POLYGONIZATION AND ANOMALOUS GRAPHENE INTERLAYER SPACING OF MULTI-WALLED CARBON NANOFIBERS*[1]

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Abstract

The graphene interlayer spacing in pure graphite is known to have a minimum value of d_{min} =0.3354 nm, while defective graphites typically have larger interlayer spacings. Using transmission electron microscopy, we find that the nanofibers are polygonized after heat treatment above 2800K. And X-ray diffraction study reveals that the interlayer spacing of the treated carbon nanofibers is distinctly smaller than d_{min}. To explain this unusual observation, we investigate the structural properties of carbon nanotubes using a multi-scale approach rooted in extensive first-principles calculations, specifically allowing the nanotube cross-sections to polygonize. We show that, it is energetically accessible at high temperatures to polygonize the nanotubes with large cross-sections (30-200 nm), accompanied by reductions in the graphene interlayer spacing. These unique predictions are confirmed in further experimental observations.

Keywords: carbon nanofibers, graphitisation, heat treatment

I. Introduction

Recent discoveries of low-dimensional carbon materials, such as fullerenes[1] and nanotubes,[2] have generated much research effort in exploring their physical and chemical properties. In particular, a fundamental understanding of their structural properties is essential in order to fully utilize their device potentials in nanotechnology.

For several different types of carbon-based nanostructures, one fundamental quantity is the graphene interlayer spacing, corresponding to the d_{002} peak observed in x-ray diffraction (XRD). This quantity has a broadly accepted minimum value of d_{min} =0.3354 nm [3] for single-crystal graphites having true ABAB stacking.[4] This prevailing view has led to the classification of a variety of "graphitic" materials, ranging from those with good *ABA*B stacking and *d*002 near 0.335 nm [3] to "turbostratic" materials with no interplanar ordering and *d*002 up to 0.344 nm.[5] For example, when graphene layers roll up to form multi-walled carbon nanotubes (MWCNTs), the inter-layer spacing increases exponentially from d_{min} as the tube radius decreases.[6]

There are a few notable exceptions of graphites reported to have d_{002} values lower than d_{min}.[7–9] The earliest examples were "Kish" graphites deposited on the surfaces of molten steel, which show a *d*002 value of 0.33528 nm.[7] However, molten steel was known to contain abundant Fe and Si impurities, which evidently applied a high internal pressure to the Kish graphite. After removing the impurities by either heat treatment or acid washing, the lattice spacing expanded back to the nominal value of graphite.[7] More recently, it was reported that heat treatment of a mixture of demineralized anthracite and minerals such as rutile (TiO_2), calcite ($CaCO_3$), or hematite (Fe_2O_3) leads to graphene interlayer spacings of 0.3352, 0.3350, or 0.3349 nm, respectively ±0.0001 nm.[8] Furthermore, applying high external pressure or high-energy electron irradiation could cause a significant reduction in the interlayer spacing of graphite or a confined structure such as a spherical shell and, ultimately, could induce a transition to diamond.[9]

In this communication, we report that the interlayer spacing of less than graphite d_{min} observed after heat treating the carbon nanofibers (CNF) at temperatures higher than 2800K, and rationalize the observation within a

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unified theoretical model of carbon nanotubes. First, using x-ray diffraction, we find that the graphene interlayer spacing in multi-walled carbon nanofibers heat treated above 2800 K is distinctly smaller than *dmin*. The model developed is multiscale in nature, and is characterized by the introduction of a local curvature that allows the nanotube cross sections to polygonize. We show that, whereas normal nanotubes are favored energetically at low temperatures, the configuration entropy associated with Stone-Wales (SW) defects can make the polygonal shape of the large nanotubes or nanofibers metastable at intermediate temperatures, and globally favorable at sufficiently high temperatures. Furthermore, such polygonal carbon nanotubes exhibit clear reductions in the graphene interlayer spacing. These predictions are convincingly confirmed in further experimental studies of carbon nanofibers with varying cross sections and at different heat treatment temperatures.

