Supporting information for

Effect of Graphene Oxide Coatings on the Structure of Polyacrylonitrile Fibers during Pre-oxidation Process

Mengmeng Qiao[1], Haijuan Kong[2,] *, Xiaoma Ding[1], Luwei Zhang[1], Muhuo Yu[1,] *

* Corresponding author: Haijuan Kong, E-mail: Konghaijuan@sues.edu.cn; Muhuo Yu, E-mail: dhuyumuhuo@163.com

Materials and methods

Materials

The graphite powder (99.5%, Jiangsu Legend Technology Co., Ltd., China). Sodium nitrate (99.98%), potassium permanganate (99%), sulfuric acid (98%), hydrogen peroxide (30%), hydrochloric acid (10%) and acetone (≥ 99.50%) were all acquired from Sinopharm Chemical Reagent Beijing Co., Ltd, China.

Methods

The graphene oxide (GO) used in this article was successfully prepared by the modified Hummers′ method[1].

Characterizations

The characteristic functional groups of the graphite and GO were recorded by Fourier transfer infrared (FTIR, Nicolet 6700, America) using the method of KBr troches with a range of 4000-500 cm^{-1}. The crystal structure of the graphite and GO was examined by X-ray diffraction (XRD, D/max 2550 VB, Bruker Co., Japan) using CuKα radiation (λ = 0.15418 nm) at 40 kV and 150 mA. The morphology and structure of the GO were studied by transmission electron microscopy (TEM, Talos F200S, German) and atomic force microscopy (AFM, Agilent 5500, Japan).

Results and discussion

TEM and AFM Analysis of the GO

TEM is often used to observe the morphology and evaluate the size of the nanoparticles. AFM as an analytical instrument can be used to study the surface structure of the solid materials including insulation materials. The TEM and AFM images give the microscopic morphology and basic dimensions of GO, as shown in Fig. 1. As can be seen from the TEM images, the single layer GO is a transparent sheet, however, it is easy to agglomerate, and the color of the agglomerated GO is dark since the GO has a relatively large specific surface area. The AFM images give the shape of the single layer GO with an irregular polygon and the thickness dimension about 25 nm, which is corresponding to some related reports[2, 3]. From the AFM and TEM images we can see that the single layer GO has been successfully prepared.

FI-IR Analysis of the GO and Graphite

The chemical structure of the compound can be determined according to the characteristic absorption frequency (wavenumber) of the Fourier infrared spectrum. Fig. 2 shows the FT-IR spectra of the GO and graphite. The infrared spectrum of the graphite has four characteristic peaks at 3432, 2924, 2860 and 1630 cm^{-1}, which are corresponding to the stretching vibrations of C-OH, symmetric -CH_2, asymmetric -CH_2 and the skeleton vibration of C=C[4, 5], respectively. When the graphite is oxidized, it forms a chemical bond with the O, which produces a large number of oxygen-containing functional groups, such as carboxylic acid groups, C=O of carboxyl groups

and phenolic hydroxyl groups, C=O of alcoholic hydroxyl groups and C-O-C of epoxy resin. Therefore, the infrared spectrum of the GO is very different from that of the graphite. The infrared spectrum of the GO has several new characteristic peaks at 1732, 1225, 1046 and 865 cm^{-1}, which are attributed to the C=O stretching vibration of the carboxylic acid group[6, 7], C-O stretching vibration of the carboxyl and phenolic hydroxyl groups[8], C-O stretching vibration of alcoholic hydroxyl group[9], and C-O-C stretching vibration of the epoxy[10], respectively.

XRD Analysis of the GO and Graphite

At present, X-ray diffraction (including scattering) has become an effective method for studying the microstructure of crystalline materials and certain amorphous materials. After the oxidative stripping of the graphite, the microstructure changes significantly due to the change of functional groups and the effect of stripping. Therefore, the preparation of the GO can be analyzed by XRD and the XRD spectra of the graphite and GO are shown in Fig. 3. The XRD spectrum of the graphite shows a sharp diffraction peak at $2\theta = 26.5°$, which corresponds to the (002) crystal plane reflecting the crystallization of graphite. After the graphite is oxidized, the diffraction peak at $2\theta = 26.5°$ is replaced by the diffraction peak at $2\theta = 10.5°$ corresponding to the (001) crystal plane of the GO. It can be known from $2d\sin\theta = n\lambda$ that the distance d between crystal faces increases when θ becomes smaller. The main reason for the change of peak is that the graphite will have oxygen added during the oxidation process to form many oxygen-containing functional groups and cause the space between the crystal faces to increase during the oxidation process.

