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Highly efficient synthesis of carbon nanocoils on alumina spheres

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Abstract

Carbon nanocoils (CNCs) and carbon nanotubes (CNTs) can be selectively synthesized on the surfaces of alumina spheres using $Fe_2(SO_4)_3/SnCl_2$ catalyst with different molar ratios of Fe to Sn by a thermal chemical vapor deposition method. With increasing the catalyst concentration, the average coil diameter, fiber diameter and pitch of the CNCs are increased. Furthermore, different productivities of CNCs can be obtained on the alumina spheres with diameters of 2 mm, 1 mm and 500 μm. It is discovered that with decreasing the diameter of alumina spheres, the thickness of the carbon layer is also decreased, resulting in a negative effect on the yield of the CNCs. High yield of CNCs grown on the 500 μm alumina spheres can be achieved by increasing the catalyst concentration to improve the thickness of the carbon layer.

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1. Introduction

Owing to their unique helical structures, carbon nanocoils (CNCs) have many excellent mechanical and electromagnetic properties [1-5], indicating potential applications in microwave absorption materials, super capacitors, near-infrared detectors, elastic composites, etc [6-11]. In order to realize the wide range of applications, the method for high-yield and large quantity synthesis of CNCs becomes an important issue.

Among a variety of methods to grow CNCs, chemical vapor deposition (CVD) method is considered to be a suitable way to industrially synthesize CNCs. Until now, high purity of CNCs are mainly obtained on a flat substrate fixed in a furnace. In our previous researches, different kinds of substrates, including ITO [12], SiO_2 [13], copy paper [14], and the sheets made of plant fibers [15] et al., have been successfully applied to synthesize CNCs in the fixed bed CVD method. However, the quantity of the CNCs is limited by the surface area of the substrate, impeding the large-scale production of CNCs. Compared with the fixed bed method, using a fluidized bed reactor in CVD is an efficient method to achieve the continuous and high-yield growth of carbon materials including carbon nanotubes (CNTs) and carbon nanofibers. This method has been widely applied in the mass production of CNTs. Large amount of vertically aligned CNTs arrays were grown by Zhang et al. among the layers of vermiculite in a fluidized bed reactor [16, 17]. Also, multiwalled carbon nanotubes (MWNTs) were synthesized on Al_2O_3 supported Ni catalysts from C_2H_2 and C_2H_4 feedstocks in a fluidized bed by Liu et al [18]. For the growth of CNCs, because of the fact that the

fluidized bed reactor can provide floating substrates to fix the bases of the CNCs, which is necessary for the growth of these CNCs [19]. Therefore, the fluidized bed method is an excellent choice to achieve the high production of CNCs. In this method, the floatable substrate is a key issue. Compared with other plate substrates, the inorganic heat-resistant spheres, such as Al_2O_3 and SiO_2, can better meet the requirement for synthesizing CNCs. Considering the cost and weight, the alumina spheres would be the best choice for the synthesis of CNCs by means of fluidized bed reactor. The micro coiled carbon fibers were synthesized on $NiSO_4/Al_2O_3$ precursor by Hanus et al [20]. Bai successfully synthesized the CNCs on alumina sheet [21]. However, the systemic research on the synthesis of CNCs on alumina spheres has not been reported to date. In this paper, the efficient conditions for growth of CNCs on alumina spheres coated with $Fe_2(SO_4)_3/SnCl_2$ have been researched, which may provide a foothold for the large quantity synthesis of CNCs in a fluidized bed reactor.