II. Experimental Observation of Interlayer Spacing Reduction of Multi-walled Carbon Nanofibers

The carbon nanofibers studied here were approximately 100 nm in diameter, with an average initial aspect ratio exceeding 100. The fibers were produced by Applied Sciences, Inc. (PYROGRAF PR-24 and PR-19, see http://www.apsci.com). The as-grown fibers had a duplex morphology comprised of an inner core, which was deposited by an Fe-based catalytic particle, covered with a layer of vapor-deposited turbostratic carbon. These fibers were heat treated under Ar in a furnace that used a graphite heating element. Different batches of fibers were treated at 3000, 3100, and 3500 K, respectively. The MWCNTs were heat treated at 3037 K for 1 h in a similar furnace. The microstructures of the fibers before and after heat treatment up to ~3500 K were examined using transmission electron microscopy (TEM) and scanning electron microscopy (SEM). The as-grown fibers had the geometry of stacked cups, with circular cross sections, as seen in the SEM image (Fig. 1a). After heat treatment, such fibers were well graphitized, as shown in the TEM image (Fig. 1b).

To measure the interlayer spacing of the nanofibers, XRD was carried out using a Sintag PAD diffractometer with Cu $_{Ka}$ x-radiation. The results are shown in Fig. 1c. The as-grown nanofibers were placed in a furnace and warmed to each target temperature where they were held for 1 h. Then the fibers were cooled down to room temperature for measurement.[10]. As the temperature reached above 2800 K, the measured interlayer spacing became 0.3350 nm, reduced from that of natural graphite at 0.3354 nm, corresponding to the dotted line in Fig. 1c. Further increases in heat temperature led to the same degree of reduction to within the experimental error of $4x10^{-5}$ nm the error bars are within the size of the data points in Fig. 1c. The stable reduction was observed all the way up to 3500 K, the highest heating temperature reached in our experiments.

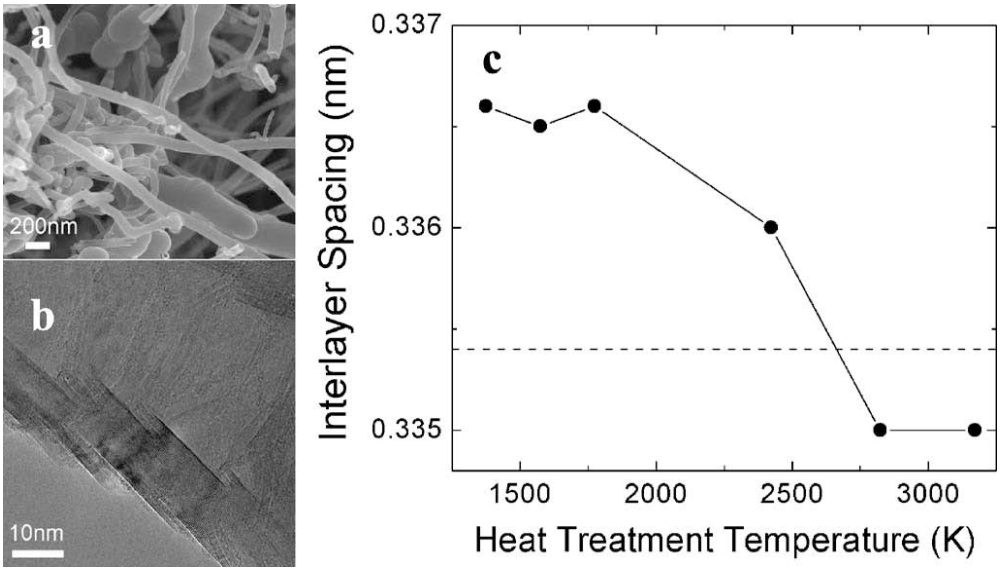

Figure 1. Electron micrographs showing that as-grown fibers have circular cross sections: (a) and heat treated fibers are well graphitized (b). (c) Experimentally measured interlayer spacing of the fibers as a function of the heating temperature. The dotted line marks the spacing of natural graphite. The error bar is within 4°—10-5 nm, smaller than the size of the data points.

It is confirmed that the stacked-cup nanofiber samples contained no metal impurities. Furthermore, the samples were neither exposed to electron irradiation nor to external pressure; therefore, none of the existing mechanisms can be invoked to explain the interlayer spacing reduction observed here. An obvious difference between ideal planar graphene and nanotube and/or nanofiber structures is the existence of finite curvatures in the latter case. Nevertheless, as shown in Ref. 6 and in the data in Fig. 1c with T>2800 K, standard carbon nanotubes or nanofibers only exhibit increased interlayer spacings over d_{min}.

