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Structure and electrical properties of heat-treated fullerene nanowhiskers as potential energy device materials

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Abstract

Fine carbon tubes "fullerene shell tubes (FSTs)" have been found among the C_{60} nanowhiskers heat-treated under vacuum at a temperature higher than 600 °C. FSTs with open ends have been found as well as FSTs with closed spherical ends. It has been also found that the FSTs can be easily prepared by the heat treatment of the C_{60} whiskers prepared by using C_{60} powders containing $(\eta^2\text{-}C_{60})Pt(PPh_3)_2$. Since the high temperature-treated fullerene (nano)whiskers exhibit a high specific surface area and a good electrical conductivity, they are expected to be utilized as new electrode materials for fuel cells.

Keywords: Fullerene; Fuel cell

1. Introduction

New nanocarbon materials such as carbon nanohorns and carbon nanotubes have been attracting much attention as promising electrode materials for polymer electrolyte fuel cells and lithium ion secondary batteries.[1–3] To fabricate nanocarbons with a high specific surface area and a high electrical conductivity is a key technology to develop excellent energy sources.

On the other hand, since the discovery of C_{60} nanowhiskers in a colloidal solution of lead zirconate titanate (PZT) containing C_{60} in 2001,[4] we have reported various forms of fullerene nanowhiskers including nanowhiskers of C_{70} and $C_{60}[C(COOC_2H_5)_2]$.[5,6] These fullerene nanowhiskers can be easily synthesized at room temperature by using the liquid–liquid interfacial precipitation method (LLIP method).[7] Not only the above one-component fullerene nanowhiskers but also C_{60} nanowhiskers with dissolved $C_{60}[C(COOC_2H_5)_2]$, $C_{60}C_3H_7N$ or C_{70} molecules have been successfully prepared by the LLIP method.[8,9] The LLIP method is a powerful tool to prepare various fullerene nanowhiskers comprising different kinds of fullerene molecules.

On the other hand, in the course of examining the thermal properties of C_{60} nanowhiskers, we found that fine carbon tubes are formed among the C_{60} nanowhiskers heat-treated in vacuum. The new nano carbon tubes are named "fullerene shell tubes", referring to the name of "C_{60} shell".[10] Also we found that carbon tubes composed of C_{60} molecules can be prepared by using $(\eta^2\text{-}C_{60})Pt(PPh_3)_2$ in the course of fabrication of C_{60} nanowhiskers that contain $(\eta^2\text{-}C_{60})Pt(PPh_3)_2$ molecules.

Since the above new tubular carbons can get a high specific surface area and a high electrical conductivity, they are expected to be utilized as promising electrode materials for polymer electrolyte fuel cells.

The present paper shows the structural and electrical properties of the new carbons that are derived from fine whiskers of C_{60}.

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2. Experimental procedure

The LLIP method was performed for the fullerene powders with compositions of C_{60}-0–3 mol.% (η^2-C_{60})Pt(PPh_3)$_2$ to get various linear forms of fullerene precipitates. C_{60} powder with a purity of 99.5% (MTR Ltd., Ohio) and as-received powder of (η^2-C_{60})Pt(PPh_3)$_2$ (MTR Ltd.) were used. A toluene solution (5 mL) saturated with fullerene was prepared and put into a transparent 10 mL glass bottle. The toluene solution and isopropyl alcohol (IPA) were cooled to about 15 °C. Next, IPA was gently added to the fullerene-saturated toluene solution by use of a pipette in order to form a liquid–liquid interface between the toluene solution and IPA. The glass bottle was allowed to stand at 20 °C for ten days in an incubator with a transparent plastic window (SANYO MIR-153, SANYO Electric Co. Ltd., Japan) to obtain fullerene precipitates (nanowhiskers or needle-like crystals of fullerene).

