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Reduction and disorder in graphene oxide induced by electron-beam irradiation

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ABSTRACT

Structural changes caused by an electron beam with an absorbed dose of 500 kGy were investigated in graphene oxide (GO). In this paper, GO and irradiated GO were characterized by X-ray diffraction, Raman spectroscopy and X-ray photoelectron spectroscopy, respectively. It was found that the interlayer spacing of GO was decreased because of the alteration of functional group percent and the reduction effect. The graphitic structure of GO was also found to be disordered slightly. In addition, the samples were reduced partially after irradiation and electron-beam irradiation of GO appeared to be a promising procedure for large-scale synthesis of graphene.

1. Introduction

Graphene oxide (GO) is single- or few-layer graphite oxide which exhibits excellent performance. The tunable oxygenous functional groups of GO facilitate the modification on the surface and make it a promising material for composites with other materials [1,2]. It also works as the mediator to produce graphene, which is one of the most fascinating materials [3,4]. Transmission electron microscopes (TEM) is undoubtedly a useful tool for the investigation of nanostructures, but has the disadvantage that structural alterations of the specimen by inevitable electron irradiation can be severe and lead to misinterpretations [5]. Moreover, electron irradiation can be deliberately used to alter the chemical, mechanical and electronic properties of nano-materials [6]. However, few reports on the response of GO to electron-beam irradiation have appeared so far. In this paper, GO was irradiated by an electron beam with an absorbed dose of 500 kGy. The structural changes were investigated and the functional group alteration was illustrated.

2. Experimental

GO was synthesized with a Hummers method [7] and provided by Nanjing Xianfeng Nano Com. Ltd, China. The irradiation was performed by an industrial BF-5 electron accelerator operating at 5 MeV, with an adsorbed dose of 500 kGy and a beam current of 200 μA in ambient temperature in air. This procedure was different from the one recently reported in literature [6]. Temperature in irradiation was not controlled or monitored. The chemical character and morphology of GO and irradiated GO (IGO) were analyzed by X-ray diffraction (XRD, 1.54059Å Cu Kα 1 as wavelength), Raman (RENISHAW in Via Raman Microscope, recorded using 514 nm laser excitation with a power of 5 mW), and X-ray photoelectron spectroscopy (XPS, Thermo ESCALAB 250), respectively.

3. Results and discussion

The XRD spectra of GO and IGO are shown in Fig. 1. After irradiation in air, the intensity and diffraction angle of the peak (at approximately 11°), which represents the interlayer spacing of GO [8,9], went up and a small decrease of the interlayer spacing ranging from 8.22 to 7.91 Å (~3.8%) was apparent. This is possibly attributed to the alteration of functional groups. In addition, for XRD, the interlayer spacing of the materials is proportional to the degree of oxidation. Compared with pristine GO, the decreased interlayer spacing indicates less oxidized and so more reduced eventually, which agree with those reported in literature [3] and [9]. There also appear another two bands at 26° and 43° which are corresponding to the rather limited ordering for the limited few-layers in GO and the turbostratic band of disordered carbon materials, respectively [10]. These two bands display almost no change after irradiation.

Raman spectra of GO and IGO have been recorded in Fig. 2. The G band (sp^2-hybridized carbon) at 1580 cm^{-1}, and the D band (sp^3-hybridized carbon) at 1350 cm^{-1} [11] were recorded. As shown in Raman spectra, the intensity ratio of D to G band (I_D/I_G) and full width at half maximum

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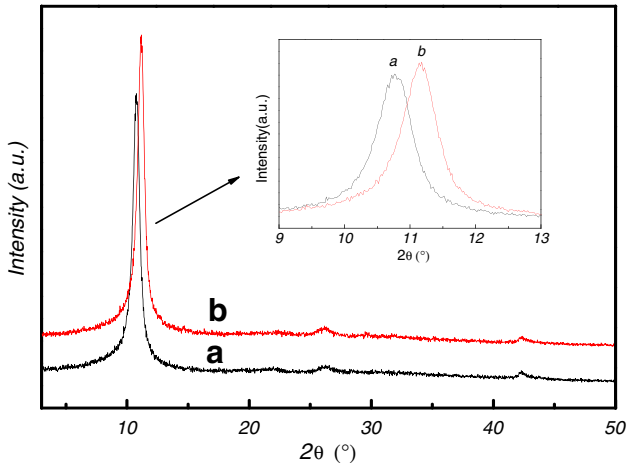

Fig. 1. XRD spectra of GO, (a) pristine and (b) irradiated by an electron beam.

of G band ($FWHM_G$) of GO slightly increased from 0.93 and 58.82 cm^{-1} to 0.98 and 59.78 cm^{-1} after electron irradiation, respectively. These results suggest that electron-beam irradiation is able to produce a limited amount of damage which causes the relative disorder. In addition, the occurrence of reduction effect during the irradiation process was also reflected in the increase of I_D/I_G. This change should be possibly attributed to a decrease in the average size of the sp^2 carbons upon IGO, but more numerous in number compared with pristine GO. The phenomenon is in good accordance with that indicated in literature [12].

