

High Efficient Synthesis of Carbon Nanocoils by Catalysts Produced by a Fe and Sn Containing Solution

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Abstract: Carbon nanocoils (CNCs) were prepared by thermal chemical vapor deposition (CVD) using a Fe and Sn containing solution as the catalyst predecessor. The solutions of Fe₂(SO₄)₃/SnCl₂, FeCl₃/SnCl₂ and Fe(NO₃)₃/SnCl₂ with the mol ratios of 3:0.1 to 3:1 were used as catalysts. Comparing the catalysts in different composition ratios with the grown deposits after CVD, we found that the optimum mol ratio between Fe and Sn is 6:0.1. It is noted that the catalyst combination of Fe₂(SO₄)₃ /SnCl₂ obviously increases the quantity of the grown carbon deposits indicating that it has the largest catalytic activity among the three kinds of combinations. Large surface area of catalyst films formed by release of SO₃ from the decomposition of Fe₂(SO₄)₃ over the temperature of 480 °C is very good for the carbon nanocoils growth and the introduction of sulfide impurities are the key factors leading to the high efficient growth for carbon nanocoils. It is known that Fe-additions lead to the growth of carbon nanotubes or nanofibers, while Sn induces their helical growth and a little sulfur impurities may induce the efficient growth of carbon nanocoils.

Introduction

Carbon nanocoils are coiled carbon nanotubes, which exhibit outstanding mechanical and electromagnetic properties due to their peculiar helical morphologies in addition to the excellent properties of carbon nanotubes. They are expected for uses in high-performance composites, electromagnetic absorbers, field emission devices for flat panel displays and nano or micro electromechanical systems such as nanosized springs, generator for electromagnetic waves, etc [1-3]. Recently, carbon nanocoils have attracted much more efforts for the overall studies. The investigation of growth mechanism and the morphology of carbon nanocoils have been reported in a lot of papers [4-6]. These carbon nanocoils are mainly synthesized by high-temperature catalytic decomposition of hydrocarbons on a transition metallic catalyst, and their diameters, lengths and density have been controlled to a certain extent. However, the question of synthesis of carbon nanocoils in large quantity still remains unsettled, which is obstacle this kind of material to the overall applications. From the all reported methods for the synthesis of carbon nanocoils, chemical vapor deposition (CVD) was considered to be a possible and efficient method for mass production of carbon nanocoils, because this method is process controllable, simple in operation and easy to be scaled up for industrial production. In this method, it is a crucial step to select highly efficient catalysts for the growth of carbon nanocoils. Among the metal catalysts used in the growth of carbon nanomaterials so far, iron, cobalt, nickel, titanium, tungsten are comparatively effective for the growth of carbon nanocoils [7,8]. M. Zhang *et al.* have successfully synthesized carbon nanocoils in high yield using iron-coated indium tin oxide as the catalyst [9]. However, it needs expensive and time-consuming vacuum evaporation to prepare Fe-Sn-In-O film, which is also not suitable for mass synthesis. L. Pan *et al.* have studied the growth mechanism of carbon nanocoils and pointed out that iron is crucial in the formation of a nanotube and indium tin oxide induces the helical growth of the nanotube, the yield of carbon nanocoils is determined by the elemental ratio of

Sn and In [4,10]. On the base of the overall results, Okazaki *et. al.* have developed Fe-Sn-O fine particles for synthesizing carbon nanocoils, which provided an effective and low cost method of catalyst preparation for synthesizing carbon nanocoils in large quantity. It was confirmed that Fe-Sn-O was an efficient catalyst even without the addition of In. [11]. On the other hand, the research on carbon nano or microcoils by Motojima *et. al.* has suggested that the addition of a small amount of sulfur compound impurities such as thiophene or H₂S in acetylene is indispensable for the growth of coiled carbon fibers in high yield, but excessive amounts of impurities may act as a poison on the catalyst that can not induce the synthesis of carbon microcoils [8,12]. In addition, they have also found that a phosphorus trichloride (PCl₃) impurity also accelerated the growth of coiled carbon fibers [13]. In this paper, a kind of effective and economic catalyst has been designed for the synthesis of carbon nanocoils in high efficiency under taking the advantages of the overall researches.

