds. This suggests that the unzipping mechanism may also be responsible for breaking of oxidized CNTs [9].

In this work we have proposed a mechanism to explain the observed fault lines and cracks on GO. It is shown that strain generated by the cooperative alignment of epoxy groups can initiate cracks on GO. The continuation of unzipping processes can be achieved by binding of a new epoxy group during the oxidation or hopping of an existing epoxy group and subsequent locking. Given that an open epoxy ring is substantially weaker than a closed ring, our work gives insight into chemical shortening of carbon nanotubes via oxidative processes.

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[16] Depending on the way the tensile stress is relieved, a thin film made of multiple layers may crack or buckle. See Ref. [10].
[19] The hopping of an epoxy group has a comparable energy barrier as single vacancy diffusion in graphite [G. D. Lee et al., Phys. Rev. Lett. 95, 205501 (2005)]. Based on a quick estimate of the fast stretching mode of C-C bonds, the hopping rate of an epoxy group on graphite is roughly once every 100 sec at room temperature.
Continuum and atomistic modeling of interacting graphene layers

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To investigate multishell models of multiwalled carbon nanotubes, we consider the buckling of a pair of graphene layers interacting by van der Waals forces. The layers are modeled as continuum sheets whose interaction is determined by a Lennard-Jones interatomic potential. Important in our treatment is the effect of nonequilibrium spacing between the layers, an issue whose physical and technological importance is suggested by a number of recent articles [see in particular, J. Zou et al., Nano Lett. 6, 430 (2006), and the references therein]. Using standard local bifurcation techniques, we construct bifurcation curves that describe the deformation of the layers as the edges of the layers are compressed. The bifurcation curves agree qualitatively with the sequence of deformations predicted by atomistic simulations. This agreement suggests the validity of multishell continuum models of multiwalled carbon nanotubes.

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I. INTRODUCTION

Carbon nanotubes have remarkable mechanical properties, most notably an extraordinary tensile strength combined with the flexibility to sustain large compressive loads and bending deformations elastically.1–3 These properties naturally suggest certain applications, for example, using nanotubes as reinforcing fibers in composite materials or as probes in atomic force microscopy. Such applications have in turn motivated many investigations of how carbon nanotubes deform and buckle under axial loads.

Axial buckling problems have been studied for both single-walled and multiwalled nanotubes. Such problems for single-walled nanotubes are more readily described because of the relatively simple structure of a single-walled tube. Basic to this structure is graphene, a two-dimensional array of carbon atoms in a periodic hexagonal arrangement. A single-walled carbon nanotube can be visualized as a rectangular section cut from a larger graphene sheet and wrapped into the shape of a hollow cylinder. One of the first papers to treat the axial buckling of single-walled nanotubes is Ref. 4, in which the authors use molecular dynamics (MD) simulations to address two questions: what is the basic shape of an axially buckled single-walled nanotube, and can this buckling be accurately described by modeling the nanotube as a continuum. The authors conclude that linearly elastic shell theory can qualitatively predict the deformations observed in their MD simulation as well as the critical axial strains at which buckling occurs.

Other work on the axial buckling of a single-walled nanotube includes Refs. 5 and 6. These papers, similar in spirit to Ref. 4, contain the use of MD simulations or experiments to determine the basic geometry of compressively loaded nanotubes as a function of the length, diameter, and thickness of the tube. In particular, atomistic studies predict that under compressive loading, a nanotube with small aspect ratio buckles like a thin shell, a nanotube with an aspect ratio above a certain threshold buckles like a rod, and a nanotube with a very large aspect ratio undergoes a “wire-like” buckling with folding patterns similar to patterns observed in biomolecules such as DNA, RNA, and peptides. This interesting folding behavior has been explored in more detail in Ref. 7.

The treatment of axial buckling problems for multiwalled nanotubes is more challenging. A multiwalled nanotube is formed by nesting from two to as many as fifty single-walled nanotubes of different diameters along a common axis. The walls of adjacent tubes in a multiwalled nanotube are typically only a few angstroms apart. Consequently, adjacent walls interact through van der Waals forces, which are interatomic forces between pairs of nonbonded carbon atoms. Although these forces are much weaker than the forces between the covalently bonded neighboring carbon atoms within the wall of a given tube, van der Waals interactions appear to strongly influence the deformation of a multiwalled nanotube during axial compression and bending.

To explore the importance of van der Waals interactions for axial buckling, Ru in Ref. 8 proposed modeling each wall of a multiwalled nanotube as a thin linearly elastic shell. The equation for the radial displacement of each wall contains terms that describe the van der Waals forces between that wall and each of its nearest neighbors as a linear function of the relative radial displacement between the walls. By specializing these equations to a double-walled nanotube and using standard buckling analysis, Ru concludes in Ref. 8 that if the two tubes buckle in the same manner and if the two tubes are at their equilibrium spacing prior to buckling, then the critical axial strain at which buckling occurs for a double-walled tube is the same as the corresponding strain for just a single tube with the same elastic moduli. Ru9,10 and Wang et al.11,12 apply the same multishell model to explore the axial buckling of multiwalled nanotubes embedded in an elastic medium, or subject to external or internal pressure.
Synthesis of graphene-based nanosheets via chemical reduction of exfoliated graphite oxide

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Abstract

Reduction of a colloidal suspension of exfoliated graphene oxide sheets in water with hydrazine hydrate results in their aggregation and subsequent formation of a high-surface-area carbon material which consists of thin graphene-based sheets. The reduced material was characterized by elemental analysis, thermo-gravimetric analysis, scanning electron microscopy, X-ray photoelectron spectroscopy, NMR spectroscopy, Raman spectroscopy, and by electrical conductivity measurements.

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1. Introduction

Graphite-like nanoplatelets have recently attracted attention as a viable and inexpensive filler in composite materials [1–3] that can be used in many engineering applications, given the excellent in-plane mechanical, structural, thermal, and electrical properties of graphite [4]. These excellent properties may be relevant at the nanoscale if graphite can be exfoliated into thin nanoplatelets, and even down to the single graphene sheet level [5].

Graphite nanoplatelets have often been made from expanded graphite, which in turn was produced from graphite intercalation compounds via rapid evaporation of the intercalant at elevated temperatures. For example, rapid thermal expansion of sulfuric acid-intercalated graphite, followed by a suitable treatment to produce platelets/nanoplatelets from the expanded material (ball milling or exposure to ultrasound) has been recently demonstrated [6–13]. Although this simple method has been applied on a large scale to commercially available sulfuric acid-intercalated graphite, it never results in complete exfoliation of graphite to the level of individual graphene sheets. The extent of thermal expansion (and therefore the platelet thickness) is dependent on the type of graphite used and on the intercalation procedure [14,15]. With few exceptions [3], the graphite nanoplatelets obtained via this process typically consist of hundreds of stacked graphene layers (assuming that the thickness of one layer is equal to the interlayer separation in graphite, 0.34 nm) and average between 30 and 100 nm in thickness.

In addition to the thermal expansion route, the delamination of intercalated graphite can sometimes be achieved by inducing a gas-producing chemical reaction within its interlayer galleries (chemical expansion). For example, a low-temperature chemical expansion route to graphite nanoplatelets and nanoscrolls, based on potassium-intercalated graphite, has been reported [16,17]. However, this approach could not be reproduced in our laboratory even


Planer nano-graphenes from camphor by CVD

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Abstract

Next to conducting polymers and carbon nanotubes (curved, closed graphenes), the material that can bring revolution in electronics is planer graphene (PG)/planer few layer graphenes (PFLG). Synthesis of PG and PFLG by simple, economical and re-producible method was a challenge. We synthesized PFLG films from camphor pyrolysis on nickel substrates by simple, cost effective thermal CVD method and studied using HR-TEM, visible Raman spectroscopy, XRD and FE-SEM. This opens the possibility that the controlled and large area synthesis of PGs and PFLGs is possible by CVD based methods, for possible large area electronic applications.

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1. Introduction

Graphene is a single layer of carbon atoms densely packed into a benzene ring structure. Graphene can be made by extracting individual plane(s) of carbon atoms from graphite crystals and are generally used to describe properties of many carbon nanomaterials, including graphite, large fullerenes and nanotubes. Carbon nanotubes can be thought of as graphene sheet(s) rolled up into nanometer sized cylinders. Many of the applications that are thought for carbon nanotubes, can be considered for graphenes. Planer graphene has been presumed not to exist in free-state, being unstable with respect to formation of curved structures such as soot, fullerenes and nanotubes. The first attempt to produce individual graphene sheet by exfoliation dates to the work done by Brodie [1] in 1859. Since then, different attempts were made for the synthesis of planer single layer graphenes and PFLGs [2–5], with little success. To our knowledge, Novoselov et al. reported recently the most successful method for the synthesis of PFLG [6,7]. They have made planer few layer graphene (PFLG) films and are observed to be metallic in nature. Ballistic charge transport, linear current–voltage (I–V) characteristic and huge sustainable currents (>10^8 A/cm^2) makes them an interesting candidate for applications in electronic devices. Graphene transistors show modest on-off resistance ratio (less than ~30 at 300 K) which is sufficient for logic circuits. It is also possible to increase this ratio by using p–n junctions, local gates or point contact geometry. Further, the transistor fabricated using PFLG is the ‘first metallic transistor’ made in which the active material was a metallic graphene, i.e. the channel was made from a metallic material [6,7]. The transistor application of graphene is very exciting, in analogy to carbon nanotubes. Planer graphenes have many unique properties [8–13]. The application of single sheet graphenes in nanocomposites as a filler is demonstrated by Schniepp et al. [14]. Application of nano-graphenes for the storage of molecular hydrogen is also suggested [15,16]. Single graphene sheet has been detected by Horiuchi et al. in a carbon nanofilm [17]. Jang et al. obtained US patent for a complex process for the fabrication of nano-scaled graphene plates [18]. Controlled, easy and low cost synthesis of graphene/PFLG is still a challenge and not much efforts have been made in this direction. The chemical approach developed by Prof. Mullen for synthesis of ‘graphene molecules’ is very interesting and important [19]. However, in the last 10 years, chemical vapor deposition (CVD) based methods are developed to synthesize curved closed graphenes (i.e.}
sheets on Ni-substrates. The role of the Ni substrate is yet to be fully understood.

