

DOI: 10.1002/adma.200702149

Turning PMMA Nanofibers into Graphene Nanoribbons by In Situ Electron Beam Irradiation

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Much of the discussion of the future prospects of nanotechnology is currently centered around carbon-based nanostructures,^[1–3] including fullerenes, nanofibers, nanotubes, and graphenes. In the past 10–20 years, fullerenes^[4–6] and nanotubes^[7–10] have attracted a great deal of attention because of their special properties, however, they are still far from finding large-scale application in nanoelectronics because it is hard to precisely control their diameter, position, and conductive type. Recently, graphene has become a new rising star on the horizon of materials science and condensed-matter physics.^[11–13] It is a perfect two-dimensional (2D) material, which is of interest for both theoretical research and electronic applications. Its combined properties of ballistic transport at room temperature with chemical and mechanical stability make it a promising candidate for nanoelectronics. These remarkable properties can also extend to bilayer and few-layer graphenes. Until now, graphenes have been fabricated by micromechanical cleavage of bulk graphite,^[12–14] epitaxial growth on metal substrates by chemical vapor deposition (CVD),^[15,16] and thermal decomposition of silicon carbide (SiC).^[17,18] Compared to carbon nanotubes, graphenes are comparatively easy to fabricate and manipulate in a designed and controlled way. Considering the abilities of large-scale fabrication and high integration, bilayer or few-layer graphenes with narrow width are more realistic for applications. However, although graphenes can be obtained by the three abovementioned methods, the fabrication of graphenes is still in its relative infancy and there is much to be learnt about how to control the number of layers and the width of the graphene. In this Communication, we report a method of preparing graphene nanoribbons in a fine-tuned way by in situ electron beam irradiation of ultrathin poly(methyl methacrylate) (PMMA) nanofibers. We chose PMMA as the irradiation material because it is a standard high-resolution electron resist. Combined with

electron beam lithography (EBL) overexposure, it would have the possibility of being applied in the production of high-resolution graphitic nanostructure circuits.

PMMA nanofibers were prepared by electrospinning.^[19,20] In situ electron beam irradiation was carried out in a commercial transmission electron microscope (JEOL JEM 2010F) operated at an accelerating voltage of 200 kV. Figure 1a shows a PMMA nanofiber with an average diameter of ca. 7 nm. When it was irradiated by an electron beam with an intensity of about $10^6 \text{ e nm}^{-2} \text{ s}^{-1}$ for 60 s (the corresponding dose was about 1000 C cm^{-2}), its diameter decreased and it was gradually carbonized and graphitized (Fig. 1b). As the electron irradiation continued for another 60 s, the diameter further decreased and it was graphitized perfectly (Fig. 1c). The lattice fringes along the axis of the nanofiber were clearly observed with the same interlayer spacing of ca. 0.33 nm. The selected area electron diffraction (SAED) pattern of the graphitized nanofiber (Fig. 1d, corresponding to the selected area in Fig. 1c) is shown in Fig. 1e. From the pattern, two main diffraction spots corresponding to the (0002) facet can be seen, which indicates that this graphitized nanofiber was of single-crystalline nature and the graphite sheets were well formed by the action of the electron beam. The selected area was small, so it was difficult to obtain the diffraction spots from other facets. As far as we are aware, there are no previous reports of transforming PMMA nanofibers into carbon nanofibers and graphitic nanoribbons. These results lead to four interesting issues as outlined below. First, how was PMMA carbonized? Second, why did the diameter of the nanofiber decrease? Third, how could it form a perfect graphene nanoribbon? And fourth, what was its three-dimensional (3D) structure?

