

LARGE-SCALE SYNTHESIS OF HELICAL CARBON NANOFIBERS OVER Fe-Cu NANOPARTICLES

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Introduction

In recent years, helical carbon materials have attracted tremendous attention due to their novel physical and chemical properties such as super-elasticity, electric conductivity and interesting processability. They can be used as sensitive and micro-magnetic sensors, electromagnetic wave absorption materials, hydrogen storage materials, elastic materials, etc. [1–5]. Helical carbon materials were usually synthesized by the pyrolysis of hydrocarbons (such as acetylene, benzene and methane) over catalyst of metallic copper, iron, nickel, and cobalt nanoparticles. However, reports on the synthesis of regular helical CNFs synthesized over Fe-Cu catalysts at relatively low temperatures are rare.

Experimental

Briefly, 0.015 mol $FeCl_2 \cdot 4H_2O$, 0.015 mol $CuCl_2 \cdot 2H_2O$ and 0.045 mol citric acid monohydrate were well mixed (stirring at 60 °C for 6 h) with 200 mL of absolute ethanol. The mixture was kept at 80 °C for several hours and then at 150 °C until a xerogel was formed. The xerogel was heated in air at 500 °C for 4 h for the generation of the catalyst precursor. By a similar approach but with $FeCl_2 \cdot 4H_2O$ to $CuCl_2 \cdot 2H_2O$ molar ratio equals to 0.01:0.02, 0.05:0.025 and 0.001:0.029 (the amount of citric acid monohydrate was kept as before), the other catalyst precursors were obtained, respectively.

For the synthesis of carbon products, 0.05 g of the powder of a catalyst precursor was dispersed on each of the two ceramic plates (3 cm in width and 6 cm in length) placed inside a quartz reaction tube (6 cm in inner diameter and 80 cm in length, equipped with temperature and gas-flow controls). Subsequently, the catalyst precursor was in situ reduced in H_2 at 400 °C for 2.5 h for the generation of the corresponding catalyst. Then the gas supply was shifted from H_2 to acetylene for the synthesis of the carbon species. The decomposition of acetylene was carried out over the catalysts at 250 °C for 4 h at atmospheric pressure, and the products were collected after the system was cooled down to room temperature (RT).

Results and Discussion

In this paper, we report that by means of acetylene decomposition at 250 °C over the Fe-Cu nanoparticles (Fe:Cu molar ratio=1:1, 1:2, 1:5 and 1:29) derived from a combined sol-gel/reduction method, carbon nanofibers (CNFs) and helical carbon nanofibers (HCNFs) can be synthesized selectively in large quantities. As shown in Figure 1a, over Fe-Cu nanoparticles of Fe:Cu molar ratio=1:1, the carbon nanofibers aggregate together in a form of cluster. In other words, curved CNF bundles can be synthesized selectively in large quantity over the catalyst. As shown in Figures 1b&c, at Fe:Cu molar ratio=1:2 or 1:5, the major product is curved CNFs; there is occasional sighting of HCNFs (inset of Figures 1b&c) but not CNFs bundles. With increase of Cu content in the Fe-Cu catalysts, there is enhancement in selectivity to HCNFs (Figures 1d & e). As shown in Figure 1f, a catalyst nanoparticle is embedded at the node of the HCNFs. The results show that the content of Cu in the Fe-Cu catalysts has a great influence on the formation of the various carbon species.

