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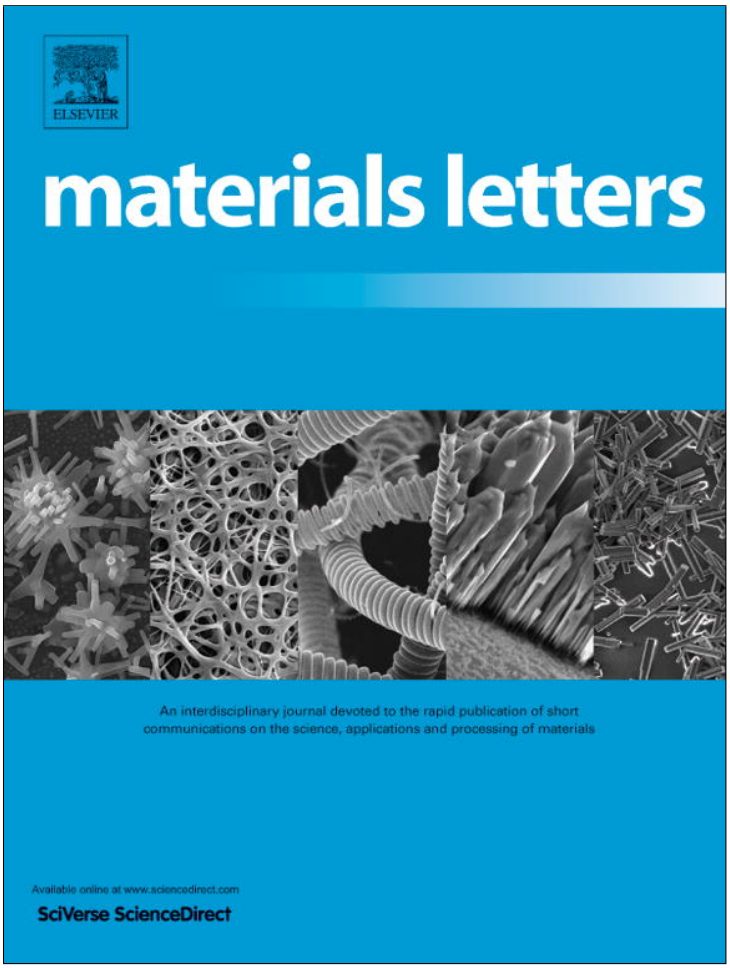

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Preparing graphene with notched edges and nanopore defects by γ-ray etching of graphite oxide

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ABSTRACT

Graphene nanostructures with notched edges and nanopore defects were produced by the γ-ray irradiation of the graphite oxide in polar solvents. Because of the grafting of the long polymer chains, the thickness of the graphene monolayers is shown to be significantly increased. In addition, the graphitization degree got increased in unetched regions of the irradiated graphene due to the annealing effect induced by irradiation from the Raman investigation. Spontaneously interlocking between the etching graphene and polymer matrix will be arisen with the formation of these nanostructures. The development of graphene with large contact area and nanopore volume may be of use in composites and sensors.

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1. Instruction

The discovery of graphene with its combination of extraordinary physical properties and ability to be dispersed in various polymer matrix has created a new class of polymer composites [1]. It was widely used in composites due to its easily controlled electronic, chemical, or mechanical properties [2,3]. In the development of high mechanical performance polymer composites, the good dispersion and a strong interface between nanofillers and polymer matrix are two key issues [4]. However, the trim edge of graphene weakens the interfacial interaction between graphene and the polymer matrix and the efficient use in sensors. In this paper, our attention focuses on the γ-ray etching on the edge and plane of graphene in the presence of polar solvent like styrene. The resulted graphene with notched edges and nanopore defects may highly improve the effect of the interface in the functional composites.

2. Experimental

Graphite oxide (GO) used in our experiment were prepared by the chemical method as described in [5]. The samples were prepared with the dispersion of 100 mg GO in 100 ml styrene/toluene (50 ml:50 ml) solution using an ultrasonic bath for 5 min. The mixture was then exposed to ^{60}Co γ-ray source under the condition of an absorbed dose 200 kGy with 2.0 kGy/h dose rate at room temperature, which had been proved to affect the structures of carbon systems significantly in our previous work [6,7]. After the irradiation, the sample was washed with acetone, ethanol and distilled water to remove the physically adsorbed polystyrene away and the resulting (or irradiated) graphene was achieved. For comparison, the pristine graphene was produced by sonicating GO in water for 2 h. The morphologies and the microstructures of the graphene were characterized by atomic force microscopy (AFM) and Raman spectroscopy before and after irradiation, respectively. All of these procedures have been conducted more than twice to make sure the reproducibility of the experimental results.