The prepared fullerene precipitates were heated in vacuum for 30 min at temperatures between 600 and 1100 °C at a heating rate of 20 °C min^{-1} in evacuated fused silica tubes by use of a muffle furnace. The heating temperature was determined from a thermo gravimetric analysis (TG) performed on the precipitates dried at room temperature in air (TGD-9000, ULVAC, Japan). The TG analysis was done under evacuation by a turbo-molecular pump (TMH071P, PFEIFFER VACUUM, Germany) at a heating rate of 10 °C min^{-1}.

The heat treatment for the fullerene precipitates at 600 and 700 °C were done in an infrared image furnace (QHC-P610C, Shinkuriko Co. Ltd., Japan) under rotary pump vacuum, while the heat treatment at 900 and 1100 °C were done in evacuated sealed silica tubes.

The heat-treated fullerene precipitates were ultrasonically dispersed in toluene and pipetted onto TEM carbon microgrids and observed by a high resolution transmission electron microscope (HRTEM, JEM-4010, 400 kV, JEOL, Tokyo, Japan).

The electrical resistivity of the samples were measured by using a micromanipulator (MMS0024-01, SANYOU Co. Ltd., Japan) equipped with a 2 channel source/monitor unit (Agilent Technologies, E5272A) by using gold electrodes.

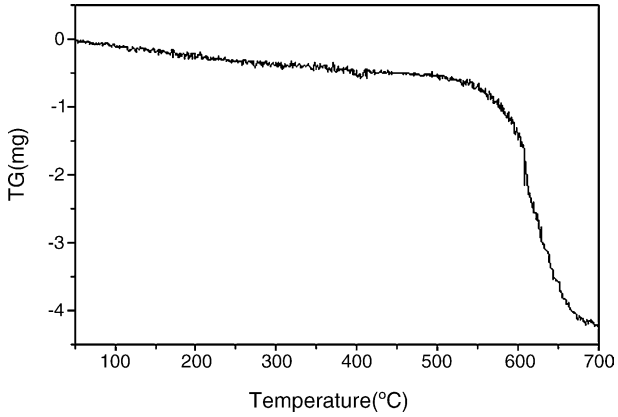

Fig. 1. TG curve for the C_{60} nanowhiskers obtained under evacuation by a turbo-molecular pump.

3. Results and discussion

A thermo gravimetric analysis for the C_{60} nanowhiskers that were obtained by using the pure C_{60} powder (99.5%) and dried at room temperature is shown in Fig. 1. It is found that the C_{60} nanowhiskers begin to decompose at a temperature higher than 550 °C in vacuum. The decrease in the TG-curve with increasing temperature shows the evaporation of solvents contained in the sample. As shown in the experimental procedure, the heat-treatment temperature was fixed to be higher than 600 °C from this TG experiment.

Fig. 2 shows a typical example of FST that was found among the C_{60} nanowhiskers heated in vacuum at 600 °C. The length of the FST is about 7.3 μm and much shorter as compared with the usual C_{60} nanowhiskers prepared by the LLIP method.[7] This is because the as-prepared FSTs were broken into shorter FSTs through the ultrasonication for the TEM specimen preparation. The average outer and inner diameters of the FST of Fig. 2 are 190 and 156 nm, respectively. The average wall thickness is 17 nm. The amorphous carbon substances sticking to the FST must have been originated from the C_{60} nanowhiskers that were decomposed during the heat treatment. A selected-area electron diffraction pattern (SAEDP) of Fig. 3(a) for the FST shows a pattern similar to the SAEDP of Fig. 3(b) for graphite powder. The tube wall is

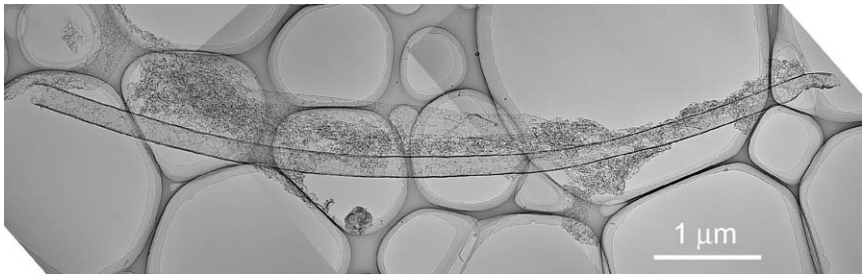

Fig. 2. TEM image of a “fullerene shell tube (FST)” prepared by heating a C_{60} nanowhisker at 600 °C for 30 min in vacuum.

