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Linear carbon allotrope – carbon atom wires prepared by pyrolysis of starch

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Abstract

A new method is reported to produce linear carbon allotrope from the pyrolysis of starch catalyzed by Fe. The pyrolytic product termed as carbon atom wires (CAW) is composed of winding lines with the diameter around 2.0 Å, indicated by magnified HRTEM images. The experimental results of UV and Raman spectra revealed a conjugated sequence of cumulated double bonds $(=C=C=)_n$ presented in the hexane extract of CAW. Arguments about the sp hybridization bonding structure of CAW can also be supported by EELS and FT-IR measurements.

1. Introduction

Among all elements, carbon constructs the greatest varieties of compounds in the world. It is well known that carbon allotrope can be bonded with sp^3 (diamond) or sp^2 (graphite, spheroidal fullerenes [1,2] and fullerene nanotubes, including multi-wall [3] and single-wall nanotubes [4,5]) hybridization. Another allotropic form of carbon based on sp hybridization was produced from graphite sublimation [6] in 1969 and synthesized from the oxidative couplings (Hay techniques) of silyl-protected alkynes [7] in 1972. Since then, intensive researches have been performed on its preparation [8–10], spectroscopy [11,12] and calculation [13]. Some reviews [14–17] outlined the advancement on the subject. Although the linear structure of sp-bonded carbon allotrope is fascinating and attractive, and the allotrope was synthesized as early as in 1960s, the properties and applications of the linear carbon are not well revealed due to difficulties of its instability and massive preparation. Here, we report a new method capable of massively producing linear carbon allotrope from pyrolysis of starch.

The discovery happened in our efforts to prepare carbon nanotubes from solid carbonaceous species. In our experience, the diameter of carbon nanotubes produced depends upon the size of catalyst used during a pyrolytic process of carbonaceous species. When we tried our best to make the catalyst more and more finely and homogeneously distributed in carbonaceous species and in the meantime to prevent it from aggregation in the preparation process, we found less and less carbon nanotubes in the sight of transmission electron microscope (TEM) of products with our efforts, instead, appearing more and more cloudy pieces whose morphology could not be established in the magnification of 5×10^4 times. When the sample was examined with a high resolution transmission electron microscope (HRTEM), it was found that the cloudy pieces were of fine structures.

The terms of 'carbyne', 'polyyne', 'alkynes' and 'poliynes' are often used to report the researches of the carbon allotropy with sp-bonded structure in literatures. To high-light the characteristic morphology of the linear shape and of the diameter size on atomic scale, and to

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avoid the argument on if the linear chain is constructed in cumulated double bonds $(=C=C=)_n$ or in the alternative single and triple bonds $(-C\equiv C-)_n$, it is better to term our product as carbon atom wires (abbreviated to CAW later on in the Letter) rather than as the nomenclatures mentioned above in the literatures. Carbon atom wires can exist stably in the forms capped by hydrogen atoms or other radicals.

2. Experimental

Ten grams potato starch as a carbonaceous species used in a pyrolytic process to produce carbon atom wires (CAW) was mixed homogeneously with 2.12 g aqueous solution of 4.0 wt% $Fe(NO_3)_3$, i.e., in the mass ratio of starch:Fe = $1:2 \times 10^{-3}$. The pyrolysis took place in a tube-furnace, isolated from atmosphere, under a stream of Ar/H_2 mixture (Ar 80 mL/min, H_2 40 mL/min) at the reaction pressure of 0.2 MPa. The reaction temperature was controlled in steps by a programmer, first, heating in the rate of 15 °C/min up to 500 °C and keeping the temperature for 6 h to reduce $Fe(NO_3)_3$ into Fe, then, raising the temperature in the same heating rate up to 800 °C, keeping it constant again for another 16 h to pyrolyze starch, and at last, cooling to the room temperature in the furnace. In the last 6 h at 800 °C, the gas stream contained only Ar gas, while H_2 was stopped adding into the reactor. About 1.2 g product was obtained and purified with 6 M HCl at the reflux temperature for 6 h to remove the catalyst Fe.

