Preparation and Growth Mechanism of Nanohelical Structures*

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Introduction

The study of helical structures such as micro-coils and nano-coils has received increasing attention in recent years [1,2]. The coiled fibers are chiral with three dimensional helical/spiral morphology and possess unique characteristics, such as super-elasticity [3,4,5], wide band absorption of electromagnetic waves [6,7], hydrogen adsorption [8] and so on. These unique properties make coiled fibers a very attractive material for potential applications.

Researchers synthesized micro-coiled fibers in last decades. The fibers are generally prepared by high-temperature (>500 ºC) catalytic decomposition of organic gas such as acetylene or benzene. In this work, the helical nanofibers were synthesized by catalysis of Cu nanoparticles, under lower temperature. Their structures were characterized with SEM, FT-IR, *etc*., and the growth mechanism of the related helical nanofibers was suggested.

Experimental

As a catalyst precursor, the copper(II) tartrate was prepared by a precipitation method [9]. The preparation of the nanofibers was carried out under atmospheric pressure in a quartz tube，which was set into the horizontal furnace and heated at the designed heating rates. A ceramic boat paved with a layer of the catalyst precursor was placed into the reaction tube. The heating continued until the catalyst precursor was decomposed into copper particles. Acetylene was then induced into the tube and decomposed to produce the nanofibers.

The morphologies of the fibers were observed by environmental scanning electronic microscope (ESEM, Fei, Quanta 200) with an accerlerating voltage of 20.0 kV. The chemical constituents of the helical fibers were confirmed through FT-IR analysis (Nicolet 5700, USA) from 4000 to 400 cm^{-1} at a resolution of 4 cm^{-1}.

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Results and discussion

The helical fibers with regular coils (Fig. 1a) are obtained under several conditions: the heating rate is less than 3 ºC/min, the atmosphere for decomposition of the catalyst precursor is acetylene, and the reaction temperature is between 195 ºC and 271 ºC. In contrast, the straight fibers (Fig. 1b) are obtained if the heating rate for the catalyst precursor increases up to 3 ºC/min under argon atmosphere.

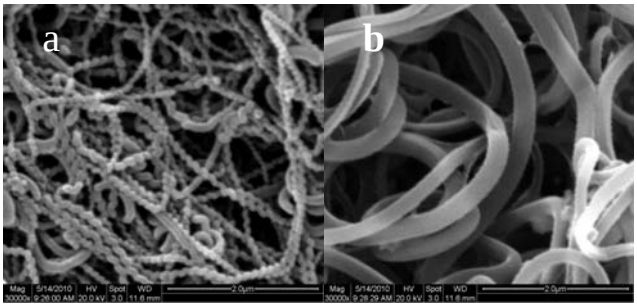

Fig. 1. SEM images of two kinds of nanofibers prepared at 271 ºC using catalysts generated from: a) under acetylene at lower heating rate (< 3 ºC), b) under argon at higher heating rate (> 3 ºC).

Fig. 2 shows a typical FT-IR spectrum of the nanofibers prepared at 271 ºC, in which the peaks at 2926.3, 2870.6, and 1451.8 cm^{-1} are ascribed to the C–H vibration in CH_2, the peak at 1601.3 cm^{-1} is assigned to C=C stretching vibration, the peaks at 3018.8 cm^{-1} and 1030.0 cm^{-1} are resulted from C–H stretching and deformation in C=C, respectively, and the C–H deformation in CH_3 induces the peak at 1375.7 cm^{-1}.

The IR analysis reveals that the chemical structure of the nanofibers contains both C=C and saturated CH_2,

CH_3 groups. The OH group associating to 3447.8 cm^{-1} may arise from the oxidation in air, which is consistent with the mechanism of traditional polyacetylene oxidation [10]. In addition, the elementary analysis reveals that the C/H molar ratios of the as-prepared coiled fibers are 1.139 at 200 ºC, 1.210 at 250 ºC and 1.252 at 300 ºC. These results confirm the existence of the unsaturated groups and their oxides that formed in air. Thus we suggest that the nanofiber is a kind of organic compound comprising C=C group with minor oxidization.

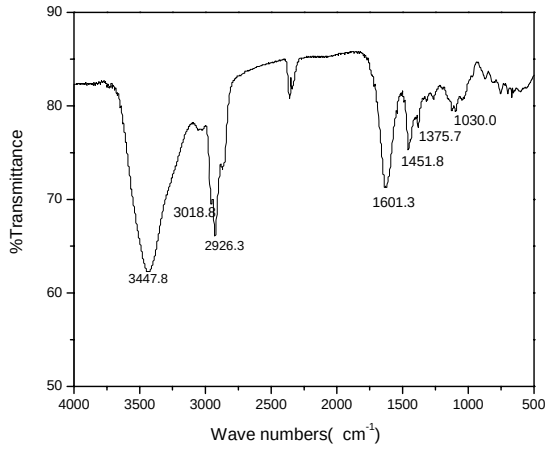

Fig. 2. Typical FT-IR spectrum of the helical nanofibers prepared at 271 ºC.

Our observation confirms that the shape of the catalyst changes during the early stage of the fiber growth (Fig. 3). Most of the nanofibers change from straight to helical shape after the reaction starts for 5 to 15 min. Once the polyhedron of the copper particle is formed, the absorbability of acetylene is disparate on different planes, leading to dissimilar rates both in the polymerization and the fiber growth on different planes, so the helical fibers generate. In general, we draw the conclusion that the acetylene adsorption favors the formation of polyhedron copper nanoparticles on which the helical nanofiber forms and grows.

Conclusion

The high purity helical nanofibers of organic compounds were synthesized by coordination polymerization of acetylene catalyzed by the generated copper nanopolyhedra. Different heating atmosphere and heating rate will result in different morphologies of fibers (helical and straight).

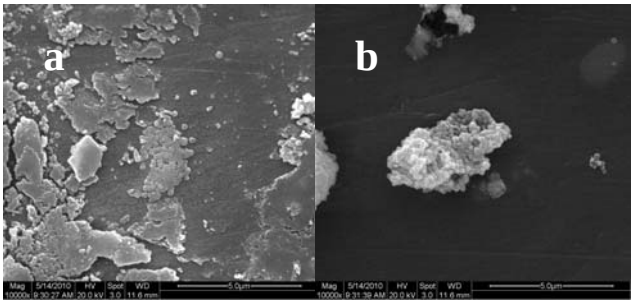

Fig. 3. SEM images of the samples grown for 0 min (a) , 5 min (b) , the typical shape change of the particle during the reaction.

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