3. Results and discussion

The AFM images of pristine and irradiated graphene are shown in Fig. 1. The thickness of the pristine and irradiated graphene layers is about 1.31 and 1.90 nm, respectively. It is noteworthy that the height value may be higher than that of the pristine graphene monolayers but lower than bilayers due to the polystyrene chains grafted on nanosheet surfaces [1]. This grafting mechanism should be explained as the formation of free radicals via radiolysis of monomers, the production of radicals on nanosheet surfaces and the covalently bonding of the functionalized polymers on the surface of nanosheets by γ-rays in the solvent surrounding the sample surface [8]. In addition, amount

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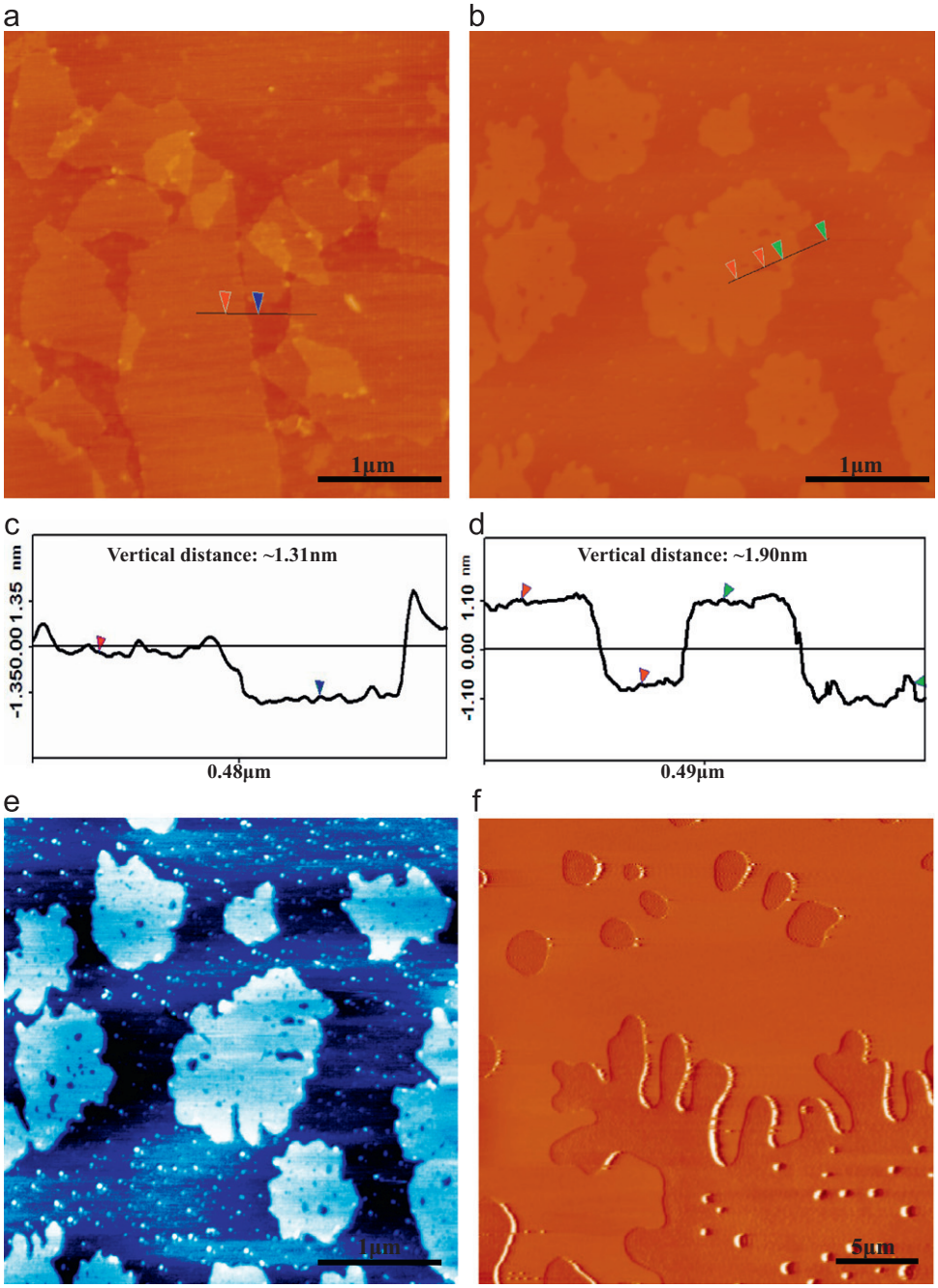