III. Theoretical Modeling

The above observations motivated us to investigate theoretically the feasibility that the nano• bers develop polygonal cross sections under high-temperature heat treatment, and in turn, the corresponding increase in the local curvature associated with the polygonal deformation causes a reduction in the interlayer spacing. The **Stone Wales** (SW) defect is a defect that occurs in carbon materials when four adjacent six-member hexagon rings break and reconstruct to form two pentagons and two heptagons, or vise versa. It is known that for planar graphene layers or CNTs with large cross sections, the two most common types of defects that can be thermally acdtivated[10], vacancy and SW defects, have the formation energies of 7.8 and 10.4 eV, respectively.[11] These high formation energies suggest that the corresponding defect densities are entirely negligible even at the high temperature of 3000 K. Nevertheless, the formation energies can depend strongly on the curvature of the carbon nanomaterials, as already suggested for the case of conventional CNTs. We have carried out systematic studies of such curvature dependences for both types of defects using LDA-DFT approaches. For the SW defects, the formation energy decreases exponentially as the curvature increases, and the dependence can be well • tted using the relation $E_d = E_0 (e^{-K_1/c_1} + e^{-K_1/c_2})$, where E_0=5.196 eV, c_1 =0.029, and c_2=0.002 (for the zigzag and armchair CNTs), giving a formation energy of less than 2 eV for local curvature K_1 >0.03 (K_1 is defined in reference 12). In contrast, the formation energy of the vacancy defects has a weaker dependence on the curvature, and is still ~5 eV even for a CNT with the smallest radius. Therefore, even at high temperatures and with large curvatures, only the SW defects can have a noticeable density. Now we evaluate the contribution to the free energy due to the con• guration entropy associated with the creation of the SW defects. When N_d defects are introduced to an N-atom system, there are Ω ways to distribute them, given by $\Omega = N!/(Nd!(N - Nd)!)$. For large N, the corresponding entropy increase is $S_d = -0.5 k_B N(\rho \ln\rho + (1-\rho)\ln(1-\rho))$, and the defect density is $\rho = Nd/(N/2)$ (the factor 1/2 re• ects that only N/2 bonds are available for the creation of SW defects). For single-walled CNTs, the polygonal structures are energetically more costly because of the strain energy associated with the polygonization, but have higher entropies due to lower defect formation energy. Therefore, the competition between internal energetics and defect formation will determine the relative stability of the SWNTs at a given temperature. Quantitatively, we have for the total free energy

$F = \Delta E_{pol} + E_d N_d - TS_d$, where the internal energy ΔE_{pol} is different for different shapes of the CNTs $\Delta E_{pol}/L = \sum_{p=1}^{N_p} \varepsilon(p, w_0) K_1(p)$, while the second term reflects the formation energy of the SW defects. Based upon these assumptions and further incorporate empirical potentials to accommodate larger structure, we have calculated that the CNTs with large cross sections can be polygonized at sufficiently high temperatures, while those with small cross sections cannot, even at the high temperature of 3500 K, because of the existence of high (over 12 eV) kinetic barriers to reaching the metastable or stable polygonal states. Further, for CNTs or CNFs with larger diameter (~100 nm), the polygonization has renders the stronger interaction between graphene and as a result, has a smaller than d_{min} interlayer spacing.

IV. Conclusions

In conclusion, we have shown experimentally that polygonization of multi-walled carbon nanotubes or nano• bers can be induced at suf• ciently high heat-treatment temperatures and with suf• ciently large diameters. These trends are consistent with the predictions of a uni• ed picture of carbon nanotubes and carbon polygons, developed through multiscale simulations rooted in extensive • rst-principles calculations. One central • nding is the stabilization of polygonal shapes at high temperatures by the con• guration entropy associated with the creation of the Stone-Wales defects. As a consequence of the polygonization, the interlayer spacing of the MWPNTs contracts to a value distinctly smaller than the established graphene interlayer spacing, as also con• rmed theoretically. We expect that the phenomena of polygonization and potential interlayer spacing reduction established here for the MWCNTs will be applicable to other related tubular and/or • ber systems as well, such as BN nanotubes or nano• bers.[13]

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