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Systematic Post-assembly Modification of Graphene Oxide Paper with Primary Alkylamines

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Graphene oxide paper can be systematically modified with alkylamines in both solution- and vapor-phase, with the latter process being significantly slower. After removal of physisorbed amine, the increases in gallery spacing, physical thickness, and mass of amine-modified papers can be directly correlated to the length of the intercalated alkyl chain. While the tensile strength of the modified papers slightly decreases with increasing amine lengths, their "effective graphene oxide moduli" were essentially unchanged, suggesting that graphene oxide is the sole contributor to the stiffness of amine-modified papers.

Introduction

The bottom-up assembly of nanosized building blocks offers a versatile route to the fabrication of a variety of functional macrostructures that are inaccessible via conventional top-down synthetic techniques, especially in the case of hybrid and nanocomposite materials. In particular, flexible paper- or foil-like assemblies have been formed from exfoliated lamellar clays,[1] carbon nanotubes,[2] stacks of expanded graphite platelets,[3] platelets of graphene oxide,[4] and platelets of reduced graphene oxide,[5] to afford materials that exhibit excellent mechanical, electronic, and, in some cases, optical properties. We have recently reported the preparation of graphene oxide paper,[4] also by pressure-assisted assembly of aqueous suspensions of graphene oxide platelets,[6] which are produced by the exfoliation of graphite oxide (GO). Flow-directed filtration of water-dispersed graphene oxide induces self-assembly of individual platelets into a stacked, layered structure with near-parallel platelet arrangement, yielding a self-supporting, mechanically strong paper upon drying. Since the assembled graphene oxide platelets retain all their oxygen-containing functional groups (epoxy, hydroxyl, carbonyl, and carboxyl) on their basal planes and edges,[7−10] this paper should be modifiable via covalent reaction, allowing for the preparation of functionalized graphene oxide papers. Alternatively, assembled graphene oxide paper could also be reduced to graphene paper by several methods.[11]

In spite of the rich chemistry available through its oxygen-containing funtionalities,[7] systematic studies of structure-property relationships in modified graphene oxide papers have been largely overlooked, with previous work focusing only on improving upon their already excellent mechanical properties.[6,12] This is surprising because chemical derivatization of graphene oxide can also significantly alter the nanoscale properties of these platelets in addition to improving the macroscopic mechanical strength of the paper. For example, attachment of hydrophobic alkyl chains to the graphene oxide platelets can change their nature from hydrophilic to hydrophobic and greatly affect the interaction between the platelets. In this way, chemical modification of graphene oxide can lead to new functionalized materials with different mechanical, electrical, and barrier properties than the parent, unmodified material.

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In preparing functionalized graphene oxide paper, one can envision two possible routes. In the first approach, graphene oxide platelets are chemically modified prior to assembly into paper.[5,6] A key requirement of this approach is that the chemically modified platelets be dispersible in a solvent prior to assembly via filtration. The second approach entails chemical modification after the fabrication of graphene oxide paper, which requires the chemical reagent to be capable of diffusing into the regions of the paper macrostructure between the stacked and overlapped platelets and reacting with the functional groups on the platelet surface. Such modification has been performed with alkali earth metal ions, which cross-link adjacent graphene oxide platelets within the paper structure, giving rise to a mechanically strengthened paper.[12]

We have previously observed that water and certain polar solvents can penetrate the structure of graphene oxide paper.[13] The intercalation of solvent causes the paper to swell and eventually lose all of its mechanical integrity. This swelling should be attributed to expansion of the interlayer galleries by the solvent, as interlamellar sorption of organics has been shown to increase interlayer spacing in dry, unexfoliated GO powder.[14] Although both the mechanical integrity and morphology of our paper can be restored after drying, the wet paper can disintegrate in the solvent if not handled carefully. Incorporating reactive reagents into such solvents could likely allow for their co-intercalation into the interlayer regions of the paper and subsequent reaction with oxygen-containing functional groups. This would enable the aforementioned second approach to be an ideal strategy for systematic modification of graphene oxide paper, producing functionalized derivatives while maintaining the overall layered morphology.

Herein, we report a systematic study on the intercalation of primary alkylamines in both solution and vapor phase into graphene oxide paper. The modified materials exhibit a direct relation between the intercalated alkyl chain length and gallery spacing, physical thickness, sample mass, and tensile strength. Surprisingly, in spite of the large interlayer spacings produced by intercalation of amines, the Young's moduli of the modified papers remained constant.