2. Experimental

The catalyst precursor was prepared by dissolving iron sulfate and stannous chloride mixture into deionized water. The concentration of the solution was changed from 0.2 to 0.05 mol/l and the molar ratio for iron to tin was decreased from 1:0 to 3:1. High-purity alumina spheres with diameters of 500 μm, 1 mm and 2 mm were applied as the substrates to synthesize carbon products. First of all, the alumina spheres were calcined in air at 710 ^{o}C for 30 min and then washed by acetone, alcohol, and deionized water in turn. After drying, they were immerged in the prepared catalyst solution and heated at 50 ^{o}C for 10 min. Then the substrates were taken out from the solution and dried in air at 50 ^{o}C. For the calcination process, the substrates coated with catalyst were calcined at 710 ^{o}C for 30 min in an argon atmosphere with an Ar flow rate of 365 sccm. At last, the carbon deposits were achieved in a CVD system at 710 ^{o}C for 1 h by introducing acetylene and argon gases with flow rates of 15 and 325 sccm, respectively. The samples were cooled to room temperature in the argon atmosphere.

The carbon deposits and their cross-section views were characterized by a field-emission scanning electron microscope (FE-SEM; NOVA NanoSEM 450), and a transmission electron microscopy (TEM, Tecnai G220 S-Twin).

3. Results and discussion

3.1 The influence of the molar ratio of Fe to Sn

Figures 1(a) to (e) show the SEM images of the as-prepared carbon products on the surfaces of the alumina spheres using Fe/Sn catalyst with different molar ratios of 1:0, 60:1, 30:1, 10:1, and 3:1, respectively. All the alumina spheres are approximately 2 mm in diameter and the solution of catalyst precursor is 0.2 mol/l in concentration. When there is no Sn in the catalyst, only carbon particles and a few of CNTs are synthesized as observed in Fig. 1(a). With increasing the content ratio of Sn, high production of CNCs can be obtained successfully as shown in Figs. 1(b) to (d), proving that Sn can induce the helical growth of the CNTs [12]. Furthermore, the CNCs obtained under different molar ratios of Fe/Sn own various morphology features. Under the molar ratio of 60:1, spring-like CNCs with a large average coil diameter of 390 nm and an average pitch of 480 nm are more easily synthesized

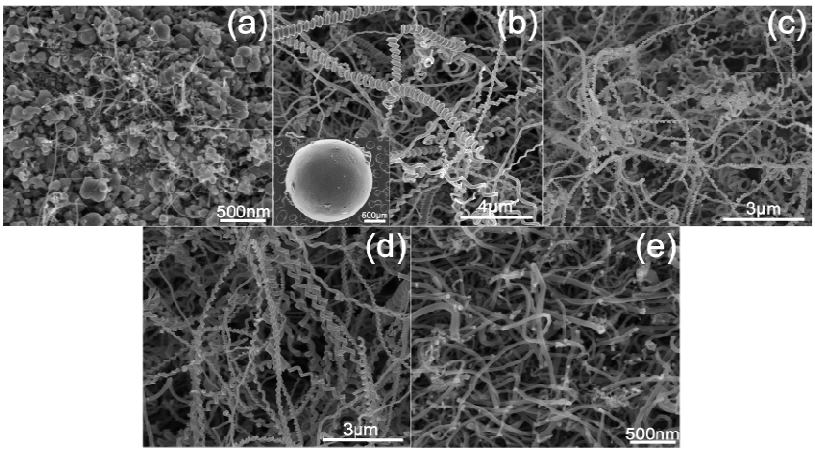

Fig. 1 SEM images of the carbon deposits on the alumina spheres using different molar ratios of Fe/Sn, (a) 1:0, (b) 60:1, (c) 30:1, (d) 10:1, (e) 3:1. The inset in (b) is the full view of the alumina sphere with carbon deposits.

than the molar ratios of 30:1 and 10:1. However, when the molar ratio of Fe/Sn is

decreased to 3:1, CNCs in the carbon products disappear again and only carbon nanowires are grown as displayed in Fig. 1(e). It is known that without Sn, CNTs can be grown from the isotropic Fe catalyst particle with high activity. When a small amount of Sn is added, the nonuniform distribution of Sn on the surface of the Fe catalyst particle improves the anisotropy of the catalyst particle, which promoting the helical growth of CNTs [22]. With the increasing of Sn content in the catalyst, the excess Sn would be uniformly distributed on the surface of Fe catalyst particle and then weaken the anisotropy of the catalyst particle, leading to the disappearance of CNCs. Moreover, more Sn bonded to the Fe catalyst particles impedes the catalytic activity of Fe and the rule of carbon precipitation, resulting in the formation of amorphous carbon nanowires as shown in Fig. 3(d). In addition, it is observed from the inset in Fig. 1(b) that the carbon products are grown evenly on the spheres.