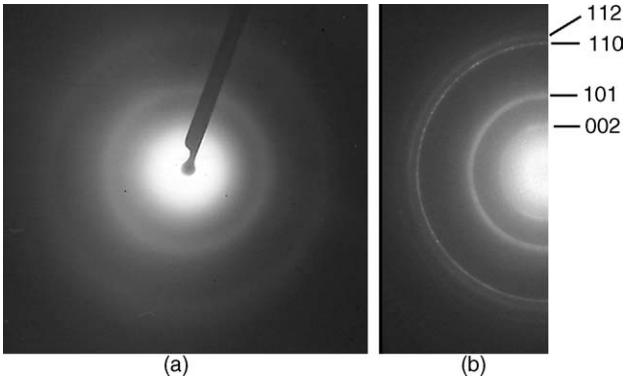

Fig. 3. SAEDPs for (a) the fullerene shell tube of Fig. 1 and (b) graphite powder.

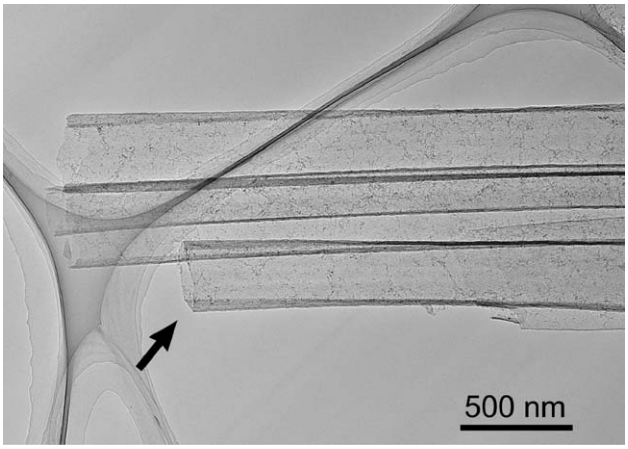

Fig. 4. TEM image of fullerene shell tubes prepared by heating C_{60} nanowhiskers at 600 °C for 30 min in vacuum.

found to be composed of amorphous carbon with disordered graphitic structure.

The edge structure of FSTs can be seen in Fig. 4. The FST indicated by arrow shows an open end.

Though most of the FSTs were found to be open-ended fragments of longer tubes, a FST with a closed end and a wall thickness of 10–20 nm was found as shown in Fig. 5. The HRTEM image Fig. 5(c) shows that the tube wall is amorphous. The enlarged image of Fig. 5(b) shows a spherical end of FST with a curvature radius of 80 nm, indicating that the FST has a cylindrical structure. It is conjectured that this rounded structure was formed from a C_{60} nanowhisker with a cylindrical surface.

A FST formed by heating at 700 °C is shown in Fig. 6. This FST has a wall thickness of 18 nm like the FSTs prepared at 600 °C. It is to be noted that the end of FST indicated by arrow has a flaked structure. This morphology indicates that the wall of FST was hard and fractured in a brittle mode by the ultrasonication for the TEM sample preparation.

Haluška et al. first reported that a shell structure "cocoon", i.e. "C_{60} shell", was formed by sublimating C_{60} crystals in a vacuum sealed glass tube.[11] The "cocoon" was transparent and developed from the thin surface layer of the original C_{60} crystals from which the inner part of C_{60} was sublimated. Sakuma et al. showed that the major part of the shell structure "cocoon" was amorphous carbon by Raman spectroscopy.[10] This result agrees with the above observation of Fig. 3(a).

