

Graphene Oxide Sheets Chemically Cross-Linked by Polyallylamine

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We report that a homogeneous aqueous colloidal suspension of chemically cross-linked graphene oxide sheets was generated by addition of polyallylamine to an aqueous suspension of graphene oxide sheets followed by sonication of the mixture. This is the first example for producing a homogeneous colloidal suspension of cross-linked graphene sheets. As a demonstration of the utility of such a colloidal suspension, “paper” material samples made by simple filtration from such a suspension of cross-linked graphene oxide sheets showed excellent mechanical stiffness and strength.

Graphene or chemically modified graphene (CMG) sheets have been investigated due to their physical, electrical, and mechanical properties.^{1–5} On the basis of the outstanding mechanical properties of graphene sheets,² they are a promising building unit to fabricate new, mechanically useful materials, such as composites,^{6,7} “paper”-like materials,^{8–10} mechanical actuators,¹¹ nano/microrobots, and electromechanical systems (NEMS/MEMS).¹¹ Introduction of cross-linking at the molecular level has been used to enhance the mechanical and physical properties of polymers or paper materials. For example, the mechanical properties of ultrahigh-molecular-weight polyethylene (UHMWPE), which has been used in medical applications such as bearing components in various arthroplasties,^{12,13} have been enhanced by cross-linking.¹² Chemical cross-linking of graphene oxide sheets in premade graphene oxide paper samples using a small amount of divalent ions produced mechanically enhanced papers.⁹ Such cross-linking, however, usually causes a lack of solubility/dispersibility in solvents, which, in turn, can lower the processability of such materials. Indeed, addition of divalent ions to an aqueous colloidal suspension of graphene oxide sheets produced agglomerates due to cross-linking between the sheets.⁹ Also, uniform dispersion of the cross-linker in the materials is probably relevant to achieving close to optimal load sharing for mechanical applications. The generation of homogeneous systems containing the resulting cross-linked materials in solvents is a highly promising approach for achieving better processability as well as a more uniform dispersion of the cross-linkers. The successful production of a homogeneous aqueous colloidal suspension of graphene oxide sheets chemically cross-linked by polyallylamine (PAA), as well as good mechanical properties of its paper material produced by simple filtration, is reported here.

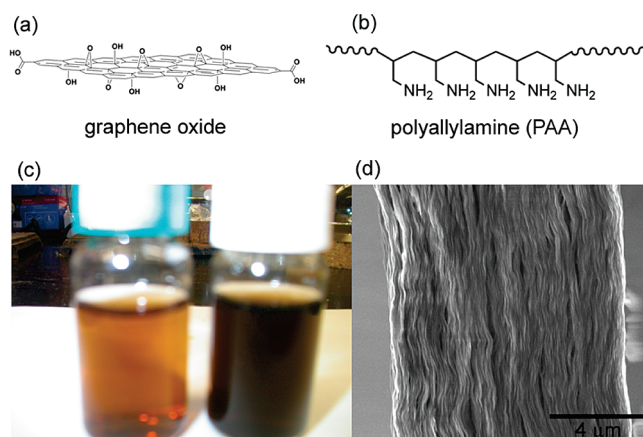


Figure 1. (a) Schematic model of a sheet of graphene oxide showing oxygen-containing functionalities. (b) Chemical structure of polyallylamine (PAA). (c) A photo of an aqueous colloidal suspension of (left) graphene oxide and (right) PAA-modified graphene oxide at the same concentration of GO (3 mg, 15 mL of water). (d) A SEM image of the cross section of a fractured PAA-modified graphene oxide paper sample.

