Synthesis of graphene soluble in organic solvents by simultaneous ether-functionalization with octadecane groups and reduction

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ABSTRACT

Octadecane-functionalized graphene (OD-G) soluble in organic solvents was produced by combining the Hummers process for graphite oxidation and a simultaneous ether-functionalization and reduction approach with 1-bromooctadecane in pyridine and dimethylformamide (DMF). The exfoliated OD-Gs were testified to be monolayer sheets by transmission electron microscope (TEM) and atomic force microscopy (AFM). The functionalization with octadecane (OD) groups and the effective deoxygenation of graphene oxide (GO) were confirmed by Fourier-transform infrared spectroscopy (FTIR), X-ray diffraction (XRD) and thermo-gravimetric analysis (TGA). It is proved that the effective reduction and functionalization of GO could be simultaneously completed during the refluxing process. The functionalization with OD groups can effectively prevent the aggregation of GO during the reduction.

Keywords

Graphene, Nanomaterials, Atomic force microscopy, XRD, Functionalization, Reduction

1. INTRODUCTION

Due to its fascinating physical, optical and mechanical properties, graphene has attracted a lot of research interests [1]. Since it was first obtained by mechanical exfoliation of graphite in 2004 [2], many other approaches have been utilized to produce high-quality graphene, for example, chemical vapor deposition (CVD) [3], epitaxial growth [4], transfer printing [5], solvothermal [6] and oxidation-dispersion-reduction [7]. Among these methods, the oxidation-dispersion-reduction process is widely used for it possesses great potential for large-scale synthesis of graphene.

The oxidation of graphite can introduce some oxygen-containing groups in the planar graphite [8], which makes it easy to be exfoliated and dispersed in water and other polar protic solvents. The exfoliated graphene oxide (GO) is nonconductive and has to be reduced and deoxygenated to gain conductive graphene. However, during the reduction

process, the exfoliated GO can be easily aggregated into graphite again. The organic functionalization of GO is proved to be effective to prevent the aggregation during reduction [9]. To date, the reported organic functionalized methods of graphene include the reaction of GO with isocyanate groups [10], amide coupling between carboxylic acid and alkylamine [11,12], aryl diazonium functionalization [13], and the functionalization through the 1, 3 dipolar cycloaddition of azomethine ylide [14]. After organic functionalization, the functionalized GO need to be reduced into conductive graphene. It is interesting to complete the organic functionalization and reduction at the same time.

In this work, we report the application of etherification reaction between 1-bromooctadecane (BOD) and GO to produce graphene soluble in organic solvents (Scheme 1). During the reaction process, the ether-functionalization occurs between GO and BOD accompanying by the simultaneous deoxygenation of GO. The synthesized octadecane-functionalized graphene (OD-G) can be stably dispersed in organic solvents. This method is facile, reproducible and effective to produce graphene soluble in organic solvents for some special applications in solar cells and light emitting devices.

2. EXPERIMENTAL PROCEDURES

2.1. Materials

Sodium nitrate ($NaNO_3$, 99%), potassium permanganate ($KMnO_4$, 99%), hydrogen peroxide (35%), pyridine (99%) and 1-bromooctadecane (BOD, 99%) were purchased from Aldrich. Purified natural graphite (SP-1) was purchased from Bay Carbon Company. All solvents were purchased from Aldrich.

2.2. Synthesis of octadecane-functionalized graphene (OD-G)

The GO was synthesized according to the modification of Hummers' methods [15]. In a typical preparation of OD-G, 50 mg of GO and 100 ml of dimethylformamide (DMF) were added to the flask with sonication for 1 hour to get a homogeneous dispersion. Five hundred milligrams BOD and 30 ml pyridine were added into the reaction mixture. The mixture was then heated to 115 ℃ and kept refluxing for 24 hours. To purify the OD-G, 100 ml ethanol was added to the mixture, followed by filtration with 0.45 μm PTFE membranes. The filter cake was washed with ethanol and acetone twice, separately. The as-prepared OD-G was then dissolved in tetrahydrofuran (THF) or dichlorobenzene (DCB) by sonication for 30 minutes.