Considering the possibility of structural difference between the surface part and the inner part of C_{60} crystals, we have examined a cross-sectional profile of a C_{60} whisker as shown in Fig. 7(a). The cross-sectioned sample was prepared by use of an ultramicrotome (Leica Ultracut UCT, Wetzlar, Germany) for the C_{60} whiskers embedded in an epoxy resin. The SAEDP indexed with a face-centered cubic (fcc) system of Fig. 7(b) shows that the growth axis is parallel to the [1 1 0] close-packed direction of C_{60} molecules in a fcc

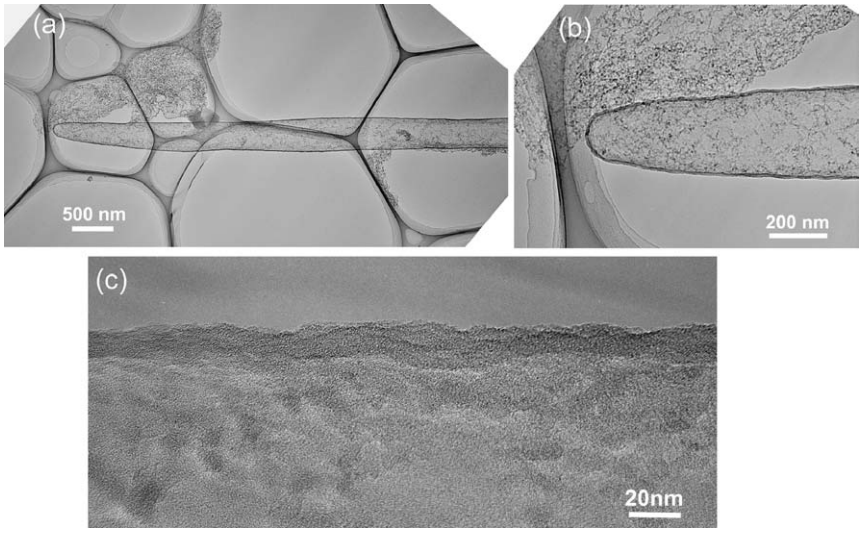

Fig. 5. (a) TEM image of a FST with a closed end that was prepared by heating a C_{60} nanowhisker at 600 °C for 30 min, (b) magnified TEM image of the spherical end with a curvature radius of 80 nm. Part (c) shows a HRTEM image for a part of the FST.

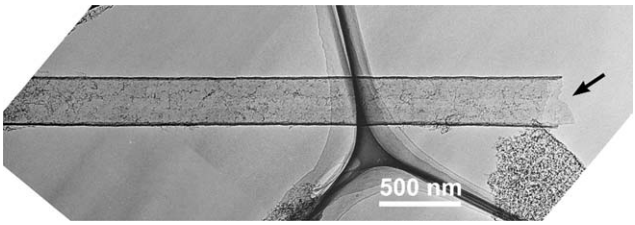

Fig. 6. TEM image for a FST prepared by heating a C_{60} nanowhisker at 700 °C for 30 min in vacuum.

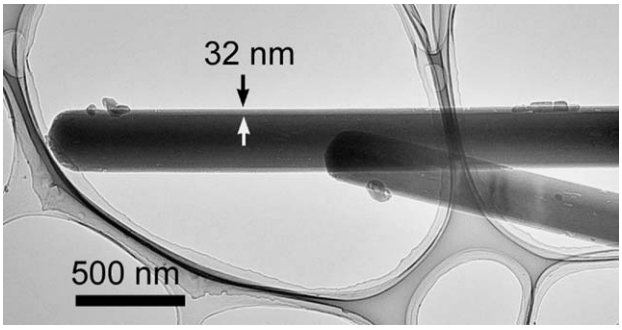

Fig. 8. TEM image of a crystalline C_{60} nanowhiskers after the heat treatment at 900 °C for 30 min in vacuum. A HRTEM observation of Fig. 9 was done for the arrowed whisker.

structure. This result coincides with our knowledge that the C_{60} molecules are densely aligned along their close-packed direction that is parallel to the whisker growth axis.[7] The whisker is covered by a thin layer with a thickness of 68 nm. The surface layer has a contrast brighter than the inside of the whisker, indicating a structural difference between the surface part and the inside part in the whisker. These observations support that the surface of C_{60} nanowhiskers has a structure different from their inner structure and that the FSTs are formed by a thermal modification of surface thin layers and the sublimation of inside C_{60} molecules.

