

High Magnetization Helical Carbon Nanofibers Produced by Nanoparticle Catalysis

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Received: January 1, 2006; In Final Form: April 28, 2006

Helical carbon nanofibers were synthesized by means of acetylene pyrolysis at 450 °C using Fe nanoparticles as catalyst. There is no need to modify the Fe nanoparticles by a chiral reagent. The carbon nanofibers generated are crystalline and symmetric, with the (110) plane of Fe particle being the mirror plane. There would be a change in the shape of the nanofibers if the temperature at the beginning or during the synthesis were altered. Compared to the helical carbon nanofibers reported elsewhere in the literature, our samples show higher magnetization.

Introduction

The investigation of chirality and chiral molecules is primarily an attempt to understand the origin of life. The studies are mostly conducted at molecular levels and related to chemical as well as physical aspects of chirality. With the detection of nanosized chiral structures, questions are raised as related to their formation. Scientists have paid much attention to coiled carbon fibers and tubes because of their novel chiral morphologies and distinct physical properties.^{1–11} By the addition of a dilute gas such as hydrogen, argon, thiophene, or H₂S, coiled carbon fibers were prepared in the catalytic decomposition of organic vapors such as acetylene and benzene at high temperatures (>600 °C) over transition metals or alloys (e.g., Ni and its alloys). Furthermore, Qin et al.^{12–15} reported the synthesis of helical polyacetylene nanofibers at 250 °C over copper nanoparticles that had been modified with chiral tartaric acid and showed that helical carbon nanofibers could be obtained by heating the polyacetylene nanofibers at or above 900 °C. It was said that the decomposition process occurred at relatively low temperatures, and the resulting nanofibers were amorphous. Herein, we report the first time the synthesis of helical carbon nanofibers (referred hereafter as coiled nanofibers) of symmetric structures by the pyrolysis of acetylene over Fe nanoparticles derived from a combined sol–gel/reduction method. The pyrolysis reaction conducted at a relatively low temperature of 450 °C is highly reproducible. No dilute gas, such as argon, nitrogen, or sulfur compounds, was needed. Synthesized at this temperature, the coiled nanofibers are crystalline.

Fe catalysts have been widely used in the preparation of one-dimensional carbon nanostructures such as carbon nanofibers,¹⁶ carbon nanohorns,¹⁷ and three-dimensional microcoils.¹⁸ The fibers obtained are generally straight, tubular, and/or microcoiled. To the best of our knowledge, the use of Fe nanoparticles for the synthesis of coiled nanofibers of high symmetry without the employment of a chiral reagent has never been reported before.

Experimental Section

To prepare the catalyst precursor, 0.01 mol FeCl₂·4H₂O and 0.015 mol citric acid monohydrate were well mixed (stirring at 60 °C for 6 h) with 100 mL of absolute ethanol. The xerogel obtained after ethanol removal (at 80 °C) was heated in air at 450 °C for 3 h for the generation of ferric oxide. Then 50 mg of the ferric oxide powder was dispersed on a ceramic plate, which was transferred to a horizontal reaction tube located inside a tubular furnace. The whole system was equipped with proper temperature and gas-flow control facilities. After the ferric oxide was reduced in H₂ at 450 °C for 4 h, acetylene was introduced into the reaction tube and the pyrolysis of acetylene at 450 °C was retained for 6 h under atmospheric pressure. Usually, about 1.582 g of the coiled nanofibers sample was produced in each run.

The morphologies of the samples were examined by a transmission electron microscope (TEM) and high-resolution TEM (HRTEM, model JEOL-2010, Japan) operated at an accelerating voltage of 120 kV and 200 kV, respectively, and by field-emission scanning electron microscopy (FE-SEM model 1530VP, LEO, Germany) operated at an accelerating voltage of 15 kV and was equipped with a JEOL JFC-1600 auto fine-coater. The magnetic properties of the samples were measured at 300 K by a Quantum Design MPMS SQUID magnetometer (Quantum Design MPMS-XL, U.S.A.) equipped with a superconducting magnet capable of producing fields of up to 50 kOe. FTIR spectra of samples (in KBr pellets) were recorded using a Nicolet 510P spectrometer.