Fig. 1. (a and c) Tapping mode AFM topographic images and height profiles of graphene from the sonicated GO for 2 h, under AFM scanning size of 5.5 μm × 5.5 μm, (b and d) tapping mode AFM topographic images and height profiles of graphene from the irradiated GO in tetrahydrofuran (THF), under AFM scanning size of 5 μm × 5 μm, (e) the strengthened image of image (b), (f) tapping mode AFM topographic of graphene from the irradiated GO in THF, under AFM scanning size of 50 μm × 50 μm.

of functionalized single-layer graphene sheets are emerged due to the self-exfoliation of GO induced by the grafting of long-chain polystyrene (Fig. 1(b)). In contrast to pristine graphene (Fig. 1(a)), the irregular nanopore appeared in plane, and the trim edge was cut so that graphene with notched edges was prepared owing to the radiolysis promoting C–C bond breaking in the nanosheets under γ-rays (Fig. 1(b)) [9]. These irregular nanopores and cut edges of irradiated graphene could be observed more clearly in Fig. 1(e). Fig. 1(f) showed that small graphene sheets separated from the whole lamellas due to the γ-ray etching, and the structure of the small graphene sheets is in accordance with that in Fig. 1(b). Therefore, γ-ray irradiation is capable of creating radiation defects at certain points which is proved by the illustrations of AFM. Spontaneously interlocking between the etching graphene and polymer matrix will be arisen with the formation of these nanostructures. The development of an interlocking microstructure of graphene-based composite makes graphene potentially more favorable for altering the matrix properties—such as the mechanical, rheological and permeability properties, and degradation stability [10].

Fig. 2 shows the Raman spectra of graphene before and after γ-ray irradiation. The bands at 1579 and 1348 cm^{-1} in the Raman spectra (Fig. 1(g)) are assigned to the G band (associated with the vibration of sp^2 carbon atoms in a graphitic 2D hexagonal lattice) and D band (related to the vibrations of sp^3 carbon atoms of defects and disorder) [11]. It was found that the D mode is increased apparently due to the formation of the disorders induced by the bond breaking under γ-rays [12], which was

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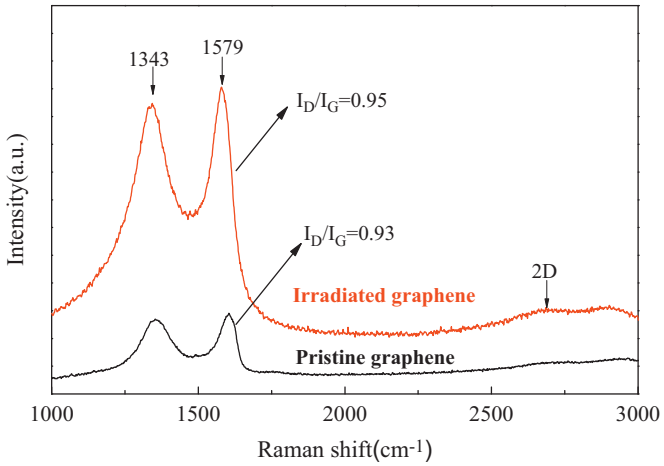

Fig. 2. Raman spectra of pristine and irradiated graphene.

supported by formation of notched edges and nanopore defects in AFM results. However, the intensity ratio of D band to G band (I_D/I_G) in the Raman spectra increased negligibly from 0.93 to 0.95 after the irradiation. This may be attributed to the reality of using edge and basal plane defects to allow an analogous photo-polymerization process without disturbing the conjugation of the as-prepared material. In addition, the restoration of the sp^2 carbon in certain area of irradiated graphene could even been observed from the increased G band intensity owing to the annealing effect under γ-rays. This annealing effect was further supported by the increase of 2D peak at $\sim$2680 cm^{-1} due to the lattice vibration induced by electronic energy deposition of γ-rays [13].

4. Conclusions

Summing up, graphene with notched edges and nanopore defective nanostructure was obtained by exposing the mixture of GO and polar solvent to ^{60}Co γ-ray source at room temperature. Owing to the self-exfoliation of GO induced by the grafting of polystyrene, a number of graphene monolayers were emerged. The γ-ray irradiation made contribution to not only the etching of graphene defects, but also the restoration of sp^2 carbon in graphene due to the annealing effect. And the resulted graphene produced by this method can potentially be used to develop polymer composite materials and sensors.

Acknowledgments

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