New Method To Prepare Graphite Nanocomposites

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Recently, graphite nanosheets have been intensively studied because of their unusual electrical, thermal, and mechanical properties.[1] Although carbon nanosheets were obtained as a by-product during preparation of fullerene and carbon nanotubes,[2] many methods have been developed exclusively to prepare graphite nanosheets, which include micromechanical cleavage,[1d,e] chemical vapor deposition (CVD),[3] solvent thermal reaction,[4] thermal desorption of Si from SiC substrates,[5] and chemical routes via graphite intercalation compounds (GIC)[6] or graphite oxide (GO).[1a] Among these, the latter route by chemical treatment of natural graphite[6,1a] is most promising for fabricating graphenes in large quantities for industrial applications, as graphite is naturally abundant and chemical treatment is convenient. Although many GICs have been synthesized so far,[7] dispersing graphene nanosheets uniformly in a polymer matrix is still difficult. However, uniform dispersion of GO nanosheets in polymer matrices is relatively more successful.[1a,8] This is generally attributed to the excellent exfoliation character of GO; that is, it can be easily exfoliated in dilute polar solutions.[1a,8,9] Moreover, even single graphenes could be obtained by exfoliation and subsequent chemical reduction, resulting in significantly increased conductivity.[1a,9c] The other advantage is that the oxygen-containing functional groups on the surface of the GO sheet[10] make it compatible with many polymers. Nonetheless, chemical reduction of GO sheets in water always results in their irreversible coagulation and restacking,[9c] making the sheets difficult to redisperse. In addition, the reduction of GO with hydroquinone even directly transforms it to crystalline graphite with an interlayer spacing of only 3.39 Å.[11] Thus, the prevention of reduced GO sheets from restacking is critical to obtaining graphitic nanocomposites.

We have recently obtained a uniform dispersion of nanosheets in a polymer matrix by in situ redox reaction between GO sheets and the monomer.[12] A solution method was also used to prepare polystyrene/graphite nanocomposites by chemical reduction of exfoliated and dispersed isocyanate-treated GO sheets in a solution.[1a] This method is more suitable for polymers which are soluble in organic solvents. However, for polymers that have little solubility in those solvents, direct polymer melt compounding is more appealing because of its compatibility with commercial processing techniques and eco-friendliness. This Communication demonstrates a new melt mixing method for fabrication of polymer/graphite nanocomposites (Scheme S1 and Experiments, see Supporting Information). It has two steps: (1) synthesis of sulfur/graphite composite, unlike the conventional process, here GO undergoes redox reaction with polysulfides ions, and the resultant sulfur nanoparticles are dispersed on the surface of graphenes; and (2) the prepared sulfur/graphite composite is utilized as fillers to fabricate polymer nanocomposites by a melt mixing method.

As shown as Figure 1a, GO exhibits a sharp diffraction peak, corresponding to an interlayer spacing of 0.77 nm. No such peak is seen for the sulfur/graphene composite (Figure 1b), indicating that the periodic structure of GO is lost and graphene sheets are exfoliated. In addition, all the diffraction peaks in curve *b* can be indexed as orthorhombic sulfur (JCPDS 08-0247), confirming the existence of α-sulfur in the composite. This is different from the previous work,[11] where GO was reduced by S^{2-} to graphite with $d_{002} = 0.38$ nm. It is believed that the in situ produced sulfur adsorbed