Representative TEM images of the carbon nanostructures on the alumina spheres using the catalyst with Fe/Sn molar ratios of 1:0 and 3:1 are respectively displayed in Figs. 2(a) and (c). The enlarged image of the area indicated by the box in Fig. 2(a) shown in Fig. 2(b) indicates that the multi-walled CNTs are successful synthesized on the alumina spheres without Sn. However, if the molar content of Sn gets larger to one third of Fe, only amorphous carbon nanowires are obtained observed from the enlarged image in Fig. 2(d), which is consistent with the result in Fig. 1(e). Therefore, changing the molar ratio of Fe/Sn in catalyst can affect not only the morphology of grown carbon nanomaterials, but also the structure of these materials.

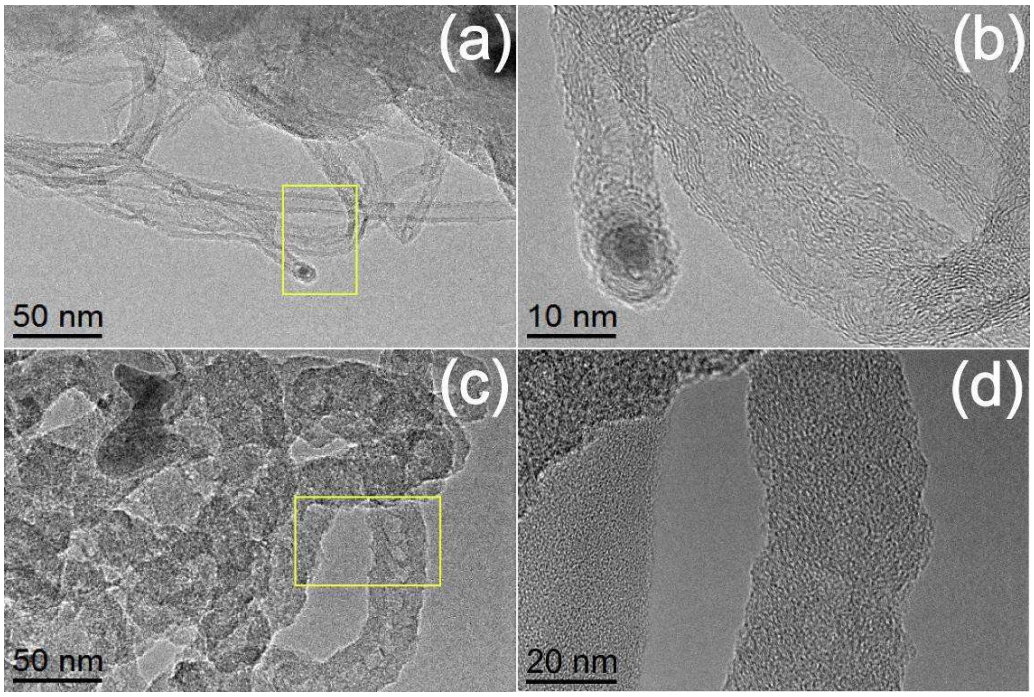

Fig. 2 TEM images of the carbon products on the alumina spheres using the catalyst with Fe/Sn molar ratios of (a) 1:0 and (c) 3:1. (b) and (d) are the enlarged images of the areas indicated by the boxes in (a) and (c), respectively.