In past, atomically thin graphite films (single layer graphenes) have been produced by thermal decomposition of the (0001) face of a 6H-SiC wafer [21]. However, such synthesis was carried out in ultra-high vacuum (UHV) conditions. The present experiment reported by us is advantageous in the sense that it does not require vacuum system. In an another effort, diamond nanoparticles were converted to single nano-graphenates at 1600°C [22]. However, such very high synthesis temperature is a serious drawback. In the present experiments, we have been able to get PFLG films at about half the temperature of this (i.e. 800°C). In yet another experiment, formation of very small (about 20–30 Å in diameter) graphitic islands were observed and studied by scanning tunnelling microscopy (STM). Such graphitic islands were formed by hydrocarbon decomposition on Pt (111) surface [23]. It should be noted here that the formed structure was in the form of very small islands and not a continuous film. Although, at present, we have not got single layer graphene; we have been able to get PFLG down to about 20 graphene layers. Efforts are underway to synthesize single layer graphene film by this method. Even though, the present PFLG films are deposited on Ni (conducting) substrates and are not much directly useful for fabricating electronic devices like FET, we believe that this is the first experiment for the successful synthesis of PFLG films by CVD method.

4. Conclusions

In conclusion, for the first time, we experimentally demonstrated that planer few layer nano-graphenes (PFLGs) can be synthesized by simple thermal CVD method. Method is simple, cost effective and has capability to scale-up. Further, such synthesis has been carried out from a natural, environmental friendly, low cost precursor – Camphor. Efforts are now directed towards understanding the growth mechanism of the PFLG film and to synthesize defect free films over a silicon wafer size area.

Acknowledgements

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Appendix A. Supporting information

HR-TEM pictures of PFLG films. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.cplett.2006.06.081.

References

Soluble graphene derived from graphite fluoride

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Abstract

Soluble graphene layers were formed by reacting graphite fluoride with alkyl lithium reagents. IR spectral studies confirmed the covalent attachment of alkyl chains to the graphene layers. Raman scattering and XRD studies of the starting materials and products revealed that the chemical process partially restores the sp² carbon network. The solubility and extinction coefficient were determined by UV–vis–near infrared spectroscopy. Annealing of bulk samples further extends the sp² lattice due to dealkylation as followed by Raman, XRD and mid-infrared spectroscopy. The present study demonstrates a one-step chemical treatment of graphite fluoride that allows the manipulation of a soluble form of graphene.

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1. Introduction

The unique sp² structure of covalent carbon–carbon lattice, graphene, serves as the building block for several forms of carbon materials including graphite, and multi- and single-walled carbon nanotubes. The strong covalent bonds between carbon atoms provide graphene with high mechanical, thermal and chemical stability. It is considered to be one of the strongest known materials per unit weight with a theoretical Young’s modulus of 1060 GPa [1] and also conducts electricity through the π-electron cloud resulting in a wide range of applications with great promise for quantum electronics [2–5].

In the normal 3-D form of graphite the graphene sheets stack to produce an insoluble material that is difficult to process; solution phase manipulation of carbon based materials such as carbon nanotubes [6–11], have already been demonstrated through chemical functionalization reactions. Recently, similar chemical functionalization reactions of graphene layers have been attempted by several research groups in order to solubilize graphene sheets [12,13].

Exfoliation of graphite is necessary for the production of graphene sheets that are desirable for the fabrication of nanocomposites and electronic devices. Separation of the graphene layers is currently accomplished by intercalation of graphite with acid or alkali metals followed by an exfoliation step [14,15], but exfoliated graphite does not disperse in organic solvents and re-aggregates readily. Functionalization of the basal plane is necessary to increase the solubility and prevent the formation of π–π interactions and scrolling [15]. Such functionalization can also result in the loss of the intrinsic electronic properties upon the formation of sp³ carbon centers, although in some cases the electronic properties of the functionalized graphene could be recovered by simple reduction or annealing [13]. Covalent intercalation compounds of graphite such as graphite oxide and graphite fluoride are appropriate starting materials for this approach and recently, the potential of graphite oxide has been demonstrated in several reports [16–18]. In the present study we

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A large variety of nanoparticles hold extraordinary promise for practical applications in catalysis, materials science, medicine, and so on. It is, however, necessary to assemble them into supramolecular aggregates with desired structural properties. In this work we explore the self-assembly of spherical nanoparticles induced by interactions that, due to entropic effects, may become anisotropic. The spherical nanoparticles considered attract each other via square-well potentials, mimicking dispersive interactions. To induce anisotropic effects, short polymer brushes are bound to the nanoparticles but only on the equatorial plane. The brushes are treated as tangent-hard-sphere chains. Nanoparticles with such morphology could be synthesized experimentally. Monte Carlo calculations are conducted to assess the properties of the self-assembled nanostructures as a function of the length of the brushes and of the depth of the particle–particle square-well potential. Our results indicate that for strongly attractive particle–particle interactions it is possible to obtain supramolecular spherulites (employing short brushes) or uniform dispersions (using long brushes). At some intermediate lengths of the polymer brushes, the formation of one-dimensional wires occurs. Our results are useful for designing responsive nanoparticles that reversibly assemble yielding uniform dispersions, nanowires, or spherulites depending on the solution conditions.

1. Introduction

Low-dimensional nanostructures (e.g., carbon-based nanomaterials[1,[2]) exhibit superior properties due to their reduced size and large surface-to-volume ratios, which render them promising candidates for nanoscale electronic, optical, and mechanical devices. Nanowires,[3] for example, can function as nanoscale interconnects while retaining size confinement in the radial direction.[4]

We are interested in the self-assembly of spherical nanoparticles in solution. Our goal is to learn how to direct the reversible nanoparticle aggregation (e.g., to yield dispersions, spherulites, or nanowires) by manipulating solution conditions (e.g., temperature or ionic strength). The results will help to design temperature-responsive materials for sensing and optical devices.[5] To obtain one-dimensional (1D) aggregates it is necessary to induce anisotropic interactions between the nanoparticles,[6–8] which can be attained, for example, by using non-uniform electric fields (dielectrophoresis). Dielectrophoresis can be used to connect carbon nanotubes to electrical pads,[9] and to fabricate Au[10] and CdS[11] wires from colloidal systems. In the case of stabilizer-depleted semiconductor nanoparticles, experimental evidence,[12] corroborated by Monte Carlo simulations,[13] indi-
tained when nanoparticles with 4 side chains of 12 segments each are in solutions characterized by $\epsilon = -1.2kT$. The top panel is for results obtained at $\Phi = 0.0011$, the bottom one for those obtained at $\Phi = 0.0044$. As discussed above, at $\Phi = 0.0011$ we see the formation of short 1D wires. Contrary to the expectations based on the RDFs presented in Figure 7, the snapshot obtained at $\Phi = 0.0044$ (bottom panel) leads us to conclude that as the volume fraction increases the nanoparticles do associate. However, the nanowires obtained at these conditions are composed of 2–3 nanoparticles along the radial direction and are much longer compared to those obtained at lower volume fractions. This association renders the RDF peaks less intense. These results, discussed in conjunction with Figure 7 and Figure 8, suggest that the radial distribution function, used here to assess the association between nanoparticles in solution, is not the optimum mathematical tool to characterize the morphology of anisotropic supramolecular aggregates. More sophisticated methods include the average asymmetry and the degree of prolate or oblateness[39,40] often used to characterize the morphology of polymers in solution.[41,42]

3. Conclusions

We studied the self-association of spherical nanoparticles in solution. The nanoparticles are decorated by four side chains. Our results indicate that for short side chains. We focused our attention on conditions at which the nanoparticles are at infinite dilution within a solvent (i.e., nanoparticle volume fraction less than 0.005). Our results indicate that it is possible to induce the formation of uniform dispersions, spherical aggregates (spherulites), and 1D nanowires by altering the solution conditions. The morphology of the supramolecular aggregates depends on various parameters: the well depth $\epsilon$ and the well width $\lambda$ that describe nanoparticle–nanoparticle interactions, and the length of the four side chains. Our results indicate that, for colloidal nanoparticles characterized by $\lambda = 1.025$ with 4 side chains longer than 12 segments, uniform dispersions are observed for well depths $\epsilon$ shallower than $-10kT$, 1D nanowires for $\epsilon$ between $-10$ and $-14kT$, and spherulites for deeper well depths. Additional calculations, not reported here for brevity, show that, when the other parameters are kept constant, the formation of spherulites is preferred over that of 1D wires for shorter side chains, deeper well depths, and wider well widths. For the parameters considered here, uniform dispersions are obtained when the well depths are less attractive than $-8kT$. Our results may serve as a guide for future experimental verification. In fact, they suggest that the phase diagram for the nanoparticles studied in this work may be very rich, and therefore useful for manufacturing responsive materials for a variety of practical applications. It seems, for example, possible to manufacture nanocomposite materials in which a small amount of fillers (the nanoparticles) can change significantly the macroscopic properties (e.g., thermal or electrical conductivity) of a polymeric matrix via the formation of percolated supramolecular aggregates.

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Buckling instabilities in coupled nano-layers

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Abstract

We study the dynamic buckling of a pair of dissimilar Euler–Bernoulli beams subject to compressive edge loading whose transverse displacements are coupled through non-linear interactions, a problem motivated by the mechanics of graphene layers. The transverse coupling models van der Waals interaction and is derived from a Lennard-Jones 12–6 potential. The beams are assumed to be a fixed distance apart at their ends, although this distance is not necessarily equal to the equilibrium distance as identified from the Lennard-Jones potential. Therefore, the equilibrium configuration is not necessarily straight. Via a Galerkin method, the governing equations are reduced to a system that can be used to calculate equilibrium configurations as well as the stability of these configurations. We show that the buckling instability in this model is significantly affected by the presence of the interaction force as well as the separation of the graphene layers at the boundaries.

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Keywords: Graphene layers; Buckling; van der Walls interactions

1. Introduction

With the advancement of recently developed techniques for isolating and manipulating individual graphene layers, such structures could become an important component in composite materials as well as in the design of nanoscale machines and devices [1–4]. Thus, there is a need to understand the mechanics of graphene layers. We study the dynamic buckling of a pair of dissimilar layers, modeled as Euler–Bernoulli beams whose transverse displacements are coupled non-linearly. To motivate this problem, we note that the non-identical layers can be viewed as describing cross-sections of say, a graphene layer and a polymer layer. In the special case of identical components, the beams can be viewed as describing cross-sections of two graphene layers [5].