As to the first issue, it is well known that for some polymers, such as polyacrylonitrile (PAN)^[21,22] and polypyrrole (PPy),^[23] fibers can be transformed into amorphous carbon fibers under high temperature in vacuum. Also hydrocarbon gas can be decomposed into amorphous carbon under high-intensity electron irradiation, which is known as electron-beam-induced deposition (EBID).^[24,25] Both of the abovementioned processes involve chain-scission of polymers. PMMA is a positive electron resist, and therefore the macromolecular chains can also be scissored into small molecular chains under electron beam irradiation. As long as the irradiation density is suitable and the irradiation time is long enough (overexposure), most of the oxygen and hydrogen atoms are lost as vapor and only carbon atoms remain. In fact, the overexposure process has been researched and applied for many years,^[26–28] to transform

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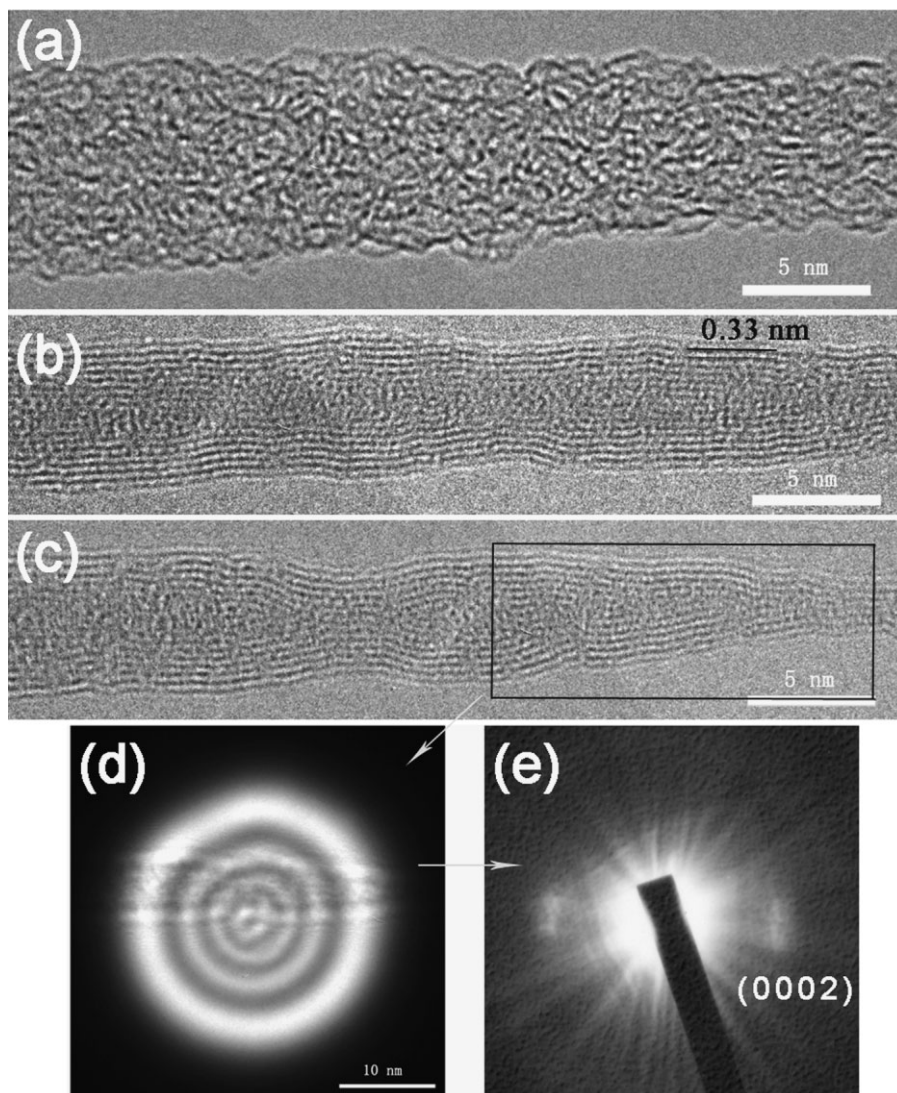


Figure 1. HRTEM images of the PMMA nanofiber: a) original state with diameter about 7 nm, b) after 60 s electron irradiation, c) after 120 s electron irradiation. d) Selected-area electron microscopy image. e) Electron diffraction pattern for the area outlined in (c).