To determine the quantities of various elements such as C, O, H and Fe, the measurements of X-ray photoelectron spectroscopy (XPS) and elemental analysis were performed on PHI 550 ESCA/SAM electron (energy) spectroscopy, Perkin–Elmer 240C and an inductively coupled plasma (ICP) atomic emission spectrometer Jorrell-Ash Model J-A1100, respectively.

To have a sample with narrow distribution of carbon chain length, the product was mixed with hexane and heated in reflux to extract small molecules of CAW. Filtrate of the mixture was used to measure its UV and Raman spectra on Perkin–Elmer LAMBDA 17 and on OLYMPUS BX41 JOBIN YVON RAMAN DIVISION, respectively. The proportion, soluble in hexane, is about 0.35 wt% in the product purified by HCL. This result does not mean that the pyrolytic product contained so little CAW, but implies that the most part of CAW possess long carbon chains. The sample for FTIR, HRTEM and EELS measurements is the whole product, not the small molecules of CAW in the hexane extractive only. The FTIR spectrum was taken by the spectrograph Nexus 670 FT-IR (Nicolet) with 32 scans and the resolution of 4 cm^{-1}. A CAW sample was ground with 100 times its bulk of pure potassium bromide and pressed into a disk for the measurement. To free from moisture, the sample and KBr used were dried in a vacuum oven at 150 °C for 48 h.

The JEOL 3000F TEM was equipped with a field emission gun and a Gatan energy filter and EELS spectra were acquired in diffraction mode at the accelerating voltage of 300 kV, with the collection angle of 4 mrad and 0.2 eV per pixel. Common chemical methods [18] were used to determine the quantities of alcoholic hydroxyl group –OH by the acetic anhydride method catalyzed by pyridine and the carboxylic acid group –COOH by neutralization with aqueous NaOH solution.

3. Results and discussion

Fig. 1 is of HRTEM photographs at different areas of carbon atom wires prepared from the pyrolysis of potato starch, in which the winding lines appear to have the same thickness, around 2 Å. Considering their thickness value being comparable to the size of a single

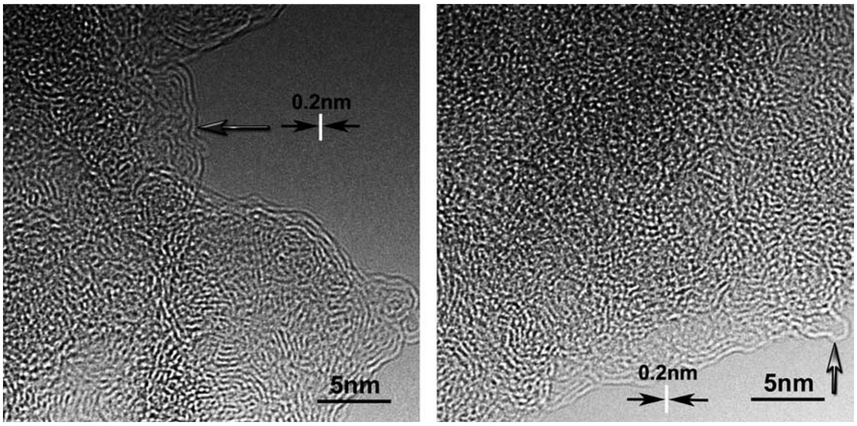

Fig. 1. HRTEM photographs at different areas of carbon atom wires prepared from the pyrolysis of potato starch.

carbon atom, we term the winding lines shown in Fig. 1 as carbon atom wires.