Our treatment of such problems is closely related to research on the mechanics of carbon nanotubes. Soon after the discovery of carbon nanotubes in the early 1990’s, researchers began to investigate how nanotubes deform and buckle under various loading conditions. Interesting early papers that consider the buckling of nanotubes include [6–9]. Much of this early work is atomistic and computational. However, current limits on computing power prohibit running such simulations over time and length scales appropriate to many buckling problems for graphene structures.

As an alternative, a number of authors study the deformation of nanotubes and graphene layers using continuum mechanics and, in particular, various beam or shell theories. Recent examples include [10–12]. Relevant for our work is a series of papers by Ru et al. [13–18], in which shell theory is used to explore the axial buckling of multi-walled carbon nanotubes under various conditions. In these papers, Ru and coauthors proposed modeling each wall of a multi-walled carbon nanotube as a thin linearly elastic shell. To explore the importance of van der Waals interactions for axial buckling, the equation for the radial displacement of each wall contains terms that describe the van der Waals forces between that wall and each of its nearest neighbors as a linear function of the relative radial displacement between the walls [19]. Recently, Han and Lu [20] modified Ru’s multi-shell approach to treat torsional buckling and Shen [21] used the multi-shell approach with a more sophisticated shell
5. Conclusions

This work considers the stability of a pair of graphene layers subject to van der Waals forces, which couple the displacements of the structures. The layers are assumed to be supported with pinned-pinned boundary conditions and the distance between the ends is not assumed to be at the equilibrium distance of the van der Waals potential. The layers are represented with Euler–Bernoulli beams and the van der Waals interaction force is approximated with a quadratic expansion about the distance between the layers at the boundaries. The results have been presented for \( x = 0 \) and \( \gamma \neq 0 \), corresponding to identical layers with non-identical axial loading. However, the behavior illustrated above is qualitatively similar for non-identical layers.

At the equilibrium configuration of the system the van der Waals forces do not vanish, so that this state is not identified with the trivial undeformed configuration. Instead, the equilibrium configuration depends on the end separation, the coefficients of the van der Waals approximation, and the tension acting on the layers. For end spacings greater than the equilibrium potential distance the layers attract one another, while for end spacings less than this distance the layers are repulsive. Using a single-mode Galerkin approximation, the stability of the fundamental mode is determined and we are able to characterize the buckling loads in terms of both the non-linearity in the van der Waals approximation as well as the end spacing of the nanotubes. Finally, the analytical results are in qualitative agreement with predictions obtained through MD simulations. Future work will include quantitative comparisons between the two, which will necessitate continuum parameter values that are reflective of the results observed in the MD simulations.

References


Fig. 6. Variational stability, \( m = 1 \) \( (f_1 = 2.00, f_2 = -1.00, \alpha = 0.25, \gamma = -0.25) \); (a) \( f_0 = -0.25 \); (b) \( f_0 = 0.25 \).

Fig. 7. Critical \( T \) \( (x = 0.00, f_1 = 2.00, f_2 = -1.00, n = 1, m = 1) \); (a) \( \gamma = 0.25 \); (b) \( \gamma = 0.125 \).
Improved mechanical and functional properties of elastomer/graphite nanocomposites prepared by latex compounding

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Abstract

The facile latex approach has been adopted to finely incorporate graphite nanosheets into elastomeric polymer matrix to obtain high-performance elastomeric nanocomposites with improved mechanical properties and functional properties. Scanning electron microscopy, transmission electron microscopy and X-ray diffraction experiments show that the nanostructures of the final nanocomposites exhibit a high degree of exfoliation and intercalation of graphite in the nitrile-butadiene rubber (NBR) matrix. Mechanical and dynamic-mechanical tests demonstrate that the NBR/graphite nanocomposites possess greatly increased elastic modulus and tensile strength, and desirably strong interfaces. The unexpected self-crosslinking of elastomer/graphite nanocomposites was discovered and then verified by oscillating disc rheometry and equilibrium swelling experiments. After critically examining various polymer types by X-ray photoelectron spectroscopy, electron spin resonance and Fourier transform infrared spectroscopy, a radical initiation mechanism was proposed to explain the self-crosslinking reaction. These NBR/graphite nanocomposites possess significantly improved wear resistance and gas barrier properties, and superior electrical/thermal conductivity. Such versatile functional properties make NBR nanocomposites a promising new class of advanced materials.

Keywords: Nanocomposites; Elastomers; Graphite; Nanostructure; Latex compounding

1. Introduction

Nanocomposites have been shown to afford remarkable property enhancements compared to conventional microcomposites [1–3]. Polymer nanocomposites with layered silicates [4–9] and carbon nanotubes [10–12] have attracted great interest for the improvement of structural properties and the development of new materials with different functional properties. Graphite is a layered material with a high aspect ratio in its exfoliated state; it is also one of the strongest materials per unit weight and has unique functional properties (e.g. good electrical and thermal conductivities, and good lubricating properties) compared to layered silicates [13]. In addition, graphite is cheap compared to carbon nanotubes. Recently, polymer/graphite nanosheet composites have made a great impact in nanocomposite research [14–27].

To date, some polymer/expanded graphite (EG) nanocomposites with good electrical conductivity have been prepared (e.g. via in situ polymerization) [14–22]. But EG does not significantly enhance the mechanical properties of the polymers due to poor dispersion of the graphite, voids trapped in the composites and weak interfacial adhesion [19–26]. Indeed, the functional performance of the
Role of Graphite Oxide (GO) and Polyaniline (PANI) in NO\textsubscript{2} Reduction on GO-PANI Composites

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Graphite oxide–polyaniline (GO-PANI) composites were obtained by mixing graphite oxide with a polyaniline salt. The extent of surface reduction of the GO and polyaniline (emeraldine) was increased by calcination at 350 °C. The surface characterization was done using Fourier transform infrared (FTIR) spectroscopy, X-ray diffraction (XRD), scanning electron microscopy (SEM), thermal analysis, potentiometric titration, elemental analysis, and adsorption of nitrogen at its boiling point. The materials were exposed to NO\textsubscript{2} to evaluate their activity for NO\textsubscript{2} retention/reduction on the surface. On all samples with the reduced form of polyaniline (emeraldine), a high efficiency for NO\textsubscript{2} reduction was observed. This efficiency was governed by the presence of PANI. Moreover, the presence of N-methylformamide solvent in the composite was determined to be an increasing factor for NO retention on the surface via its hydrogen bonding to the solvent that is interacting with the surface functional groups of graphite oxide. The calcination of GO-PANI at 350 °C reduced the GO surface, resulting in a physical mixture of graphite particles and reduced polyaniline (emeraldine). This happened because of the low thermal stability of compounds formed via the reactions of emeraldine with epoxy and carboxylic groups.

Introduction

Growing concerns about the environment and concern regarding terrorist attacks have resulted in a search for effective adsorbents for the removal of small-molecule toxic gases (nitric oxides (NO\textsubscript{x}), ammonia (NH\textsubscript{3}), hydrogen sulfide (H\textsubscript{2}S), sulfur dioxide (SO\textsubscript{2}), carbon monoxide (CO), etc.). Because, usually, those gases are to be removed under ambient conditions in the presence of moisture, their physical adsorption is limited, because of weak adsorption forces. For these reasons, reactive adsorption, which is a variation of the adsorption process, must be explored.

One group of materials that have potential applications for the removal of small-molecules gases is based on graphite oxide (GO).\textsuperscript{1–7} GO was first obtained in the 1850s, via the oxidation of graphite with such oxidants as KClO\textsubscript{3} /HNO\textsubscript{3}.\textsuperscript{1} It has a layered structure and various nonstoichiometric chemical compositions, which are dependent on the level of oxidation. Extensive oxidation of graphite may lead to total molecular dissolution of graphite with carboxylic acids and CO\textsubscript{2} as the reaction products. As a result of the various levels of oxidation, the graphene layers of GO lose their polyaromatic character, because of the incorporation of various oxygen-containing functional groups.\textsuperscript{2} Although the exact assignment of groups is controversial to some extent,\textsuperscript{2–9} it is generally accepted that the graphene layers have epoxy and –OH groups that are attached to carbons.\textsuperscript{2,3,5} According to Lerf and co-workers, the graphene layers are considered to be flat, with a slightly distorted tetrahedral configuration of carbons attached to –OH groups.\textsuperscript{3} It was also proposed that the carboxylic groups are located at the edges of the graphene layers;\textsuperscript{2} they have a strong acidic character.\textsuperscript{2,4}

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The graphene layers of GO are arranged in an organized way, with the interlayer distance (d\textsubscript{OO}) varying in the range of 6–12 Å. The main reason for those variations is in the level of hydration. Because epoxy and –OH groups exist within the interlayer space, the water molecules are attracted there by hydrogen bonding.\textsuperscript{3} Moreover, both functional groups and water molecules are in different types of motion, depending on the location of the water, which can be either embedded or distributed in interlayer voids.

The layered character of graphite oxide opened a new route for the synthesis of composite materials. This route is possible because of (i) the hydrophobic character of GO, (ii) its easy dispersion in water, and (iii) delamination in alkaline media or alcohols. Moreover, graphite layers can be easily restacked, and their degree of orientation is dependent on the drying method.

A very popular way of GO modification is the introduction of amines or conducting polymers within the interlayer space.\textsuperscript{10–14} The main goal of this type of modification is the production of functional nanometer-scale structures, devices, and particularly cathode materials for lithium secondary batteries. The introduction of large organic ammonium ions resulted in the initial exfoliation of layered structures, which were reassembled after drying.\textsuperscript{10} When primary aliphatic amines were introduced, nucleophilic substitution reaction with surface epoxy groups occurred.\textsuperscript{11} A study of GO intercalated with aniline/o-anisidine co-polymer indicated hydrogen bonds between the \textsuperscript{\texttextsuperscript{-NH, = N–}}, and –OCH\textsubscript{3} groups and oxygen functional groups of GO as the main mechanism of intercalation.\textsuperscript{12} Materials obtained in this way have electrical conductivities that are 3 orders of magnitude greater than that of pure GO. Moreover, the electrochemical response of the new material was significantly stabilized, in comparison with GO. An interesting way of the composite preparation was the formation of co-assembly layers from a colloidal dispersion of GO–amine in alcohol and cetyltrimethyl ammonium-intercalated bentonite.\textsuperscript{14}

The objective of this paper is to evaluate the role of polyaniline (PANI) and GO in GO-PANI composites in the
Conclusions

The results presented in this paper show the predominant effect of emeraldine salts and its calcined (partially reduced) counterparts on the reduction of NO\textsubscript{2} on graphite oxide—polyaniline (GO-PANI) composites. Although the GO has a positive effect on NO\textsubscript{2}/NO\textsubscript{2} retention on the surface of the composite when N-methylformamide is used as a solvent, via its retention between layers (and thus causing an increase in the number of sites for polar interactions), generally, for dried and calcined samples, its surface is inactive for NO\textsubscript{2} reduction. This is caused by the decomposition of oxygen-containing groups that are engaged in the reactions with emeraldine, which results in the conversion of GO to graphite layers, where NO\textsubscript{2}/NO\textsubscript{2} are not able to be intercalated between layers. The high activity of emeraldine is linked to its susceptibility to oxidation with pernigraniline, with NO and water as the reaction products. It is important to mention that, although, in real life, conditions other gases such as H\textsubscript{2}S or CO can be present, PANI that has been doped in GO is not expected respond well to (or to interact with) those contaminants. Although H\textsubscript{2}S can interact with the oxidized quinoid form of the polymer, it should not attack the −N–H bond in the reduced benzoic structure.

