Sonochemical Preparation of Functionalized Graphenes

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S *Supporting Information*

ABSTRACT: A convenient sonochemical method is described for the preparation of polystyrene functionalized graphenes starting from graphite flakes and a reactive monomer, styrene. Ultrasonic irradiation of graphite in styrene results in the mechanochemical exfoliation of graphite flakes to single-layer and few-layer graphene sheets combined with functionalization of the graphene with polystyrene chains. The polystyrene chains are formed from sonochemically initiated radical polymerization of styrene and can make up to ~18 wt % of the functionalized graphene, as determined by thermal gravimetric analysis. This one-step protocol can be generally applied to the functionalization of graphenes with other vinyl monomers for graphene-based composite materials.

Graphene has received enormous attention in the fields of microelectronics and composite materials;[1−7] when incorporated appropriately, graphenes can dramatically enhance the electrical, physical, mechanical, and barrier properties of polymer composites at extremely low loadings.[8−16] The properties of graphene/polymer composites, however, depend on how well the graphenes can be dispersed into the host polymers. Substantial efforts are now being made to modify graphene surfaces to improve their processability and the performance of the composites.[17−29]

Currently, chemical modification or functionalization of graphene is based on graphenes from previously prepared graphene oxide. The production of graphenes from graphene oxide is a multistep process and involves using strong oxidizing and reducing agents.[30−33] In addition, such prepared graphenes often contain a large amount of defects even after reduction compared to graphenes obtained from other methods.[5] An alternative approach to prepare graphenes is direct exfoliation of natural graphite flakes via sonication in organic solvents, surfactants/water solutions, or ionic liquids.[34−39] Both the exfoliation of graphite in liquid phase approach and the chemical oxidation of graphite method rely on the physical effects of ultrasound to break the 3D graphite structure down to a 2D graphene structure.

Ultrasound has found important applications in a diverse range of materials and chemical syntheses.[40,41] Both the physical and chemical effects of ultrasound arise from acoustic cavitation: the formation, growth, and collapse of bubbles in liquids irradiated with high intensity ultrasound.[40−42] Localized hot spots with ~5000 K and pressures of hundreds of bars are formed during bubble collapse within liquids irradiated with high intensity ultrasound; these hot spots generate highly reactive species including radicals from sonolysis of solvent vapor.[43] The chemical effects of high intensity ultrasound which is usually accompanied by the mechanical and physical effects of ultrasound, however, have not been previously utilized in graphene synthesis.

In this work, we show that by choosing a reactive medium as the solvent, the combined mechanochemical effects of high intensity ultrasound can, in a single step, readily induce exfoliation of graphite to produce functionalized graphenes. To obtain high yields of exfoliated graphenes from graphite, the surface energy of the solvent should match the surface energy of graphite, and the optimal solvents therefore have surface tensions of ~40 to 50 mJ m^{-2}.[34] In addition, the solvent must also be able to undergo sonochemical reactions during the sonication to produce radical functionalization of the graphene sheet. Styrene meets these dual criteria, having an appropriate surface tension (~35 dyn/cm at 0 °C)[44] and reactive vinyl groups capable of polymerization.