References and Notes

1. D. C. Marcano, D. V. Kosynkin, J. M. Berlin, A. Sinitskii, Z. Sun, A. S. Slesarev, L. B. Alemany, W. Lu and J. M. Tour, *Acs Nano*, 2018, **12**.
2. L. He, X. Zheng, Q. Xu, Z. Chen and J. Fu, *Applied Surface Science*, 2012, **258**, 4614-4623.
3. Y. Feng, C. He, Y. Wen, Y. Ye, X. Zhou, X. Xie and Y. W. Mai, *Composites Part A Applied Science & Manufacturing*, 2017, **103**, 74-83.
4. Y. Zhang, Z. Min, J. Zhang, S. Qian, J. Li, L. Hang, L. Bo, M. Yu, S. Chen and Z. Guo, *Journal of Polymer Research*, 2018, **25**, 130.
5. W. Song, C. He, Z. Wang, Y. Gao, Y. Yang, Y. Wu, Z. Chen, X. Li and Y. Dong, *Carbon*, 2014, **77**, 1020-1030.
6. I. F. Pinheiro, F. V. Ferreira, D. H. S. Souza, R. F. Gouveia, L. M. F. Lona, A. R. Morales and L. H. I. Mei, *European Polymer Journal*, 2017, **97**, 356-365.
7. L. S. Cividanes, D. D. Brunelli, E. F. Antunes, E. J. Corat, K. K. Sakane and G. P. Thim, *Journal of Applied Polymer Science*, 2012, **127**, 544-553.
8. A. Yang, J. Li, Z. Chen, W. Zhang and M. Ning, *Applied Surface Science*, 2015, **346**, 443-450.
9. J. Ryu and M. Han, *Composites Science & Technology*, 2014, **102**, 169-175.
10. H. Zheng, Y. Shao, Y. Wang, G. Meng and B. Liu, *Corrosion Science*, 2017, **123**, S0010938X17301221.