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Literature Cited

Single Sheet Functionalized Graphene by Oxidation and Thermal Expansion of Graphite


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A detailed analysis of the thermal expansion mechanism of graphite oxide to produce functionalized graphene sheets is provided. Exfoliation takes place when the decomposition rate of the epoxy and hydroxyl sites of graphite oxide exceeds the diffusion rate of the evolved gases, thus yielding pressures that exceed the van der Waals forces holding the graphene sheets together. A comparison of the Arrhenius dependence of the reaction rate against the calculated diffusion coefficient based on Knudsen diffusion suggests a critical temperature of 550 °C which must be exceeded for exfoliation to occur. As a result of their wrinkled nature, the functionalized and defective graphene sheets do not collapse back to graphite oxide but are highly agglomerated. After dispersion by ultrasonication in appropriate solvents, statistical analysis by atomic force microscopy shows that 80% of the observed flakes are single sheets.

Introduction

Graphene, the basal plane of graphite, is composed of a honeycomb arrangement of carbon atoms and is the basis of carbon nanotubes (CNTs). Graphene single sheets are expected to have tensile modulus and ultimate strength values similar to those of single wall carbon nanotubes (SWCNTs) and are also electrically conducting. Much like SWCNTs, graphene sheets serve as fillers for the enhancement of mechanical and electrical properties in composite materials. Recent studies in which single sheets of graphene have been prepared by the removal of one sheet at a time by a “Scotch tape” method have shown promising electrical properties that could be useful for developing novel electronic devices. Motivated by the promise of graphene as an alternative to SWCNTs, in a recent study we reported a method to produce functionalized single graphene sheets (FGSSs) in bulk quantities through thermal expansion of graphite oxide (GO). In this report, we provide a detailed analysis of the expansion mechanism and a detailed characterization of the resultant material.
Starting with Brodie\(^{14}\) in 1859, there has been an extensive body of literature concerning graphite and graphite modification.\(^{15-21}\) GO formation involves the reaction of graphite with strong oxidizers such as sulfuric acid, nitric acid, potassium chlorate, and potassium permanganate. The introduction of oxygen containing functional groups (such as hydroxyl and epoxide) results in an increase in the d-spacing of GO as well as a change of hybridization of the oxidized carbon atoms from planar sp\(^2\) to tetrahedral sp\(^3\). To prepare GO, we employ the Staudenmaier oxidation method which uses a mixture of sulfuric acid, nitric acid, and potassium chlorate.\(^{22}\)

There have been numerous attempts to exfoliate or expand graphite starting with GO or graphite intercalation compounds. Such materials find application in electromagnetic interference shielding,\(^{23}\) oil spill remediation,\(^{24}\) and sorption of biomedical liquids.\(^{25}\) The terms exfoliated and expanded graphite are often used interchangeably.\(^{15-21}\) Many publications describe the process of making expanded graphite material with accordion- or worm-like structure.\(^{26-28}\) These materials are not completely exfoliated and contain extensive domains of stacked graphite layers as depicted by the native graphite X-ray diffraction (XRD) peaks. The majority of these partially exfoliated graphite materials are made by intercalation of graphite with sulfuric acid in the presence of fuming nitric acid.\(^{29-37}\) The intercalated materials are then heated, and an expansion of the graphite is observed. Although the heating results in a substantial volumetric expansion, the resultant material is described as worm-like or accordion-like, and the typical surface areas (<100 m\(^2\)/g)\(^{38}\) are significantly lower than the theoretical limit of 2630 m\(^2\)/g that should be observed if all the graphene surface were exposed.\(^{38}\) This is due to the domains of retained graphite spacing which results in nonuniform expansion in the c-axis.

We originally described the thermal expansion that successfully yields single graphene sheets.\(^{33}\) In this paper, we expand upon two aspects of the FGS production that contribute to our understanding of the exfoliation process: (i) Although the pressure buildup due to the evolution of gases was shown to be the main mechanism for exfoliation, a fundamental understanding of the kinetics of the decomposition rate and how it compares against the diffusional release of the gases was not provided. (ii) The presence of single graphene sheets was demonstrated, but a statistical analysis of the entire system was lacking. To produce large quantities of FGS consistently, in this paper we focus on these two critical issues. To determine the minimum temperature required for exfoliation, we compare the diffusion rate of evolved gases to the experimentally determined decomposition rate of GO. To quantify the degree of exfoliation, we study the surface area and morphology of the material both in the as-produced dry state and in the solvent-dispersed state and determine the distribution of both the sheet thicknesses and the sheet diameters of the dispersed material.

**Experimental Section**

Reagents. Natural flake graphite (NFG), sized at 400 µm (grade 3061) and 45 µm (grade 230), was kindly provided by Asbury Carbons (P.O. Box 144, 405 Old Main St., Asbury, NJ 08802). Fuming nitric acid (>90%), sulfuric acid (95–98%), potassium chloride (98%), and hydrochloric acid (37%) were obtained from Sigma-Aldrich and used as received.

Expansion and Exfoliation of Graphite. GO was prepared according to the Staudenmaier method.\(^{13,22}\) Graphite (5 g) was reacted with concentrated nitric (45 mL) and sulfuric acid (87.5 mL) with potassium chlorate (55 g). The 500 mL reaction flask was placed in an ice bath, and the potassium chlorate was added slowly over 15 min to avoid sudden increases in temperature. [Caution! Addition of the potassium chlorate results in the formation of chlorine dioxide gas, which is explosive at high concentrations.\(^{39}\)] Purring the head space of the reaction vessel with an inert gas, keeping the reaction vessel cool, and adding the potassium chlorate slowly can help minimize the risk of explosion; however, proper safety equipment including acid resistant gloves, apron, and face shield should be worn while adding the potassium chlorate.] On completion of the reaction, the mixture was added to excess water, washed with a 5% solution of HCl, and then repeatedly washed with water until the pH of the filtrate was neutral. The GO slurry was spray-dried with an inlet air temperature of 300 °C and outlet air temperature of 100 °C, with an air flowrate of 80 kg/h and an atomizer wheel at 25,000 rpm (Niro portable spray dryer, Niro, Inc., 9165 Runsey Rd., Columbia, MD 21045). The dried sample was stored in a vacuum oven at 60 °C until use. The GO suspension used for microscopy studies was prepared directly from the GO slurry prior to spray-drying. The spacing of the 0002 graphite lattice was monitored using XRD (Rigaku Miniflex diffractometer, Cu
The plasma oxidation process of highly oriented pyrolytic graphite (HOPG) has been investigated through a combination of multiscale (micrometric to atomic) imaging by atomic force and scanning tunneling microscopies (AFM/STM) and STM tip-scratching of the HOPG substrate. Complementary information was obtained by Raman spectroscopy and X-ray photoelectron spectroscopy (XPS). Repetitive imaging of the same HOPG location following a series of consecutive plasma treatments allowed an accurate determination of the plasma etch rates along both the $a$ and $c$ crystallographic directions of the graphite lattice. The etch rates were typically in the range of a few nm per min along the $a$ axis, and the equivalent of 1–6 graphene layers per min along the $c$ axis. The results pointed to the existence of two main plasma etching regimes, related to short (<20–30 min) and long (≥30 min) treatment times. This was inferred not only from the measured plasma etch rates but also from the observation of fundamental differences in the atomic-scale surface structure of the plasma-treated HOPG samples, and from the general mechanical behavior of the materials under the action of the AFM tip. In particular, atomic-scale STM imaging suggested a change from a defected, but essentially graphitic, surface in the first regime to an amorphous carbon surface in the second regime. Together with AFM and STM, Raman spectroscopy and XPS provided a consistent picture of the surface structure and chemistry of the plasma-modified HOPG in the two regimes. The implications of these results as well as the possible mechanism that drives the plasma etching process in the two regimes are discussed.

1. Introduction

The surface modification of graphite presents particular interest from a fundamental science perspective as well as from the point of view of practical applications. In the former case, surface-modified graphite has proved to be a suitable model system for both experimental and theoretical studies related to a wide variety of issues. These include carbon combustion, 1–4 the performance of structural materials employed in spacecraft, 5–7 the templated growth of nanostructures, 8 the electrochemistry of carbon materials, 9 the investigation of nanoparticle–substrate interactions, 10–13 and of carbon-supported catalysts, 14,15 or the adsorption of molecules on carbon surfaces. 16–18 In the realm of direct applications, graphite is used, for instance, as the negative electrode in lithium ion batteries, where different types of surface modification of the graphitic anode are currently being investigated with the aim of improving the efficiency of such devices. 19,20 Another area of interest has emerged very recently with the advent of methodologies that allow the preparation and processing of very thin graphite flakes, with thicknesses ranging from several nanometers down to the single graphene level. 21–23 One of the potential applications proposed for this two-dimensional counterpart of graphite is as a filler in composite materials. 23–26 Again in this case, an appropriate functionalization of the graphite flake surface is thought to be necessary in order to achieve composites with optimum performance. 24–26

In many of the examples mentioned above, oxidation was used as the basic method to modify and manipulate the surface of graphite. Thus, graphite oxidation is considered a topic of scientific and technological relevance. 1–7,27 In particular, oxidation by plasmas is rather attractive, since it offers several advantages over other types of oxidation (e.g., electrochemical, thermal, or wet chemical oxidation): it is a nonpolluting process,
it is potentially scalable, and reaction times are shorter. As various recent examples demonstrate, plasma oxidation is a useful approach to enhance and/or fine-tune the surface properties not only of graphite but also of other sp²-based carbon materials of interest, such as carbon nanotubes and activated carbon fibers.