Polystyrene functionalized graphenes were prepared by irradiating natural graphite flakes in freshly distilled styrene (15 mL) with high intensity ultrasound (Sonic & Materials VCX-750, 1 cm^2 Ti horn at 20 kHz and 50 W/cm^2 at 0 °C for 2 h under Ar flow) (see Supporting Information (SI) for experimental details and setup (Figure S1)). Typical yields of the functionalized graphenes are ~10% based on the initial graphite used in this small-scale sonochemical synthesis. These polymer functionalized graphenes are very stable, can be easily dispersed into different common organic solvents (~2 mg/mL in dimethylformamide, and similarly soluble in THF, toluene, and chloroform), and do not precipitate even after 6 months (Figures S2 and S3).
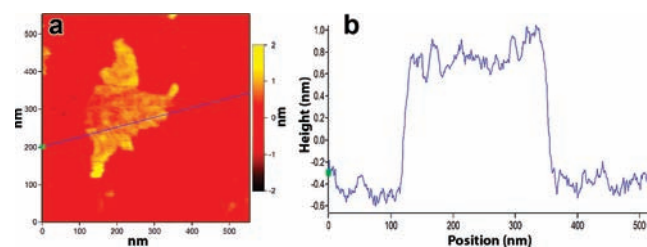
The black graphene colloid solution was investigated by transmission electron microscopy (TEM). TEM samples were prepared by placing a few drops of the solution onto copper grids with an ultrathin holey carbon film. Figure 1a and 1b show the TEM images of a single-layer and trilayer graphene respectively. The formation of single- and few-layer graphenes was further confirmed by selected area electron diffraction (SAED) (Figure 1 insets and Figure S4). The Figure 1a inset shows the SAED pattern of the graphene sample, and the {1100} spots appear to be more intense than the {2110} spots which is the fingerprint of single-layer graphenes.[34,45] For comparison, in the Figure 1b inset, the {2110} spots are more intense than the {1100} spots which is characteristic of multilayer graphenes.[34,45] At the same time, folded and disordered graphenes were also observed under TEM (Figure S5). TEM analysis of the graphenes revealed that ~80% of the exfoliated graphenes are less than 5 layers, as determined by measuring the distinguishable edges of the exfoliated graphenes (Figure S6).[34,35,38]
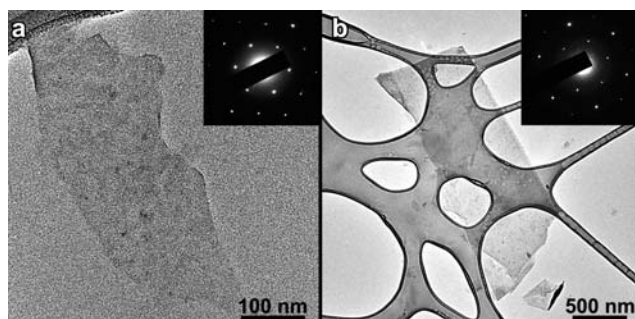
Figure 1. TEM images of (a) single-layer graphene and (b) trilayer graphene with SAED insets confirming single-layer and few-layer graphenes, respectively. Lacey carbon served as the support.


Figure 3. (a) FT-IR spectra in KBr pellet and (b) TGA of graphite (black line) and polymer functionalized graphene (red line), with a heating rate of 10 °C/min under N_2.

Figure 2. (a) AFM image of a functionalized single-layer graphene on Si wafer. (b) Line scan height profile along path indicated in (a).

Figure 4. (a) Raman spectra of graphite (black line) and polystyrene functionalized graphene (red line). (b) XPS spectra of graphite and (c) polystyrene functionalized graphene.

Atomic force microscopy (AFM) was also used to examine the thickness of these styrene-functionalized graphenes. Figure 2a reveals a graphene with a thickness that varies from 1.0 to 1.4 nm according to cross-sectional analysis, which is slightly higher than the reported apparent thickness of single-layer graphene.[5,46] This apparent height difference is probably caused by the absorbed polystyrene chains on the surface of graphene. In addition to the thickness difference, the presence of functionalized polymer chains is further supported by the roughened graphene surface. The absorbed polymer chains on the surface of graphene will result in surface roughness because the functionalization sites via radical coupling on the surface of graphene are randomly distributed on the surface.[47] In contrast, unmodified graphenes always show a smooth and flat surface.[20] Few-layer graphenes were also observed under AFM characterization (Figure S7).