Experimental Section

Materials. All chemicals were used as received from commercial sources unless otherwise noted. SP-1 graphite powder was purchased from Bay Carbon (Bay City, MI). Butyl-, octyl-, and dodecylamine were obtained from Aldrich (Milwaukee, WI).

Preparation of Graphene Oxide Paper. GO was prepared via a modified Hummers method,[15,16] where graphite powder was vigorously stirred with H_2SO_4 and $KMnO_4$ at 30 °C for 3 h to yield GO. The oxidized product was treated with H_2O_2 to remove residual permanganate ions before copious washing with a dilute acid solution (1 M HCl). After filtration, the GO product was dried in air before further use.

Aqueous dispersions of graphene oxide platelets were prepared by ultrasonic agitation of an aqueous GO suspension (3 mg/mL, Fisher Scientific FS60 ultrasonic cleaning bath). Graphene oxide paper was fabricated by filtering this dispersion through a polycarbonate filter (Isopore Membrane Filters, 142 mm diameter, 200 nm pore size, Millipore) using a Fisherbrand Pressure Holder (Fisher Scientific, 1.5 L reservoir, air pressure of 30 psi). Following its preparation by filtration, graphene oxide paper was air-dried and the polycarbonate filter was removed by dissolution in a minimal amount of methylene chloride.

Solution-Phase Amine Intercalation. Graphene oxide paper was cut into 1 cm × 4 cm strips, which were soaked at room temperature for 24 h in methanol solutions of butyl-, octyl-, or dodecylamine (0.1 M, 5 mL). Samples were supported by a wire mesh during amine functionalization to discourage sample degradation. After intercalation, the samples were soaked in pure methanol (~10 mL × 3) for 2 min each (to briefly rinse the sample surface), before being air-dried and analyzed. Alternatively, the samples can be soaked in methanol (~10 mL × 3) for 24 h (to extensively wash the sample and remove physisorbed amine) with solvent exchanged every 8 h.

Vapor-Phase Amine Intercalation. Strips of graphene oxide paper samples were exposed to dodecylamine vapor by placing them in a closed scintillation vial next to a drop of dodecylamine for 2 weeks at room temperature.

Physical Characterization. Spacing between adjacent platelets in the paper structure was determined by X-ray diffraction (XRD) using a Rigaku 2000 diffractometer with nickel-filtered Cu Kα radiation (λ = 1.5418 Å). Paper thickness was monitored via scanning electron microscopy (SEM) using a Nova NanoSEM 600 (FEI Co.) microscope. Mechanical testing was performed using a 2980 dynamic mechanical analyzer (DMA, TA Instruments). Elemental analysis (carbon and nitrogen content) was performed by Atlantic Microlab (Norcross, GA).

Results and Discussion

The formation of covalent or hydrogen bonds between GO and primary alkylamines at room temperature are well-known reactions that are ideal for assessing the post-assembly modification of graphene oxide paper.[17−20] As amines readily intercalate between the graphene oxide platelets comprising GO, these layers are pushed apart to generate derivatives with well-defined *d*-spacings, an easily characterized morphological feature. Two schemes have been proposed for this interaction in the literature. Bourlinos et al. suggested that amines covalently reacted with graphene oxide layers in GO via amination of epoxide groups on the basal plane.[17] In contrast, Matsuo et al.

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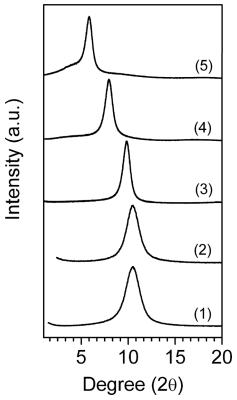

Figure 1. (1 and 2) XRD patterns of graphene oxide paper before (1) and after (2) soaking in methanol for 24 h. (3−5) Solution-phase modified graphene oxide papers treated with butylamine (3), octylamine (4), and dodecylamine (5) after soaking in methanol for 24 h.

observed that the amines primarily interact through hydrogen bonding with hydroxyl groups, also found mainly on the basal plane.[18] In both schemes, the amine would be in highest concentration within the regions between the platelets, resulting in observed increases in *d*-spacing after amine reaction and intercalation.