Nonetheless, our current understanding of the plasma oxidation process of carbon materials is still relatively limited compared to the other types of oxidation. Previous studies on graphite have mostly established the main morphological changes on the micrometer and nanometer scales induced by oxygen plasma exposure. In another study, atomic-scale scanning tunneling microscopy (STM) was employed to reveal the very initial stages of microwave plasma oxidation of graphite. It was concluded that the attack starts with the creation of monatomic vacancies on the graphite surface that subsequently develop into multiatomic vacancies. However, several important questions of plasma oxidation were not addressed in this or any other earlier study. For example, the plasma etching rates along both the a and c directions of the graphite lattice, i.e., along directions parallel and perpendicular to the basal plane, respectively, have not yet been compared or determined. Accurate knowledge of these etch rates could be useful, for instance, in the patterning of ultrathin graphite films, which are actively investigated at present as promising candidates for applications in nanoscale electronics.

Another unresolved question is how etching proceeds on the atomic scale in later stages of plasma oxidation. This point is not trivial, one, considering that plasmas are nonequilibrium media, and therefore the observations made in the very early stages of plasma oxidation could easily damage/exfoliate the plasma-oxidized HOPG samples, then in the tapping mode indicated that imaging with the former approach to enhance and/or fine-tune the surface properties not only of graphite but also of other sp²-based carbon materials of interest, such as carbon nanotubes and activated carbon fibers.

In this work, we address these and other issues of the plasma oxidation of graphite by mainly employing atomic force microscopy (AFM) and STM at scales ranging from the micrometer level down to the atomic scale. Moreover, to answer some of the posed questions, we have used an STM tip-scratch method that serves two principal purposes: first, it creates marks on the graphite surface that allow the repetitive location and imaging of the same spot after consecutive plasma treatments of a given sample. Second, this procedure also generates features that in turn were generated with a magnetron. The MW radiation was transferred through a waveguide from the magnetron to the quartz chamber where the plasma was created and the HOPG samples were placed. The treatments were accomplished at a MW power of 100 W and at a working pressure in the chamber of 1.0 mbar. O₂ (99.999% pure) was used as the plasma gas. HOPG samples were exposed to the oxygen plasma for typical periods of 10 or 30 min and then analyzed. Afterward, the same HOPG specimen was submitted to an additional plasma treatment and analyzed again. This process was usually repeated several times, so at the end the sample had been consecutively treated and analyzed up to 5 times.

Following each individual plasma treatment, the HOPG samples were investigated by AFM/STM under ambient conditions (relative humidity ~40%, temperature ~22–24 °C) both at random surface locations and repeatedly at given spots that were predefined on the untreated HOPG surface by an STM tip-scratch method. The STM tip-scratching of pristine HOPG as well as the AFM/STM imaging of the plasma-treated material were carried out in a Nanoscope III Multimode system, from Veeco Instruments (Santa Barbara, CA). To create predefined spots by tip-scratching, a Pt/Ir (80/20) STM tip was approached to the freshly cleaved HOPG surface in discrete (~100 nm) steps while monitoring the tip apex/sample region with an optical microscope coupled to the AFM/STM apparatus. In this way, the tip was allowed to contact and scratch the HOPG surface, and it was normally retracted as soon as damage to the material could be observed with the optical microscope. This process mostly led to the exfoliation of an area of the HOPG surface with a lateral size of several micrometers and a depth in the range from several to a few tens of nm. The tip-scratched (exfoliated) area could then be easily located with the optical microscope for repeated AFM/STM visualization.

For imaging of the plasma-treated samples by AFM, the tapping mode of operation was preferred over the contact mode. Experiments in which the same area was scanned first in the contact mode and then in the tapping mode indicated that imaging with the former could easily damage/exfoliate the plasma-oxidized HOPG samples, particularly those treated at shorter times (e.g., 10 min). Damage to the samples could be minimized to an acceptable level with the tapping mode, although it could not be completely avoided in some cases, as will be shown later. For this reason, the AFM images shown in this work correspond to the tapping mode. The tapping mode images were recorded with rectangular silicon cantilevers, which had spring constants of about 40 N m⁻¹ and resonance frequencies around 250 kHz. The contact mode was used for imaging and for the measurement of force-displacement curves. In this case, triangular silicon nitride cantilevers with nominal spring constants of 0.12 N m⁻¹ were employed. The adhesion forces were calculated as the average of a few hundred individual measurements at random surface locations.

2. Experimental Section

The graphite samples used in the present study were grade ZYH highly oriented pyrolytic graphite (HOPG), obtained from Advanced Ceramics Corp. (Cleveland, OH). Just before any manipulation, the HOPG specimens were cleaved in air to obtain fresh, pristine surfaces. Oxygen plasma treatments of HOPG were carried out in a Technics Plasma 200-G apparatus (Kircheim bei München, Germany). The plasma was activated by 2.45 GHz microwave (MW) radiation, which in turn was generated with a magnetron. The MW radiation was transferred through a waveguide from the magnetron to the quartz chamber where the plasma was created and the HOPG samples were placed. The treatments were accomplished at a MW power of 100 W and at a working pressure in the chamber of 1.0 mbar. O₂ (99.999% pure) was used as the plasma gas. HOPG samples were exposed to the oxygen plasma for typical periods of 10 or 30 min and then analyzed. Afterward, the same HOPG specimen was submitted to an additional plasma treatment and analyzed again. This process was usually repeated several times, so at the end the sample had been consecutively treated and analyzed up to 5 times.

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Graphite Nanoplatelet—Epoxy Composite Thermal Interface Materials

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Natural graphite was intercalated, thermally exfoliated, and dispersed in acetone to prepare graphite nanoplatelets (GNPs, G_n) of controlled aspect ratio. Thermal conductivity measurements indicate that few graphene layer (GG, where n ~ 4, with a thickness of ~2 nm) function as a very efficient filler for epoxy composites. When embedded in an epoxy matrix, the G_4 GNPs provide a thermal conductivity enhancement of more than 3000% (loading of ~25 vol %), and a thermal conductivity \( \kappa = 6.44 \text{ W/mK} \), which surpasses the performance of conventional fillers that require a loading of ~70 vol % to achieve these values. We attribute the outstanding thermal properties of this material to a favorable combination of the high aspect ratio, two-dimensional geometry, stiffness, and low thermal interface resistance of the GNPs.

1. Introduction

The progress in miniaturizing device components has aggravated the problems associated with heat dissipation in the electronics industry, and this has produced a need for improved thermal interface materials (TIMs) in modern chip packaging. Current TIMs are based on polymers, greases, or adhesives filled with thermally conductive particles such as silver, alumina, or silica which require 50–70 vol % of filler to achieve thermal conductivity values of 1–5 W/mK.1 A number of nanomaterials have been explored as candidates for improving the thermal conductivity of polymer composites, and carbon nanotubes (CNTs) have emerged as an efficient filler because of their superior thermal conductivity (~3,000 W/mK along the tube axis) and high aspect ratio.2–10 However, the cost of CNTs is inhibiting industrial applications. In the present manuscript, we show that graphite nanoplatelets (GNPs), prepared from exfoliated natural graphite, provide excellent thermal enhancement when embedded in an epoxy matrix. We demonstrate an industrially viable procedure for the bulk processing of natural graphite that yields few-layer GNPs of similar aspect ratio to that of single-wall carbon nanotubes (SWNTs) but with twice the increase in the thermal conductivity when embedded in an epoxy composite.10 The application of these materials promises an economical route to a new class of efficient thermal management materials.1

Graphite, an allotrope of carbon, consists of superimposed lamellae of two-dimension (2D) carbon—carbon covalent networks, referred to as graphene, which stack along the c-axis as a result of strong van der Waals forces, and the separation of these layers is a considerable challenge.11 The focus on the extraordinary electronic properties of graphene11–21 has prompted a search for efficient routes to bulk materials, and chemical processing has already been employed to study the solution-phase properties of single-layer graphene11 and to prepare individual oxygenated graphene sheets, which were utilized for the fabrication of electrically conductive composites with a very low percolation threshold.19

Exfoliation of graphite is an alternative route to the separation of graphene layers;22–27 however, the lack of functional groups in the graphene sheets promotes the reaggregation of the material into micron-sized clusters. Significant efforts have already been applied to embed nanometer-sized graphite particles in polymer matrices using a variety of techniques,25,28,29 and these composites, which contain nanometer-sized particles (5–10 nm), have been reported to show enhanced thermal and electrical conductivities.25,28–30 In the present manuscript, we report a systematic investigation of the exfoliation and dispersion of natural graphite to prepare graphite nanoplatelets of desired aspect ratio, and we provide the first study of the effect of the aspect ratio of the 2D-graphitic filler material on the thermal conductivity. The controlled exfoliation and dispersion process described in this study plays a key role in manipulating the thickness of the GNPs, and we demonstrate the power of this technology in achieving a remarkable thermal conductivity enhancement in epoxy composites.

2. Experimental Section

2.1. Graphite Nanoplatelets Preparation. Natural graphite flakes with an average size of 500 \( \mu \text{m} \) were obtained from Asbury Graphite Mills Inc., NJ, and Vulcan XC72R carbon black was obtained from Cabot Corporation. In a typical experiment, 1 g of natural graphite flakes was treated overnight at room temperature with 12 mL of a mixture of concentrated sulfuric and nitric acids (3:1). The intercalated graphite was filtered, washed with distilled water, and air-dried for 2 days. The intercalated graphite was exfoliated by thermal shock on rapid exposure to temperatures of 200, 400, and 800 °C in nitrogen for 2 min.24

The exfoliated graphite was dispersed in acetone by high-shear mixing for 30 min followed by bath sonication for 24 h.
presumably due to the more rigid 2D structure of the nanoplatelets, which minimizes the bending and preserves the high aspect ratio. We suggest that the dimensionality and rigidity of the 2D GNPs are responsible for the superior thermal conductivity enhancement compared to that of the one-dimensional SWNTs (Figure 4a). We posit that the few-layer GNPs represent the optimum nanographite for advanced composites, because it has been shown that individually exfoliated graphene sheets roll up into nanoscrolls and thereby reduce the dimensionality of the material.13

Further enhancement in thermal conductivity of GNPs-based composites may be possible if the interfacial bonding between the GNPs and the polymer matrix is improved. This might be achieved by introducing chemical functionalizations on the surface of the nanoplatelets as proposed for the SWNT-based composites.35 The chemistry of SWNTs is now well developed,36 and similar functionalization schemes can be applied to graphite nanoplatelets. In the few-layer GNPs, the inside layers function as highly conductive channels for thermal transport, while the chemically functionalized outside layers can facilitate the phonon transfer from the GNPs to the polymer matrix, an additional advantage in comparison with the individual graphene sheet. Theoretical modeling predicts that the thermal conductivity of composites increases with the filler aspect ratio,38 whereas we observe a trend toward saturation of the thermal conductivity enhancement at an aspect ratio between 30 and 200 (Figure 3), and thus GNP-800 with an aspect ratio of ~200 is close to the optimum filler for TIM applications. We anticipate that it will be possible to optimize the GNPs for utilization in other advanced composites and to develop economical solutions for applications that require high strength or electrically conductive materials.

