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Surface effect on the self-reinforcing behavior of graphene oxide membranes

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ABSTRACT

Cyclic microbridge tests were applied to investigate the mechanical properties of the 100-to-400-nm-thick graphene oxide membranes. The effective Young's moduli of different thickness graphene oxide membranes were derived and proved to be size dependent. The self-reinforcing behavior of graphene oxide membranes, which exhibits as an increase in Young's modulus after cyclic loading, was observed and turned out to be in a relationship with thickness. A theoretical analysis is presented to explain the size dependence of the self-reinforcing Young's moduli. This work is meaningful for the applications of graphene oxide membranes and the development of basic elements of the micro/nano-electro-mechanical systems.

1. Introduction

As a member of graphene family, the graphene oxide (GO) is a complex consisting of various oxygen groups that adhered strongly to the basal plane and the edge of graphene. Due to these hydrophilic functional groups, individual GO sheets can be easily assembled into multilayer membranes through simple filtration or the liquid/air interface self-assembly technique.

Recently, the multilayer GO membranes have attracted much research attention due to their outstanding mechanical properties. Dikin et al. [1] investigated the mechanical properties of micron thick samples of the graphene oxide paper and found that the Young's modulus is much higher than the values of bucky paper, flexible graphite foil and vermiculite paper. The thickness has no significant impact on the effective Young's modulus when it is larger than 1 μm. Chen et al. [2] prepared the 5-to-10-μm-thick GO membranes through a facile self-assembly process and found them to have a Young's modulus of 12.7 GPa. Gong et al. [3] investigated the mechanical properties of GO papers with various thicknesses (0.5–100 μm) by bulge and tensile test. In their study, the Young's moduli were found to decrease with thickness, ranging from 44.6 to 8.5 GPa. To date, the reported average effective Young's moduli of micron-scale multilayer GOs are in a wide range of 2.5–42 GPa [4,5]. This variance is rooted in, e.g., wrinkles [6], water content [7], interlayer interactions [8,9], temperature [10,11], measurement method [12], and so on.

In general, for the micro/nanostructural materials with a large ratio of the surface area to the bulk, the surface effect can be substantial [13]. A lot of research has been done on the elastic characteristics of micro- and nanoscale materials including experiments [14–16], theoretical analysis [17–19], and computer simulations [20–22]. These experiments and computer simulations showed that the elastic moduli of these materials varied with the diameter of the nanowires or the thickness of the films due to the surface effect. Chen et al. [23] treated the nanostructure as a core-surface composite structure. The overall elastic behavior of nanostructures is a superposition of surface areas and the core component where the core exhibits the same elastic properties as the corresponding macroscopic bulk material. Miller et al. [19] introduced the surface elastic modulus to evaluate the importance of the surface effect. When the thickness of GO membrane reaches the submicrometer or nanometer scale, the Young's modulus alters with the change of thickness. Wang et al. [24] used in situ atomic force microscopy to measure the 900 nm-thick GO micro-beams. The average modulus of graphene oxide paper was determined to be 7.43 GPa. Chen et al. [25] prepared the foam films of GO with a thickness of about 400 nm. The Young's modulus was evaluated to be 13.9 GPa. Cao et al. [26] measured the GO paper with a varying thickness (between 24 and 75 nm) by uniaxial tensile loading. In this case, the surface effect on elastic properties of submicrometer-

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scale GO membranes needs further investigation.

As is well known, the self-reinforcing behavior is widely found in polymer materials whose macromolecular movements (e.g. straightening and reorientation) lead to a larger stiffness by improving the alignment of curved and unaligned polymer chains at large strain level [27]. Dikin. et al. [1] found that the GO membranes exhibit the self-reinforcing behavior, where the Young's modulus increased by 20% after five cyclic loading experiments. According to Dai's research [28], the unique self-reinforcing behavior for GO membranes is attributed to the straightening and reorientation of graphene sheets and is further tuned through tailoring the interlayer adhesion. Wu et al. [29] applied the polarized Raman spectroscopy and the X-ray diffraction to characterize the self-reinforcing behavior of graphene oxide membranes. The results showed that the alignments of the graphene sheet along loading direction improved when the GO membrane was subjected to a unidirectional tension. However, the impact of surface effect on self-reinforcing behavior of submicrometer-scale or nanometer-scale GO membrane is unknown.

In this study, 100-to-400-nm-thick GO microbridge samples were fabricated using the semiconductor technology and the focused ion beam micro-nano processing technology. The effective Young's moduli were determined by fitting the force-deflection curves with the micro/nanobridge deformation model. The impact of thickness on the effective Young's modulus was investigated and explained by the surface effect. Finally, the relationship between thickness and the self-reinforcing Young's modulus is obtained.

