Oxidation and disorder in few-layered graphene induced by the electron-beam irradiation

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Structural changes caused by an electron beam with the high irradiation energy of 5 MeV were investigated in few-layered graphene. Both the original and the irradiated few-layered graphene were characterized by x-ray diffraction, Raman spectroscopy, and x-ray photoelectron spectroscopy. It was found that a typical diffraction peak of graphene oxide emerged and this may be attributed to a partial oxidation in few-layered graphene which was induced by the irradiation. In addition, the graphitic structure of few-layered graphene was found to be disordered according to the increased intensity ratio of D to G band. © *2011 American Institute of Physics*. [doi:10.1063/1.3587798]

Graphene, a single atomic layer of sp^2-hybridized carbon, has attracted tremendous attention owing to its strictly two-dimensional structure and a wide range of unusual properties. Graphene research has developed at a truly relentless pace.[1–6] Few-layered graphene (FLG), which is composed of several individual graphene layers, is now also under intensive investigation.[7] Transmission electron microscope is undoubtedly a useful tool for investigation of free standing graphene sheet, but has the disadvantage that structural alterations of the specimen by inevitable electron irradiation can be severe and lead to misinterpretations.[8,9] Moreover, electron irradiation can be deliberately used to alter the chemical, mechanical, and electronic properties of nanomaterials. The problem of changes in graphene lattice induced by the low and medium energy electron-beam irradiation was originally addressed by Teweldebrhan and Balandin.[10] The structure and electrical properties of graphene were also found to be tuned by the medium energy electron-beam irradiation.[11–16] In this letter, FLG was irradiated by an electron beam with the high energy of 5 MeV. The structural changes were investigated and the alterations of functional group percent were illustrated.

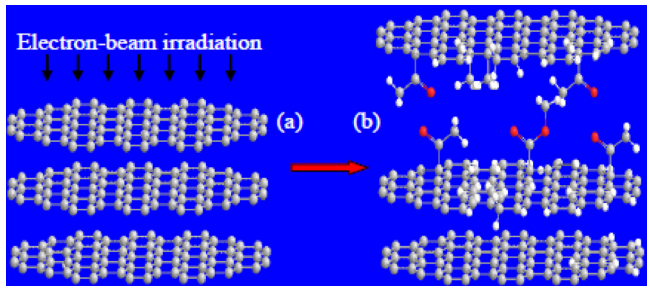

FIG. 2. (Color online) Illustration of the irradiation process, (a) pristine and (b) irradiated FLG.

FLG was synthesized with the method of chemical exfoliation[17] 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 a fluence of 5.01 C/cm^2 and a beam current of 200 μA in ambient

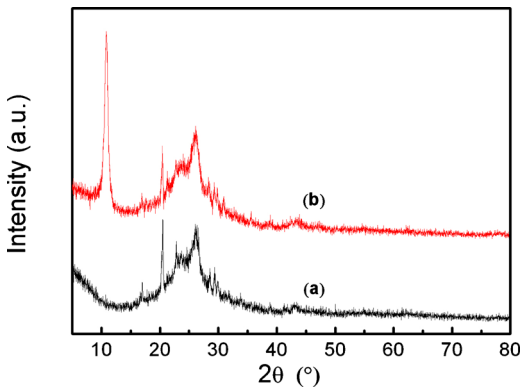

FIG. 1. (Color online) XRD spectra of FLG, (a) pristine and (b) irradiated by an electron beam.

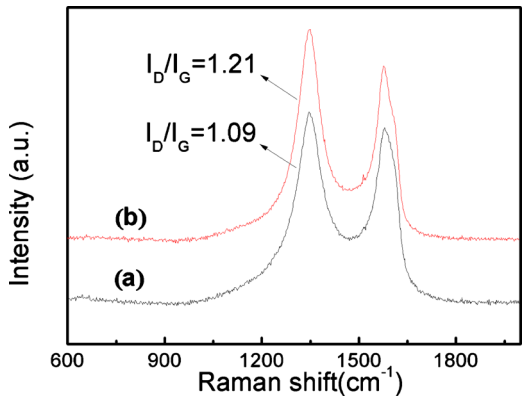

FIG. 3. (Color online) Raman spectra of FLG, (a) pristine and (b) irradiated by an electron beam.

