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RESEARCH PAPER

Effect of annealing temperature on the mechanical properties of flexible graphene films

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Abstract: Free-standing graphene films (GFs) as functional materials require high mechanical performance for a convenient industrial processing. GFs were prepared from graphene oxide films by annealing temperatures from 1300 to 1700 °C, and were characterized by AFM, XRD, SEM, Raman spectroscopy and mechanical testing. Results indicate that the samples have a maximum tensile strength and fracture strain of 22.41 MPa and 2.44%, respectively and a minimum thermal conductivity of 744 W m^{-1} K^{-1} for an annealing temperature at 1500 °C. This is related to physical interlocking which results, from surface wrinkles of the graphene layers.

Key Words: Graphene film; Annealing temperature; Wrinkle; Mechanical properties

1 Introduction

Owing to many perfect properties, graphene films (GFs) have attracted tremendous attention in the fields of lithium ion battery[1], supercapacitor[2], biosensor[3], thermal management[4], water purification[5] and electromagnetic shielding[6] et al. Thermal annealing treatment of graphene oxide (GO) films was proven to be a convenient approach towards the preparation of flexible free-standing graphene films. It is proven that 1 000 °C is a critical turning-point for the effective de-oxygenation and reduction of the film[7]. At 1 000 °C in the carbonization, most of the oxygen-containing functionalities on graphene oxide sheets were removed, the sp^2 conjugation structure on the basal plane of the two dimensional crystal[7-9] was restored and a high conductivity for electrons and photons was attained. However, there is a simultaneous decrease in the mechanical stiffness for the film, which is attributable to the loss of interlayer hydrogen-bonds among graphene sheets. The film will become very fragile and is difficult to remain its integrity in industrial processing, which is unfavorable for commercial applications.

Fortunately, the mechanical properties of the film can be improved with a further increase in annealing temperature. For example, it was reported that GFs annealed at 1 000 °C shows the tensile strengths of 5.34 MPa [10]. However, the value was increased to 36.89-58.20 MPa with increasing carbonization temperature up to 1 800 °C in another literature [4]. In the wide temperature range between 1 000 and 1 800 °C, there is still no systematical investigation for the evolution of mechanical properties for the film.

It is proposed that wrinkles can be tuned on the basal plane of graphene sheets with various surface densities of chemical functional groups and defects [11, 12]. They are believed to play a key role on the mechanical properties of the reduced GO film [13, 14]. However, a comprehensive study on the evolution of microstructure for the film, towards tunable mechanical properties, is still absent.

In this contribution, the GO films were prepared by vacuum filtration. Afterwards, the evolution of mechanical properties of these films after carbonization at 1 300, 1 400, 1 500, 1 600 and 1 700 °C, were systematically investigated together with microstructure characterization with AFM, XRD, SEM, Raman spectroscopy. The mechanical properties of GFs in relation to the annealing temperature and micro-structure have been studied. An understanding of the mechanism behind the phenomenon is also important, which makes the practical applications of GFs possible in many fields.

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2 Experimental

2.1 Preparation of GFs

Graphite oxide was synthesized from a purified natural graphite using modified Hummers' method[15]. Then graphite oxide was exfoliated in deionized water by ultra-sonication for 30 min to obtain GO suspension (1.5 mg mL^{-1}). GO films were prepared by vacuum assisted flow-filtration of GO suspension followed by drying at room temperature. GFs were obtained by annealing the GO films. The annealing process was as follows. The GO films were heated from room temperature to the highest temperature at a rate of 5 ^{o}C min^{-1} under argon atmosphere, kept for 60 min at the highest temperature, then cooled to 500 ^{o}C at a rate of 5 ^{o}C/min and naturally cooled from 500 ^{o}C to room temperature. The whole cooling process proceeded with the protection of argon flow. Based on the highest temperature employed, the samples prepared above were described as G1300, G1400, G1500, G1600 and G1700.

2.2 Structure and property characterization

The as-obtained samples were characterized by using a scanning electron microscope (SEM, JSM-7001F, 3.0 kV), an atomic force microscope (AFM, NanoWizardIII, JPK Instruments), a X-ray diffractometer (XRD, Cu *K*a radiation, D8 Advance, BRUKER/AXS, Germany), and a Raman spectrophotometer (LabRAM HR UV-NIR, HORIBA JobinYvon, France). Static mechanical uniaxial in-plane tensile tests were performed with a dynamic mechanical analyzer (DMA, Q800, TAinstruments).

