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Helical Carbon and Graphitic Films Prepared from Iodine-Doped Helical Polyacetylene Film Using Morphology-Retaining Carbonization

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Carbon films are interesting materials because of their special physicochemical and mechanical properties. They have been used in various applications such as electrochemical energy storage,¹ field-effect transistors,^{2,3} cell electrodes,^{2,4} catalyst supports,⁵ gas-absorbent materials,^{1b} and wear-resistant coating.⁶ Many carbon thin films or membranes supported by substrata have been reported that consist of evaporated amorphous carbon^{1b} and macroscopically aligned or random networks of carbon nanotubes.⁷ The freestanding carbon thin film, with a peculiar spiral structure such as hierarchical helical bundles of nanofibrils, is expected to afford novel electrical and electromagnetic properties. However, it has been considered difficult to prepare a freestanding carbon thin film through the carbonization of an organic polymer film. This is because carbonization at high temperature⁸ causes thermal decomposition and volatilization of hydrocarbon gases, destroying the morphology of the original film.

On the other hand, since iodine doping of the polyacetylene (PA) film results in a remarkable increase in electrical conductivity,⁹ it has been generally adopted to increase the electrical conductivity of a variety of conjugated polymers. Here we will shed light on a new aspect of this doping by disclosing its indispensable role in maintaining the nanostructure and morphology of precursors during carbonization. We have used the nanofibril-fabricated helical PA film (Figure 1a–c) to prepare the freestanding helical carbon thin film. Helical PA film, recently developed using a novel polymerization method, has a spiral morphology, in which bundles consisting of nanofibrils with diameters < 100 nm are twisted and concentrically curled.¹⁰

The helical carbon thin films were prepared by carbonization of the iodine-doped helical PA film at high temperature. Experimental details are described in the Supporting Information (SI). The atomic ratio of doped iodine to carbon in the PA film was ~0.25. The thermal behaviors of the undoped and doped PA films during carbonization were examined using thermogravimetry and differential thermal analysis (TG-DTA). The outgases generated during the heating of the doped PA film up to 500 °C were also examined using GC–MS.

The doped PA film is almost completely carbonized at temperatures above 800 °C. The thermal behavior observed in the TG-DTA curve for the doped PA film is quite different from that of the undoped PA film (Figure S1). No indication of the thermal decomposition is observed in the DTA curve for the doped PA film. Surprisingly, the fibrous morphology of the original structure remains unchanged even after the carbonization and then the heat

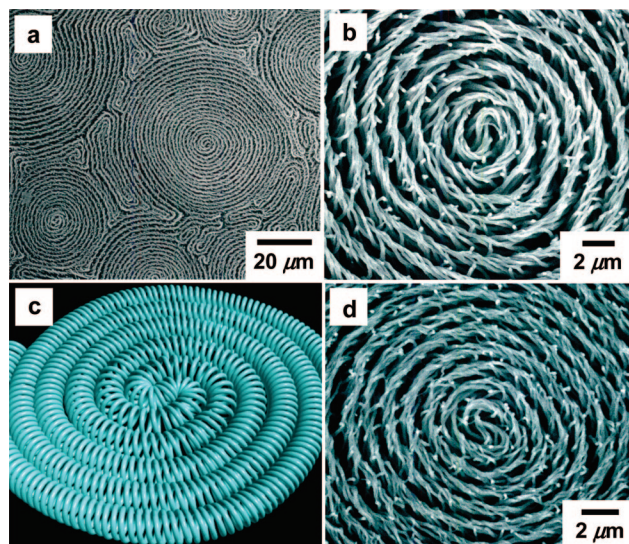


Figure 1. (a) SEM image of the helical PA film and (b) enlarged one. (c) Schematic representation of the helical morphology consisting of twisted bundles of the PA nanofibrils. (d) SEM image of helical graphitic film prepared through a morphology-retaining carbonization of iodine-doped helical PA and then heat treatment at 2600 °C.

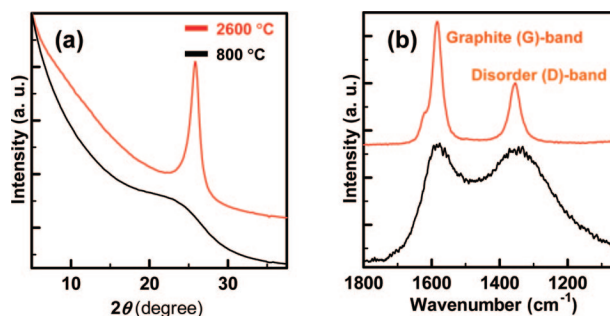


Figure 2. (a) X-ray diffraction intensity curves and (b) Raman scattering spectra for the films carbonized at 800 °C (black) and those heat-treated at 2600 °C after the carbonization (red).

treatment (Figure 1d). In addition, the weight loss of the films due to carbonization at 800 °C is very small, amounting to only 20% of the weight of the film before iodine doping. Thus the nanofibril-fabricated carbon film is obtained through the carbonization of the doped PA film. X-ray diffraction of the carbon film prepared from the doped PA film at 800 °C has no crystalline reflection (Figure 2a). The Raman scattering spectrum of the carbon film shows a strong, broad peak at 1350 cm⁻¹ attributed to the disordered structure (D-band), together with a comparable peak at 1580 cm⁻¹