Pristine graphene oxide paper displays an XRD pattern with a solitary peak at ~0.8 nm,[4] the exact location of which is dependent on both the method of preparation and on humidity level.[21] After treatment with butyl-, octyl-, or dodecylamine in solution and a brief methanol rinse (6 min), the modified graphene oxide paper samples exhibit *d*-spacings shifted to 1.00, 1.30, and 2.01 nm, respectively. Soaking the treated samples in methanol for 24 h decreases the measured *d*-spacings to 0.98, 1.10, and 1.51 nm, respectively (Figure 1), which compare well with the data reported by Bourlinos et al. for butyl-, octyl-, and dodecylamine.[17] That the decrease in gallery spacing is achieved by increasing the methanol soaking period suggests that initial intercalation of amines occurs by both chemisorption and physisorption, where the physisorbed molecules can be removed from the galleries by the solvent. No further shifting occurs with additional soaking in methanol past 24 h, indicating that the majority of physisorbed amines are removed after this period, with primarily chemisorbed amines remaining in the gallery. Interestingly, dodecylamine-treated paper possesses a larger-than-expected gallery spacing (~40% larger than that of octylamine-treated paper). This can be attributed to the increased entanglement of long-chain amines within the gallery (see below), which results in a considerable amount of dodecylamine physisorbed within the gallery even after extended soaking.

A direct correlation exists between the number of carbon atoms in the alkyl chain of the chemisorbed amine and the observed *d*-spacing of the paper (Figure 2). This trend is present for papers both briefly rinsed in methanol (5 min) and soaked for 24 h and is expected to give rise to a concurrent increase in macroscopic paper thickness.

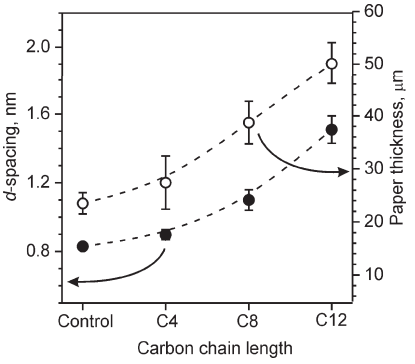

Figure 2. Plot of gallery spacing (*d*-spacing) (●) and average thickness of graphene oxide paper samples (○) versus the intercalated amine's alkyl chain length. All data were collected after samples were soaked in methanol for 24 h. The dashed lines are included as visual guides.

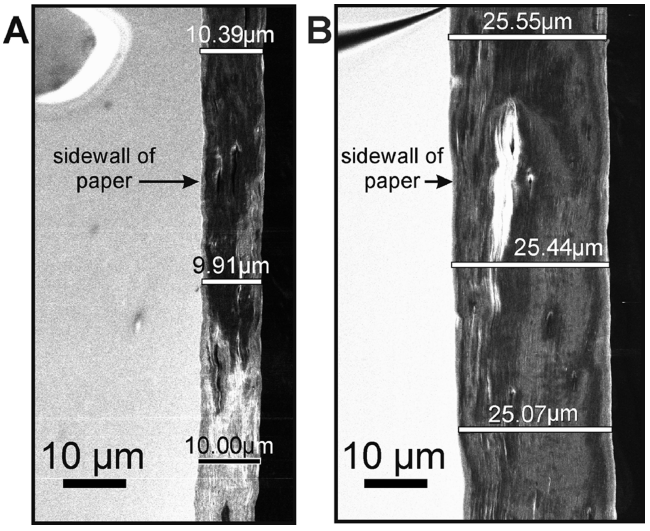

Figure 3. SEM images of the fracture surface of a ~10 μm-thick graphene oxide paper sample before (A) and after (B) solution-phase treatment with dodecylamine.

To verify this hypothesis, SEM images were collected before and after amine treatment (Figure 3). A graphene oxide paper sample, initially 10.10 ± 0.25 μm thick, increases in thickness to 25.35 ± 0.25 μm after treatment with dodecylamine. The extent of this increase (251%) compares well to that expected from the increase in *d*-spacing from 0.83 to 2.01 nm (242%) after dodecylamine modification. The SEM images also confirm retention of the desired original morphology−near-parallel arrangement of graphene oxide platelets−of unmodified graphene oxide paper.

