Synthesis of Y-shaped carbon nanofiber films by the decomposition of acetylene with copper catalysts

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In this study carbon nanofiber films were synthesized via chemical vapor deposition with acetylene as carbon resource and copper film as catalyst. The resultant films were characterized using scanning electron microscopy. It was observed that the carbon nanofiber films were composed of a large number of Y-shaped nanofibers, and the diameter of Y-shaped nanofibers was about 300 nm. Copper nanocrystals were always located at the nodes of Y-shaped fibers, and they were faceted with regular shapes, such as triangular and rhombic. Each copper catalyst particle can lead to the growth of three fiber branches over different crystal facets, and thereby form the Y-shaped carbon nanofibers.

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1. Introduction

Since the report of fullerene [1] and carbon nanotubes [2], carbon nanomaterials have attracted a lot of attention in the filed of chemistry, physics, materials science and engineering because of their unique structural and physical properties [3]. Their potential applications have given rise to an intense research activity on catalytic synthesis of carbon nanofibers with different morphologies via chemical vapor deposition (CVD) methods. To our knowledge, branched carbon nanofibers [4], helical carbon nanofibers and straight carbon nanofibers [5] have been synthesized in recent years. However, the Y-shaped carbon nanofibers were rarely synthesized by copper catalyst through a CVD process. In general, the most important factor for the formation of carbon nanofibers through the CVD process is the size and shape of metal catalysts which determine the morphology of carbon nanofibers [6]. For instance, when copper nanoparticles were used to catalytically synthesize carbon nanofibers, small catalyst particles are apt to synthesize helical carbon nanofibers, but large ones to straight carbon nanofibers [7-12]. In this paper, copper nanofilms were obtained on silicon substrate via a physical vapor-condensation method. Copper nanoparticles transformed their morphologies during the CVD process, and the reshaped catalysts can lead to the formation of high yield Y-shaped carbon nanofibers as a film on the silicon substrate. Furthermore, catalytic growth mechanism of Y-shaped carbon nanofibers is discussed.

2. Experimental

2.1 Preparation of Copper Catalysts

Firstly, silicon wafers were ultrasonically washed by acetone, then washed with deionized water and dried by flowing air. Secondly, the cleaned silicon wafer was placed onto a supporting substrate inside a thermal evaporation chamber. Before preparation, the thermal evaporation chamber was pumped to a vacuum degree of 10^{-3} Pa, then backfilled with a working gas (argon). The copper target materials were melted and evaporated by high temperature. Then copper nanoparticles were formed by the nucleation and growth processes. Finally, copper nanofilm made of copper nanoparticles was deposited on the silicon wafer using a physical vapor-condensation method [11]. The obtained copper film with a thickness of about several hundreds nanometers was then transferred to a CVD chamber without additional treatment.

2.2 Growth of Y-shaped carbon nanofibers

Y-shaped carbon nanofiber films were synthesized using a CVD apparatus [8]. The silicon substrate covered with copper film was placed in the middle of reaction tube. The tube was pumped to 10^{-3} Pa. Acetylene as carbon source was introduced into the reaction tube until internal pressure equaled to external pressure. Then reaction tube was heated from room temperature to 300 ^{o}C and maintained at 300^{o}C for about 10 min. After the reaction, the reaction tube was naturally cooled to room temperature.

2.3 Structural characterization

The morphology of silicon substrate coated with copper nanoparticles and carbon nanofibers were studied by scanning electron microscopy (SEM). The SEM characterizations were examined on a FEI Quanta 200.

3. Results and discussion

As given in Fig. 1, silicon substrate was uniformly coated with copper nanoparticles with irregular shapes and uniform particle size distribution. The particles aggregated to each other, and the diameters of copper particles range from 300 nm to 500 nm.

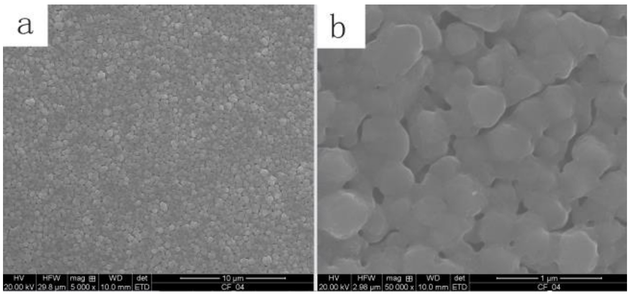

Fig. 1. SEM images of a copper nanofilms formed on silicon wafers: (a) low magnification and (b) high magnification.

When the temperature was increased to 300 ^{o}C, carbon nanofibers were obtained on copper nanofilms. Fig. 2 is the top-down view of the products prepared from a 10-min reaction, on which the bright spots corresponds to catalysts, and a fiber film with dark contrast was observed surrounding the catalyst. All copper particles seem to have the same catalysis activity in the synthesis of carbon fibers, and the fibers were randomly distributed on the substrate surface. It infers that there are free spaces among the fibers, which can significantly contribute to increase specific surface area of fiber films. These characteristics can result in potential applications in many filed, such as catalyst and adsorption.

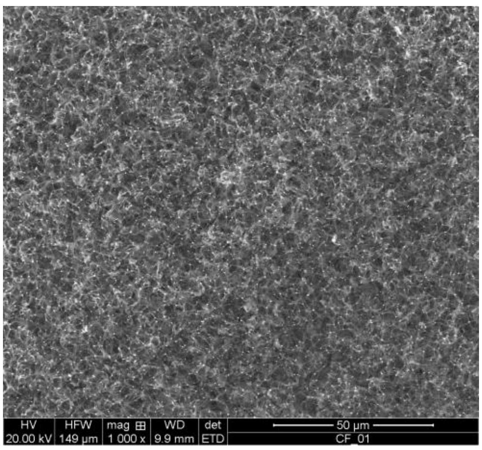

Fig. 2. SEM image of a carbon nanofiber film formed on silicon substrate.

