Novel Synthesis of Conductive Poly(arylene disulfide)/Graphite Nanocomposite*

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Abstract: A new process for the dispersion of graphite in the form of nanosheets in a poly(arylene disulfide) matrix was developed via in situ polymerization of monomer at the presence of exfoliated graphite oxide in NaOH solution. The nanoscale dispersion of graphite layers within poly(arylene disulfide) was confirmed by the X-ray diffraction patterns and TEM examinations. According to the conductivity test, the conductivity of the final poly(arylene disulfide)/graphite nanocomposite was increased by about 7 orders of magnitude compared with GO.

Key words: graphite oxide; nanocomposite; transmission electron microscopy
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Since the first report of polyamide-organoclay nanocompsites by Fujiwara and Sakomoto in 1976[1], the polymeric nanocomposites have attracted considerable attention owing to their significant contribution to technological applications. In our previous studies, polymer/clay nanocomposites have been prepared with the pronounced improvements in physical and chemical properties that are distinct from those of either the matrix or the corresponding macro or micro composite[2-4]. Although graphite is also composed of layered nanosheets just like layered silicates and many kinds of graphite intercalation compounds (GIC) were synthesized[5-11], only a few polymer/graphite nanomomposites have been reported because organic molecules are hard to be directly intercalated into the graphite. The graphite layers are jointed together with inter spacings of only 0.335 nm, and moreover, the graphite layers are both lack of the affinity and space for hydrophilic or hydrophobic organic molecules or polymer to intercalate. The bonds holding between the graphite layers (in the direction of c axis) can be broken up by strong oxidation followed by generating the hydrophilic graphite oxide (GO) of lamellar structure. According to the amount of water in the layers, the interlayer spacing (d_L) ((002) interference) varies from 0.61 to 0.11 nm. It readily disperses in NaOH solution (d_L = 1.23 nm in 0.05 mol/L NaOH solution, $d_L = \infty$ in 0.01 mol/L NaOH)[12]. The intercalated GO allows it to be used as the host of many kinds of nanocomposite and exhibits very rich intercalation chemistry.

It has been very recently reported that some polar organic molecules and polymers, such as poly(vinyl alcohol)[13-15], poly(acrylamide)[16], poly(acrylic acid)[17] can be inserted into the GO lamellaes to form intercalated or exfoliated GO nanocomposites. Intercalation of hydrophobic polymer, like poly(vinyl acetate), into GO was also achieved by *in-situ* polymerization of the vinyl acetate monomer in GO that was intercalated with long-chain aliphatic alcohols in previous work[18]. It was further reported that GO can be restored graphite sheet structure upon thermal treatment[19]. So it is possible to use polymer/GO intercalation nanocomposites as a precursor to prepare polymer/graphite nanocomposites. In our previous work, polymer/graphite oxide intercalation compounds were synthesized, and then the polymer/graphite nanocomposite was obtained by the reduction of graphite oxide[18,20,21]. GO has also been proved to be an oxidizing reagent and can be reducing by the ammonia, KI and got rearomatization[22,23]. Nevertheless, there is little information on the synthesis of the polymer/GO nanocomposite via the oxidizing characteristic of GO so far.

Poly(arylene disulfide)s have high resistance to environmental degradation, good low temperature properties, low water-vapor transmission, excellent resistance to acids, bases, and organics, as well as good adhesion to metals, glass and concrete[24-26]. Moreover, organic aliphatic disulfide polymers are novel positive material for

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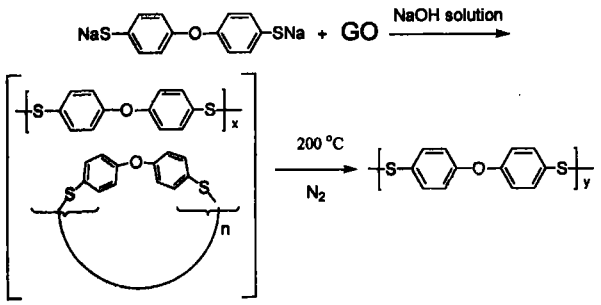
secondary battery. The theoretical energy content of these materials far exceeds that of conventional battery materials as well as those of other candidate materials such as the conducting polymers. Aromatic disulfides (or their polymers), such as the diphenyl disulfide and 2, 5-dimercapto-1, 3, 4-thiodiazole (DMTD), have recently been extensively studied and used as a active cathode material for rechargeable lithium batteries[27-31]. They show potential applications in the fields of electrode materials in rechargeable batteries. However, most poly (arylene disulfides) s are insoluble in common solvents and therefore are incapable of solution processing to be directly used as the matrix for polymeric nanocomposites.