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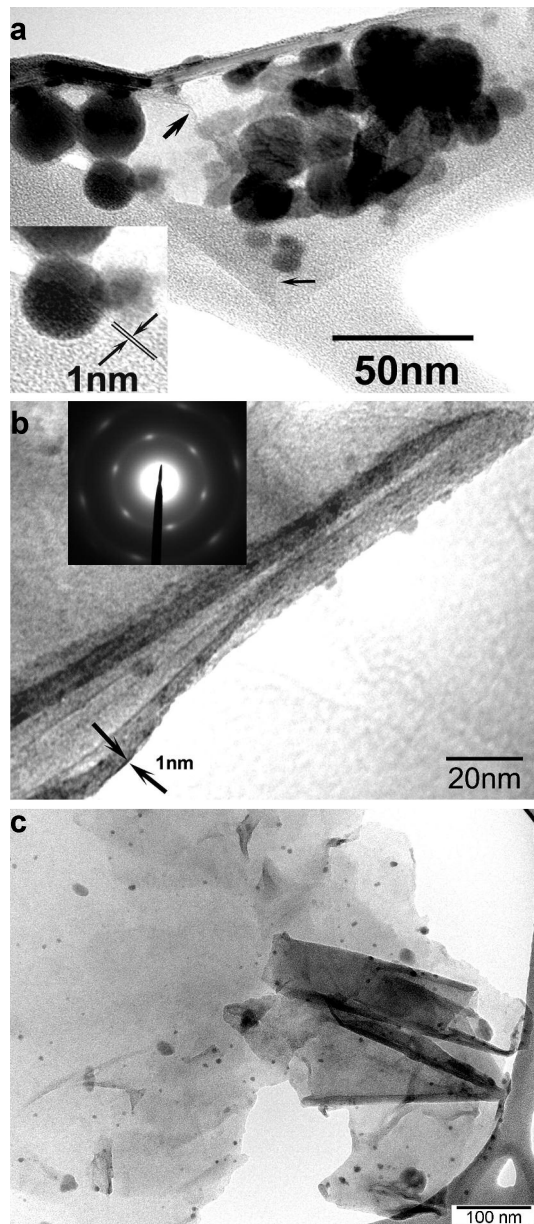(7) Shioyama, H. *Synth. Met.* **2000,** *114,* 1.
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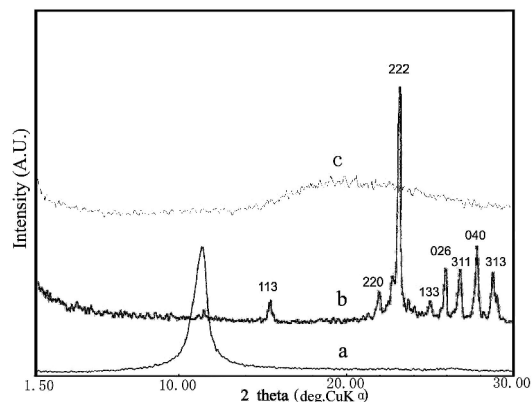
Figure 1. XRD of (a) GO, (b) sulfur/graphite composiste, and (c) polymer/graphite nanocomposite.

on the surface of exfoliated nanosheets has prevented restacking of the nanosheets. This is confirmed by TEM observations (Figure 2), which reveal the presence of sulfur nanoparticles with a diameter < 30 nm dispersed on free-standing graphene sheets. The arrows in Figure 2 clearly point to the folded sheet edge, from which the ∼1 nm thickness of the sheet is easily identified, similar to other reports.[1a] As a result of their high aspect ratio, the nanosheets generally scroll and bend to minimize the surface energy or dangling bond on the edge.[13] This is clearly seen in Figure 2a, where the top edge of the sheet is scrolled and its left edge folded. Actually, there are studies reporting the transition from graphite nanosheets to carbon nanotubes (or named scrolls).[6,14] The inset SAED image in Figure 2b matches those of the crystalline graphene sheets.[1a,2d,3a] Also, like recently synthesized sulfur nanoparticles,[15a] nanotubes,[15b] and microtubules,[15c] our in situ produced sulfur nanoparticles will enable more interesting applications.

After the reduction, the brown slurry of GO became black, indicating a regraphitization of GO. The reduction of GO is also confirmed by elemental analyses, as the C/O ratio has been used as a conventional measure of the oxidation degree of graphitic materials. The C/O in GO is 4/2.91, which is close to the previous report.[16] However, it increased to 4/1 in the composite. This is similar to the results of GO reduced by hydrazine.[9c] In the sulfur/graphene composites, the sulfur content is 60 wt %. It is noteworthy that the sulfur content can be adjusted easily by varing the x value in the polysulfide ions (S_x^{2-}). In the Raman spectrum (Figure S1, see Supporting Information), the prominent features of graphitic materials are the well-known D and G bands. The sharp D band at 1590 cm^{-1} and G band at 1350 cm^{-1} show the defective, crystalline structure of graphene nanosheets.[3,2d] The presence of a weak peak at 1136 cm^{-1} is consistent with the high density of the sheet edges.[3a] In the FTIR

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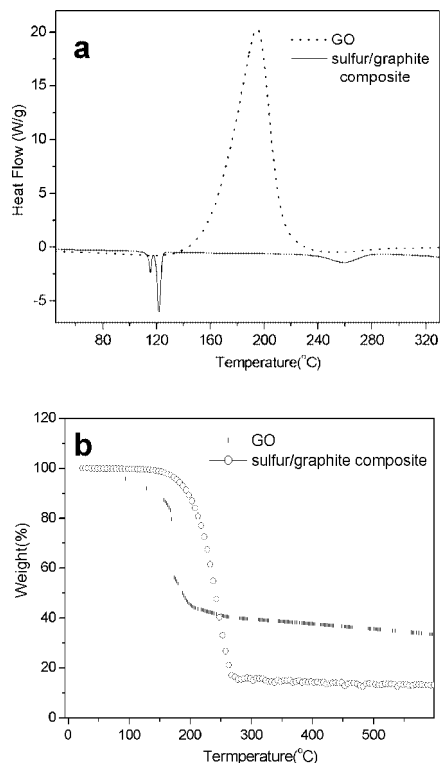(16) Liu, P. G.; Gong, K.; Xiao, P.; Xiao, M. *J. Mater. Chem.* **2000**, *10*, 933.