4. Conclusions

In summary, we report an efficient process for converting natural graphite into few-layer GNPs utilizing a simple procedure of acid intercalation, thermal exfoliation, physical separation, and dispersion. When embedded in a polymer matrix, the GNP material (G_n, where n is small) demonstrates a remarkable enhancement of the thermal conductivity at low-volume loadings and significantly outperforms carbon nanotube-based fillers. This material offers an economical solution for the development of a new generation thermal interface materials for electronic packaging and advanced composites.

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References and Notes

Electronic and Transport Properties of Boron-Doped Graphene Nanoribbons

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We report a spin polarized density functional theory study of the electronic and transport properties of graphene nanoribbons doped with boron atoms. We considered hydrogen terminated graphene (nano)ribbons with width up to 3.2 nm. The substitutional boron atoms at the nanoribbon edges (sites of lower energy) suppress the metallic bands near the Fermi level, giving rise to a semiconducting system. These substitutional boron atoms act as scattering centers for the electronic transport along the nanoribbons. We find that the electronic scattering process is spin-anisotropic; namely, the spin-down (up) transmittance channels are weakly (strongly) reduced by the presence of boron atoms. Such anisotropic character can be controlled by the width of the nanoribbon; thus, the spin-up and spin-down transmittance can be tuned along the boron-doped nanoribbons.

Several experimental groups have successfully produced isolated, and stable at room temperature, 2D crystals of graphene [1–5]. Edges on graphene sheets can be viewed isolated, and stable at room temperature, 2D crystals of graphene sheets revealed bright stripes along its edges, suggesting a high density of edge states near the Fermi level [6]. The electronic properties of nanoribbons are ruled by the atomic geometry along the edges: namely, zigzag or armchair. Hydrogen terminated zigzag nanoribbons are metallic or semiconducting depending on the edge spin orientation [7].

Graphene has attracted enormous attention due to its potential for future application in nanoelectronics. Its functionality as nanosensors or spin filter devices can be tailored controlling the electronic properties of graphene nanoribbons (GNR) by different proposals. One of those is the use of impurities that inject electrons or holes in the system changing its electronic properties, with the advantage that they can also play the role of adsorption sites, making it possible to tailor a nanosensor. The case of boron impurities [8–10] we study is interesting because they affect the nanoribbon metallic behavior and also break the polarized transport degeneracy, suggesting the use as a spin filter device.

In this Letter we present a detailed study of the electronic and transport properties of boron-doped GNR. The electronic structures and the equilibrium geometries were obtained through ab initio total energy density functional theory [11] calculations [12]. Similarly, the transport properties were investigated through ab initio methods, where the electronic structure of contacts, and the atomic relaxations of the whole system are taken into account [18–20], including the electronic spin dependence. Transport calculations were performed using the TRANSSAMPA code, which is based upon nonequilibrium Green’s functions, see details in Ref. [19]. In order to include the electrodes, the transport properties of (3,0), (5,0), (7,0), (9,0), and (11,0) nanoribbons were described with 90, 126, 162, 198, and 234 atoms per supercell, respectively.

A structural model of (3,0) GNR is shown in Fig. 1. Following the classification proposed in Ref. [21], for the (3,0) nanoribbon we have three rows of hexagonal rings of carbon atoms, giving rise to a honeycomb stripe with zigzag boundaries on both sides. The $sp^3$ hybridization in a graphene sheet leads to three $\sigma$ bonds and the $\pi$ and $\pi^*$ bands near the Fermi point. The electronic band structure is such that graphene sheets are metallic for wave vectors parallel to the $z$ direction ($IK$ direction), being ruled by those $\pi$ and $\pi^*$ orbitals [22]. Similar hybridizations, viz.: $sp^2 \rightarrow \sigma$ and $2p \rightarrow \pi/\pi^*$, are expected when the edge dangling bonds of GNR are saturated with hydrogen atoms. Consequently, the electronic band structure of hydrogenated nanoribbons resembles the band structure of graphene sheet [23].

The unpaired $\pi/\pi^*$ edge electrons give rise to a magnetic ordering on the system. The two most stable spin density configurations are Ferro-$F$, and Ferro-$A$. In Ferro-$F$ the spins at both edges are coupled ferromagnetically [Fig. 1(a)], whereas in Ferro-$A$, the spins are in opposite directions between the edges [Fig. 1(b)]. For both systems, the flat energy bands near the Fermi level are ruled by the edge $\pi$ and $\pi^*$ orbitals of nanoribbons, Fig. 2. Although the Ferro-$A$ exhibits the lowest total

FIG. 1. Structural model of (3,0) GNR. (a) Ferro-$F$, and (b) Ferro-$A$ spin configurations.
In conclusion, based upon ab initio theoretical calculations we examined the energetic stability, the electronic and the transport properties of boron-doped GNR. The substitutional boron atoms occupy the edge sites of nanoribbons. The presence of boron atoms at nanoribbons edges leads to a transition from a metallic to semiconductor nanoribbon and also breaks the symmetry of spin-up and spin-down transmittance channel. The substitutional boron atoms play a role of a scattering center primarily for spin-down transmittance channel. The substitutional boron atoms occupy the edge sites of nanoribbons and also breaks the symmetry of spin-up and spin-down transmittance channel. Those results suggest that, through a suitable doping process, it is possible to tailor the electronic current along GNR. For instance, giving rise to a dominant spin–polarized electronic current along the GNR, opening a possibility of building spin filter devices based upon GNR.

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[12] We have used a GGA approximation [13]; norm-conserving [14] fully separable [15] pseudopotential; periodic-boundary conditions; a supercell approach with a single layer of graphene with 70 and 98 atoms for (3,0) and (5,0) nanoribbons, respectively, separated by 15 Å from their images; all calculations were performed using the SIESTA code [16], and we employ a DZP basis function [17] and a mesh cutoff of 170 Ry for the grid integration; the Brillouin zone was sampled using ten special k points. We have verified the convergence of our results with respect to the number and choice of the special k points. All atoms of the nanoribbon were fully relaxed within a force convergence criterion of 20 meV/Å.
[24] Considering a B bulk at the α-phase and a graphene sheet as sources to calculate the boron and carbon chemical potentials, respectively, the formation energy of a boron impurity at a GNRs edge is 0.23 eV.
Electrostatic deposition of graphene

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Abstract
Loose graphene sheets, one to a few atomic layers thick, are often observed on freshly cleaved HOPG surfaces. A straightforward technique using electrostatic attraction is demonstrated to transfer these graphene sheets to a selected substrate. Sheets from one to 22 layers thick have been transferred by this method. One sheet after initial deposition is measured by atomic force microscopy to be only an atomic layer thick (≈0.35 nm). A few weeks later, this height is seen to increase to ≈0.8 nm. Raman spectroscopy of a single layer sheet shows the emergence of an intense D band which dramatically decreases as the number of layers in the sheet increase. The intense D band in monolayer graphene is attributed to the graphene conforming to the roughness of the substrate. The disruption of the C–C bonds within the single graphene layer could also contribute to this intense D band as evidenced by the emergence of a new band at 1620 cm⁻¹.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Recently, graphene (graphite sheets that are one-atom thick layers of sp² bonded carbon) has attracted a tremendous amount of attention [1]. The structure and the physical properties of graphene have been theoretically studied over several decades, as this 2D structure provided the building block for the formation of 3D graphite, 1D nanotubes, and 0D bucky balls [2]. Graphene is predicted to have remarkable properties such as large thermal conductivity comparable to the in-plane value of graphite, superior mechanical properties and excellent electronic transport properties [3]. The charge carriers in graphene are predicted to have zero effective mass and the transport properties are expected to be governed by the relativistic Dirac equation rather than the Schrödinger equation [4, 5]. Mechanical cleavage has been widely used to separate a few layers of graphene from highly oriented pyrolytic graphite (HOPG). Ribbons and terraces with step edges of graphene have been obtained by peeling off the surface layers of HOPG using scotch tape [6]. Alternative methods such as exfoliation [7] and epitaxial growth on single-crystal silicon carbide substrates [8] have produced multi-layer graphene sheets, but not single layer sheets. Recently, Stankovich et al developed a technique to make large amounts of single layer graphene sheets embedded in a polymer matrix [9]. All of these methods are tedious and labour-intensive. Furthermore, none of these methods address how to place the graphene sheets in a desired location, which is of great importance in constructing electrical experiments and assembling heterogeneous electronic systems. In this paper we discuss an electrostatic approach to deposit sheets of graphene on a given substrate.

2. Background

This deposition method was motivated by the observation with scanning tunnelling microscopy that there are numerous small sheets of graphene, of from one to several layers, on the surface of freshly cleaved HOPG. The sheets are loosely bound to the bulk graphite and can be removed from the surface rather easily by applying an electrostatic field (from an STM tip).

Graphene pieces on two different HOPG surfaces are shown in figure 1. The STM was operated in constant current mode and the bias voltage applied to the tip was 0.11 V. Shown in figure 1(a) are triangular graphene sheets, once and twice folded. The area of the STM picture is ≈200 nm × 200 nm. In figure 1(b) a graphene ribbon, ≈50 nm wide and more than...
Figure 5. Raman spectra of graphene sheets with varying numbers of sheets (a). The details of the shifting of the G band (b).

sheet is the presence of a new peak at $\sim 1620 \text{ cm}^{-1}$. This band has been observed previously in vapour grown carbon fibres [10], and more recently in nitrogen-doped SWNTs [11]. This $1620 \text{ cm}^{-1}$ feature has been identified with a maximum in the phonon density of states associated with midzone phonons. The presence of defects (like broken C–C bonds) within the single graphene layer could also contribute to the intense D band. As $n$ increases, the number of defects due to missing C atoms or broken C–C bonds becomes a smaller fraction of the total number of carbon bonds present in the sample, which leads to an increasingly intense G band.