PMMA from a positive resist to a negative resist and the remainder cannot even be dissolved in acetone. However, the mechanism of this process has never been studied in detail because it is so complicated. In this Communication, we use high-resolution transmission electron microscopy (HRTEM) to show how overexposure can turn PMMA into carbon, which leads to the transformation of PMMA from a positive to a negative resist.

For the second and third issues, it is also well known that high-energy electron beam irradiation can cause a “knock-on” effect, which results in graphitization of amorphous carbon and atom sputtering.^[29–34] Considering the mass loss of the oxygen and hydrogen and the atom sputtering, the decrease of diameter of the nanofiber was reasonable. As to the ordering of graphite layers, we believe it is related to the ordering of the molecular chains of PMMA. A single 950 K PMMA chain has 9500 MMA monomers, and the length of the chain can be

several micrometers with a diameter of ca. 1 nm. When PMMA molecular chains form a sub-10 nm nanofiber, the chains are thought to self-assemble. Besides, such chains tend to self-assemble by electric-field-induced stretching in electrospinning, which is just like DNA^[35,36] and single-walled carbon nanotubes.^[37,38] To investigate whether PMMA molecular chains were ordered, two crossed nanofibers were irradiated (Fig. 2c). Figure 2a is the initial state and Figure 2b is the state after irradiation for 10 min. From Figure 2b, it is found that the lattice fringes were disordered in the crossed part (corresponding to the selected area in Fig. 2c) but highly ordered in the uncrossed parts (marked by 1, 2, 3, and 4). The SAED pattern (Fig. 2d) for the crossed part (outlined area in Fig. 2c) shows concentric rings, which indicates the structure was polycrystalline. These results suggest that ordering of PMMA chains occurred and it was a necessary condition for forming graphene nanoribbons.

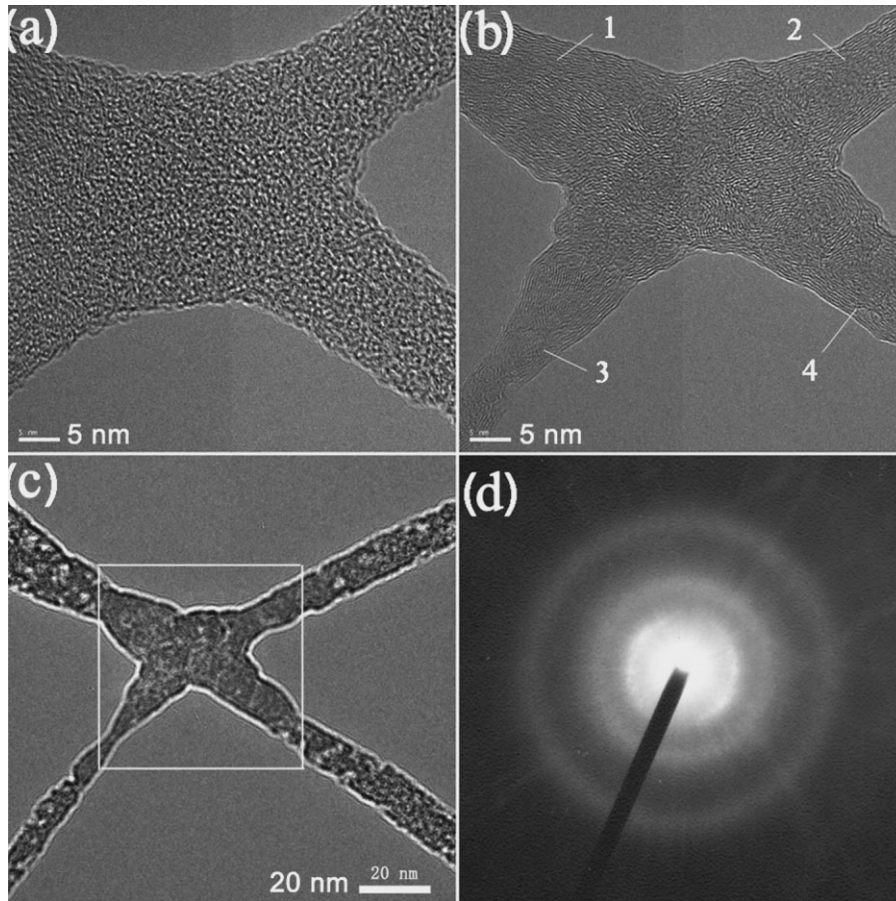


Figure 2. HRTEM images of two crossed PMMA nanofibers: a) original state, b) after 10 min of electron irradiation. c) Low-magnification image of the crossed nanofibers. d) Electron diffraction pattern for the area outlined in (c).