Increased masses in amine-treated samples further supports that amine molecules are indeed able to completely infiltrate the graphene oxide paper gallery and remain after extensive methanol washing. After amine treatment, mass increases of 6.6, 13.9, and 38.6% were observed for graphene oxide paper samples treated with butyl-, octyl-, and dodecylamine, respectively. Elemental analyses of these same samples revealed $C_{graphene}/N$ ratios of 17.8, 15.9, and 13.9. While this trend may suggest that amines with longer alkyl chains intercalate into the paper structure more readily, this is counterintuitive. The decreased $C_{graphene}/N$ ratios are more likely due to the

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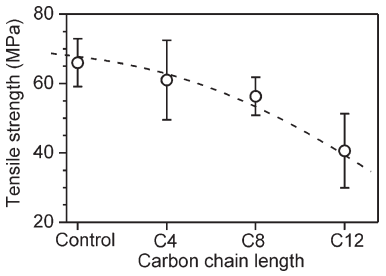

Figure 4. Tensile strength calculated using the physical cross section of the sample along the fracture edge. Values are plotted against carbon number (alkyl chain length) of the intercalated amine. The dashed line is included only as a visual guide.

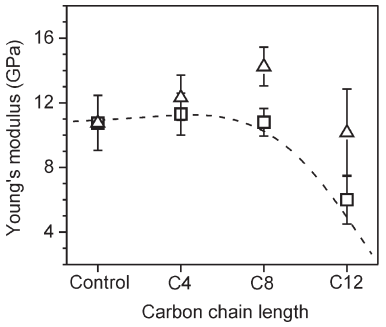

Figure 5. Modulus values (E) determined by linear fitting of the stress−strain dependence in the "elastic" regime. Values denoted with □ are calculated using the physical cross section and are Young's modulus values. Values denoted with △ are calculated using the thickness of an unmodified control sample and represent "effective graphene oxide modulus". The dashed line is included only as a visual guide.

tangling of alkyl chains, an effect that would become increasingly predominant with longer alkyls and would inhibit complete removal of physisorbed amines from the gallery during methanol washing. Such entanglement may artificially increase the gallery spacing, as observed in dodecylamine-treated graphene oxide paper, even after 24 h of soaking in methanol (Figure 2).

The tensile strengths of amine-modified graphene oxide papers can be directly related to the lengths of the intercalated alkylamines. Unmodified graphene oxide paper, prepared in this study by pressure-assisted filtration, exhibits an average tensile strength of 66 MPa (Figure 4) and Young's modulus value of 11 GPa (Figure 5), both lower than those for vacuum-assisted, filter-assembled papers.[4] As chain length of the intercalated amine increases, the strength of the modified paper decreases from the 66 MPa parent value, with the weakening likely due to decreased interactions between adjacent graphene oxide platelets. Such interactions comprise either direct hydrogen bonding between platelets, hydrogen bonding through intercalated H_2O molecules, or interlocking of adjacent platelets, a typical feature of graphene oxide paper,[4] and would decrease as the d-spacing increases. Surprisingly, intercalation with dodecylamine only decreases the tensile strength by ~40%, a relatively small amount considering the significant increase in d-spacing (~180%).

The Young's moduli of amine-treated papers exhibit a distinctly different trend, with values largely unaffected by the presence of butyl- and octylamine (Figure 5). However, intercalation of dodecylamine induces a drastic

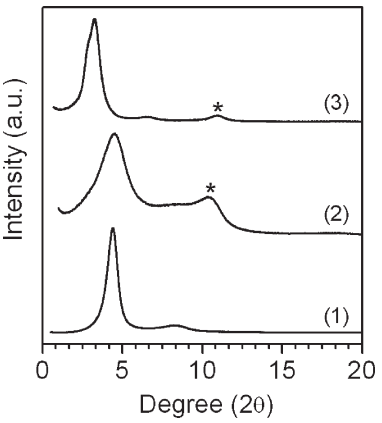

Figure 6. XRD patterns of dodecylamine-modified graphene oxide paper produced by (1) solution-phase intercalation (24 h) and vapor-phase intercalation after (2) 12 h and (3) 2 weeks. None of the samples were exposed to a methanol wash. Peaks marked with (*) denote the residual character of unmodified graphene oxide paper.