Graphite oxide (GO) contains a wide range of oxygen functional groups both on the basal planes and at the edges of graphene oxide sheets;^{14–17} thus, hydrophilic graphene oxide is readily exfoliated in water.¹⁸ The reactive oxygen functional groups (Figure 1a) of graphene oxide, including hydroxyl, epoxy, and carboxylic acid groups, can be chemically modified to produce homogeneous colloidal suspensions in various solvents and to influence the properties of graphene-based materials. For example, reaction of GO with isocyanate groups produced isocyanate-modified graphene oxide sheets that are well-dispersed in polar aprotic solvents.¹⁹ Chemical reduction of the isocyanate-modified graphene oxide in the presence of a polymer produced an electrically conductive nanocomposite of polystyrene/graphene.⁶ Reaction (amide coupling) between carboxylic acid groups of graphene oxides and octadecylamine after SOCl₂ activation of the COOH groups produced graphene

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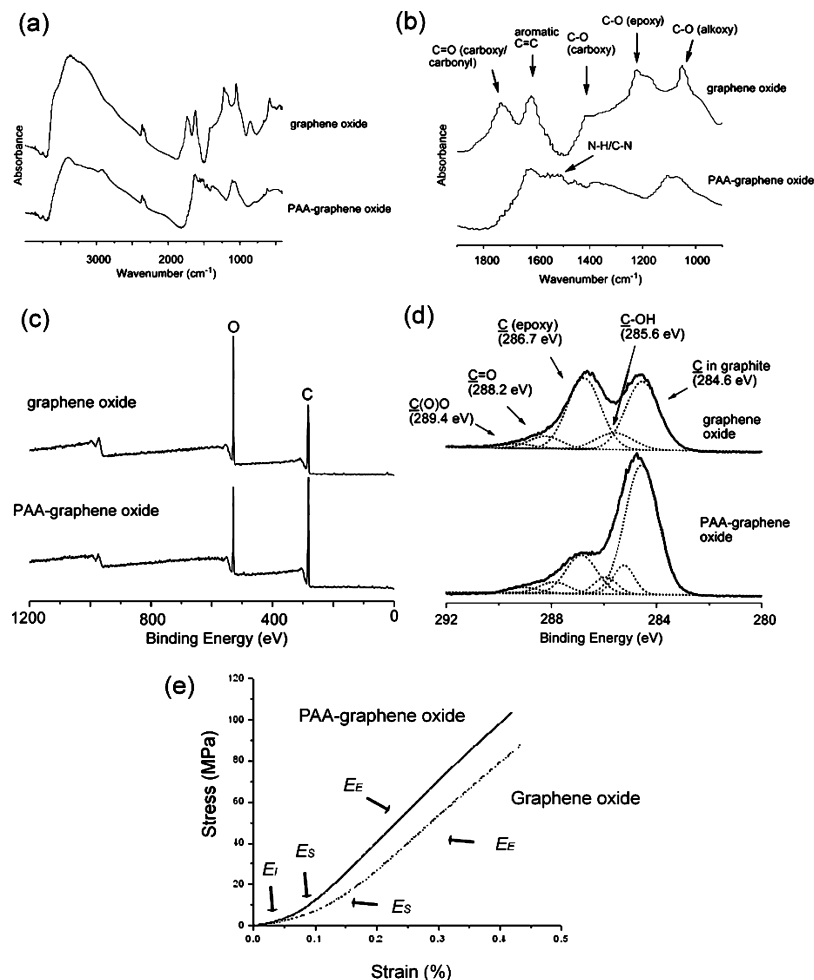


Figure 2. FT-IR spectrum of graphene oxide and PAA-modified graphene oxide paper samples (a) at the full region and (b) at the magnified region. Chemical structure of polyallylamine (PAA). XPS spectra of graphene oxide and PAA-modified graphene oxide paper samples. (c) Wide region and (d) deconvoluted spectra in the C1s region. (e) Stress-strain curves of unmodified and PAA-modified graphene oxide paper samples from tensile testing.

oxide modified with aliphatic groups that could be dispersed in organic solvents.²⁰ Recently, several routes to colloidal dispersions of reduced graphene oxide sheets (which are electrically conductive as individual sheets or in aggregates) have been reported using electrostatic stabilization between reduced graphene oxides,²¹ chemical reduction of sulfonated graphene oxides,²² reduction of K⁺ ion-modified graphene oxides,²³ and noncovalent functionalization of reduced graphene oxide with a pyrene derivative.²⁴ On the basis of such prior work, we have exploited the chemical reactivity of various oxygen functional groups present on the graphene oxide sheets to produce cross-linked “graphene” sheets as a building block for new materials.