Concerning the fourth issue, namely the 3D structure of the nanoribbon, our results indicate the nanoribbon was formed by graphite sheets stacking layer by layer and the sheets were parallel to the incident electron beam. Because the initial state of the graphene nanoribbon was a columned nanofiber, the width of the middle graphene was the greatest and the outermost graphene was narrowest. A schematic diagram of the cross section of the ribbon is shown in Figure 3a. As the irradiation time increased, the graphenes peeled from both sides to the middle layer by layer and the width became narrower and narrower, as shown schematically in Figures 3b–d. Perhaps the critical question here is why the graphene sheets were parallel to the incident electron beam. Based on calculations, simulations, and experiments,^[39,40] irradiation damage of columned atomic layers such as carbon nanotubes is anisotropic because the ejection threshold energy for atoms on the top and bottom surfaces is less than that for the atoms on the sides; namely, atoms facing the electron beam are preferentially removed compared to atoms on the sides. For this reason, the graphene layers tend to align parallel to the electron beam.

When the irradiation process was controlled carefully, the number of graphene layers could be fine-tuned precisely, as

shown in Figure 4. The original diameter of the nanofiber was about 16 nm. To increase the rate of graphitization, a smaller spot size was used to obtain higher electron intensity. When the spot size was small enough, the electron intensity obeyed a Gaussian distribution. The electron intensity at the middle of the spot was obviously larger than that at the edge, which resulted in a faster rate of graphitization and atom sputtering,

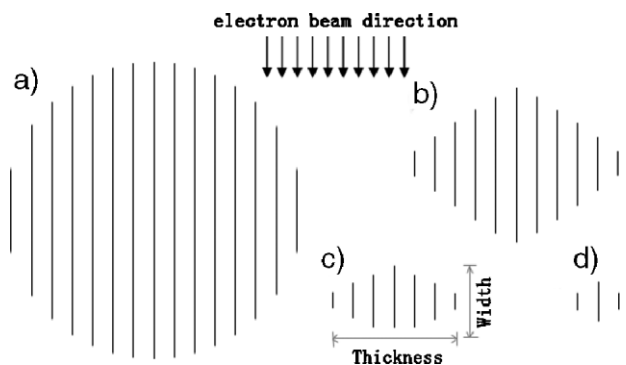


Figure 3. Schematic diagram of the cross section of the graphene nanoribbon. With increasing irradiation time, from (a) to (d), the thickness and the width of the graphene nanoribbon decreased gradually.