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TABLE I. The change in functional group percent.

Functional groups	Graphite C—C	Amorphous C—C	—C—OH	–C=O	—COOH
Binding energy (eV)	284.1–284.6	285.3–285.7	286.0–286.7	287.4–288.0	288.7–289.4
FLG (%)	62.76	16.66	7.71	4.52	8.35
Irradiated FLG (%)	61.87	13.70	13.43	7.36	3.74

temperature in air. This procedure was different from the one recently reported in literature.[10] Chemical character and morphology of the original and the irradiated FLG were analyzed by x-ray diffraction (XRD, 1.540 59 Å Cu $K\alpha 1$ as wavelength), Raman (RENISHAW inVia Raman Microscope, recorded using 514 nm laser excitation with a power of 5 mW), and x-ray photoelectron spectroscopy (XPS, Thermo ESCALAB 250).

XRD spectra of the original and the irradiated FLG are shown in Fig. 1 and the irradiation process is illustrated in Fig. 2. Both the original and the irradiated FLG have diffraction peak at $2\theta=26.4°$ (d=0.34 nm). The peak with d=0.34 nm is corresponding to the normal graphite spacing, and this is consistent with the ordering for the few-layers in FLG [see Fig. 2(a)].[2] However, there is a diffraction peak for irradiated FLG at $2\theta=12.0°$ (d=0.74 nm). For XRD, the interlayer spacing of the materials is proportional to the degree of oxidation.[18] The peak with d=0.74 nm should come from the intergraphene oxide (GO) diffraction, corresponding to the typical diffraction peak of GO.[9] This XRD result indicates that the electron-beam irradiation results in partial oxidation in FLG to yield GO structure [see Fig. 2(b)].

Raman spectra of the original and the irradiated FLG are shown in Fig. 3. The G band (sp^2-hybridized carbon) at 1580 cm^{-1}, and the D band (sp^3-hybridized carbon) at 1350 cm^{-1} are recorded.[3] As shown in Raman spectra, the intensity ratio of D to G band (I_D/I_G) of pristine FLG is much higher than the one indicated in the recent work.[10] It is due to the fact that the graphitic structure was not fully restored and significant defects were introduced during the preparation procedure.[19] I_D/I_G was found to be increased from 1.09 to 1.21 after electron irradiation. The observed modification may be attributed to the formation of vacancies, which were induced by knock-on damage because of the high energy irradiation.[10,20] The mechanism of I_D/I_G increase is different from that in Ref. 10 due to a higher electron energy used in this work.

The XPS results of the samples support the conclusions that FLG was oxidized partially and the graphene structure was disordered slightly. The C 1*s* peak of each FLG sample was analyzed using a peak synthesis procedure, which combines Gaussian and Lorentzian functions.[21] The changes in the percent of functional groups were illustrated in Table I. Due to the oxidation effect of electron-beam on FLG, the gross percent of the C—C (graphite C—C and amorphous C—C are contained) was decreased from 79.42% to 75.57%. Furthermore, the decrease in graphite C—C indicates the disorder of graphene structure. However, the XPS results show that there is a slight decrease in the O/C ratio (from 9.26% to 8.59%) after irradiation. This is not contrary to the oxidation results which were summarized above. It is possibly due to the fact that oxygen groups between the interlayers of FLG cannot be explored. It may also be attributed to the sharp decrease in —COOH and the increase in —C—OH.

In summary, high energy electron-beam irradiation is a powerful tool to modify the structure and composition of FLG by creating vacancies and changing the percent of functional groups. FLG was found to be partially oxidized and disordered from the appearance of typical GO diffraction peak and the increase in I_D/I_G after irradiation. This work revealed that more attention should be paid to the structure alteration induced by electron-beam irradiation. Moreover, high energy electron-beam irradiation may be a promising way for the large-scale functionalization of FLG.

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