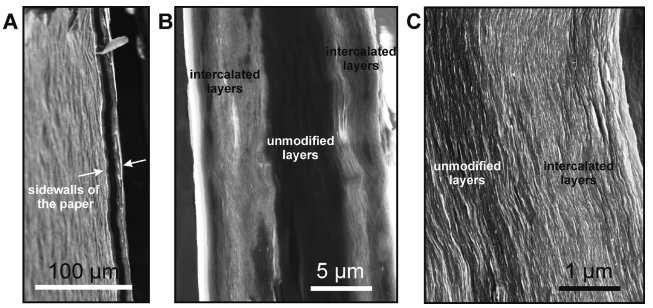

Figure 7. SEM images taken at different magnifications to illustrate incomplete intercalation of dodecylamine vapor into graphene oxide paper after 12 h of exposure. The contrast between the unmodified and intercalated layers can be attributed to the accumulated charging in the amine-modified layers.

drop of nearly ~50%. This sudden decrease may be attributed to incomplete removal of residual physisorbed dodecylamine from the interlayer spacing during washing. As mentioned above, this can lead to artificially low $C_{graphene}/N$ ratios and thus artificially large sample thickness values for Young's modulus calculation. Indeed, when Young's moduli are normalized to the thickness of an unmodified graphene oxide paper (15.7 μm), instead of the physical cross section, this drastic drop is no longer observed (Figure 5). The "unchanged" nature of this "effective graphene oxide modulus" suggests that graphene oxide is the primary contributor to the stiffness of amine-modified papers, while the amine only serves to expand the structure. In this context, the interlamellar amine molecules can facilitate load sharing between the stacked and overlapped graphene oxide platelets, suggesting that graphene oxide paper can be used as a storage medium (for charges and chemicals) without having its mechanical stiffness compromised by inter-gallery loading.

As mentioned in the introduction, post-assembly modification of graphene oxide paper in solution phase entails a vulnerable period during which the sample is fragile and easily destroyed when handled. Vapor-phase intercalation would provide an alternate means to circumvent this

processing issue. To this end, we attempted to prepare a dodecylamine-modified graphene oxide paper by exposing the pristine paper to dodecylamine vapor. Exposure for 12 h produces modified papers with surprising XRD patterns that contain a strong peak for residual unmodified graphene oxide (marked by a * in Figure 6, pattern 2). SEM images of such samples (Figure 7) reveal incomplete intercalation, clearly seen as contrast differences in the images. We note that the *d*-spacing of the vapor-treated paper is much larger than that for unrinsed, solution-phase-treated, dodecylamine-modified paper (Figure 6, pattern 1). As the former paper was not washed with methanol, such large spacing suggests significant physisorption of amine within its gallery structure.

Continued exposure of graphene oxide paper to dodecylamine vapor for 2 weeks increases the mass of the modified paper to 130% of the parent material. The XRD pattern of this modified paper shows a *d*-spacing of 2.77 nm, though a weak residual peak for unmodified graphene oxide paper remains (marked by a * in Figure 6, pattern 3). The presence of these graphene oxide peaks even after two weeks of exposure suggests that vapor-phase intercalation of alkylamines is an exceedingly slow process that is hindered by the low volatility of the intercalating species. Furthermore, amine treatment in the vapor-phase does not take advantage of the considerable penetration power of solvent, which itself can cause swelling of the paper structure (see the Introduction) and would likely facilitate migration of the dissolved amine to the reactive graphene oxide surface. In this sense, the absence of solvent during vapor-phase intercalation would be predicted to lower the rate of reaction between the amine and the graphene oxide surface.

Conclusions

In conclusion, we have demonstrated that post-assembly modification of graphene oxide papers with primary alkylamines can be successfully achieved via solution- or vapor-phase intercalation, with the latter process being significantly slower. After removal of physisorbed amines from the gallery, modified papers systematically exhibit direct correlations between the length of the intercalated alkyl chain and intergallery spacing, physical thickness of the paper, sample mass, and tensile strength. The tensile strength of the amine-modified papers suffers slightly as the length of the amine increases, with longer chains increasing the gallery spacing and making the paper weaker. However, the stiffness of the modified papers remains relatively unaffected, with little change in "effective graphene oxide modulus". These results suggest that graphene oxide paper can be used as an effective storage medium (for charges and chemicals) retaining its good mechanical stiffness in spite of intergallery loading.

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