2.3. Characterizations

Transmission electron microscopy (TEM) images were obtained using a JEOL 2010-H microscope (TEM) operating at 200 kV. The samples for the analysis were prepared by dropping dilute solutions of OD-G in DCB onto 400-mesh carbon-coated copper grids and leaving the solvent to dry. Atomic force microscopy (AFM) was carried out using a non-contact mode on a PSIA XE-150 scanning probe microscope. The AFM samples were prepared by spin coating the dispersion solutions of OD-G in DCB onto Si

substrates covered with 300-nm thick SiO_2. X-ray powder diffraction (XRD) patterns were taken on a Rigagu D/MAX 2500 V/PC diffractometer using Cu Ka radiation. FTIR spectra were recorded on a Bruker FT-IR spectrometer (Nicolet IS10) with solid powder samples. TGA was performed under dry air using a NETESCH STA 409 PC thermogravimeter with sample quantity from 5 to 6 mg. The samples were heated from room temperature to 900 ℃ at a rate of 10 ℃/min. The UV-Vis absorption spectra were taken at room temperature with the concentration of 0.1 mg/ml in THF using an UV/Vis/NIR spectrometer (JASCO. Corporation V-570). The current-versus-voltage (*I–V*) curves of thin films of GO and OD-G were measured on an MSTECH probe station. The dispersion solutions of exfoliated GO and OD-G were filtered to make the respective thin films, and each of these films was annealed at 120 ℃ to remove residual solvents.

3. RESULTS AND DISCUSSIONS

The morphologies of GO and OD-G are observed by TEM. As shown in Fig. 1a, the image of GO sheets is smooth with the average size of about 1 μm. The verge is quite clear while some tend to fold and roll. After functionalized with OD groups, the size of OD-G is about 0.5 μm, which is smaller than that of the original GO (Fig. 1b). During the functionalization, the reaction between oxygen groups from GO and BOD could split the larger graphene into smaller graphene sheets. Similar results were reported by Sun X.M. et al. [16]. The introduction of OD groups can effectively prevent the aggregation of GO during reduction. The AFM image of OD-G is shown in Fig. 2. The thickness of OD-G sheets is measured as ~1.7 nm according to the two-line scan, which is larger than the reported thickness (0.6 nm) of the graphene sheets by the annealing method in ultrahigh vacuum [16], and close to the data (2.0 nm) of octadecylamine functionalized graphene [11]. This suggests that the OD-G sheets are in monolayer. The larger thickness of OD-G is caused by the introduction of OD groups.

The FTIR spectra are tested for confirming the effective reduction and ether-functionalization with OD groups of GO. From Fig. 3a, the FTIR spectrum of OD-G presents the doublet bands at 2854 and 2923 cm^{-1}, which are attributed to the antisymmetric and symmetric C-H stretching vibrations of the $-CH_2-$ groups from OD groups [17]. The band centered at 1200 cm^{-1} is resulted from the C-O-C asymmetric stretch [18]. This suggests the ether-functionalization occurs between GO and BOD. In addition, the band at 1574 cm^{-1} is connected to the C=C skeletal vibration of reduced graphene sheets [19]. This indicates that GO has been effectively reduced during the functionalization process in pyridine at 115 ℃. McAllister et al. [20] reported the deoxygenation by the nucleophilic substitution between epoxy groups of GO and alkylamine or diaminoalkane. So we speculate that the reduction is associated with the nucleophilic attack of GO by pyridine. Meanwhile, for the FTIR spectra of OD-G at 50 ℃, the lack of bands at 1574 cm^{-1}, 2854 cm^{-1} and 2923 cm^{-1} suggests that GO is neither functionalized with OD groups nor reduced by pyridine at this temperature.

Fig. 3b shows the XRD patterns of GO and OD-G produced at 115 ℃. It can be seen that the XRD pattern of OD-G produced at 115 ℃ shows a broader peak of graphitic {002} diffraction plane at $2\theta=21.95^{o}$ which is resulted from the disordered stacking of

reduced graphene sheets [21]. This further confirms the effective reduction during the ether-functionalization. Additionally, the weak peak at $2\theta=8.76^{o}$ is associated with the {001} diffraction plane of OD-G. The corresponding interlayer spacing is 10.1 Å, which is larger than that of original GO due to the successful ether-functionalization with OD groups.

Thermo-gravimetric analysis (TGA) is used to measure the weight ratio of the functional groups. Fig. 3c gives the TGA curves of GO and OD-G. It can be seen that the mass loss of OD-G at 200 ℃ [22], which resulted from the removal of oxygen-containing groups, decreases significantly to 5% in comparison with that of GO. In addition, for the OD-G sample, the nearly 25% weight loss from 200 ℃ to 500 ℃ is assigned to the oxidative decomposition of the OD groups [12]. The TGA analysis further confirms that GO was successfully functionalized and effectively reduced during the etherification reaction with BOD, which is in accordance with the FTIR and XRD analyses.