Results and Discussion

Figure 1 shows the TEM image of two coiled nanofibers attached to an iron nanoparticle. It is common to have two coiled nanofibers grown on one catalyst nanoparticle. With one coiled nanofiber on each side, the iron nanoparticle appears to be at the node of the nanofibers. The diameter of the coiled nanofibers is roughly the size of the Fe nanoparticle. A closer examination reveals that the iron nanoparticle inside the nanofiber is oval in shape and is about 40 nm in size, and the two “arms” of coiled nanofibers are mirror-image to each other. They are identical in cycle numbers and are almost equal in coil diameters, coil lengths, and coil pitch; the direction of coiling, however, is opposite.

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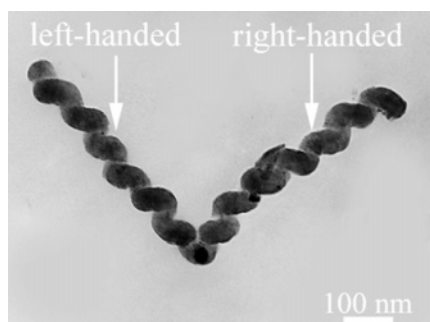


Figure 1. Typical TEM image of a pair of coiled nanofibers grown on an iron nanoparticle.

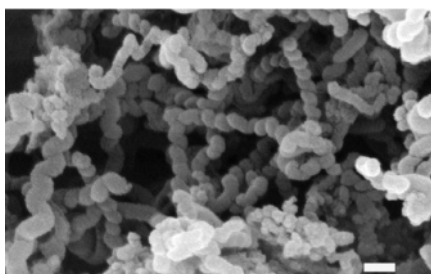


Figure 2. FE-SEM image of representative coiled nanofibers. (The bar denotes 200 nm.)

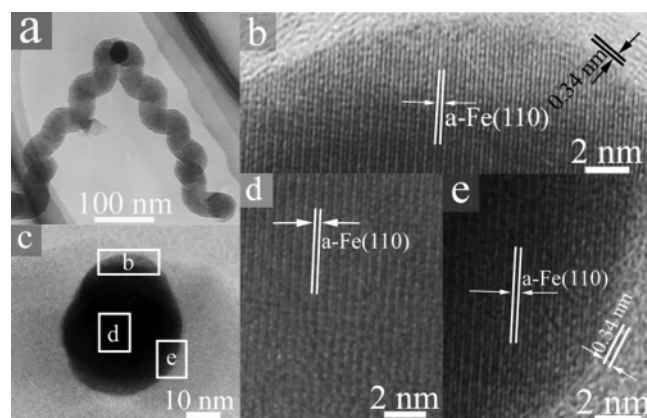


Figure 3. Microstructure of a catalyst nanoparticle located at the node of coiled nanofibers; (a) TEM image; (c) HRTEM image; (b, d, and e) magnified images of areas marked in figure (c), respectively.

Figure 2 shows the FE-SEM image of the coiled nanofibers. Most of the nanofibers are regularly and tightly coiled and hence show very short coil pitches. The diameter of the coils (i.e., the outer diameter of the helix) is about 80 nm, whereas that of the fibers is ca. 40 nm.

Figure 3 shows the microstructure of an Fe nanoparticle. The HRTEM images (Figure 3b, d, and e) reveal that the (110) plane of the single-crystalline Fe nanoparticle appears to be the mirror plane of the two coiled nanofibers. Parts b and e of Figure 3 show the graphitic layers wrapping the Fe nanoparticle; the interplanar distance of the graphitic layers is ca. 0.34 nm.

From Figure 4, one can see that the coiled nanofiber is not amorphous but rather polycrystalline (Figure 4b), although at a relatively low reaction temperature. The coiled nanofiber develops along the direction of growth and is composed of graphitic layers (Figure 4c and d) that are peripheral and circulate around the axes of the fiber. The magnified HRTEM images of the end and coiled sections show again an interplanar distance of graphitic layers of ca. 0.34 nm.