An UV spectrum of the hexane extract of CAW is shown in Fig. 2. The bands around 221, 199 and 272.5 nm indicate that the carbon atom numbers of the most wires dissolved in hexane are less than ten [7,13]. Fig. 3 is of a Raman spectrum of the extractive. The peaks of 971, 999.5, 1077.5 and 1506 cm^{-1} correspond to the stretching frequency of $=C=C=$ [17,19], but there is no apparent peak around 2100 cm^{-1} (outside the range shown in the figure) corresponding to the stretching frequency of $-C\equiv C-$ [17] observed. Although the linear sp-hybridized carbon allotropy can be depicted as a sequence of cumulated double bonds $(=C=C=)_n$ or as a chain of conjugated triple bonds $(-C\equiv C-)_n$, the former is presumably the preferred bonding configure when the carbon atom number of a chain is less than 10 [16]. The experimental results of UV and Raman spectra revealed that the most portion of carbon atom wires dissolved in hexane consisted of short chains with carbon atom numbers less than 10.

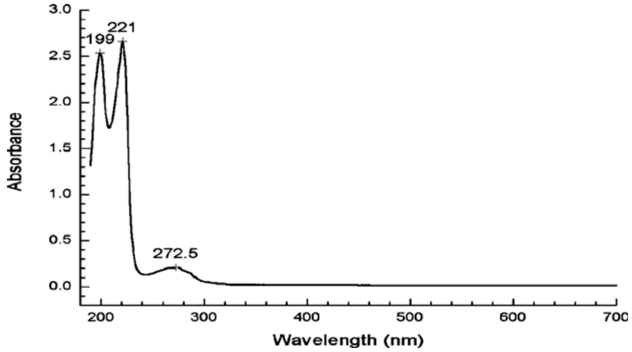

Fig. 2. An UV spectrum of the hexane extract of carbon atom wires prepared by pyrolysis of potato starch.

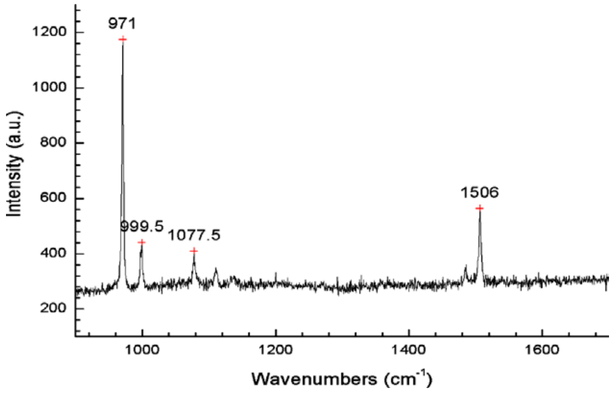

Fig. 3. A Raman spectrum of hexane extract of carbon atom wires prepared by pyrolysis of potato starch.

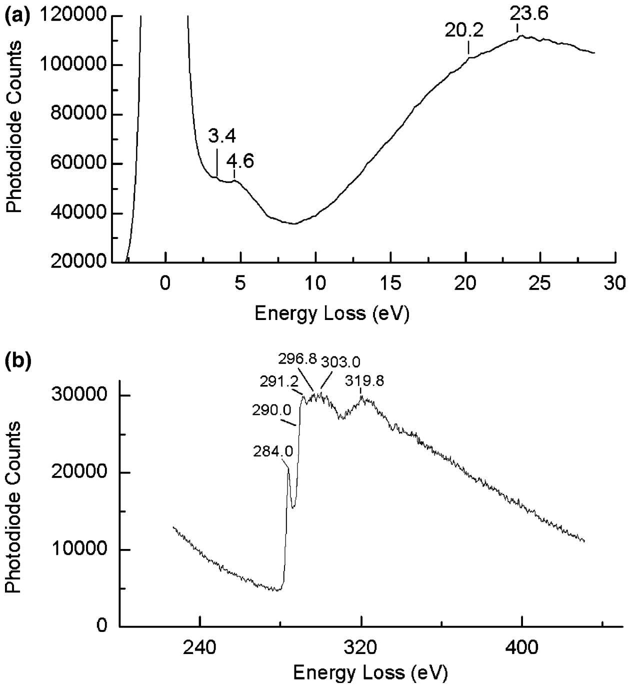

Fig. 4. The low loss region (a) and carbon K-edge (b) EELS spectra from carbon atom wires.