Most of the C_{60} nanowhiskers heat-treated at elevated temperatures turned amorphous. But crystalline C_{60} nanowhiskers were observed as shown in Figs. 8 and 9, although those crystalline whiskers were very rarely found. Fig. 8 shows that a thin surface layer of 32 nm in thickness is formed like the case of Fig. 7. The high-resolution TEM (HRTEM) image for this whisker shows the crystalline structure of the whisker. The filtered HRTEM image Fig. 9(b), however, shows a high density of dislocations are remaining in the whisker. The FFT pattern of Fig. 9(c) was indexed assuming a body centered tetragonal (bct) structure with the lattice constants $a = 0.98$ nm and $c = 1.7$ nm. The center-to-center distance (D) between adjoining C_{60} molecules along the growth axis is 0.98 nm and this D value is about 2% smaller than the D value of pristine fcc C_{60} crystals with a lattice constant $a = 1.417$ nm.[12] It is considered that the surface thin layer of the whisker is working as a passive film that protects the whisker from the decomposition and turn the 'fullerene shell' when the inside C_{60} molecules are lost by evaporation.

In addition to the above fullerene shell tubes, we have successfully prepared fullerene shell tubes by heating the C_{60} whiskers prepared by using the powder with a composition of C_{60}-1 mol % (η^2-C_{60})$Pt(PPh_3)_2$ at 900 °C. Fig. 10(a) is an example showing a tubular structure that has tiny pores on the wall with a size of about 10 nm. These tubular fine carbons showed a specific surface area of 380 $m^2\,g^{-1}$ that was measured by the BET method (Belsorp 18 plus, BEL JAPAN Inc.). As shown in the SAEDP of Fig. 10(b), the FST has a wall of amorphous carbon like the example of Fig. 2.

Although the as-prepared C_{60} whiskers have a high electrical resistivity >10^5 Ω cm,[13] they became electrically conductive by high-temperature heat treatment in vacuum. For example, a C_{60} whisker of 2.2 μm in diameter showed a resistivity of 0.037 Ω cm and a C_{60} whisker of 2.9 μm in diameter showed a resistivity of 0.042 Ω cm after the heat treatment at 1100 °C for 30 min. Hence, the high-temperature heat-treated FSTs are expected to be excellent fine carbons

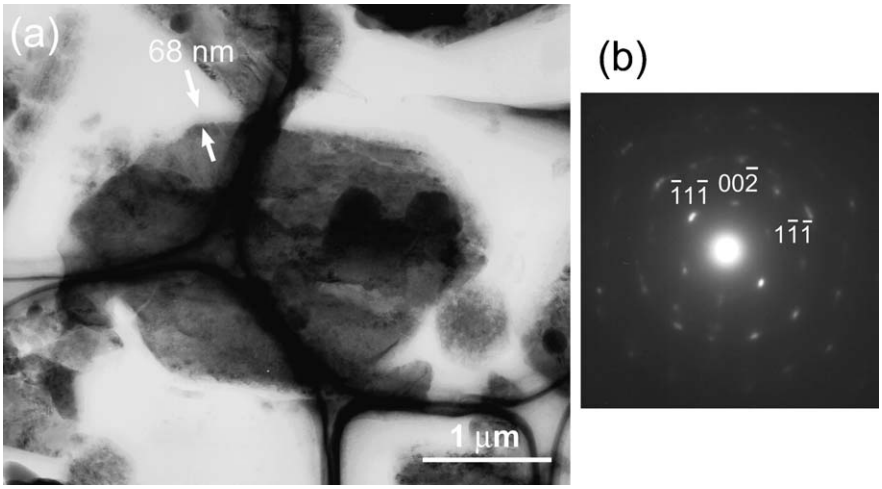

Fig. 7. (a) Cross-sectional TEM image of a C_{60} whisker, (b) SAEDP for the cross-sectioned sample of (a).