3 Results and discussion

GFs were obtained by annealing GO film under different annealing temperatures. As shown in Fig. 1a, the free-standing GF1500 exhibit a shiny metallic luster, indicating an obvious reduction of GO film. GF1500 shows a high flexibility and can be rolled without causing any visible fracture (inset image of Fig. 1a). Fig. 1b presents a typical SEM image of GF1500, which shows that it is of uniform thickness and has a relatively rough surface. Cross-section SEM image of GO1500 is shown in Fig. 1c, which shows an obvious layered structure. In Fig. 1d, graphene sheets are stacked up each other to form a layer-by-layer structure in the vertical direction. On the surface, GF1500 is found to be uniform with a dense distribution of microscopic wrinkles (Fig. 1e). Pandey et al.[16] has reported that GO sheets tend to wrinkle upon deposition from an aqueous solvent. The wrinkles inside GF1500 could be inherited from its GO film, and further develop during the thermal annealing treatment. The difference in wrinkling level of GFs is mainly resulted from the different annealing temperatures due to the same precursor film employed for preparation of GFs.

In order to further observe the development of wrinkling level of GFs annealed at different temperatures, quantitative analysis was conducted with AFM. The average roughness from the root mean square of measured values (RMS) are shown in Table 1.

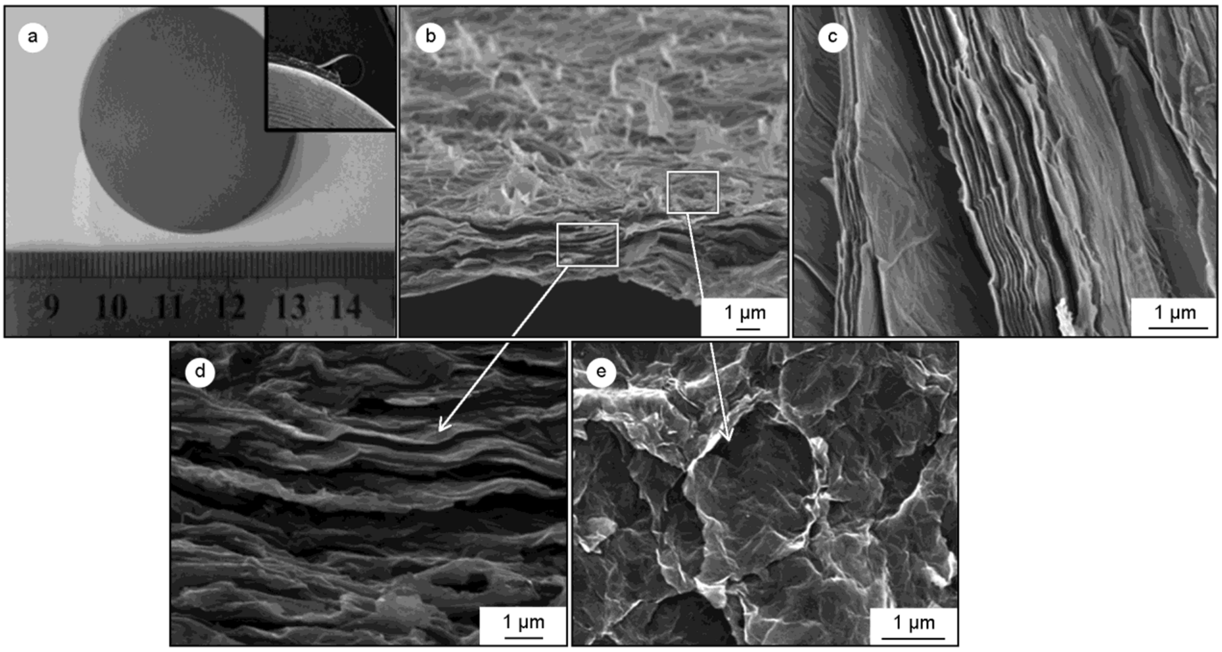

Fig. 1 Morphology and structure of G1500. (a) Photo image, inset of (a) shows a G1500 folded strip, (b) low-resolution SEM image, (c) cross section SEM image of GO, (d) high-resolution SEM image for cross-section and (e) surface morphology of the film.