In Fig. 4a, the peak of 4.6 eV and the should of 3.4 eV that are characteristic of the strong π–π* interband transition and π-interband plasmon, and the peak of 23.6 eV and the shoulder of 20.2 eV that arise from plasma resonance of all valence electrons (π + σ plasmon) can be found and are shifted to the lower energy values than the corresponding values of graphite, as the case of carbynes and carbynoid samples [17,20]. EELS spectrum of carbon K-edge shown in Fig. 4b is also characteristic of carbyne rather than graphite or diamond [17,20].

An IR absorption spectrum of CAW produced from potato starch is shown in Fig. 5. The sample measured by FTIR is the purified product itself, not its hexane extract as the sample for Raman measurement, containing long carbon atom wires. Thus, a broad absorption around 2010 cm^{-1} corresponding to the stretching vibration of $C\equiv C$ in the chain of conjugated triple bonds $(-C\equiv C-)_n$ which does not appear on the Raman

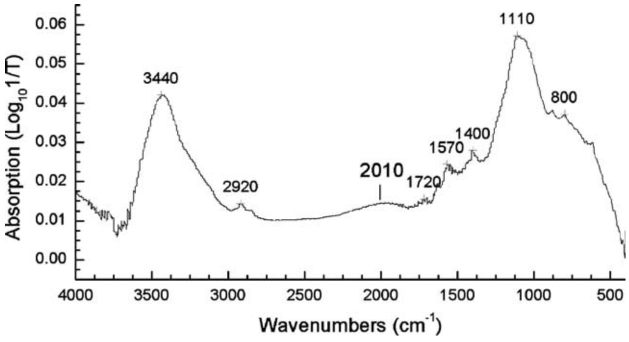

Fig. 5. An IR absorption spectrum of carbon atom wires produced from potato starch.

spectrum and the peaks around 1400–1570 cm^{-1} due to various carbon skeletons such as cumulene and polyene structure [17,21–23] can be observed. The low intensity of the broad absorption around 2010 cm^{-1} implies the highly conjugated $(–C\equiv C–)_n$ structure in the product. As to the other bands, we refer the absorption around 1110 cm^{-1} to C–C and C–O stretching vibration, the band around 3440 cm^{-1} to O–H stretching vibration, the band around 1720 cm^{-1} to C=O stretching vibration, and the band around 800 cm^{-1} to the skeletal vibration of alkyl group $–CH_3$, the deformation frequency and 'out-of-plane' vibration of the alkenyl group $=CH_2$ and OC–OH group [24,25]. These bands indicate the presence of alcoholic hydroxyl group –OH and the carboxylic acid group –COOH in our product, which were confirmed by the chemical analysis method as well. Chemical analysis detected that there were about one alcoholic hydroxyl group –OH per 16 carbon atoms, one –COOH group per 230 carbon atoms in CAW.

The measurements of XPS and elemental analysis indicated that the purified CAW contained about 93% carbon, 2% hydrogen and 5% oxygen by weight. The trace residence of the catalyst Fe was 126 ppm in the product purified by 6 M HCL once and could be reduced to 6 ppm when the product was purified twice.

It has been realized that nonreactive terminal groups or end caps, as well as the chain conformations and interactions can stabilize the linear sp structure [8,17]. The existence of the groups detected above and the winding line shape with small intervals among the neighboring wires can presumably help to explain the stability of carbon atom wires at the room temperature in air. In addition, carbon atom wires are of one dimension and have unfixed intervals among the neighboring wires, and thus it is anticipated that they are easily accessible by intercalation of different foreign atoms, molecules and ions to form composites with various desirable properties.

When we used $Co(NO_3)_2$ instead of $Fe(NO_3)_3$, and degreased cotton instead of potato starch, we got similar results.

4. Conclusion

Based on the experimental results of morphology, molecular and electron spectroscopy, the pyrolytic product of potato starch, termed as carbon atom wires, possesses the sp-bonded structure of linear carbon allotropy. The product is slightly soluble in hexane and the most portion of carbon atom wires dissolved in hexane consists of short chains with carbon atom numbers less than 10.

Acknowledgements

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