3.2 The influence of the catalyst concentration

The SEM images in Figs. 3(a) to (c) show that the CNCs with different shapes and sizes are obtained at the concentration of the catalyst solution of 0.05, 0.1 and 0.2 mol/l using the same Fe/Sn molar ratio of 60:1 on the 2 mm alumina spheres. It is found that the CNCs are mainly plait-like shapes under the catalyst concentrations of 0.05 and 0.1 mol/l as shown in Figs. 3(a) and (b), while spring-like CNCs possess the majority under the catalyst concentration of 0.2 mol/l as shown in Fig. 3(c). Fig. 3(d) shows the changes of average coil diameter, fiber diameter and pitch with catalyst concentration. It is observed that with increasing the catalyst concentration, the average coil diameter, fiber diameter and pitch of the CNCs are also increased obviously. The average fiber diameter of the CNCs obtained under the concentration

of 0.2 mol/l is two times larger than the one under the concentration

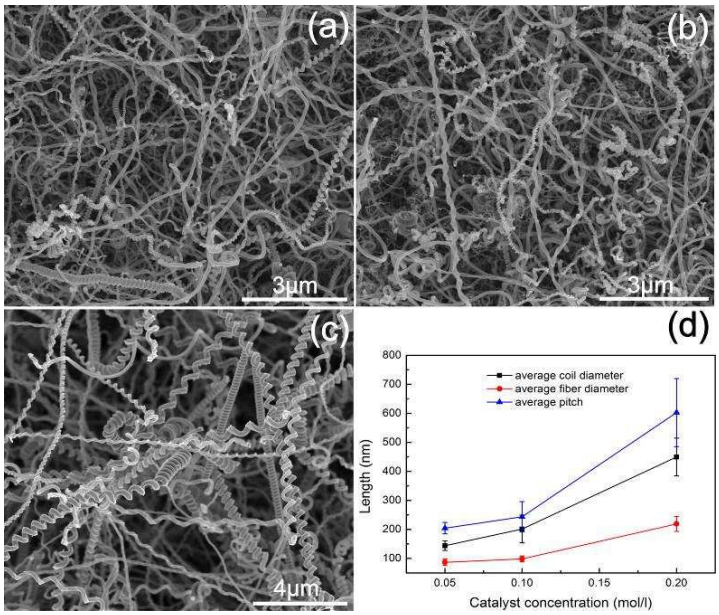

Fig. 3 SEM images of the CNCs synthesized on the alumina spheres of 2 mm in diameter using different concentrations of catalyst solution, (a) 0.05 mol/l, (b) 0.1 mol/l, and (c) 0.2 mol/l. (d) The changes of average coil diameter, fiber diameter and pitch with different catalyst concentrations.

of 0.05 mol/l. What is more, the average coil diameter and pitch of the CNCs under the concentration of 0.2 mol/l are approximately three times of the ones under the concentration of 0.05 mol/l. It is considered that the higher catalyst concentration would promote the catalyst aggregations and increase the size and anisotropy degree of catalyst particles, and then increase the diameter of the CNCs.

3.3 The influence of the alumina sphere diameter

Alumina spheres with different diameters were also applied to synthesize CNCs. The SEM images in Fig. 4 show the carbon products grown on the alumina spheres with diameters of 2 mm, 1 mm and 500 μm. It is found that with the decreasing of the diameters, the productivity of CNCs is also decreased. The CNCs on the alumina spheres with diameter of 2 mm shown in Fig. 4(a) are grown uniformly, while the

carbon wires take the majority of the carbon products on the alumina spheres with diameter of 500 μm shown in Fig. 4(c). According to the above results, the alumina spheres with larger diameter would be better choices to improve the productivity of CNCs in the fluidized bed method.