5. Conclusions

Since graphene shows unusual and interesting properties, the positioning of graphene on a suitable substrate at a selected location is important both for studying the fundamental properties of graphene and developing graphene-based devices. Electrostatic deposition of graphene provides a convenient alternative to the popular method of mechanical cleaving of HOPG, with the added benefit of selective deposition. This technique enables the number of layers deposited to be controlled. As demonstrated by the Raman experiments, the ability to place various numbers of layers on a surface, provides a useful tool for examining the physics of surfaces and interfaces. Varying the thickness of graphene from 22 to 1 layers upshifts the G band and increases the intensity of the D band. Also the $G'$ band can be seen to be split into two bands for graphene of multiple layers, while for monolayer graphene there is only a single $G'$ peak [12, 13].

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Role of the Epoxy Group in the Heterogeneous CO$_2$ Evolution in Carbon Oxidation Reactions

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A density functional theory study was carried out to evaluate different possibilities of heterogeneous CO$_2$ desorption in combustion/gasification reactions. First, we investigated the heterogeneous CO$_2$ evolution induced as a secondary reaction caused by the CO readsoption on an oxidized surface, which produces a carbonate-like surface complex. This functional group was found to decompose as CO$_2$ with an activation energy of 60 kcal/mol. Another possibility for heterogeneous CO$_2$ formation during char combustion or gasification is through the molecular O$_2$ chemisorption on a carbon active site of an oxidized graphene layer. The peroxy complex thus formed undergoes rearrangement into a dioxiranyl complex, C(2O). This complex can evolve as CO$_2$ with an activation energy of 48 kcal/mol. The CO$_2$ desorption is facilitated by the presence of an epoxy complex near the edge of the graphene layer. The epoxy complex undergoes transformation into a cyclic ether complex during the dioxiranyl decomposition. Transition states and energetic profiles of these decomposition reactions were determined. Variations of selected C–C, O–O, and C–O bonds were analyzed through the change in the bond orders calculated by natural bond orbital analysis. Overall, carbon oxidation reactions in the presence of epoxy functionalities are very important in the formation of heterogeneous CO$_2$ and of cyclic ether complexes.

1. Introduction

Combustion is the most widely used coal utilization process. Recently, however, gasification processes have received more attention due to their advantages over classic combustion technology, such as higher efficiency, higher variety of products (electricity, steam, syngas, and hydrogen), as well as better control of contaminant gases (SO$_x$, NO$_x$, and CO$_2$). Gasification is carried out with an oxidant gas such as O$_2$, H$_2$O, or CO$_2$. In both combustion and gasification, two general steps can be distinguished in the processes: first, an oxygen atom is transferred from the oxidant molecule to the carbonaceous solid causing the formation of surface complexes, C(O); then these complexes can decompose giving rise to the formation of CO and/or CO$_2$ with the consequent consumption of the carbonaceous material.$^{1,2}$ It is important to mention that in coal combustion and gasification processes, CO$_2$ production is not only caused by surface complexes decomposition. In such processes, several secondary reactions can take place giving rise to CO$_2$ formation by homogeneous reactions in gaseous phase or other types of heterogeneous reactions such as CO readsoption on previously formed complexes.$^3$

In the case of the oxidation with molecular oxygen, the first step is the dissociative chemisorption on the carbonaceous surface forming C(O) complexes that act as stable intermediates during the total process.$^4$ The general description of the process is shown by simple representations such as O$_2$ + C$_x$y → 2C(O), where C$_x$y represents an active site.$^{1,5}$ However, this description does not offer sufficient information at a molecular level of the elemental reactions taking place. In order to get an insight into the reactions that produce CO or CO$_2$, it is important to have the characterization of the complexes formed in the initial steps and their transformation during the process. To determine the nature of these complexes several experimental studies have been carried out employing techniques such as IR, NMR, X-ray photoelectron spectroscopy (XPS), scanning electron microscopy, transmission electron microscopy, temperature programmed desorption (TPD), and transient kinetics (TK),$^{3,6–18}$ among others.

One of the most common techniques in complexes characterization is TPD since it allows suggesting the nature of functional groups through their decomposition products. For example, the carboxilate groups generally decompose as CO$_2$, while ether, phenol, or carbonyl functionalities decompose as CO.$^{18}$ However, interpretation of the TPD profiles presents additional difficulties due to several secondary reactions.$^{3,7}$ B. Marchon et al.$^{20}$ used TPD to calculate desorption activation energies of CO and CO$_2$ and compared the determined values with those reported for bond energies of lactones, carboxylic acids, and semiquinones on reference compounds. A good correlation was obtained suggesting the presence of these functionalities on the carbonaceous materials during combustion or gasification processes. TPD may be used simultaneously with other techniques to obtain more detailed information of the functional groups giving rise to the CO or CO$_2$ thus formed. Kelemen and Freund$^{12}$ employed TPD and XPS to evaluate the decrease of the XPS signal of different complexes correlating them with the desorbed gases. This procedure allowed the researchers to observe that during CO$_2$ desorption the 288.8 eV C(1s) XPS signal diminishes. This signal corresponds to carbon atoms bonded to oxygen atoms by means of three bonds, suggesting the presence of carboxylate or carbonate groups that decompose as CO$_2$. These authors also found that the signal corresponding to C–O single bond (285.8 eV C(1s)), is the only signal remaining in XPS at high temperatures while CO evolution continues, allowing them to suggest the existence of an ether-
functionality, the activation energy required for the CO₂ evolution would be very high and other reactions, such as O–O cleavage, may become more favorable.

The above-described step sequence can also be analyzed following the variation of the Wiberg bond index through the reaction coordinate. The changes are shown in Figure 8 where the NBO data of the main bonds involved in the decomposition reaction coordinate. The changes are shown in Figure 8 where other bonds are almost completely cleaved after the transition state (C₆ – O₃, C₂ – C₃). This type of figure illustrates very clearly the bond transformations that take place in a chemical reaction.

In the research carried out by Haydar et al.¹⁴ to evaluate desorption steps of CO₂, they found two CO₂ desorptions with activation energies at around 48 and 61 kcal/mol which were presented without assignation to any particular complex. In the present work, we report two complexes which have CO₂ desorption activation energies similar to those found experimentally that may explain such desorptions.

Cyclic ether complexes have been reported in numerous studies by means of spectroscopic techniques.⁶¹¹²¹³ However, to the best of our knowledge their formation mechanisms have not yet been described. In this study, we show a possible route for formation of such a complex that at the same time allows us to explain CO and CO₂ desorption in carbon gasification at high temperatures.

Finally, it is crucial to point out that the role of the epoxy group is different when it is located in the center of a graphene layer. In this case, the C=C bonds at the basal plane are broken and new ether bonds (C–O–C) are formed releasing the strain involved in the three-member ring structure as observed by Li et al.²² The ether functionalities thus formed cause a deformation of the graphene layer that can explain the wrinkled and rough structure of an exfoliated graphite oxide observed by AFM.²² Furthermore these complexes are also involved in the CO₂ desorption giving rise to vacancies in the interior of a graphene sheet.²²

4. Conclusions

A step by step analysis of the oxidation of a graphene layer was carried out. This study suggests two possible routes for heterogeneous CO₂ desorption in oxidation with molecular oxygen of carbon materials. The first one takes place by means of a secondary reaction giving rise to the formation of a carbonate group at the edge of the graphene layer which decomposes as CO₂ leaving an isolated active site. The second reaction occurs through molecular chemisorption of O₂ on a graphene layer which has undergone a certain degree of oxidation, and therefore, there are other oxygenated complexes such as semiquinone and epoxy groups. Following these conditions, a mechanism for heterogeneous evolution of CO₂ and simultaneous formation of cyclic ether is proposed. This mechanism is useful to explain different experimental observations concerning CO₂ and CO desorption at high temperatures. At the same time, it explains the role of epoxy groups as oxygen reservoir in combustion and gasification reactions. Finally, the analysis of the bond order by NBO facilitates the understanding of the formation, transformation and cleavage of bonds involved in a given reaction, particularly when it is presented graphically as has been done in this research.

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References and Notes

Nanostructuring the graphite basal plane by focused ion beam patterning and oxygen etching

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Abstract
Ga⁺ focused ion beam (FIB) patterning was used to structure highly oriented pyrolytic graphite surfaces with square, periodic arrays of amorphous carbon defects (mesh sizes: 300 nm–2 μm). Controlled oxygen etching of these arrays leads to matrices of uniform, orientationally aligned, nm-sized, hexagonal holes. The properties of the resulting hole assembly (hole depths and lateral hole dimensions) have been investigated by means of atomic force microscopy, scanning electron microscopy and FIB sectioning. The hole dimensions and uniformity both depend on the FIB parameters and etching conditions. Etching temperatures from 500 to 700 °C were applied. Initial etch rates of up to 10⁶ C s⁻¹ per individual hole were observed when using oxygen pressures of 200 mbar. For an etch temperature of 590 °C the rate of etching of individual holes was found to depend measurably on the inter-hole separation. This confirms that the associated reaction kinetics is mediated by the finite diffusion length of reactive oxygen species along the graphite basal plane. Prolonged etching results in hole–hole contact and generation of mesa arrays of controllable size and shape.

(Some figures in this article are in colour only in the electronic version)

1. Introduction
There are a number of ways to fabricate randomly distributed, flat-bottomed, nm-sized holes/pits in the basal plane of highly oriented pyrolytic graphite (HOPG). It is well known that one or a few monolayer (ML) deep nanoholes can be generated in graphite samples simply by heating in gaseous oxygen. The associated oxidation processes (generating CO and to a lesser extent CO2) commence at ‘natural’ point defects and vacancies already present [1, 2]. Pits form because the horizontal etch rate along the basal plane is much faster than the vertical etch rate at the oxidation/etch temperatures used. Furthermore, there are slight differences among in-basal-plane etch rates along different crystallographic directions. Under the right experimental conditions this can lead to pits with hexagonal shapes, although more typically circular or irregular hole geometries are observed. Transmission electron microscopy (TEM), scanning electron microscopy (SEM), atomic force microscopy (AFM) and scanning tunnelling microscopy (STM) have been extensively used to investigate the corresponding pit growth kinetics [3, 4]. However, there remain many open questions with regard to the underlying oxidation mechanism [5].

