Alkyl-functionalized graphene nanosheets with improved lipophilicity

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Graphene nanosheets (GNSs) have attracted much attention in many potential applications, such as composites, transparent conductive films, field effect transistors and ultrasensitive sensors [1,2]. One practical route to harness the unique properties of GNSs would be to incorporate them into polymer materials [3]. Compared with exfoliation of graphite and epitaxial growth on SiC, the deoxygenation of graphite oxide (GO) nanosheets is widely considered as a more promising fabrication technique in that it enables mass production of GNSs at low cost [2–6]. Unfortunately, since the GO nanosheets are heavily oxygenated and the oxygen-containing groups are difficult to be completely removed during the deoxygenation process, the GNSs prepared by this strategy are decorated with some oxygen functionalities, such as carboxyl groups [4]. The presence of these oxygen functional groups facilitates the uniform dispersion of GNSs in the polar polymers [5]. However, a huge challenge still lies in the generation of satisfactory compatibility between GNSs and nonpolar polymers, which hampers the development of such composites for high-performance applications. Considering that the nonpolar polymers are much more influential and versatile in industrial applications, it is of great significance to lipophilically modify the as-reduced GNSs so that they can be homogeneously dispersed in the nonpolar polymers.

In this letter, by analogy with former works on GO nanosheets [7], we present an easy approach to covalently functionalize GNSs with long alkyl chains, which is demonstrated to be an effective way to enhance the compatibility between GNSs and nonpolar polymers. Synthesized and purified from

expandable graphite (Yingtai Co., China) by a modified Hummers method [8], GO was exfoliated into GO nanosheets in water and then chemically reduced by hydrazine under alkaline condition (using ammonia to adjust the solution pH to around 10), yielding aqueous GNS dispersions [6]. After freeze drying and vacuum drying of resultant dispersions, solid GNSs with a fluffy appearance were obtained. The amidated GNSs (GNS-C18s) were prepared by refluxing GNSs (30 mg), octadecylamine (ODA, 200 mg) and 
\[\text{N},\text{N}-\text{dicyclohexylcarbodiimide (DCC, 4.1 g)}\] in 150 ml of \[\text{N},\text{N}-\text{dimethylformamide (DMF)}\] at 90 °C under \[\text{N}_2\] for 48 h. The reaction can be expressed as follows:

\[
\text{Graphene} + \text{NH}_2(\text{CH}_2)_{17}\text{CH}_3 \rightarrow \text{Graphene} + \text{NH}(\text{CH}_2)_{17}\text{CH}_3
\]

Afterwards, the solid GNS-C18s were separated by filtration, then washed with excess ethanol and dried under vacuum.

The grafting of ODA makes the functionalized GNSs lipophilic and enables them to be homogeneously dispersed in nonpolar media. As shown in Fig. 1, after mild shaking and 30-min standing in immiscible 0.1% ammonia solution/toluene mixture, the unmodified and modified GNSs exhibit completely different affinities. Compared to the unmodified GNSs, which tend to be dispersed in polar ammonia solution (lower layer), the amidated GNS-C18s are lifted to nonpolar toluene phase (upper layer). It is a symbol of successful lipophilization of GNSs.

The formation of amide groups can also be directly determined by Fourier transform infrared spectroscopy (FTIR, Nicolet Nexus 470 spectrometer). As illustrated in Fig. 1a, there are some characteristic GNS absorptions at 1727 and 1581 cm\(^{-1}\), attributed to C=O stretch of carboxyl and C=C stretch of GNSs, respectively. After the reaction with ODA and DCC (Fig. 1b), the band of GNSs at 1727 cm\(^{-1}\) disappears and a new band at 1639 cm\(^{-1}\) assigned to C=O stretch mode of amide carbonyl is observed. Besides, the bands at 3297 (N-H stretch of amide), 2917 and 2848 (C-H stretch of alkyl chain), 1542 (N-H bending of amide), 1458 cm\(^{-1}\) (C-N stretch of amide) appear in the spectrum. These results confirm the success of this amidation reaction.