Experimental

Fe₂(SO₄)₃/SnCl₂ solution, the molar ratio of which was from 3:0.1 to 3:1 (molar ratio of Fe/Sn was from 6:0.1 to 6:1), was selected as catalyst. FeCl₃/SnCl₂ and Fe(NO₃)₃/SnCl₂ solutions were also prepared for comparison. A suspension liquid of Al₂O₃ powders, which act as support materials, was spin coated on SiO₂ substrates (sizes: 1.5mm×1.5mm). Then the catalyst solutions with a volume of 250 μl were dropped on these substrates, and dried at 40-50 °C for 10 min. Then the samples were calcined at 700 °C for 30 min in order to oxidize the catalysts. Carbon nanocoils were synthesized on these substrates by a thermal CVD system at 700°C for 30 min by introducing acetylene gas of 60 sccm in an Ar gas with a flow rate of 200 sccm. At last, the substrates were cooled slowly to room temperature in ambient Ar gas. The deposits were observed and analyzed by a scanning electron microscope and a Raman spectrometer.

Results and Discussion

Figure 1 (a) shows the SEM image for the surface of Fe₂(SO₄)₃/SnCl₂ catalyst film after calcine at 700 °C for 30 min.

Figure 1(b) is the enlarged SEM image of the square area indicated in fig. 1 (a). An alveolate surface morphology is clearly observed, which is considered to be formed by release of SO₃ from the decomposition of Fe₂(SO₄)₃ over the temperature of 480 °C. This kind of morphology is very

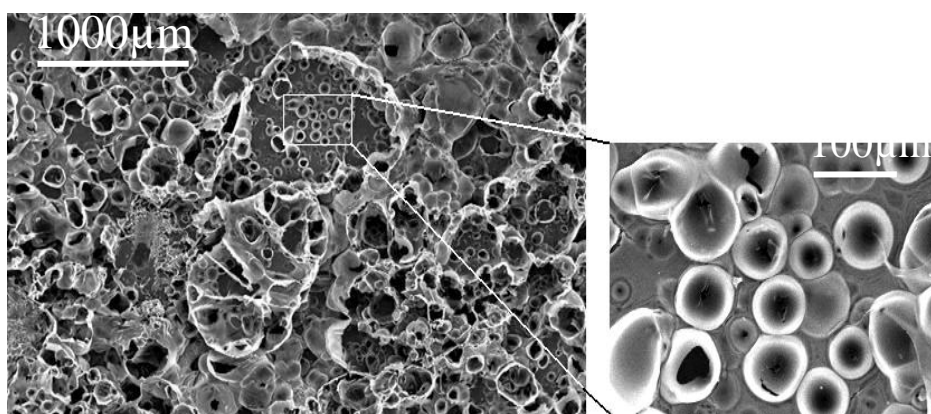


Fig 1. (a) SEM image of Fe₂(SO₄)₃/SnCl₂ calcined catalyst film which shows the alveolate morphology. (b) The enlarged SEM image of calcined catalyst film.

good for the carbon nanocoils growth because its large surface area increases the chance for the contact of catalysts with the supplied acetylene gas and hence enhances the activity of the catalysts. But such phenomenon was not observed for the FeCl₃/SnCl₂ or Fe(NO₃)₃/SnCl₂ catalysts after calcine.

The compositions of calcined catalysts were analyzed by Raman spectra. Figure 2 shows the Raman spectra for the calcined catalysts of (a) $\text{Fe}_2(\text{SO}_4)_3/\text{SnCl}_2$ and (b) $\text{FeCl}_3/\text{SnCl}_2$, respectively. It is observed that the two kinds of catalysts show almost the same Raman spectra, suggesting that composition of two calcined catalysts is basically the same. The serial large peaks appearing in the Raman spectra are attributed to Fe_2O_3 , indicating that the catalyst film is almost oxidized after