Figure 5 shows the IR spectrum of as-prepared coiled nanofibers. There are no IR signals of $-\text{CH}=\text{CH}-$, $-\text{CH}_2-$,

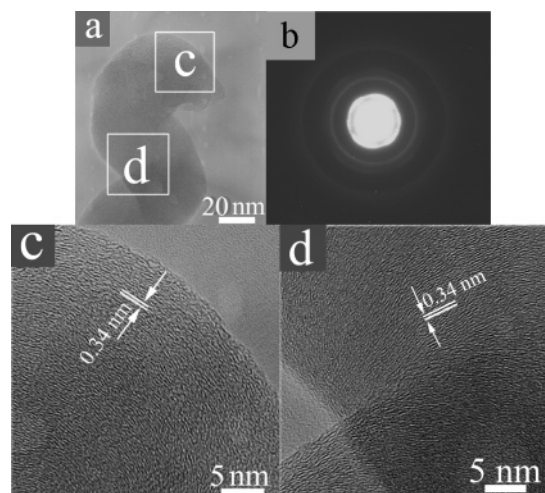


Figure 4. Microstructure of a coiled nanofiber; (a) HRTEM image; (b) selected area electron diffraction pattern; (c and d) magnified images of the areas marked c and d in figure (a), respectively.

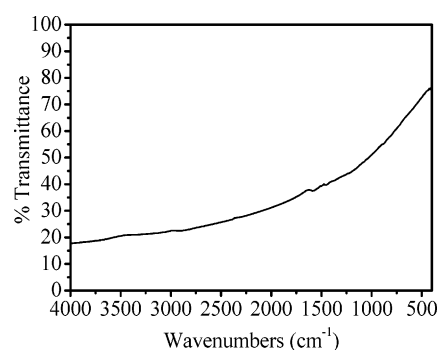


Figure 5. IR spectrum of coiled nanofibers.

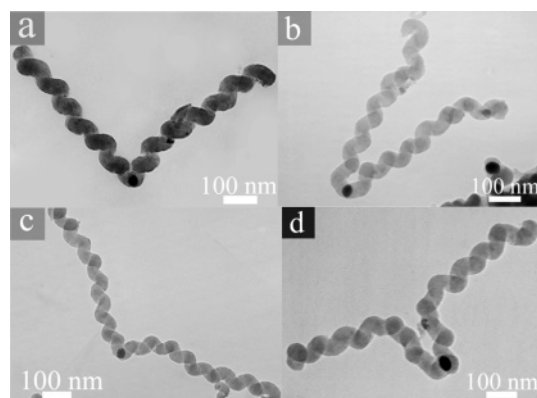


Figure 6. TEM images of coiled nanofibers; (a), (b), and (c) coiled nanofibers identical in cycle number (7 cycles) but with interangles θ of about 70°, 35°, and 130°, respectively; (d) coiled nanofibers with θ of about 35° and a change in growth direction at the third cycle.

and $-\text{CH}_3-$ entities. In other words, the coiled nanofibers are completely carbonized and the method adopted in this study is capable of producing coiled carbon nanofibers effectively.

Most of the pairs of coiled nanofibers show an interangle θ of about 70° (Figure 6a), and there are minorities with θ equal to 35° or 130° (Figure 6b, c, and d). It is interesting to observe that no coiled nanofibers with θ other than these three have been found. It is also interesting to observe that most of the coiled nanofibers stopped at the seventh cycle and the coiling direction is opposite within each pair set. It seems as if there are some unknown factors that are in control. As demonstrated in Figure 6b, the two coiled nanofibers changed simultaneously in coiling direction at the sixth cycle. On the other hand, if one

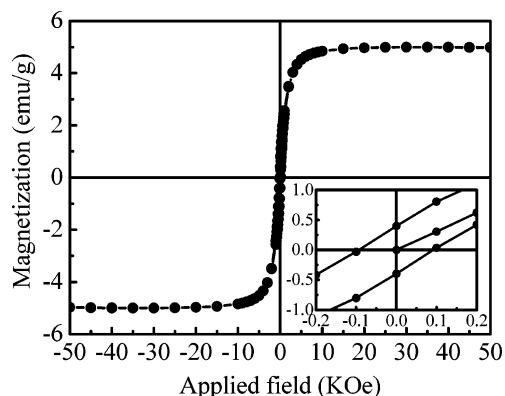


Figure 7. Typical magnetization curves of coiled nanofibers measured at 300 K.