Fig. 2 presents the dispersions of GNSs and GNS-C18s in xylene, an important nonpolar solvent which can dissolve most important nonpolar polymers, at 0.2 mg/ml loading. The nanosheets were dispersed by sonication for 30 min and the mixtures were allowed to stand for 10 min. Clearly, the dispersion of GNSs in xylene is poor. In vivid contrast, GNS-C18s can be dispersed stably in xylene, yielding a homogeneous black suspension. The films prepared by spin-coating sonicated suspensions on mica substrates were investigated by atomic force microscopy (AFM, Multimode Nano 4 in tapping mode) observation. From Fig. 2, large clumped clusters were found for the GNSs in xylene in contrast to thin sheets for GNS-C18s. As shown in cross-section analysis, the GNS-C18s have a height of about 1.3 nm. This value is a little higher than the reported apparent thickness of single-layer GNSs (~1 nm) [2–4], which may be due to the grafting of long alkyl chains.

![Fig. 1](image1.png)

**Fig. 1** – Dispersibility comparison of (a) GNSs and (b) GNS-C18s in toluene (upper layer)/0.1% ammonia solution (lower layer) system, as well as their FTIR spectra.

![Fig. 2](image2.png)

**Fig. 2** – Dispersions of (a) GNSs and (b) GNS-C18s in xylene, as well as their tapping mode AFM images and cross-section analyses (inset).
The homogeneous dispersion of modified GNSs in nonpolar polymers would provide another evidence of successful lipophilization modification. The GNSs and GNS-C18s were solution-blended in xylene with isotactic polypropylene (iPP, F401, Yangzi Petrochem. Co., China), a typical nonpolar polymer with numerous commercial applications. Briefly, 8 mg GNS-C18s were suspended and sonically dispersed in 80 ml of xylene. Afterwards, 2 g iPP was added and the mixture was stirred at 138 °C for 5 h. After precipitation in methanol, the resulting composite was filtered and dried to obtain a flocculent solid. The iPP/GNSs composite with the same filler loading was prepared for comparison. The obtained composites (denoted as 0.4G-iPP and 0.4G-18-iPP, respectively) were hot pressed into thin sheets at 200 °C and cut into dog-bone type specimens. The tensile-fractured surfaces of the two composites were observed with field emission scanning electron microscopy (FESEM, Hitachi, S-4800). As shown in Fig. 3a and b, the GNS-C18s demonstrate remarkably improved dispersion in polymer host, compared with their unmodified counterparts. Moreover, in contrast to the weak adhesion of GNSs with host iPP, the GNS-C18s are embedded tightly in the matrix and there is no sheet pull-out during fracture.

To illustrate the possible applications of our lipophilically-modified GNSs in the fabrication of high-performance nonpolar polymer composites, we used thermogravimetric analysis (TGA, Perkin–Elmer, heating from 50 °C to 600 °C at a rate of 20 °C/min in air) to investigate the thermal stability of 0.4G-18-iPP, together with that of neat iPP and 0.4G-iPP for comparison. As shown in their derivative thermogravimetric (DTG) curves (Fig. 3c), the peak temperature corresponding to the highest decomposition rate for 0.4G-18-iPP is 12 °C higher than that of iPP, and 7 °C higher than that of 0.4G-iPP. This noticeable enhanced thermal stability of 0.4G-18-iPP further confirms the improved compatibility between alkylated GNSs and iPP matrix.

In summary, GNSs were covalently functionalized with lipophilic moieties of ODA by simply using an amidation reaction. The grafting of long alkyl chains onto GNSs substantially enhances their lipophilicity. When incorporated into iPP, the amidated GNSs show homogeneous dispersion and intimate adhesion with matrix, leading to a notable enhancement in the thermal stability of the resulting composites. Our study suggests an easy but promising pathway to utilize GNSs to fabricate high-performance nonpolar polymer composites.

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REFERENCES