Aromatic thiolic salts are extremely easy to be oxidized forming the corresponding aromatic disulfides. In this article, we report the synthesis of the conductive exfoliated poly (arylene disulfide)/graphite nanocomposites. The novelty of this work arises from the facts of followings: ① obtain the high performance poly(arylene disulfide)/graphite nanocomposite with good conductivity, ② GO acts both as an oxidizing reagent for the polymerization of aromatic dithiols and as the host of the resulting nanocomposite. The chemical reactions in this process are depicted in Scheme 1. In this connection, we attempt to develop a new and convenient rout to prepare *in-situ* polyarylendisulfide/GO nanocomposites.



Scheme 1

GO was prepared from the natural graphite powder via the previously reported procedure[32]. To a 250 mL three-neck round flask containing 100 mL 0.02 mol/L NaOH 0.8 g of dried GO was added and sonicated for 50 min, and then 1.2 g 4,4′-oxybis(benzenethiol) dissolved in 100 mL of 5% NaOH aqueous solution was introduced while stirring. The resulting slurry was stirred and reacted for 8 h at an ambient temperature. Excess 1% HCl solution was then added to the mixture until the pH of the solution becomes 2. The solution was further kept stirring for another 8 h. This solution was filtered and the filtrate was washed with distilled water followed by drying at 333 K overnight. The obtained material was then heat treated under a dynamic vacuum at 200 ℃ for about 4 h to render some unreduced GO to restore graphene sheet structure, thus to obtain poly(4, 4′-oxybis(benzene) disulfide)/graphite nanocomposites with good electrical conductivity.

Fig.1 shows the X-ray diffraction (WAXD) patterns of pristine GO and the poly(4, 4′-oxybis(benzene) disulfide)/graphite. Because of the hydrophilic characteristic of GO, the water still exists even after having been dried for 4 days at 60 ℃. The interspacing of 0.841 nm of the GO indicates the presence of certain amount of water in the interlayers. After the reaction of GO with the 4, 4′-oxybis(benzenethiol) salts, the characteristic diffraction peak of GO disappears and there is no defined diffraction peak as shown in trace b of Figure 1 except for the broad peak located at about 19°. This peak is attributed to the polymer matrix, i.e., poly(4,4′-oxybis(benzene) disulfide). This verifies that the regular and periodical manner of GO is lost and the GO nanosheet can be delaminated by the resulted aromatic dithiolic salts. The nanocomposite precursor of poly(4, 4′-oxybis(benzene) disulfide)/graphite powders can be synthesized via aforementioned procedure.

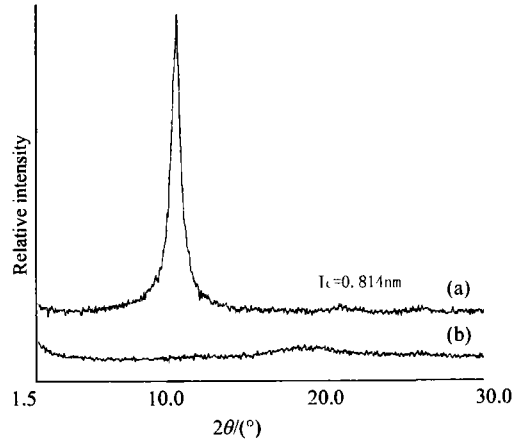


Fig.1 X-ray diffraction patterns of (a) pristine GO; (b) poly(4,4′-oxybis(benzene) disulfide)/graphite nanocomposite

In order to confirm the nanoscale dispersion of the graphite within the used polymer, transmission electron microscopy (TEM) was used to observe the morphology of the nanocomposites. From Fig.2, it can be seen that the individual graphite layers appear as dark lines and the interface between the graphite and polymer is not clear. It means the graphite layers can be well dispersed in poly (4,4′-oxybis(benzene) disulfide) and the polymer matrix can contact closely with graphite. It is interesting to note that some graphite layers in the micrograph seem snaky shape. This is different from the morphology of nanoscale graphite layers observed in previous work[33]. The sinuate morphology implies the good compatibility between the graphite sheet and the polymer matrix. Also from this

figure, the graphite layer cells exhibit a thickness of ~ 10 nm, and a length of ~ 100 nm, indicating that the graphite layers have large aspect ratios.