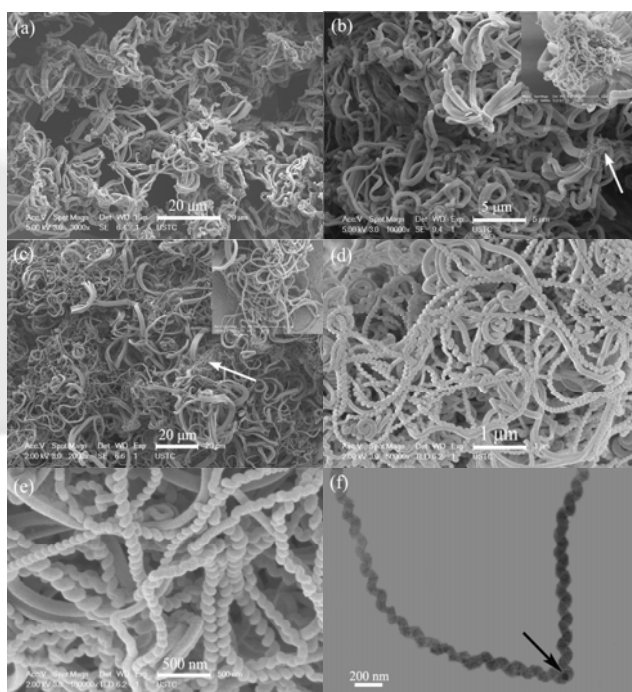


Fig. 1 FE-SEM images of carbon nanomaterials synthesized at 250 °C over Fe-Cu nanoparticles of different compositions: (a) Fe:Cu=1:1, (b) Fe:Cu=1:2, (c) Fe:Cu=1:5, (d) Fe:Cu=1:29, (e) Cu and (f) A typical TEM image of HCNFs obtained over Fe-Cu nanoparticles of Fe:Cu=1:29. (The insets of Figures 1b&c are high-magnification images taken at positions indicated by the white arrows in Figures b&c, respectively.).

In Figure 2, one can see that with rise of Cu content, there is increase in yield. The increase becomes more significant when the Cu content is above 85 wt%. In Figure 3, one can see that when C_2H_2 pyrolysis temperature is varied from 300 to 450 °C and with the other experimental parameters kept unchanged, maximum yield is found at 350 °C over the nanoparticles of

Fe:Cu=1:5. Compared to that obtained over Fe nanoparticles, the carbon species generated over the Fe-Cu nanoparticles show larger coil length. With the encapsulation of Fe-Cu nanoparticles, the HCNFs display high magnetization. The saturation magnetization (M_S) and coercivity (HC) (ZW, there is no need to put "HC" there.) of HCNFs generated over Fe-Cu nanoparticles of Fe:Cu=1:29 as shown in Figure 4 is 3.54 emu g^{-1} and 340 Oe, respectively. Thus, the approach adopted for mass production of one-dimensional helical carbon materials in this study has the advantages of being simple, low-cost, and environment-friendly.

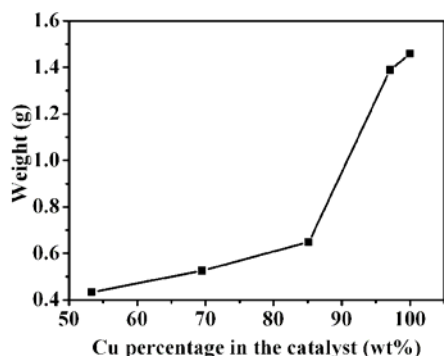


Fig. 2 Weight of samples obtained versus Cu concentration of catalysts.

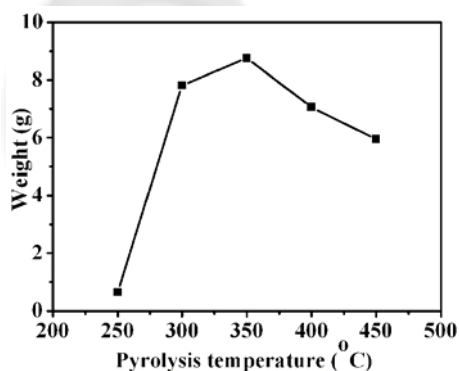


Fig. 3 Weight of samples obtained over Fe-Cu nanoparticles (Fe:Cu=1:5) versus pyrolysis temperatures.

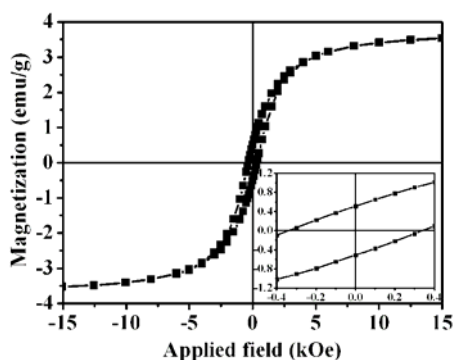


Fig. 4 Typical magnetization curves (inset is the enlarged part close to the origin) of sample obtained over Fe-Cu nanoparticles (Fe:Cu=1:29).

Conclusions

We report that by means of acetylene decomposition at $250 \text{ }^\circ\text{C}$ over the Fe-Cu nanoparticles (Fe:Cu molar ratio=1:1, 1:2, 1:5 and 1:29) derived from a combined sol-gel/reduction method, carbon nanofibers (CNFs) and helical carbon nanofibers (HCNFs) can be synthesized selectively in large quantities. Thus, the approach adopted for mass production of one-dimensional helical carbon materials in this study has the advantages of being simple, low-cost, and environment-friendly.

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