High-yield synthesis of carbon nanofibers catalyzed by copper nanowires

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Copper nanowires prepared by ac electrodeposition in anodic aluminum oxide (AAO) templates were used in catalytic decomposition of acetylene for synthesis of carbon nanofibers via chemical vapor deposition (CVD) method at a temperature of 300 °C. The experimental results indicated that one single copper nanowire could cause catalytic growth of several carbon nanofibers with the same diameters. The microstructure change of copper nanowires takes place in the experiment. The resultant products were characterized using scanning electron microscopy (SEM) and transmission electron microscopy (TEM).

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1. Introduction

Carbon nanofibers (CNFs) have been studied for a long time for a variety of applications including composite, [1] lithium batteries, [2] super capacitors, and fuel cells [3]. Recently it has attracted much attention from materials scientists to synthesize CNFs in different ways. Actually, chemical vapor deposition (CVD) has been chosen to prepare CNFs in most cases by researchers, whereas transition metals like Fe, Co, Ni, and Cu are used as catalysts [4, 5]. CNFs with different morphology and microstructure can be produced by different metal nanoparticles. Tanaka *et al [*6] reported that highly crystalline CNFs with controlled structure may be prepared with Fe and Fe-Ni alloy as catalysts at the temperature of 560 to 620 °C. Martin-Gullon *et al.* reported that using ferrocene as catalyst source, iron-derived CNFs with a core of multi-wall nanotubes were produced from natural gas and xylene at temperatures above 1077 °C [7]. Helical carbon nanofibers with a symmetric growth mode were synthesized with copper nanocrystals as catalysts [5]. Generally, the microstructure of catalysts used to grow CNFs is in the form of nanoparticles, and the particle size is uniform. However other catalysts with different nanostructures like nanowires or nanocones have rarely been reported in literature.

In this contribution, novel carbon nanofibers were synthesized with acetylene as a carbon source and copper nanowires as catalysts by CVD method. In our experiment, the copper nanowires were obtained by ac electrodeposition with anodic aluminum oxide (AAO) as templates [8]. The obtained carbon nanomaterials are characterized and the growth mechanism is discussed. At the end, we propose a new growth model.

2. Experimental

AAO templates were prepared by a two-step anodic oxidation and oxalic acid as electrolyte [9]. After that copper nanowires were synthesized by ac electrodeposition, deposition voltage was 10 V and deposition frequency was 50 Hz. The electrolyte was 0.50 M $CuSO_4$/0.50 M H_3BO_3 for copper nanowire depositions. AAO templates with deposited copper nanowires were etched in 1 M NaOH solution for a defined time, and then the copper nanowires would be released from the templates. CNFs were synthesized via CVD using copper nanowires as catalysts at a temperature of 300 °C. In this process, acetylene was chosen as a carbon source. The resultant products were characterized using scanning electron microscopy (SEM) and transmission electron microscopy (TEM).

3. Results and discussion

The morphology of AAO templates after the second anodization is shown in Fig. 1. The pore size of the AAO templates are about 80 nm in diameter, 10 um in depth and distributed uniformity. Geometrical shape of the pore with a hexagonal arrangement is observed on the surface of AAO templates with low density of defects.

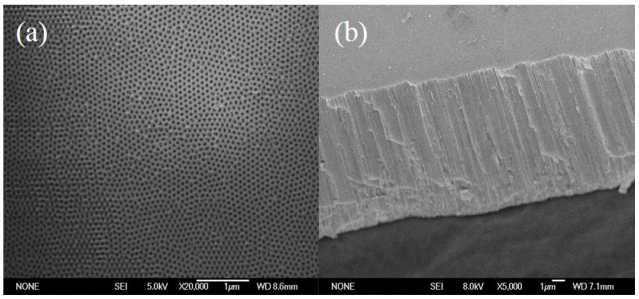

Fig. 1. SEM images of AAO templates prepared by two-step anodic oxidation: (a) top view and (b) cross section view

Copper nanowires prepared by ac electrodeposition were etched in 1 M NaOH for about 15 min to dissolve AAO templates, and then copper nanowires without templates would be obtained. Pure copper nanowires were dispersed in ethanol by ultrasound, and the dispersion solution was used for SEM and TEM sample preparations.