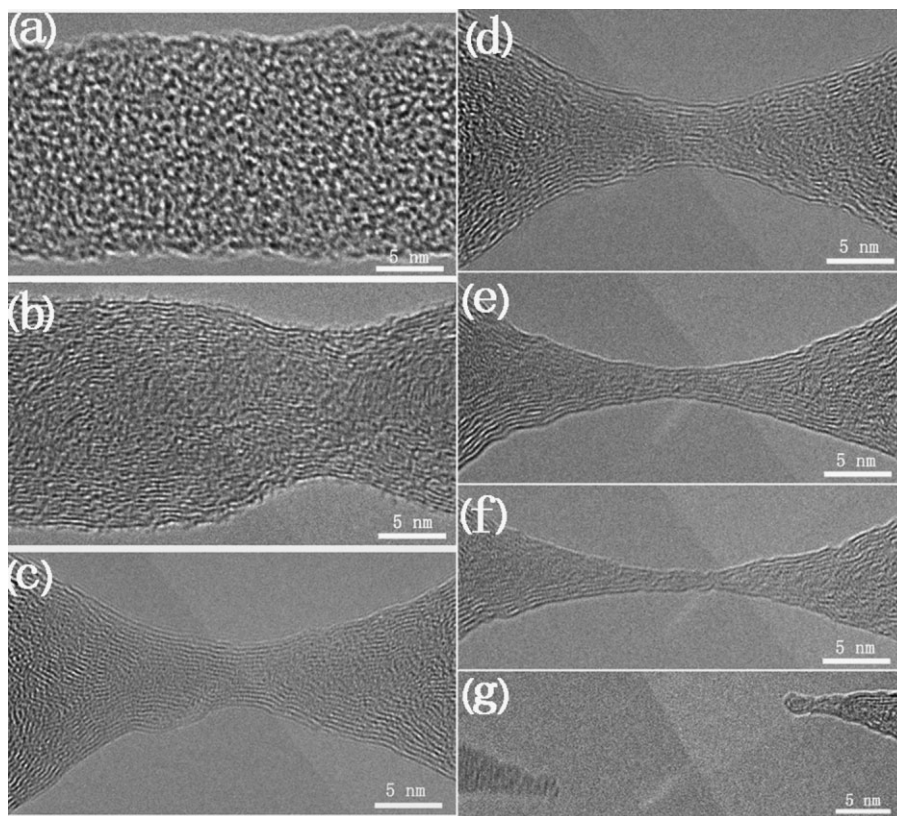


Figure 4. A sequence of HRTEM images showing the formation and fine-tuning of the graphene nanoribbon with high electron intensity irradiation. a) Original state with a diameter of about 16 nm. b–f) With increasing irradiation time, the graphene nanoribbon formed and was fine-tuned. The smallest thickness of the nanoribbon from (c) to (f) was about 5.0, 4.8, 2.4, and 1.0 nm, respectively, and the corresponding number of graphite layers was 15, 14, 7, and 3. g) The graphene nanoribbon after breaking.

so the shape of the graphene nanoribbon was like a bridge. The smallest nanoribbon (Fig. 4f) in this process was formed of only four graphene sheets, and the thickness was about 1 nm. It is thought that a single graphene sheet could be obtained if the irradiation process were controlled more precisely, but it was difficult to take pictures because the samples were fragile and tended to break. The fragility was caused by the inner tensions in the nanoribbon. Figure 4g shows a nanoribbon after it broke. There is a comparatively large distance between the two tips, which indicates a high inner tension.

In conclusion, graphene nanoribbons were formed from ultrathin electrospun PMMA nanofibers by electron beam irradiation. Since the number and width of the graphene sheets could be fine-tuned, it provides a novel method of obtaining graphenes in a controlled and designed way, which is of great interest to graphene science and technology. As far as we are aware, this is the first report of transforming PMMA into the carbon graphitic phase by electron beam irradiation. This new way of obtaining graphite nanostructures has promising potential applications in graphitic carbon nanostructure-based electronics and devices. Since PMMA is a widely used high-resolution electron resist, this graphitization technique could be combined with electron beam lithography to obtain high-resolution patterned graphite circuits. Its advantages

compared with other methods are that it is a one-step process and does not need high temperature, so it is compatible with the present micro- and nanoelectronic processes.

Experimental

PMMA nanofibers were prepared by electrospinning. 2 mL 950K PMMA C4 solution (MicroChem, 4 wt % in chlorobenzene) was mixed with 2 mL *N,N*-dimethylformamide (DMF) and subsequently vigorously stirred for 72 h. After stirring, about 0.3 mL mixed solution was loaded into a 1 mL glass syringe equipped with a stainless steel needle with 0.4 mm inner diameter. The electrospinning process was carried out with a 25 kV voltage and a 12 cm needle–substrate distance. A copper grid coated with ultrathin holey carbon film was used as a substrate to collect nanofibers. The as-electrospun nanofibers were baked on a hotplate at 50 °C for 30 min to get rid of the solvents.

Received: August 26, 2007

Revised: March 21, 2008

Published online:

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