The UV-Vis absorption spectra of GO and OD-G are shown in Fig. 3d. The absorption bands centered at 239 and 269 nm belong to the π–π^* transition of aromatic C-C bonds of GO and OD-G, respectively. The evident red shift is due to the removal of oxygen groups, which is in accordance with the result of reduced oleylamine functionalized graphene [23]. According to the current-versus-voltage curves of thin films of GO and OD-G (Fig.3f), the 200-nm-thick film of OD-G shows good conductivity of 71 S/m, while GO films is nonconductive. This further confirms that the effective deoxygenation takes place during the ether- functionalization between GO and BOD.

4. CONCLUSIONS

It has been shown that OD-G soluble in organic solvents is successfully obtained by a facile simultaneous ether-functionalization and reduction procedure in the mixture solvents of pyridine and DMF.The reduction and ether-functionalization of GO can be simultaneously completed at the same procedure. This method is facile, reproducible and promising to make graphene soluble in organic solvents for the future applications in organic solar cells and organic light emitting devices.

ACKNOWLEDGEMENTS

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List of Scheme

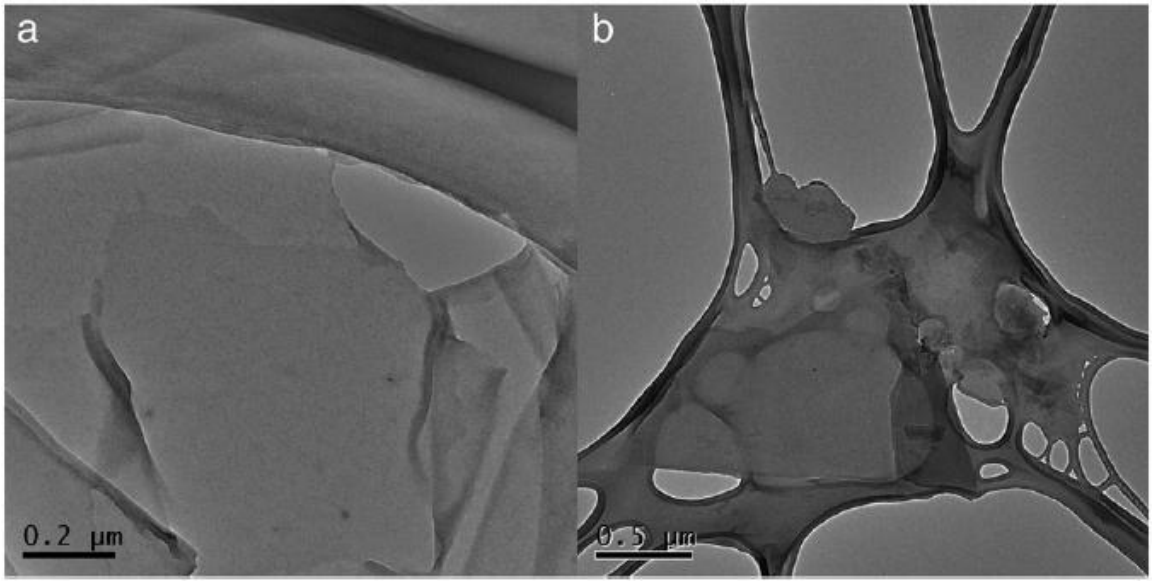


Figure 1

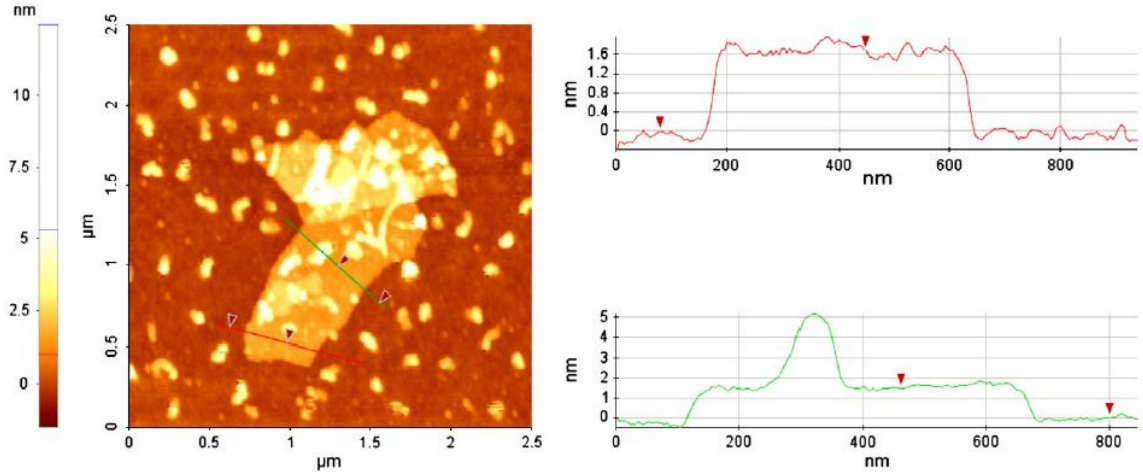

nm
10
7.5
5
2.5
0
µm
2.5
2
1.5
1
0.5
0
0
0.5
1
1.5
2
2.5
µm
nm
1.6
1.2
0.8
0.4
0
0
200
400
600
800
nm
nm
5
4
3
2
1
0
0
200
400
600
800
nm