The FT-IR spectrum of functionalized graphenes shown in Figure 3a shows the characteristic absorbance of polystyrene even after exhaustive washing: peaks at 3024, 1602, 1492 cm^{-1} and combination bands in the range of 2000 to 1700 cm^{-1} correspond to the phenyl group, the peaks at 2922 and 2850 cm^{-1} correspond to the methylene and methenyl groups, and the peaks at 1028 cm^{-1} correspond to the C−Ph groups.[48] The FT-IR spectrum of graphite or nonfunctionalized graphenes does not contain any of those absorbance peaks. This suggests the presence of polystyrene in the functionalized graphenes. In addition, polystyrene standards, sonochemically synthesized polystyrene, and polystyrene functionalized graphenes show similar ^{1}H NMR spectra (Figure S8). This further supports the presence of polystyrene on graphenes. Thermal gravimetric analysis (TGA) was used to determine the content of polystyrene in the functionalized graphenes. By comparing the weight loss of functionalized graphenes to graphite, the content of polymer is about 18 wt %. The molecular weight of polystyrene on the
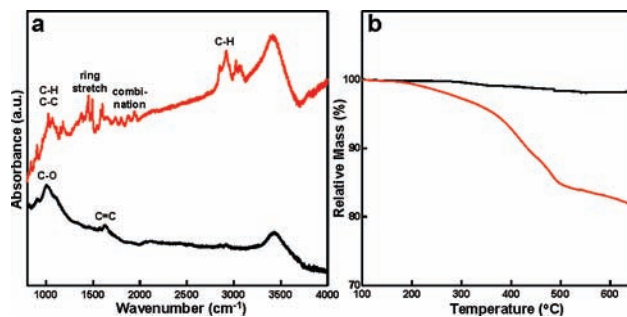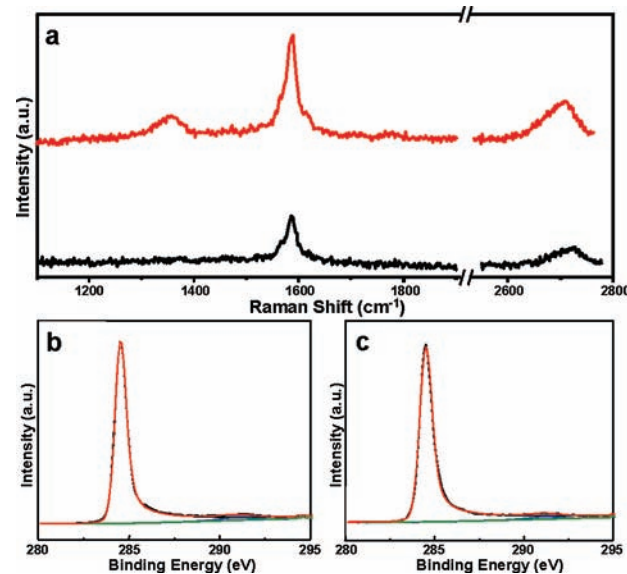
surface of graphene is difficult to measure due to the covalent bonding of the polymer and graphene. We can estimate the number average molecular weight (upper limit) from polystyrenes polymerized by sonication of styrene alone under the same conditions which is determined to be 1.5×10^5 with a polydispersity index of 2.1 (Figure S9).

Of course, any surface modification of graphene must partially destroy the sp^2 hybridization of graphene. In order to probe its overall structural integrity, we have examined the Raman, XPS, and UV−vis spectroscopy of our modified graphene. Figure 4a shows the Raman spectra of graphite and functionalized graphene. The D band is obvious in polymer functionalized graphene compared to graphite, which indicates the formation of sp^3 hybridized carbon on the graphene surface due to covalent bonding of polystyryl chains to graphene. The G band of polystyrene functionalized graphene shifts to a position slightly higher ($\sim$4 cm^{-1}) than graphite, while the 2D band of polymer functionalized graphene shifts to a lower position ($\sim$8 cm^{-1}) together with an intensity increase compared to graphite. This further supports that graphite is exfoliated to single- or few-layer graphenes.[3] The intensity ratio I_D/I_G for the polymer functionalized graphene