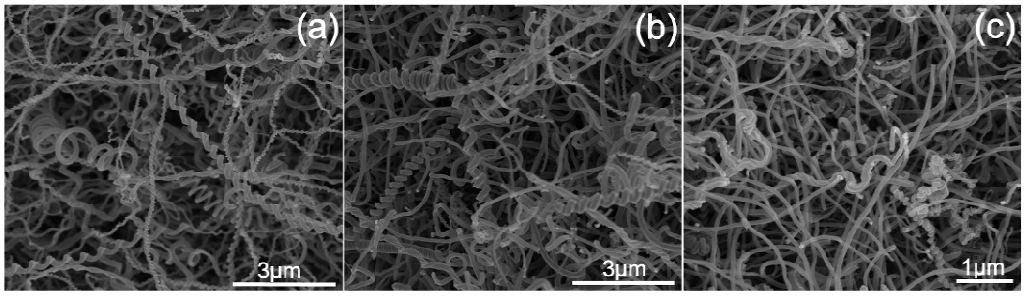

Fig. 4 SEM images of the carbon products grown on the alumina spheres with diameters of (a) 2 mm, (b) 1 mm and (c) 500 μm using 0.1 mol/l catalyst solution in which the molar ratio of Fe/Sn is 10:1.

The cross sections of the carbon products are observed to analyze the reason for the low productivity of CNCs on the alumina sphere with small diameter of 500 μm. Figs. 5(a), (b) and (c) show the SEM images of the cross sections of the carbon products deposited on the alumina spheres with diameters of 2 mm, 1 mm and 500 μm, respectively. It is discovered that the thickness of the carbon layer on the 2 mm alumina sphere reaches 10 μm. However, on the 1 mm and 500 μm alumina spheres, the thicknesses of the carbon layers are decreased to 6.7 and 5.5 μm, respectively, which are almost half of the previous one. It is known that, during the growth of CNCs, the carbon layer is essential for fixing the base of the CNCs according to Li's research [19]. When the thickness of a carbon layer is decreased to a certain degree, the carbon layer cannot provide a strong interaction between the catalyst aggregate and the base of a carbon fiber grown from there. This results in the decreasing of the yield

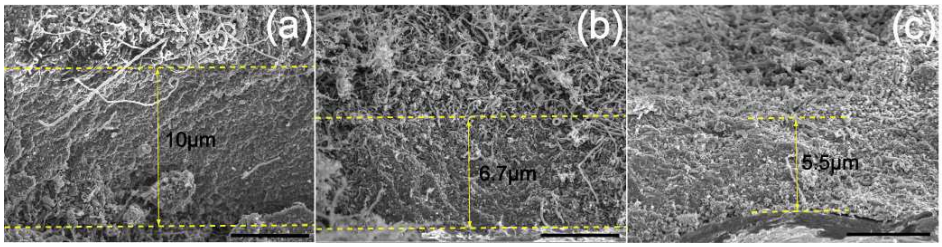

Fig. 5 SEM images of the cross section views of the carbon products on the alumina spheres with diameters of (a) 2 mm, (b) 1 mm and (b) 500 μm using 0.1 mol/l catalyst solution in which the molar ratio of Fe/Sn is 10:1. The bar in each figure is 5 μm.

of CNCs. In this work, combining with the growth result in Fig. 4(c), the thickness of the carbon layer can not be lower than 5.5 μm.

According to the above results, it is indicated that the thickness of carbon layer has a great effect on the growth of CNCs. In order to verify this viewpoint, the thickness of carbon layer on the 500 μm alumina sphere is improved to get a higher yield of CNCs. The catalyst concentration was increased to 0.2 mol/l, after which more catalyst particles can contribute to the carbon precipitation to form an expanding layer of the mixture of catalyst carbides and carbon deposits. Therefore, a compact aggregate can be formed to fix the base of the grown fiber. The SEM image of the cross section of the carbon products is shown in Fig. 6(a). As displayed, the thickness of the carbon layer is increased obviously. Furthermore, Fig. 6(b) shows that the high-yield CNCs are obtained as expected. Therefore, the method by increasing the catalyst concentration to improve the thickness of carbon layer is effective for large scale synthesis of the CNCs on the smaller sized alumina spheres.