PAA (Figure 1b) is a long alkyl chain with a number of reactive amine groups that can easily react with oxygen functional groups of the graphene oxide sheets. Adding PAA ($M_w = 17000$, 20 wt % aqueous solution, GO/PAA = 3.75 in weight; see the Supporting Information (SI)) to the aqueous suspension of the graphene oxide, which was produced by simple sonication of GO (30 mg, 3 mg/mL) in a bath sonicator, immediately led to the generation of floating particles (the particles did not settle but were visible to the eye), presumably due to agglomeration of sheets by the cross-linking between graphene oxide sheets and the polymer chains. A homogeneous colloidal suspension of the PAA-modified graphene oxide sheets was obtained by extensive (6 h, continuously) sonication of the diluted mixture (1 mg of GO/5 mL of water) and was darker

than that of unmodified graphene oxide sheets at the same concentration (Figure 1c). As one example for the use of such colloidal suspensions of cross-linked graphene oxide sheets, paper materials containing PAA-modified graphene oxide were made by filtering followed by harsh washing of the resulting samples to remove residual PAA (see the SI). GO (30 mg) was used to make paper samples for chemical analyses and measurements of mechanical properties in this work. A scanning electron microscope (SEM) image of a cross section of the paper sample (prepared by fracturing a sample in liquid N₂ using tweezers) showed a well-layered structure of the PAA-modified graphene oxide sheets (Figure 1d), similar to other graphene-based paper materials generated from colloidal suspensions.^{8–10}

The Fourier-transformed infrared (FT-IR) spectra of unmodified graphene oxide paper showed C=O, aromatic C=C, carboxy C-O, epoxy C-O, and alkoxy C-O stretches (Figure 2a,b).²⁵ After the modification of graphene oxide sheets with PAA, the relative intensity of the epoxy C-O stretch of the PAA-modified graphene oxide paper at 1222 cm⁻¹ significantly decreased. As graphene oxide has been found to contain reactive epoxy groups, its exposure to amine groups would lead to a ring-opening reaction of the reactive three-membered epoxide ring, creating new C-N bonds. The ring-opening reaction of the epoxy group from attack by nucleophiles such as amine groups has been well established.²⁶ The increase of the peak intensity at 1500 cm⁻¹, which corresponds to a stretching of

TABLE 1: Mechanical Properties of Unmodified and PAA-Modified Graphene Oxide Paper Samples^a

	E_I (GPa)	E_S (GPa)	E_E (GPa)	σ (MPa)	ε (%)
graphene oxide	5.8 ± 1.4	16.6 ± 2.2	25.6 ± 1.1	81.9 ± 5.3	0.40 ± 0.03
PAA-modified graphene oxide	11.3 ± 3.2	25.5 ± 3.9	33.3 ± 2.7	91.9 ± 22.4	0.32 ± 0.08

^a E_I = modulus in the initial region where loading is started. E_S = modulus at $\sigma = 10$ MPa in the straightening region. E_E = maximum modulus in the linear region.

the new C–N bonds and possibly residual PAA, was observed in FT-IR spectra of air-dried PAA-modified graphene oxide paper samples. In addition, significantly decreased C=O stretches, as well as shifted carboxy C–O stretches, were observed after PAA modification of graphene oxide sheets. This could be interpreted as evidence that carboxylic acid groups interact with amine groups.²⁵ In comparison with C1s X-ray photoelectron spectroscopy (XPS) spectra of unmodified graphene oxide paper, that of PAA-modified graphene oxide paper (Figures 2c,d) showed a significantly decreased component for the C of the epoxy group (286.7 eV) and a new component for the C–N bond, supporting formation of new C–N bonds between epoxy groups of graphene oxide and N groups of PAA.²⁷ The PAA-modified graphene oxide paper showed a small N1s component that was not observed in the XPS spectra of unmodified graphene oxide paper. The FT-IR and XPS spectra would support that the graphene oxide sheets are chemically cross-linked by a small amount of PAA (see below for more information about the C/N atomic ratio). Notably, a homogeneous colloidal suspension of the cross-linked graphene oxide sheets in water was produced by sonication. To our knowledge, this is the first example of producing a homogeneous colloidal suspension of cross-linked graphene sheets. This suspension should be more versatile for making materials for various mechanical applications than our previous approach that involved postmodification of premade paper samples using divalent ions.⁹