2. Experimental section

GO specimens were fabricated on 100-mm-diameter (100) Si wafers with both sides polished. Dry etching was used to create some windows in the bottom side of the Si_3N_4 layer to expose the Si underneath. After that, the wafers were immersed in KOH solution (500 g/ml) to etch Si from the bottom side of the window. After Si was etched through, the wafers were placed into HF solution to sweep away Si_3N_4. GO was prepared from the purified natural graphite (obtained from Qingdao Yingshida Graphite Co., Ltd., with a particle size of 20 μm) by the modified Hummers method [45]. The GO paper was made by filtering of the resulting colloid through a cellulose membrane filter (47 mm in diameter, 0.22 μm pore size), followed by air drying and peeling from the filter. The free-standing GO film can be easily transferred to the as-prepared Si substrate in deionized water. After the vacuum drying process (0.05 MPa, 333 K, 12 h), the microbridges were fabricated by removing material from the parent GO paper on the Si substrate using focused ion beam (FIB) integrated within scanning electron microscope (SEM). A relatively small FIB current of 260 pA was used to avoid ion beam implantation and damage of the GO samples during the microbridge fabrication [30–32]. As seen in Fig. 1 (a), four GO microbridges were created over trenches on an Si substrate by self-adhesion. A total of sixty-two bridges with a 100–400 nm thickness, 15 μm width and 20–80 μm length were prepared in the tests.

The microbridge mechanical testing was conducted using a Nanoindenter II equipped with a wedge indenter tip. The wedge of the indenter, with a width of 20 μm, is wider than the sample, and thus, the one-dimensional analysis holds. Fig. 1 (b) shows a schematic of a wedge tip indenting the GO microbridge.

3. Results and discussions

As shown in Fig. 2, a typical cyclic loading displacement curve shows the hysteresis between the first loading curve and the subsequent loading-unloading curves. Similar curves were obtained in Park's research [9], where the first loading curve deviated from subsequent loading-unloading curves. Assembled by individual GO sheets, the GO membranes are unavoidably corrugated due to the irregular distribution of the oxygen-rich groups on the surface and thermal fluctuation [33], which makes GO sheets incompletely align along the same direction [34]. In addition, when fixed on the sample holder, the thin and flexible GO membranes easily exhibit various curvatures, which have an effect on testing. Thus, during

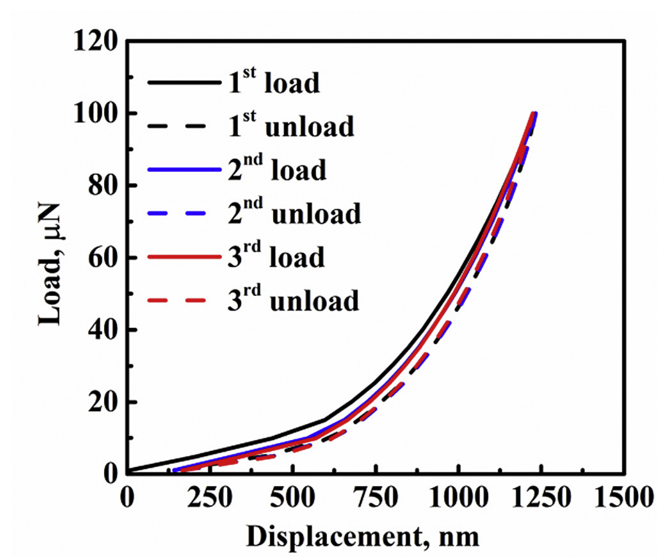

Fig. 2. Typical load versus vertical displacement curves of the microbridge. (A colour version of this figure can be viewed online.)

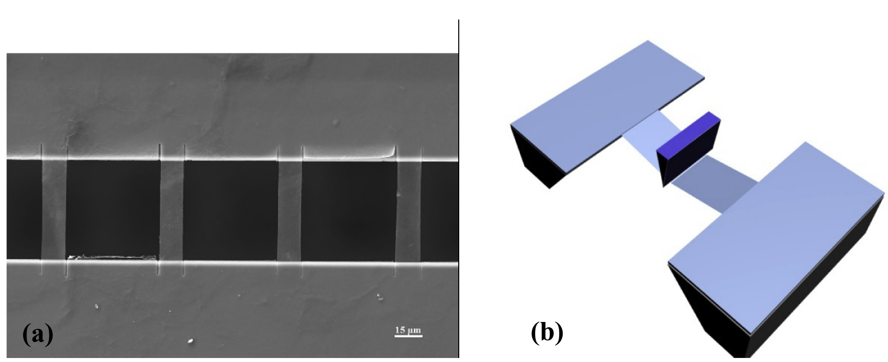

Fig. 1. (a) SEM micrograph of four GO microbridges (b) Schematic of a wedge tip indenting the GO microbridge. (A colour version of this figure can be viewed online.)