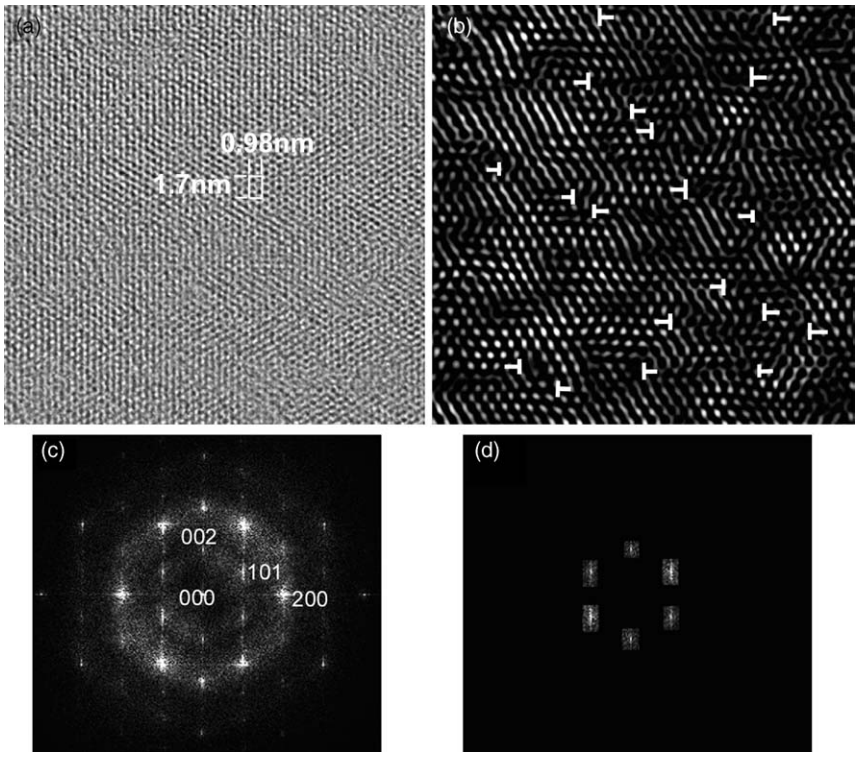

Fig. 9. (a) HRTEM images for the C_{60} nanowhisker of Fig. 8. (b) inverse filtered FFT image for photo (a) constructed by using the filtered FFT pattern (d), and (c) FFT image for part (a).

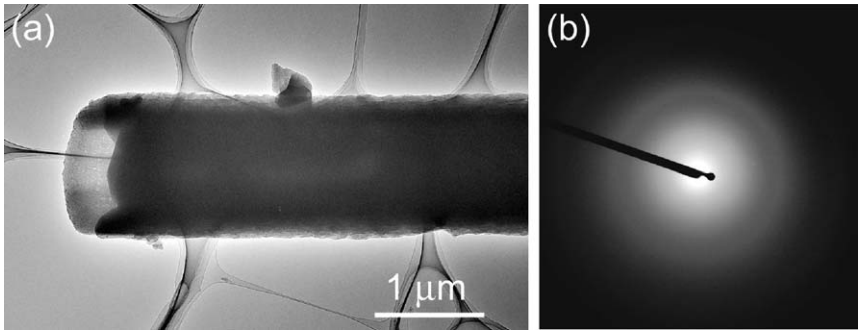

Fig. 10. (a) TEM image for a fullerene shell tube prepared by firing at 900 °C in vacuum and (b) its SAEDP.

with a high electrical conductivity and a high specific surface.