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is ∼0.78 which is much lower than that of graphene oxide and chemically reduced graphenes.[20,49−52] This indicates that the surface of polymer functionalized graphenes is not extensively destroyed. XPS spectra (Figure 4b and 4c) of graphite and polystyrene functionalized graphene show a single peak around 284.5 eV, which is associated with graphitic carbon. No additional signals from C—O or C═O groups are observed which demonstrates that the graphenes are not oxidized; recall that the sonication was carried out under Ar. The structural integrity of graphene is further supported by the UV—vis spectroscopy (Figure S10). The UV—vis spectrum of polystyrene functionalized graphene in tetrahydrofuran shows a strong absorption peak around 275 nm, which is comparable to reduced graphene oxide after the conjugated graphitic structure has been restored by chemical reduction.[31,52] This demonstrates that the structure of graphene in the polystyrene modified form has not been extensively modified compared to reduced graphene oxide.

The results of the mechanical/physical effects of ultrasound on graphite are clearly seen in the SEM images (Figure S11) of graphite flakes before and after sonication, which show that graphite flakes become smaller and thinner after ultrasonic irradiation. We can even observe a wrinkled graphene absorbed on the surface of Si wafer at low accelerating voltage. From XRD spectra (Figure S12), we can see a rhombohedral phase emerges after sonication of graphite flakes in styrene. This new phase is a thermodynamically unstable allotropic form of graphite that arises from the formation of ABCABC stacking of graphene layers instead of the normal ABAB stacking sequence (hexagonal).[53] The deformation and exfoliation of graphite are caused by the mechanical shockwaves and shear forces created by the collapse of cavitating bubbles that form during irradiation of ultrasound in liquid.[41] As shown in Figures S11 and S12, the graphite after sonication indeed has become thinner and the lateral sizes of the pieces become smaller; as a consequence, the intensity of the (002) peak decreases and the fwhm of the (002) peak increases as a result of Scherrer broadening.[54,55]

The chemical reactivity of the solvent is a key parameter in the sonochemical preparation of functionalized graphenes. We tested a variety of other solvents, including toluene, ethylbenzene, 1-dodecene, and 4-vinylpyridine to prepare functionalized graphenes. Only the easily polymerizable reactants containing vinyl groups, styrene and 4-vinylpyridine, lead to stable functionalized graphenes (Figures S13, S14, and S15). The characterization of poly(4-vinylpyridine) functionalized graphene is presented in Figures S16 and S17; FTIR demonstrates that the surface of graphenes is grafted by poly(4-vinylpyridine), and the TGA shows that the content of the polymer is ∼20 wt %.

Our sonochemical approach is a mechanochemical combination of the mechanical exfoliation of graphite using ultrasound combined with the chemical functionalization of graphenes from sonochemical reactions of the solvent; both of these processes occur at the same time during the sonication. The surface tension of styrene is an excellent match to the surface energy requirements of graphenes, which assists in the thermodynamics of exfoliation; combined with the mechanical forces (from both shear and shockwave) created by the implosive collapse of cavitating bubbles, the breakage and exfoliation of graphite flakes into single- or few-layer graphenes occur. Radicals formed during sonication of an appropriate solvent/coreactant can react with the graphene surface to form the polymer functionalized graphenes that we obtain. Alternatively, the surface of graphite may first be functionalized by the radicals followed by

exfoliation and further functionalization of the newly exposed graphene face.

In summary, a convenient single-step sonochemical approach for the preparation of polymer functionalized graphenes from graphite has been demonstrated using a reactive solvent with appropriate surface tension. The styrene used here serves both as a good solvent for exfoliation of graphite and as a monomer for formation of reactive polymeric radicals which react with the sp^2 hybridized carbon of graphene. The graphitic structure of polymer functionalized graphenes has not been extensively affected. Such functionalized graphenes have good stability and solubility in common organic solvents and have great potential for graphene-based composite materials.

■ ASSOCIATED CONTENT

Ⓢ **Supporting Information.** Detailed experimental procedures; more TEM, SEM, and AFM images; UV—vis spectra; XRD spectra; H^1 NMR spectra; and complete ref 34. This material is available free of charge via the Internet at http://pubs.acs.org.

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■ ACKNOWLEDGMENT

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