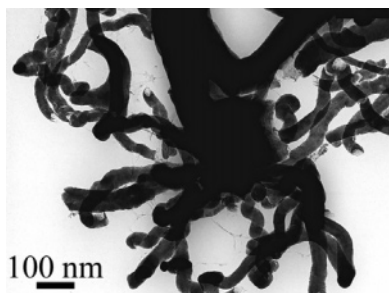


Figure 8. TEM images of carbon products obtained when acetylene was introduced initially at room temperature.

fiber changed the direction of growth, the other changed also at the same cycle number (Figure 6d).

The FE-SEM and TEM investigations reveal that the Fe nanoparticles prepared by the combined sol–gel/reduction method are effective for the growth of these coiled nanofibers. The experiment is a highly reproducible product and product selectivity is high. The results reported so far review the unique catalytic property of the Fe nanoparticles prepared by this method. The products of acetylene decomposition over the Fe catalysts reported elsewhere are carbon nanofibers,¹⁶ carbon nanohorns,¹⁷ carbon microcoils,¹⁸ and straight and/or tubular carbon nanofibers of irregular helical form.

The magnetization dependence of coiled nanofibers on field was measured at room temperature. Figure 7 shows the M – H curves at an applied maximum field of 50 KOe. The saturation magnetization is 4.99 emu/g, and the coercivity is 91.61 Oe. Compared to the coiled nanofibers of symmetric growth synthesized over nonmagnetic metals,^{12–15} the coiled nanofibers containing iron nanoparticles have higher magnetization. We tested the coiled nanofibers that had been exposed to air for over one year and found no changes in XRD features as well as magnetic properties. The high stability of the Fe nanoparticles could be a result of encapsulation in graphite layers.

We found that the temperature for the introduction of acetylene has certain influence on the morphology of the carbon products. If the initial temperature for acetylene introduction to the reaction tube was room temperature and then the temperature was raised for acetylene pyrolysis at 450 °C, the carbon products would be coiled nanofibers and the majority of them would be straight and/or irregular in form. The yield was found to be around 5.863 g in each run. Compared to the case of having 450 °C as the initial reaction temperature, these carbon fibers differ in diameters (Figure 8). Nevertheless, for the coiled nanofibers formed in this case, they also show a diameter of about 40 nm and with an iron nanoparticle encapsulated at the node.

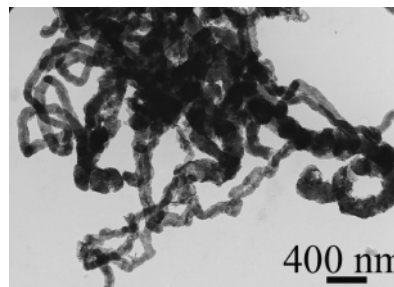


Figure 9. TEM images of carbon products in acetylene pyrolysis at 700 °C.

The effect of decomposition temperature on the morphology of carbon products was also investigated. If the pyrolysis of acetylene was conducted at 700 °C (Figure 9), there would be no coiled nanofibers but fibers with straight and/or irregular shapes. The diameters of these carbons are irregular and fall in the 100–200 nm range. The yield of carbon products was found to be around 15.753 g in each run.

Conclusion

This study reveals that the Fe nanoparticles prepared by the combined sol–gel/reduction method are effective for the growth of coiled nanofibers. Hence, compared to the Fe catalysts reported elsewhere, the Fe nanoparticles prepared in such a way are unique and coiled nanofibers can be synthesized from acetylene at low pyrolysis temperature. Compared to the coiled nanofibers obtained over nonmagnetic transition metals, the samples containing magnetic iron nanoparticles show higher magnetization.

Acknowledgment. We thank Prof. C. T. Au (Department of Chemistry, Hong Kong Baptist University) for valuable suggestions. Y.W.D. and A.G. thank the Chinese and Israeli Ministries of Science for a Binational Grant through the Sino–Israeli Program in Materials Science. This work was supported by the National Key Project for Basic Research (grant no. 2005CB623605) and the National Natural Science Foundation of China (grant no. 50471049), China.

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