Finally, nano-sized Pt particles were found to be precipitated when the C_{60} whiskers prepared by using C_{60}-3 mol %(η^2-C_{60})Pt(PPh_3)$_2$ powder were irradiated by a concentrated electron beam in a TEM. Fig. 11 shows a C_{60} whisker which turned amorphous by the electron beam irradiation. A thin part of this precipitate was observed with a high magnification and the result is shown in Fig. 12. Fig. 12(a) shows Pt nanoparticles with a size of 3.2 ± 0.8 nm finely dispersed in the irradiated C_{60} whisker (Fig. 11). The (1 1 1) lattice planes of Pt (fcc, $a = 0.39231$ nm) are shown in the magnified image of Fig. 12(b). This size of Pt nanoparticles is close to the size of Pt nanoparticles ~2 nm deposited on the carbon nanohorns[1] and 2.6 nm of those on carbon nanotubes for the polymer electrolyte fuel cell application.[14]

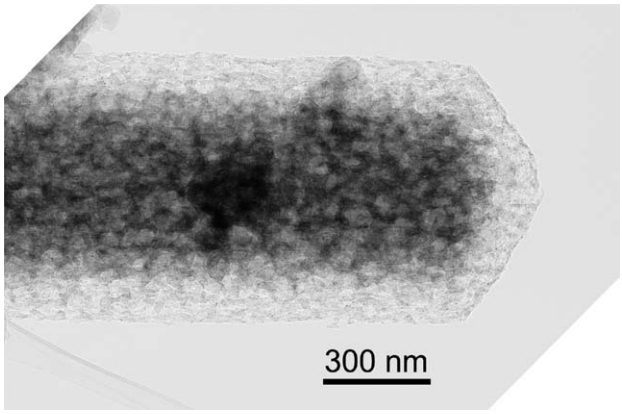

Fig. 11. TEM image of an electron beam-irradiated needle-like precipitate prepared by using the C_{60}- 3 mol.%(η^2-C_{60})Pt(PPh_3)$_2$ toluene solution.

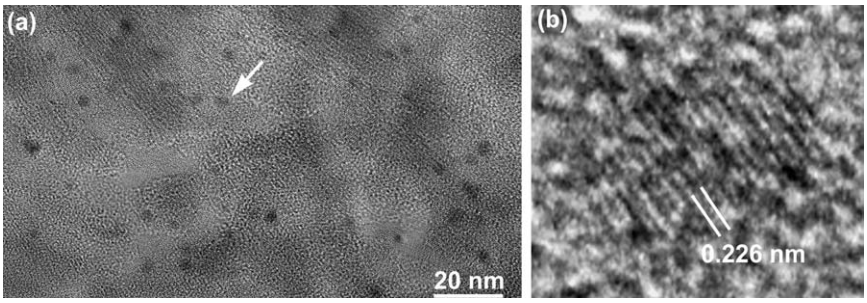

Fig. 12. (a)TEM image that shows Pt nanoparticles (shown by arrow) dispersed in the matrix of the electron beam irradiated needle-like precipitate of Fig. 11. (b) HRTEM image for a Pt nanoparticle shown in part (a).

It has been known that the cathode oxidation reduction reaction in polymer electrolyte fuel cells is enhanced by using platinum nanoparticles finely dispersed on carbon nanotubes.[14]

The above result suggests that fine C_{60} fibers with well-dispersed Pt nanoparticles can be produced by electron beam irradiation of the C_{60} nanowhiskers containing C_{60}-platinum derivatives. It is expected that Pt nanoparticles with suitable size and concentration can be obtained by controlling the concentration of C_{60}-Pt derivative molecules in the C_{60} nanowhiskers upon electron beam irradiation. Such C_{60} nanofibers with fine Pt particles may be efficiently utilized in the field of fuel cells when they acquire a high electrical conductivity by a suitable heat treatment.

Hence, the new electrically conductive tubular carbons with a high-surface area shown above must find wide application for polymer electrolyte fuel cell electrodes.