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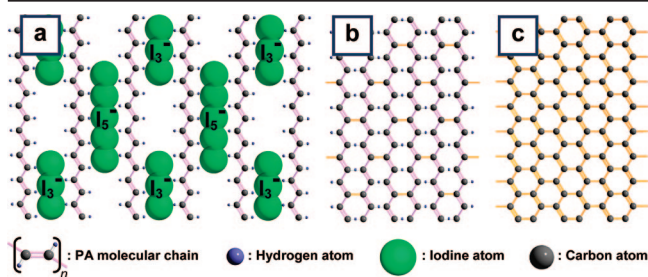


Figure 3. (a) Structural model of the iodine-doped PA. (b) Hypothetical molecular model of the specimen formed on the way to the dehydrogenation reaction from the iodine-doped PA film shown in image a. (c) Hexagonal carbon bond network formed at 800 °C after passing through the model shown in image b. (Enlarged figures are given in Figures S2 and S3.)

corresponding to the structure of the sp^2 hexagonal carbon bond network (G-band)^{1a} (Figure 2b).

It is apparent that the iodine doping prevents the PA film from thermally decomposing at high temperature. According to the structural model of the iodine doped PA film,¹¹ polyiodide ions such as I_3^- and I_5^- are situated between the PA chains, forming a charge transfer complex (Figure 3a). Iodine tends to react with hydrogen at high temperature.¹² Since an outgassing of hydrogen iodide has been detected by GC–MS during heating of the doped PA film, it can be assumed that hydrogen contained in the doped PA is removed to some extent as hydrogen iodide from the PA chains and that the PA chains partially cross-link between the neighboring chains (Figure 3b). Furthermore, most of the hydrogens are removed with increasing temperature. As a result, the networks of sp^2 hexagonal carbon bonds are formed during carbonization (Figure 3c). These results indicate that the carbon film prepared from the iodine-doped PA film at 800 °C exists in an almost amorphous state.

The carbon film prepared at 800 °C can be further graphitized by heat treatment at 2600 °C, as shown in Figure 2. The two peaks at 1350 and 1580 cm^{-1} become sharp in the Raman spectrum (Figure 2b). The sharp diffraction peak corresponding to the (002) face of a graphitic crystal¹³ indicates that the graphitic crystallization occurs in the carbon film through heat treatment at 2600 °C (Figure 2a). It should be emphasized that the carbon film heat-treated at 2600 °C has almost the same helical structure as those of the original PA film and the carbon film prepared at 800 °C (Figure 1c,d).

An individual nanofibril in the carbon film can be dispersed by ultrasonication in ethanol. A TEM image of carbon nanofibril and its electron diffraction pattern (EDP) are shown in Figure 4a and b, respectively. The EDP shows two pairs of the (002) reflection of the graphitic crystals, having an intersection angle in the range 45°–60° along the fibril axis (Figures 4b and S5b). From the results of the EDP and a high resolution TEM image (Figure 4c), a schematic representation of a single helical graphitic nanofibril can be deduced (Figure 4d). The original undoped PA film has an electrical conductivity of $<10^{-5}$ S/cm.⁹ Meanwhile, the carbon film and the graphitic one have conductivities on the order of 10 and 10^2 S/cm, respectively.

In summary, we have demonstrated that the iodine doping is quite effective in increasing carbon yield and in preserving both the helical nanofibril structure and the spiral morphology of the helical PA films. Moreover, the carbon film obtained by carbonization at 800 °C can be graphitized by heat treatment at 2600 °C while still retaining their original nanofibril-fabricated structures. Iodine-doped PA and as-synthesized PA films are unstable under atmospheric conditions. This is the reason why the PA films are less feasible for practical use. However, the carbon and graphitic

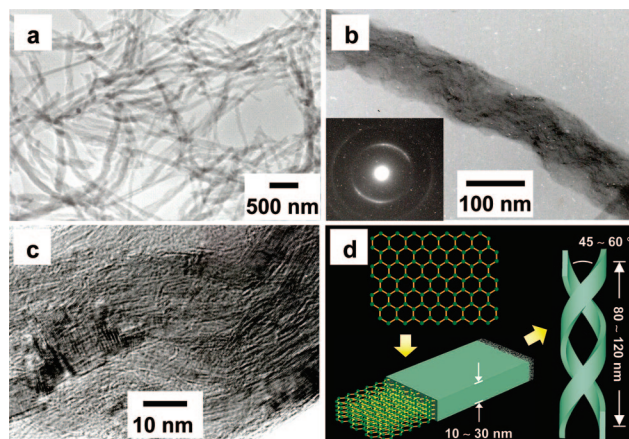


Figure 4. TEM images of (a) the dispersed helical graphitic nanofibrils and (b) a single helical graphitic nanofibril with its electron diffraction pattern (inset). (c) High resolution TEM image of the helical graphitic nanofibril. (d) Schematic representation of the helical structure consisting of graphitic nanofibrils. (Enlarged figures are given in Figures S4–S7.)

films prepared from the iodine-doped PA films are stable under atmospheric conditions. It is therefore expected that these carbonized films might exhibit intrinsic functions characteristic of the helical structure and that they might be also be used in practical carbon materials.

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Supporting Information Available: Experimental details, iodine doping, and carbonization. These materials are available free of charge via Internet at <http://pubs.acs.org>.

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