SEM imaging at high magnifications (Fig. 3) demonstrates that the fiber film was composed of numerous Y-shaped carbon nanofibers with a diameter of 300 nm. Note that copper nanoparticles always located at the nodes of Y-shaped fibers. The Cu nanoparticles were always faceted with regular shapes. The majority of them had a triangular projection, as showed in Fig. 3c. Besides, there were a few rhombic (Fig. 3b) and polygonal (Fig. 3d) copper nanoparticles. In comparison to initial copper precursors (Fig. 1b), Cu catalysts changed shapes from an irregular morphology to a regularly faceted form after the CVD process. The morphology of the fibers seems to be related to the shapes of copper catalysts.

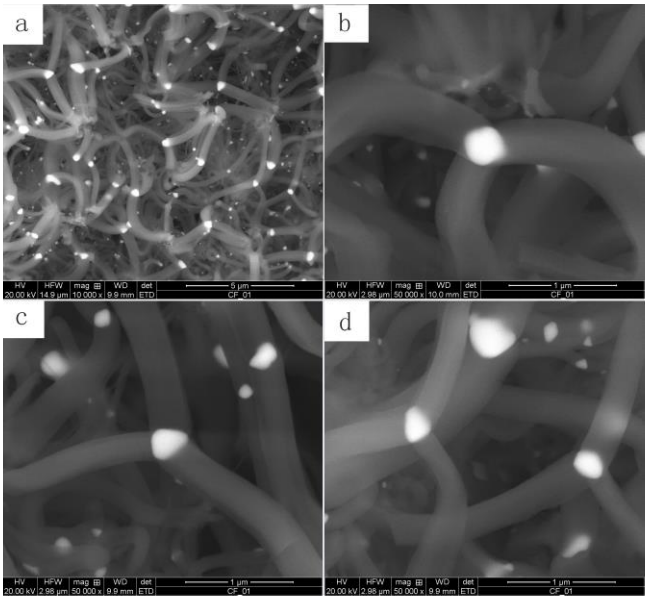

Fig. 3. SEM images of carbon nanofibers obtained on a silicon substrate. (a) Y-shaped carbon nanofibers with a diameter of circa 300 nm, copper catalyst nanoparticles with different shapes: (b) square, (c) triangular and (d) polygonal.

In order to examine the effects of reaction temperatures on the shape change of copper catalysts, the copper nanofilms were heated to the reaction temperature under vacuum condition without the introduction of acetylene. As shown in Fig. 4, the copper nanoparticles did not exhibit a shape alteration from an irregular shape to a regular faceted form. In Hansen's study, the reversible shape changes of copper nanocrystals were observed at 220^{o}C. The shape changes were observed only in response to the changes under gaseous environment [13], which suggested that the copper nanocrystals were thermally stable in shape at 220^{o}C. In this paper, the shapes of copper nanocrystals were changed during the nanofiber growth, which indicates that the carbon resource acetylene played an important role in the shape change of copper nanocrystals. Namely, the shape changes of copper nanocrystals were caused by the surface reconstruction during the carbon nanofiber growth and the driving force should be the surface energy induced by the acetylene adsorption on different exposed crystal faces of copper nanocrystals [5]. The shapes of copper nanocrystals determined the morphology of fibers. In Fig. 3c, the three crystal facets of triangular copper nanocrystal had the same abilities in decomposition of acetylene to grow carbon fibers, so the Y-shaped fibers were composed of three straight branches with the same diameters. But, in Fig. 3b, T-shaped fibers were synthesized by rhombic catalysts due to different growth rate over the surface of catalyst. The fibers would bend towards the side of low growth rate, and the T-shaped fibers were finally obtained.

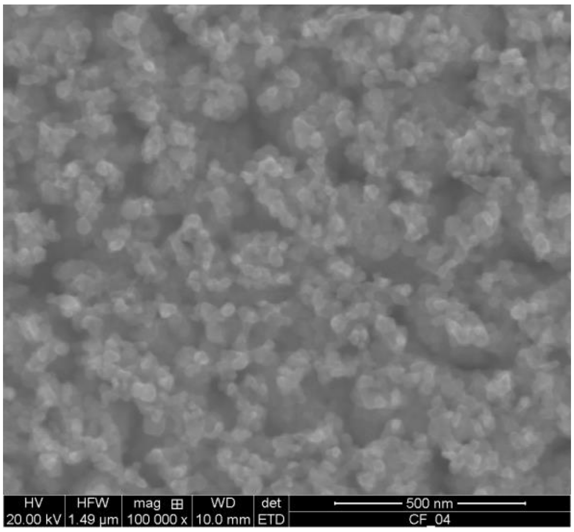

Fig. 4. SEM image of a copper nanofilm after heat treatment at the reaction temperature under vacuum condition.

4. Conclusions

Regular Y-shaped carbon nanofibers can be prepared by the decomposition of acetylene using copper nanocrystals coated on silicon substrates. The shape change of copper nanocrystals occurred during the fiber growth process, and the carbon resource acetylene played an important role in the shape change of copper nanocrystals. The copper nanocrystals always located at the nodes of Y-shaped fibers, and each copper nanocrystal can lead the growth of three fiber branches with the same diameters.

Acknowledgments

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