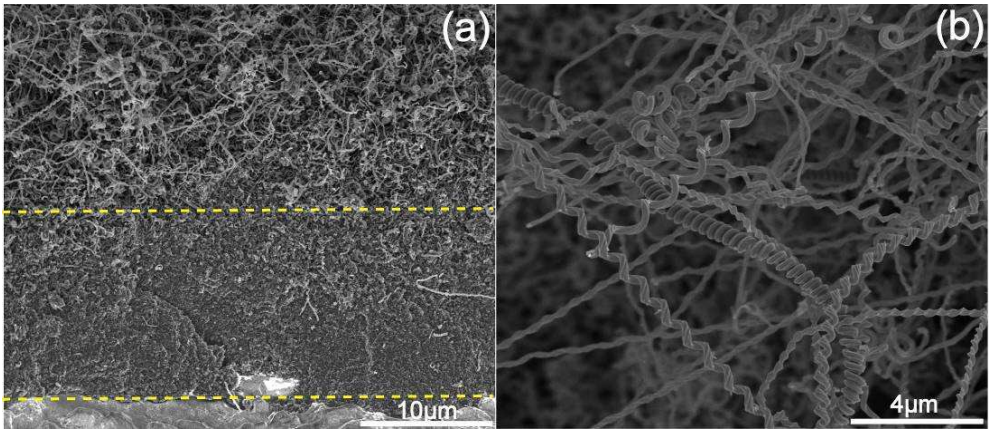

Fig. 6 SEM images of (a) the cross section of the carbon products on the alumina spheres of 500 μm in diameter using the catalyst precursor solution with concentration of 0.2 mol/l and (b) the CNCs grown on the surface of the alumina sphere.

4. Conclusion

We have successfully synthesized the CNCs on the alumina spheres with different diameters using different molar ratios of Fe/Sn. MWCNTs with the minimum diameter of 10 nm are obtained under the molar ratio of Fe/Sn 1:0. And high production of CNCs are synthesized when the molar ratios of Fe/Sn are 60:1, 30:1 and 10:1. It is discovered that with the increasing of the catalyst concentration, the average coil diameter, fiber diameter and pitch of CNCs are also increased. In addition, the thickness of carbon layer is decreased with the decreasing of the diameter of the alumina spheres, resulting in a reduced yield of CNCs. By improving the catalyst concentration, the thickness of the carbon layer on the 500 μm alumina spheres is increased to achieve a high yield of CNCs. In general, the alumina spheres with a larger diameter would be more favorable to be applied to improve the productivity of CNCs in the fluidized bed method.

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Figure captions:

FIG. 1 SEM images of the carbon deposits on the alumina spheres using different molar ratios of Fe/Sn, (a) 1:0, (b) 60:1, (c) 30:1, (d) 10:1, (e) 3:1. The inset in (b) is the full view of the alumina sphere with carbon deposits.

FIG. 2 TEM images of the carbon products on the alumina spheres using the catalyst with Fe/Sn molar ratios of (a) 1:0 and (c) 3:1. (b) and (d) are the enlarged images of the areas indicated by the boxes in (a) and (c), respectively.

FIG. 3 SEM images of the CNCs synthesized on the alumina spheres of 2 mm in diameter using different concentrations of catalyst solution, (a) 0.05 mol/l, (b) 0.1 mol/l, and (c) 0.2 mol/l. (d) The changes of average coil diameter, fiber diameter and pitch with different catalyst concentrations.

FIG. 4 SEM images of the carbon products grown on the alumina spheres with diameters of (a) 2 mm, (b) 1 mm and (c) 500 μm using 0.1 mol/l catalyst solution in which the molar ratio of Fe/Sn is 10:1.

FIG. 5 SEM images of the cross section views of the carbon products on the alumina spheres with diameters of (a) 2 mm, (b) 1 mm and (b) 500 μm using 0.1 mol/l catalyst solution in which the molar ratio of Fe/Sn is 10:1. The bar in each figure is 5 μm.

FIG. 6 SEM images of (a) the cross section of the carbon products on the alumina spheres of 500 μm in diameter using the catalyst precursor solution with concentration of 0.2 mol/l and (b) the CNCs grown on the surface of the alumina sphere.