Figure 2. TEM images of sulfur/graphite composites.

spectrums (Figure S2, see Supporting Information), GO shows four sharp peaks, 3420 cm^{-1}, 1724 cm^{-1}, 1618 cm^{-1}, and 1051 cm^{-1}, which correspond to −OH, C=O, free water and C−O−C group, respectively.[10,12] In contrast, for the composites, the peaks of C=O and C−O−C are absent, and a new peak at 1569 cm^{-1} appears, which is attributed to the ring stretching of aromatic C=C.[9c,10,12] These changes also support the reduction of GO and the partial removal of the oxygen functional group with restoration of the aromatic graphene network.

DSC of GO (Figure 3a) shows one strong extherthomic peak at 190 °C, which is caused by the decomposition of the organic groups on the GO sheets. For the composite, the two peaks at 115 and 121 °C come from the melt of α-sulfur and β-sulfur, respectively, while the peak at 260 °C is due to the evaporation of sulfur. No extherthomic peak is found, indicating good thermal stablility of the graphitic materials in the composites. The TG curve of GO exhibits a major

Figure 3. (a) DSC and (b) TG curves of GO and sulfur/graphite composite.

Figure 4. TEM image of the polyarylenesulfide/graphite nanocomposite.

weight loss around 170 °C (Figure 3b), which is attributed to the removal of organic groups, while the weak weight loss below 100 °C is due to the physically adsorbed water in the sample. For sulfur/graphite composites, there is only one major weight loss around 200 °C, which is due to sulfur evaporation. These results show that, after the reduction treatment, the graphitic nanosheets become hydrophobic and thermally stable, which make them suitable for direct melt processing with polymers. Also, the conductivity of the sulfur-modified graphene nano sheets is 69 S/m indicating a striking contrast to the electrically insulating GO.[1a] The good conductivity enables the graphite nanocomposite for use as an electrode material in lithium batteries[17] and vulcanization agent for fabrication of conductive polymer nanocomposites.[18] Other applications include serving as effective mercury sorbents, since previous studies have shown that introduction of sulfur and oxygen containing functionalities on carbon surface[19] can greatly improve its Hg uptake capacity. For

sulfur and graphenes in nanoscales they will exert more pronounced functionalities.

To show the feasibility of melt mixing of the fabricated sulfur/graphite composite with polymer, poly(arylene sulfide)/ graphite nanocomposite was prepared. First, the sulfur/ graphene composite was mixed with the melt of the polymer precusor, cyclic oligomer of poly(aylene sulfide). When the mixture was heated to 180 °C, a ring opening polymerization and cross-linking reaction occurred between sulfur and the polymer precursor[20] (see Supporting Information Scheme S1). XRD of the resultant polymer/graphene nanocomposite shows no diffraction peak of sulfur, except for a broad peak located at ∼20° (Figure 1c) due to the amorphous polymer matrix. This confirms sulfur has reacted with the polymer. Interestingly, no peaks corresponding to GO or graphite are found, affirming the exfoliated nature of graphenes was preserved in the resulting polymer nanocomposite.The TEM micrograph in Figure 4 confirm this, where the curly black lines represent the cross-sections of the graphite nanosheets, which are 1−3 nm thick and finely dispersed in the polysulfide matrix. The thick lines may be caused by the crumpling, wrinkling, or folding of the nanosheets. These nanosheets are significantly thinner than those (>30 nm) obtained from exfoliated graphite or GIC.[21]

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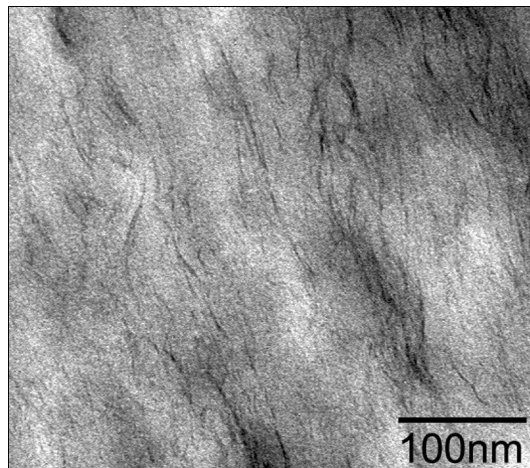
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