4. Conclusions

As shown above, the C_{60} nanowhiskers can be transformed to tubular structures "fullerene shell tubes" and become electrically conductive by heating at high temperatures in vacuum. The formation mechanism of fullerene shell tubes can be understood by assuming a thermal modification of surface thin layers of C_{60} nanowhiskers and the sublimation of inside C_{60} molecules.

Since the FSTs exhibit a high surface area and a good electrical conductivity, they are expected to be used as excellent fuel cell catalyst carriers.

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References

1. Yoshitake, T., Shimakawa, Y., Kuroshima, S., Kimura, H., Ichihashi, T., Kubo, Y. *et al.*, Preparation of fine platinum catalyst supported on single-wall carbon nanohorns for fuel cell application. *Physica B*, 2002, **323**(1–4), 124–126.
2. Matsumoto, T., Komatsu, T., Arai, K., Yamazaki, T., Kijima, M., Shimizu, H. *et al.*, Reduction of Pt usage in fuel cell electrocatalysts with carbon nanotube electrodes. *Chem.Commun.*, 2004, 840–841.
3. Yoon, S.-H., Park, C.-W., Yang, H., Korai, Y., Mochida, I., Baker, R. T. K. *et al.*, Novel carbon nanofibers of high graphitization as anodic materials for lithium ion secondary batteries. *Carbon*, 2004, **42**, 21–32.
4. Miyazawa, K., Obayashi, A. and Kuwabara, M., C_{60} nanowhiskers in a mixture of lead zirconate titanate sol–C_{60} toluene solution. *J. Am. Ceram. Soc.*, 2001, **84**, 3037–3039.
5. Miyazawa, K., C_{70} nanowhiskers fabricated by forming liquid/liquid interfaces in the systems of toluene solution of C_{70} and isopropyl alcohol. *J. Am. Ceram. Soc.*, 2002, **85**, 1297–1299.
6. Miyazawa, K., Mashino, T. and Suga, T., Structural characterization of the $C_{60}[C(COOC_2H_5)_2]$ whiskers prepared by the liquid–liquid interfacial precipitation method. *J. Mater. Res.*, 2003, **18**, 2730–2735.
7. Miyazawa, K., Kuwasaki, Y., Obayashi, A. and Kuwabara, M., C_{60} nanowhiskers formed by the liquid–liquid interfacial precipitation method. *J. Mater. Res.*, 2002, **17**, 83–88.
8. Miyazawa, K., Mashino, T. and Suga, T., Liquid phase synthesis of the nanowhiskers of fullerene derivatives. *Trans. Mater. Res. Soc. Jpn.*, 2004, **29**(2), 537–540.
9. Miyazawa, K., Fullerene Nanofibers as Potential Materials for Fuel Cell Electrodes. *Fourth Knowledge Foundation's Annual International Conference on Nanostructured Materials 2003*. Miami Beach, FL, USA, November 9–10, 2003, proceedings in press.
10. Sakuma, H., Tachibana, M., Sugiura, H., Kojima, K., Ito, S., Sekiguchi, T. *et al.*, Growth and structures of C_{60} shells. *J. Mater. Res.*, 1997, **12**, 1545–1550.
11. Haluška, M., Kuzmany, H., Vybornov, M., Rogl, P. and Fejdi, P., A double-temperature-gradient technique for the growth of single-crystal fullerites from the vapor phase. *Appl. Phys. A*, 1993, **56**, 161–167.
12. McCready, D. and Alnajjar, M., *Powder Diffraction File No. 44-558*, International Centre for Diffraction Data, Newton Square, PA, 1994.
13. Miyazawa, K., Kuwasaki, Y., Hamamoto, K., Nagata, S., Obayashi, A. and Kuwabara, M., Structural characterization of C_{60} nanowhiskers formed by the liquid/liquid interfacial precipitation method. *Surf. Interf. Anal.*, 2003, **35**(1), 117–120.
14. Li, W., Liang, C., Qiu, J., Zhou, W., Han, H., Wei, Z. *et al.*, Carbon nanotubes as support for cathode catalyst of a direct methanol fuel cell. *Carbon*, 2002, **40**, 791–794.