Research Article

Functionalization of Graphene with Nitrile Groups by Cycloaddition of Tetracyanoethylene Oxide

Xiaojun Peng, Yang Li, Guoliang Zhang, Fengbao Zhang, and Xiaobin Fan

*State Key Laboratory of Chemical Engineering, Key Laboratory for Green Chemical Technology,
School of Chemical Engineering & Technology, Tianjin University, Tianjin 300072, China*

Correspondence should be addressed to Xiaobin Fan; xiaobinfan@tju.edu.cn

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Graphene has got considerable attention in both experimental and theoretical fields for its extraordinary properties. Covalent functionalization is an efficient strategy to render graphene additional properties and overcome its shortcomings such as zero band gap and nondispersibility in solvents. This study reports the synthesis and characterizations of a new kind of functionalized graphene, graphene-TCNEO, obtained by 1,3-dipolar cycloaddition. The graphene-TCNEO was systematically characterized by FTIR, Raman, XPS, SEM, TEM, and EDS mapping, and the covalent linkage between graphene and tetracyanoethylene oxide was firmly verified. Considering the great diversity of nitrile chemistry, the obtained graphene-TCNEO could be further transformed into other graphene-based derivatives with interesting properties.

1. Introduction

Graphene has got considerable attention from both experimental and theoretical fields for its extraordinary properties, such as large surface area, unique mechanical, thermal, optical, and electronic transport properties [1–3]. Although these properties endow graphene great potential in many practical applications, its inertness nature, zero band gap, and nondispersibility in solvents [4] weaken its competitive strength in the synthesis of composites, semiconductors, sensors, and so forth [5–8]. Therefore, functionalization of graphene [9] has attracted widespread attention in the past few years. Covalent functionalization [10–12] of graphene with organic atoms or molecules is of particular interest, as it can combine the unique properties of each component while overcoming the shortcomings of graphene as mentioned above. Through direct attachment of organic atoms or molecules to the C=C bonds of graphene [13, 14] and the rich covalent reactions of oxygen-containing groups in graphene oxide [15–17], a variety of strategies to functionalize graphene for different application purposes have been demonstrated. In this study, we report a method to introduce abundant nitrile groups to pristine graphene by cycloaddition reaction of graphene with tetracyanoethylene oxide [18–20] (TCNEO) (Scheme 1).

2. Experimental Details

The process for the functionalized graphene material is shown in Scheme 1. The mixture of desired 10 mg graphene prepared by the methods of high temperature expansion [21], 60 mg TCNEO, and 200 mL solution of 1,2-dibromoethane were added into a 250 mL round-bottomed flask and stirred and heated at 140°C to reflux for 24 h under N₂ atmosphere. After the reaction completed, the reaction mixture was filtered through nylon membrane. The obtained filter cake was washed several times by anhydrous ethanol and deionized water, respectively. The final product was suspended in deionized water through sonication and dried under vacuum freeze-drying to obtain the desired graphene-TCNEO.

The graphene and functionalized graphene were characterized by infrared spectrum (FTIR) (Thermo-Nicolet 380), X-ray photoelectron spectroscopy (XPS) (PerkinElmer, PHI 1600 spectrometer), Raman spectroscopy (NT-MDT NTEGRA Spectra), scanning electron microscopy (SEM) (Hitachi S4800), high-resolution transmission electron microscopy (HRTEM) (Philips Tecnai G2 F20), and energy dispersive spectroscopy (EDS) (Hitachi S4800).

SCHEME 1: Synthesis of graphene-TCNEO hybrid materials.

FIGURE 1: FTIR spectra of graphene and graphene-TCNEO, the peaks located at the 1399 cm^{-1} by the residual of solvent in the purge process.

FIGURE 2: XPS general spectra and curve fit of N 1s core-level spectra for graphene (a) and functionalized graphene (b), C 1s core level for graphene (c) and functionalized graphene (d), and O 1s core level for graphene (e) and functionalized graphene (f).

FIGURE 3: The Raman spectrum of graphene and grapheme-TCNEO.

FIGURE 4: SEM images of graphene (a) and functionalized graphene (b), TEM images of graphene (c) and functionalized graphene (d).

3. Results and Discussions

Graphene and tetracyanoethylene oxide were mixed and dispersed in 1,2-dibromoethane, followed by continuous reactions at 140°C for 12 h in the N₂ atmosphere. After being purified by repeated filtration and redispersion, the final product was obtained. As can be seen from Figure 1, the obtained grapheme-TCNEO shows the characteristic vibration of nitrile groups from TCNEO at 2210 cm⁻¹. Because of the conjugation effect caused by the conjugated structure of the attached graphene sheets, the vibration of the nitrile groups shifts to relatively lower wavenumber [22, 23]. In addition, two new peaks at 1527 cm⁻¹ and 1190 cm⁻¹ are also readily observed in grapheme-TCNEO, respectively and represent the skeletal vibration of the generated polysubstituted

homocyclic ring and the stretching vibration of the introduced C–O. These results will be further supported by later X-ray photoelectron spectroscopy (XPS) and Raman analysis.

Compared with the graphene (Figure 2(a)), a new peak at about 399 eV corresponding to the binding energy of N 1s is clearly observed in the obtained grapheme-TCNEO, attributed to the introduced nitrile groups (Figure 2(b)). In the corresponding high-resolution N 1s spectrum, there is a single peak binding in 399.18 eV that suggests the presence of nitrile groups [24]. Based on the elemental ratios, the degree of functionalization is calculated to be approximately 1 TCNEO group in 85 carbon atoms. Additional evidence for the introduction of TCNEO to graphene comes from the obvious increase of C–O bonds in the C 1s and O 1s spectra of the obtained grapheme-TCNEO (Figures 2(c)–2(f)).

FIGURE 5: The SEM image of the grapheme-TCNEO (a) and corresponding quantitative EDS element mapping of C (b), N (c), and O (d).

Raman spectra analysis [25] reveals a significant increase in the intensity ratio (I_D/I_G) of graphene after functionalization (Figure 3). Considering the G band and D band that represent the sp^2 C atoms and defects, respectively, it can be anticipated that the destructions of the sp^2 hybridization structure are raised from the successful cycloaddition reactions. This result matches up with the results of FTIR and XPS discussed above. Moreover, the noticeable red shifts (15 cm^{-1}) of the G band and D band are observed after the reaction, probably due to the introduced conjugated nitrile groups that alter the conjugate structure of the graphene basal plane.

The structural change of graphene before and after functionalizations was further investigated by scanning electron microscope (SEM) and transmission electron microscope (TEM). As can be seen from Figures 4(a) and 4(b), the obtained grapheme-TCNEO shows a wrinkled structure similar to the pristine graphene sheets. TEM images (Figures 4(c) and 4(d)) demonstrate that both the grapheme-TCNEO and graphene are semitransparent due to their thin natures and have the dark veins that simply resulted from overlapped regions of the graphene sheets. The corresponding quantitative energy dispersive X-ray spectroscopy (EDS) mappings (Figure 5) confirm that elements C, N, and O are homogeneously distributed on the surfaces of the obtained grapheme-TCNEO, providing visualized evidence for the successful functionalization of graphene with nitrile groups.

4. Conclusions

In summary, we report an efficient strategy to functionalize graphene with nitrile groups. Systematic characterizations

demonstrated that the nitrile groups were homogeneously introduced to the surfaces of graphene via the cycloaddition reaction with tetracyanoethylene oxide (TCNEO). Considering the diversity of nitrile chemistry, the obtained grapheme-TCNEO may be further transformed into other graphene-based derivatives with interesting properties.

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