Fig. 1

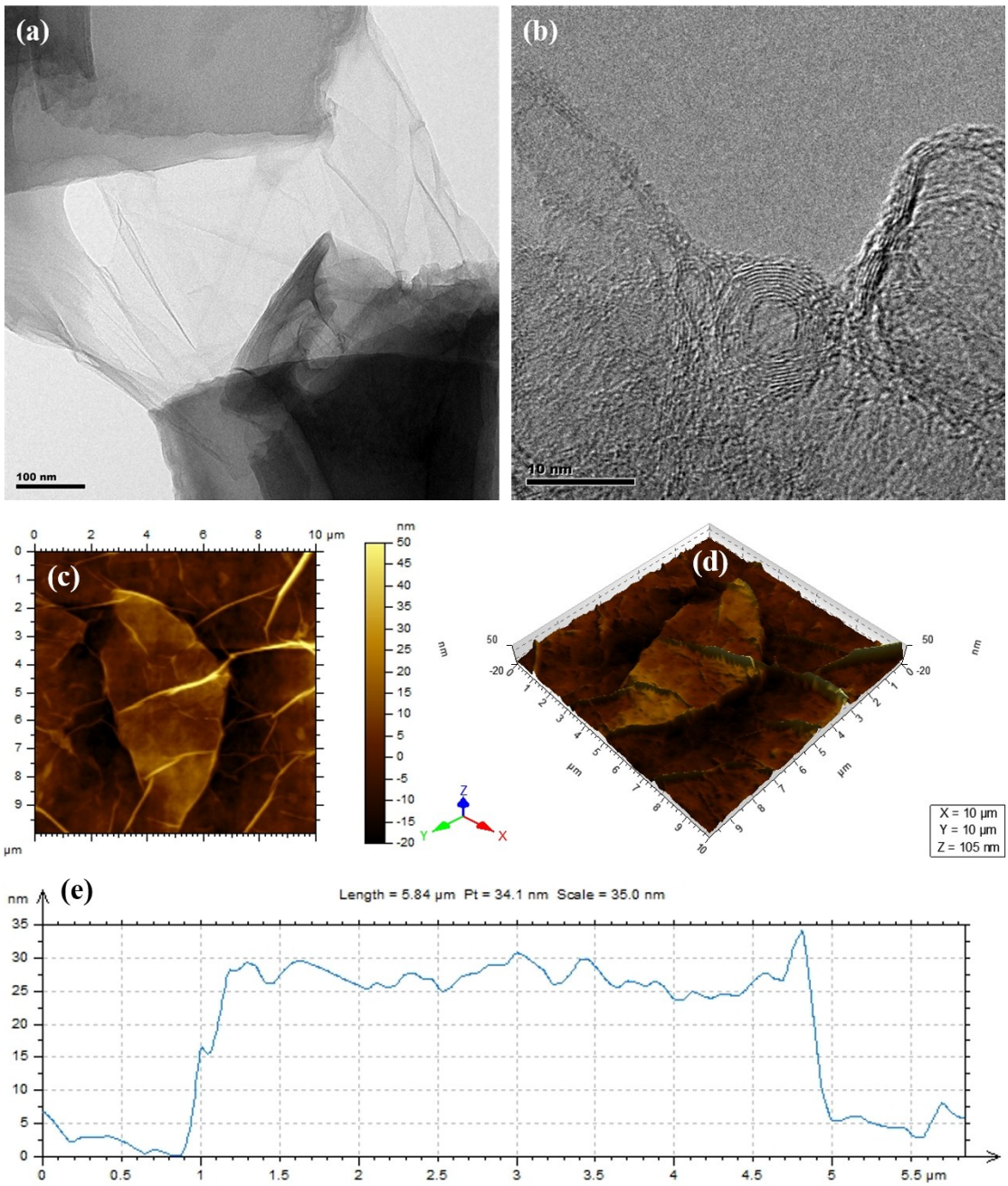

Fig. 1. TEM images (a), (b) of the GO, AFM images (c), (d) of the single layer GO and the cross-section height profile of the single layer GO (e).

Mengmeng Qiao, et al., Fig. 1

Fig. 2

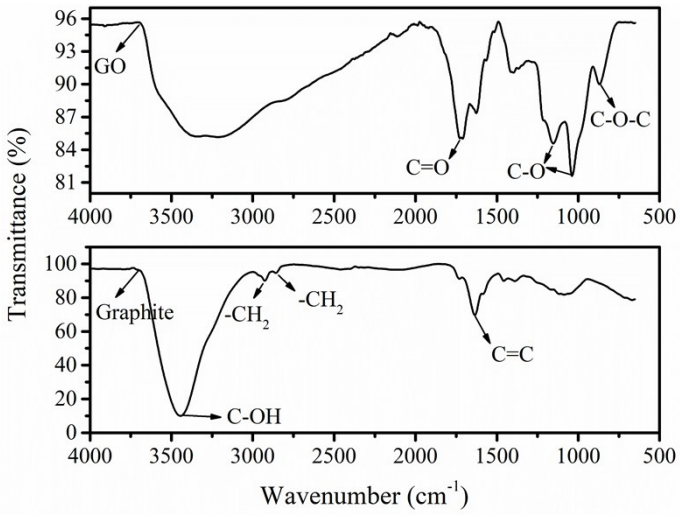

Fig. 2. FT-IR spectra of the GO and graphite.

Mengmeng Qiao, et al., Fig. 2

Fig. 3

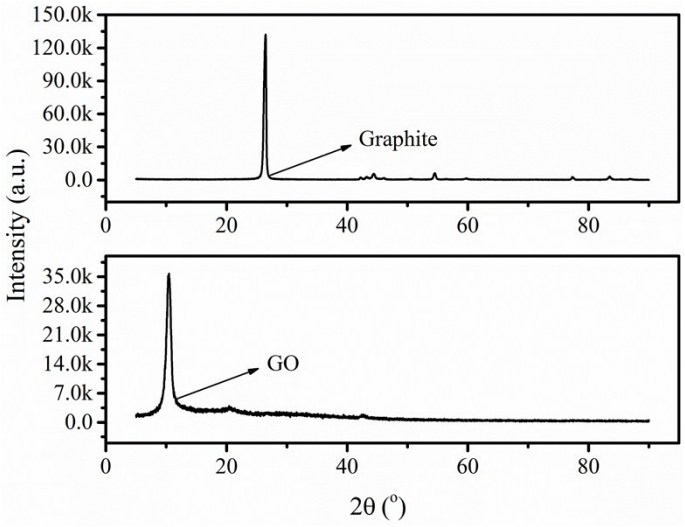

Fig. 3. XRD spectra of the GO and graphite.

Mengmeng Qiao, et al., Fig. 3