Elemental analysis of PAA-modified graphene oxide measured by combustion of the paper samples showed a similar C/O atomic ratio (1.5, including contribution from adsorbed water) to that of graphene oxide paper (1.2, including contribution from adsorbed water). In comparison with the C/O atomic ratio (~ 2.7) of GO (the contribution from adsorbed water was removed by the use of Karl Fischer titration),²⁸ the C/O value (1.5) of the PAA-modified graphene oxide paper indicates that the sample likely has interlamellar water. On the other hand, reduced graphene oxide sheets prepared by chemical^{28,29} or thermal³⁰ treatment showed a higher C/O value (about 10) compared to that of the PAA-modified graphene paper sample discussed here. While elemental analysis of the unmodified graphene oxide paper sample did not show a nitrogen component, a small amount (C/N atomic ratio, ~ 28) of nitrogen was found in the PAA-modified graphene oxide paper sample.

We have measured the mechanical properties of the paper material by tensile testing (Table 1). A paper sample prepared from unmodified graphene oxide was used as a reference. Similar to unmodified graphene oxide papers,^{8,9} a stress–strain curve of PAA-modified graphene oxide papers shows an initial straightening region followed by a “linear region” (although this region is almost linear, not perfectly elastic, we here refer to it as the linear region, Figure 2e). The PAA-modified graphene oxide paper has a modulus (E_E , an average value of five samples) of 33.3 GPa in the linear region. This value is $\sim 30\%$ higher than that (an average value of five samples, 25.6 GPa) of unmodified graphene oxide paper. Interestingly, the PAA-modified graphene oxide paper is 19–55% stiffer in the linear

region than previously reported for divalent ion (Mg^{2+} and Ca^{2+})-modified graphene oxide papers.⁹ The cross-linking of graphene oxide sheets by PAA may be playing a role in the mechanics of this stiffer material. While the unmodified graphene oxide paper exhibits a high modulus in the linear region, the modulus in the region of low strain is much smaller than that in the linear region. For example, the average moduli (E_I , 5.8; E_S , 16.6 GPa, respectively) of unmodified graphene oxide paper at the initial and straightening region are smaller than that (25.6 GPa) in the linear region, meaning that such paper samples are not, in a relative sense, stiff in the region of low strain. On the other hand, the PAA-modified graphene oxide papers had significantly higher stiffness in initial (11.3 GPa) and straightening (25.5 GPa) regions relative to unmodified graphene oxide papers. The relative enhancement of the moduli is about 95 and 54% in the initial and straightening regions, respectively. The tensile strength of the PAA-modified graphene oxide paper is $\sim 10\%$ higher than that of unmodified graphene oxide paper.

In conclusion, an aqueous colloidal suspension of chemically cross-linked graphene oxide sheets was generated by addition of polyallylamine to an aqueous suspension of graphene oxide sheets followed by sonication of the mixture. Chemical analysis using XPS and FT-IR suggests that the graphene oxide sheets are cross-linked through epoxy groups of the graphene oxide sheets. Paper material samples made by simple filtration from such cross-linked graphene oxide sheets showed increased stiffness and strength relative to unmodified graphene oxide paper samples also made by simple filtration. Although the chemical structure of the cross-linked graphene oxide and the reaction mechanism for cross-linking have not been fully revealed, this approach for producing chemically cross-linked graphene sheets and homogeneous colloidal suspensions of them could be extremely useful for fabricating mechanically useful materials such as polymer-based composites and thin films. Furthermore, a number of free and reactive amine groups of the polyallylamine chains could be a good precursor for further chemical modification.

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Supporting Information Available: The Supporting Information includes experimental details. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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