Figure 2

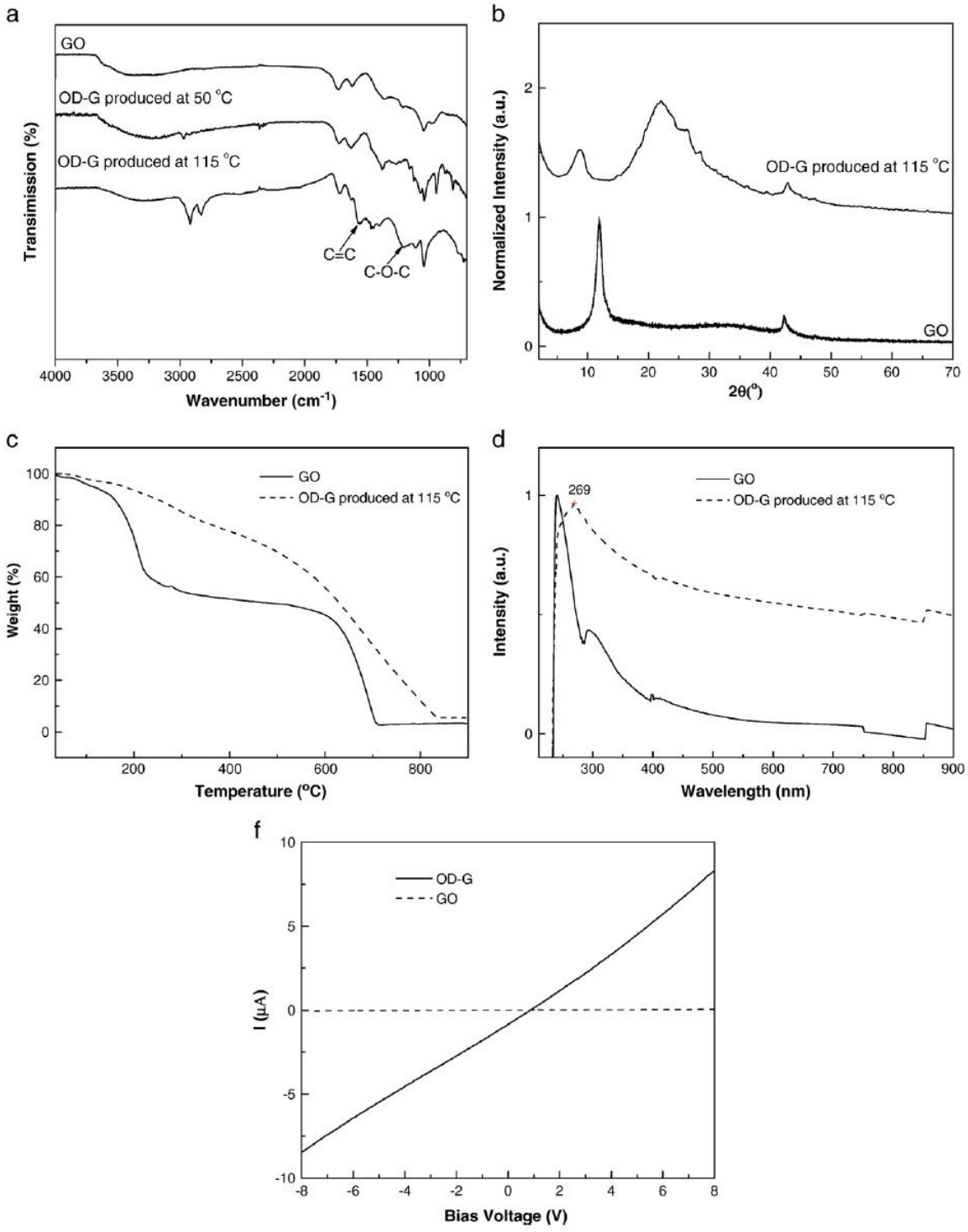
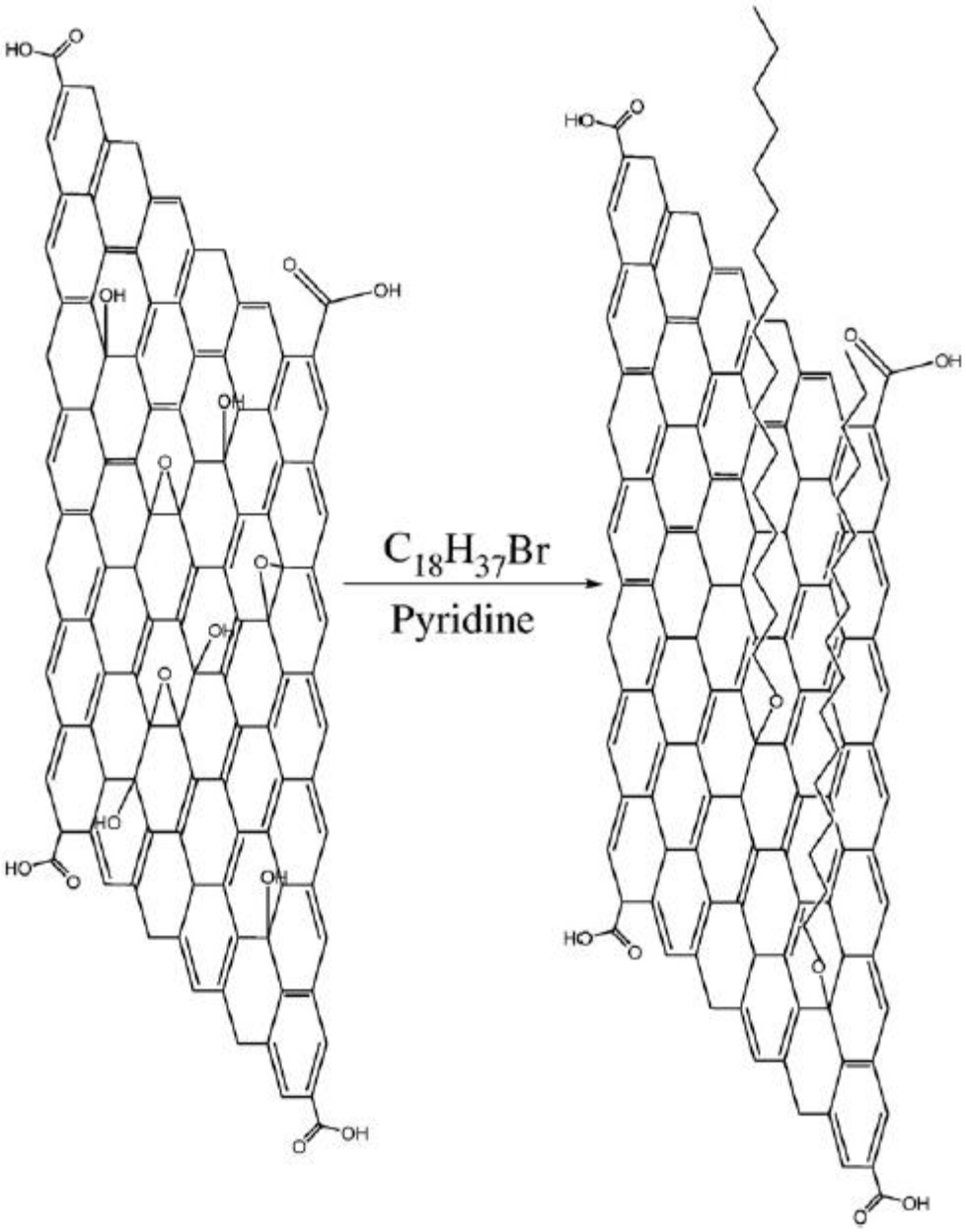

a
GO
OD-G produced at 50 °C
OD-G produced at 115 °C
C=C
C-O-C
Transimission (%)
Wavenumber (cm-1)
b
OD-G produced at 115 °C
GO
Normalized Intensity (a.u.)
2θ(°)
c
GO
OD-G produced at 115 °C
Weight (%)
Temperature (°C)
d
GO
OD-G produced at 115 °C
269
Intensity (a.u.)
Wavelength (nm)
f
OD-G
GO
I (μA)
Bias Voltage (V)

Figure 3



Scheme 1