The X-ray photoelectron spectroscopy (XPS) spectra of the samples supported the conclusions that GO was reduced partially and the GO structure was disordered slightly. The C1s peak of each GO sample was analyzed using a peak synthesis procedure, which combines Gaussian and Lorentzian functions [13]. The change of functional group percent is illustrated in Table 1. Due to the reduction effect of electron-beam on GO, the gross percent of the C—C (graphite C—C and amorphous C—C are contained) was increased from 32.82% to 35.95%. Moreover, the increase of the amorphous C—C and the decrease of the graphite C—C indicate the disorder of the GO structure. However, the XPS results showed that the O/C ratio was a little higher (from 41.54% to 43.45%) after irradiation treatment compared with the untreated sample. This may be attributed to oxygen adsorption which was caused by electron-beam irradiation in the air environment [14].

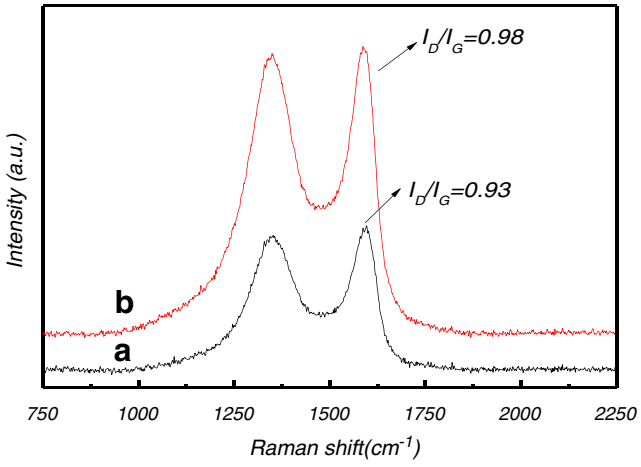

Fig. 2. Raman spectra of GO, (a) pristine and (b) irradiated by an electron beam.

Table 1
The change of functional group percent.

Functional groups	Graphite C—C	Amorphous C—C	—C—OH	—C=O	—COOH
Binding energy (eV)	284.2	285.5	286.2	287.8	289.0
GO	14.34%	18.48%	14.67%	36.40%	16.11%
IGO	12.18%	23.77%	20.12%	34.54%	9.39%

4. Conclusions

Electron beam irradiation decreased the inter-layer distance of GO from 8.22 to 7.91 Å and disordered their structure in air. The samples were also found to be reduced partially by the irradiation. In addition, the percent of oxygen groups was altered and the number of gross C—C bonds was increased from 32.82% to 35.95%. It is worth expecting that the reduction of GO with electron irradiation becomes an economical and efficient method for a large-scale production of graphene in the future.

Acknowledgments

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References

[1] Wang HL, Hao QL, Yang XJ, Lu LD, Wang X. ACS Appl Mater Interfaces 2010;2:821–8.
[2] Si Y, Samulski ET. Nano Lett 2008;8:1679–82.
[3] Marcano DC, Kosynkin DV, Berlin JM, Sinitskii A, Sun ZZ, Slesarev A, et al. ACS Nano 2010;4:4806–14.
[4] Hye-Mi J, Seung Hun H, Seong-Ho C, Hong-Lim L. Mater Lett 2010;3:357–60.
[5] Banhart F. Rep Prog Phy 1999;62:1181–221.
[6] Teweldebrhan D, Balandin AA. Appl Phys Lett 2008;94:013101.
[7] Hummers WS, Offeman RE. J Am Chem Soc 1958;80:1339.
[8] McAllister MJ, Li JL, Adamson DH, Schniepp HC, Abdala AA, Liu J, et al. Chem Mater 2007;19:4396–404.
[9] Zhang L, Li X, Huang Y, Ma YF, Wan XJ, Chen YS. Carbon 2010;48:2367–71.
[10] Xu ZW, Huang YD, Min CY, Chen L, Chen L. Radiat Phys Chem 2010;79:839–43.
[11] Stankovich S, Dikin DA, Dommett GHB, Kohlhaas KM, Zimney EJ, Stach EA, et al. Nature 2010;442:282–6.
[12] Stankovich S, Dikin DA, Piner RD, Kohlhaas KA, Kleinhammes A, Jia Y, et al. Carbon 2007;45:1558–65.
[13] Xu ZW, Huang YD, Zhang CH, Liu L, Zhang YH, Wang L. Compos Sci Technol 2007;67:3261–70.
[14] Dillon AC, Jones KM, Bekkedahl TA, Kiang CH, Bethune DS, Heben MJ. Nature 1997;386:377–9.