Increasing the lateral density of randomly distributed etchable defects beyond that ‘naturally’ occurring in HOPG
References

Electronic Transport Properties of Individual Chemically Reduced Graphene Oxide Sheets

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ABSTRACT

Individual graphene oxide sheets subjected to chemical reduction were electrically characterized as a function of temperature and external electric fields. The fully reduced monolayers exhibited conductivities ranging between 0.05 and 2 S/cm and field effect mobilities of 2−200 cm²/Vs at room temperature. Temperature-dependent electrical measurements and Raman spectroscopic investigations suggest that charge transport occurs via variable range hopping between intact graphene islands with sizes on the order of several nanometers. Furthermore, the comparative study of multilayered sheets revealed that the conductivity of the undermost layer is reduced by a factor of more than 2 as a consequence of the interaction with the Si/SiO₂ substrate.

The peculiar electronic properties of graphene sheets have attracted strong interest both in the experimental and theoretical scientific community during the past few years.1−3 Most prominently, carriers in an ideal graphene sheet behave as massless Dirac fermions.4 In the meanwhile, these unique properties could be verified by a range of experiments,4,5 and the first prototype devices such as field-effect transistors (FETs)6 and ultra-sensitive sensors7 have been successfully demonstrated. Micromechanical cleavage is currently the most effective and reliable method to produce high-quality graphene sheets.8 However, the low yield of this approach (a few graphene monolayers per mm² of substrate area), combined with the lack of methods that enable positioning of the sheets, severely limits the implementation of highly integrated graphene-based circuits.

High-yield production methods for graphene sheets are also desirable for other applications like mechanically reinforced composites9,10 or transparent, electrically conductive films.11 A promising methodology is the chemical reduction of graphite oxide,9,12,13 wherein the basal plane carbon atoms are decorated with epoxide and hydroxyl groups and the edge atoms bear carbonyl and carboxyl groups.13−15 The presence of these functional groups reduces the interplane forces and imparts hydrophilic character, thereby promoting complete exfoliation of single graphene oxide (GO) layers in aqueous media. While no high-resolution microscopic data are available for GO, theoretical studies suggest that the oxygen-containing groups are clustered into rows and islands, resulting in graphitic regions intermixed with islands of oxygen-functionalized atoms.16 Deoxygenation of GO has been accomplished by the strong chemical reducing agent hydrazine, whereupon a significant fraction of the contained oxygen is removed.12,17 However, the electrical properties of reduced GO have remained largely unexplored, despite their relevance for evaluating the viability of this chemical route to graphene, as well as for the development of graphene-based conductive composites. In this report, we describe electronic transport studies of individual single- and multiple-layer GO sheets subjected to two different types of chemical reduction. The comparison with unmodified graphene demonstrates that such procedures enable only partial recovery of the electrical conductivity due to the oxidatively introduced point defects that remain within the 2D carbon framework.

Graphite oxide was prepared via the Hummers method,18 starting from graphite flakes of 20 μm size (Sigma Aldrich). The resulting oxidized material was dispersed in water with the aid of soft ultrasonication and then deposited onto different substrates, including mica, Si/SiO₂, and highly oriented pyrolytic graphite (HOPG). While deposition onto mica and HOPG did not require any functionalization, the
responsible for the observed resistance decrease in the bilayer case. Additional interference may arise from defects in the SiO₂ layer that survive the annealing procedure.

In summary, we have presented the first electronic transport studies of chemically reduced graphene oxide sheets, which potentially provide access to large-scale production of graphene monolayers. In the fully reduced sheets, the room-temperature conductivity and carrier mobility were found to lag behind those of graphene by 3 and 2 orders of magnitude, respectively, predominantly as a consequence of lattice vacancies that cannot be healed during the reduction process. The structure of the sheets is best described by intact, nanometer-sized graphitic domains separated by defect clusters, which results in hopping conduction as the dominant charge-transport mechanism. Future high-resolution microscopic investigations could reveal further details about the defect nature and identify the location of oxygenated functionalities which presumably remain in a low concentration. Such knowledge would be of relevance for attempts to tune the electronic structure of graphene via chemical edge functionalization.²⁸²⁹

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Computational Studies of the Structure, Behavior upon Heating, and Mechanical Properties of Graphite Oxide

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A Monte Carlo based scheme for the formation of graphite oxide (GO) was developed and implemented. A Rosenbluth factor was used to select intermediate structures in an attempt to form stable, low-energy, and realistic GO. The scheme resulted in the production of GO that has an interplanar spacing of 5.8 Å, in good agreement with the experimental value (5.97 Å). Epoxide and hydroxyl functional groups dominate the basal planes, a finding that is consistent with experiment. Individual sheets are wrinkled with an average root-mean-square deviation of 0.33 ± 0.04 Å. Hydrogen bonding between hydroxyl groups and between hydroxyl and epoxide groups has significant impact on the stability of many structures. Molecular dynamics simulations, guided by forces from electronic structure calculations, were performed to examine the behavior of GO when heated to room (300 K) and thermal exfoliation (1323 K) temperatures. Hydrogen-transfer reactions that catalyze the migration of epoxide groups were observed at both temperatures. At 1323 K, the evolution of CO was also observed, and the mechanisms for this process have been elucidated. This process provides a plausible explanation of the source of the 30% carbon mass loss that occurs during the experimental thermal exfoliation of GO. The mechanical properties of GO were examined and compared to those of graphene. Although significantly weaker in tensile deformation than graphene (fracture stress = 116 GPa), GO (fracture stress = 63 GPa) potentially has great strength provided it does not contain large holes. An epoxide line defect, recently reported as playing an important role in the failure of oxidized graphene, was also examined. The observed very large fracture stress (97 GPa) suggests that this structure does not play a major role in the fracture process.

I. Introduction

Interest in graphite oxide (GO) has increased recently because of its potential as a starting material for the large-scale production of exfoliated two-dimensional graphite nanosized platelets, which have shown considerable promise as a nanocomposite filler material. Graphite oxide was first synthesized in 1859 by treating graphite (an inexpensive starting material) with KMnO4 and H2SO4 and has since been synthesized using a variety of oxidative methods. In most cases, the planar structure of graphite is preserved, with the interplanar spacing increasing from 3.4 Å (the interplanar spacing in graphite) to a value of at least 6.0 Å. This spacing increases with oxidant/acid exposure time and subsequent exposure to moisture. Although the oxidation process can be continued until CO and CO2 are eventually produced from the parent graphite, well-structured GOs have been reported with oxygen levels in approximate stoichiometries as high as C10O6H5.

Graphite oxide readily forms stable colloidal dispersions of thin sheets in water. It can be hydrophobized using n-alkylammonium cations and swollen in organic solvents, resulting in lamellar GO structures whose size can be controlled by adjusting solvent composition. Treating GO with organic isocyanates creates a material that readily forms stable dispersions in polar aprotic solvents and that spontaneously exfoliates into individual graphite oxide sheets with a thickness of ~1 nm. These sheets mix readily with many organic polymers, making possible the synthesis of graphene–polymer composites. Chemical reduction of composites containing GO can result in materials that are electrically conductive due to regraphitization. Several GO-containing composites have been shown to possess properties that make them suitable for use as cathodic materials in lithium rechargeable batteries (see, e.g., refs 2 and 16).

Rapid heating also can be used to exfoliate GO into single sheets. A heating rate greater than 2000 °C/min for 30 s in a 1323 K oven has been used to create well-dispersed sheets that exhibit a lateral extent of a few hundred nanometers. A mass loss of 30% accompanies this exfoliation and suggests that the sheets may contain a significant number of defects and that these defects could be of a significant size.

The graphene sheets in GOs are decorated with a variety of functional groups. There is extensive NMR, infrared spectroscopic, and electron diffraction evidence for the presence of COOH, OH, and C=O groups at the edges of the sheets while the basal planes are covered mostly epoxy (1,2-ether) and OH functionalities. A large number and variety of models of this material have been proposed. Although there also has been some preliminary theoretical work performed in an attempt to understand this material, much remains to be learned about its structural details.

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neighboring functional groups. At 1323 K, CO evolution from pristine sheets and those containing pre-existing defects was observed. This CO evolution provides a plausible explanation for the 30% carbon mass loss that occurs during the thermal exfoliation of GO.

The mechanical properties of GO were examined and were compared to those of graphene. Oxidation was found to decrease the strength by 46%. A nanohole formed by removing a single cluster of carbon atoms in a 128 atom sheet was found to reduce the strength by more than 63%, so the effects of nanodefects may be significantly more deleterious on strength than oxidation. The reduction in fracture stress due to epoxide line defects was found to be less than 17% as compared to a pristine sheet, which indicates that these have little effect on the strength.

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Figure 9. (a) Graphene sheet containing an epoxide line defect, (b) the pristine GO sheet, and (c) the GO sheet that was initially missing a hexagonal unit of carbon atoms that were strained to failure. Their stress versus strain behavior is shown in Figure 8.

This is important because structures that are relatively low in energy at low oxidation levels do not necessarily lead to relatively low-energy structures at higher oxidation levels. The process was repeated in stages in which additional functional groups were added to the sheets, until an experimentally observed stoichiometry was synthesized. Sheets containing various defects were also examined.

The resulting GO sheets were significantly wrinkled. The calculated interplanar spacing of 5.8 Å for the pristine sheets is in good agreement with observed experimental values (5.97 Å). A complex set of hydroxyl—hydroxyl and hydroxyl—epoxide hydrogen-bonding interactions takes place between the functional groups. Occasionally, small holes in the basal planes appear as C—C bonds break. The resulting potentially dangling bond carbons form carbonyl and alcohol groups. Other molecules, such as peroxide and water molecules, are also observed.

Molecular dynamics simulations were performed to examine the behavior of GO upon heating to room (300 K) and thermal-exfoliation (1323 K) temperatures. These MD simulations used forces obtained from SCC-DFTB electronic structure calculations. At both temperatures, reactions in which hydrogen atoms are transferred were observed. Also, epoxide groups were observed to migrate on the basal plane in processes often stabilized by hydrogen bonding or catalyzed by hydrogen-transfer reactions between the mobile epoxide oxygen and neighboring functional groups.