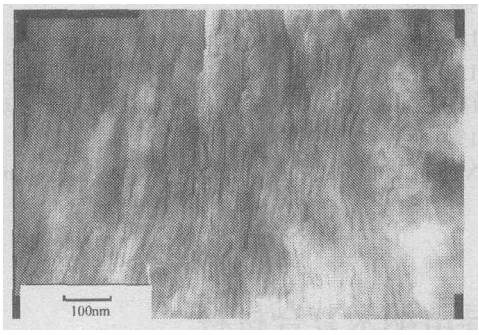


Fig.2 TEM micrograph of the poly(4,4′-oxybis(benzene) disulfide)/graphite nanocomposite

For GO, FTIR spectrum (Fig.3(a)) shows three sharp peaks of 1724 cm^{-1}, 1618 cm^{-1} and 1051 cm^{-1} assigned respectively to carbonyl group (C═O), water and epoxy group (C—O—C). The weak peak at 1398 cm^{-1} is usually attributed to the hydroxyl group (C—O—H). After reacting with the aromatic dithiolic salt, it can be found that the strong band of carbonyl group and the epoxy group reduce greatly and almost disappear. However, the weak band of the hydroxyl group in GO becomes very sharp in the nanocomposite (Fig.3(b)). From the variation of the bands at 1618 cm^{-1} and 3422 cm^{-1}, we can also conclude the highly hydrophobic property of GO is greatly decreased. The variation of the FTIR spectrum of GO is similar to the previous work, and can be explained by the reduction reaction of GO[19,21,22]. There is no adsorption peak of the thiol (S – H) observed in the FTIR spectrum, indicating that the aromatic dithiolic salts are oxidized cyclic oligomers by GO.

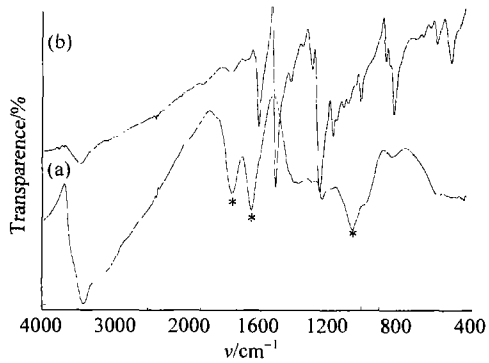


Fig.3 FTIR spectra of (a) pristine GO (b) poly(4,4′-oxybis(benzene) disulfide)/Graphite nanocomposite

Electrical conductivity data were obtained by DC measurement on 1 cm diameter plates, using a SDY-Ⅳ four-probe instrument. The resulted cyclic (arylene disulfide)/graphite blend was melt molded into discs (typically 0.1 cm thick) by compression (~ 70 MPa). The conductivity of the final poly(arylene disulfide)/graphite nanocomposite was 1 S/cm, increased by 7 orders of magnitude compared with the pristine GO (~ 10^{-7} S/cm). The great augmentation of the conductivity can be ascribed to two facts: one is the nanoscale dispersion of graphite sheets and the conducting network formed in the polymer matrix, the another is that GO can be reduced by the aromatic dithiolic salts and subsequent GO restore into graphite sheet structure via heating treatment.

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新方法合成聚芳双硫醚/石墨导电纳米复合材料

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摘 要:利用氧化石墨的氧化性及其在碱性水溶液中剥离分散的性质,将其与芳香二硫酚在碱性水溶液中反应,合成了聚芳双硫醚/石墨导电纳米复合材料。XRD 及 TEM 均证明了无机片层在聚合物基体中呈剥离分散状态。电导率测试表明所合成的纳米复合材料的电导率较氧化石墨提高了近 7 个数量级。

关键词:氧化石墨;纳米复合材料;透射电镜
中图分类号:TM242 **文献标识码**:A