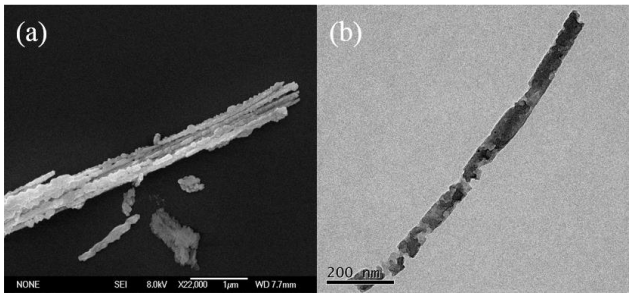

Fig. 2. SEM (a) and TEM (b) images of copper nanowires prepared by ac electrodeposition.

The copper nanowires prepared by ac electrodeposition are shown in Fig. 2. From the SEM image of Fig. 2(a) we can see that the surface of the copper nanowires is rough, and the nanostructure of copper nanowires is bamboo-like. This is because that the ac electrodeposition is periodically varied, and copper nanowires are only deposited in one half cycles. It can be observed that the copper nanowires are 70-90 nm in diameter in TEM image of Fig. 2(b).

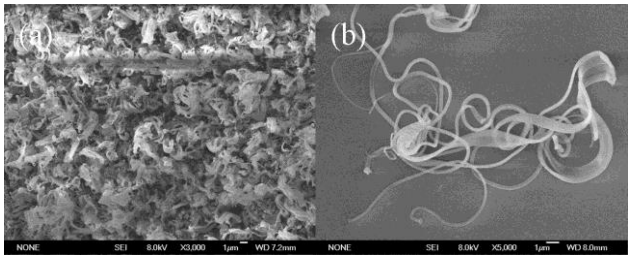

Fig. 3. SEM images of CNFs synthesized by CVD method using copper nanowires as catalysts: (a) original CNFs and (b) CNFs dispersed in ethanol by ultrasound

The CNFs synthesized by copper nanowires are shown in Fig. 3. It could be found that the growth orientations of CNFs are different in the whole picture (Fig. 3a). There are always several CNFs grown over the side of a single copper nanowire. From Fig. 3(b) we can infer that the CNFs, which grew over a single copper nanowire, have the same diameter of about 200 nm. Interestingly we never found the CNFs grew from one endpoint of copper nanowires. We proposed that the shape changes of copper nanowires have an important influence on the morphology of resulted products.

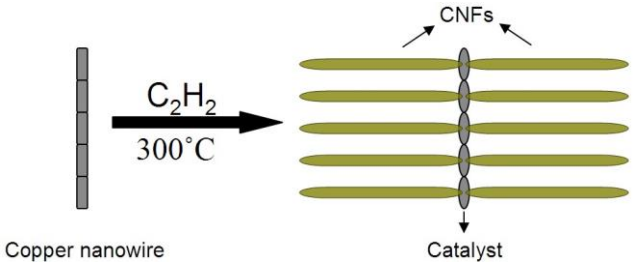

Fig. 4. Growth model of CNFs prepared by copper nanowires

To further investigate the growth model of CNFs, we establish the schematic diagram of growth mechanism of CNFs (Fig. 4). Just like copper nanocrystals in Hansen's study,[10] the bamboo-like copper nanowire can change its nanostructure during the growth process of CNFs. Every bamboo joint of copper nanowires would transform into one nanocrystal which is able to catalytically decompose acetylene, and each copper nanocrystal with the same size can catalytically grow a single CNF with the same diameter. It is worth noting that even the shape of bamboo joints of copper nanowires have been changed, but the morphology of copper nanowires still exist.

4. Conclusions

In summary, we demonstrated catalytic growth of CNFs by the decomposition of acetylene and using copper nanowires as catalysts. The nanowires were prepared by ac electrodeposition via AAO templates. Experimental results indicate one single copper nanowire can catalytically grow several CNFs with the same diameter, and the CNFs always grew over the side of copper nanowires. Moreover, the nanostructure change of copper nanowires was observed in the experiment.

Acknowledgments

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