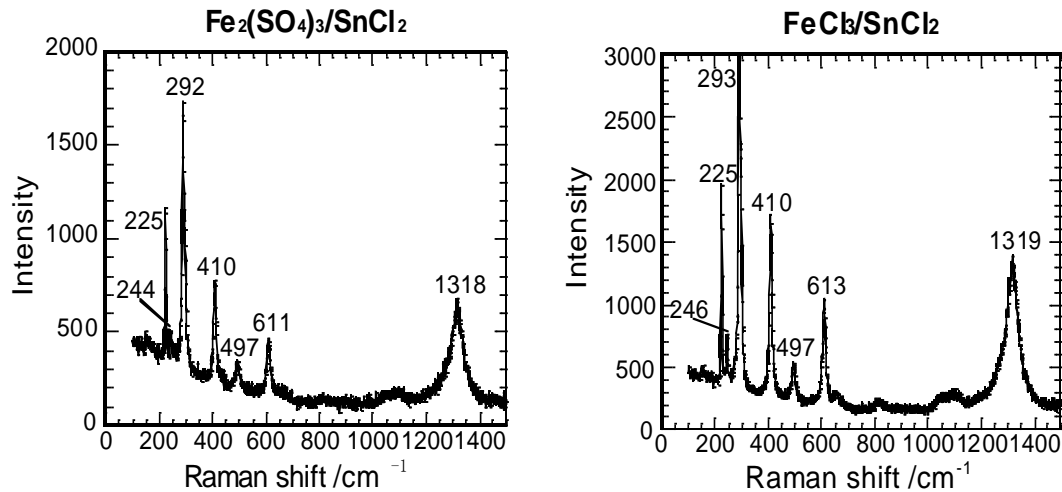


Fig 2. Raman spectra of (a) $\text{Fe}_2(\text{SO}_4)_3/\text{SnCl}_2$ and (b) $\text{FeCl}_3/\text{SnCl}_2$ catalysts calcined at $700\text{ }^\circ\text{C}$ for 30 min.

calcine process. Furthermore no peak corresponding to the Sn or Cl is detected.

In order to know the element ration in the catalyst films, energy dispersive X-ray (EDX) analysis was made. Figure 3 shows the EDX spectra of a calcined $\text{Fe}_2(\text{SO}_4)_3/\text{SnCl}_2$ catalyst. It is found that small peaks attributed to S, Si and Sn are observed in the spectra besides the large peaks of Fe and O, indicating that a few of sulfur and tin elements (approximately 3 at. %) exist in the catalyst film after calcine. Together with the Raman spectra, Fe is mainly originated from Fe_2O_3 which is decomposed by $\text{Fe}_2(\text{SO}_4)_3$, Si comes from SiO_2 substrate, Sn would be originated from its Oxide or from SnO , and S may originate from S-Fe(Sn)-O compound due to the decomposition of $\text{Fe}_2(\text{SO}_4)_3$.

Figure 4 shows the grown carbon nanocoils using the catalysts of calcined $\text{Fe}_2(\text{SO}_4)_3/\text{SnCl}_2$. By using $250\text{ }\mu\text{l}$ $\text{Fe}_2(\text{SO}_4)_3/\text{SnCl}_2$ solution as catalyst predecessor whose concentration was 0.2 mol/L , 200 mg carbon deposits were generated. The yield (weight ratio of carbon to Fe_2O_3) was ca. 2500% . It is found that more than 70% of deposits are carbon nanocoils with various diameters and pitches.

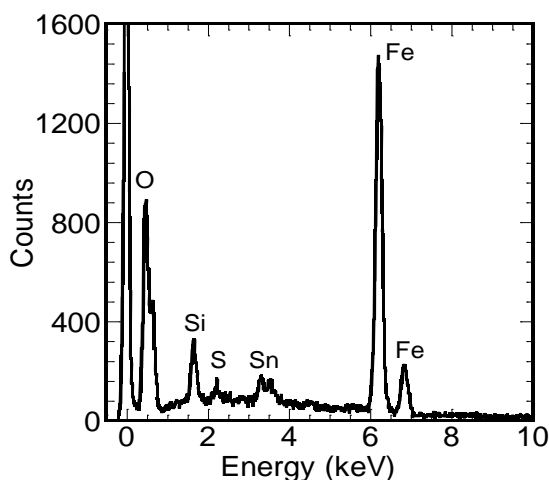


Fig 3. EDX spectra of calcined $\text{Fe}_2(\text{SO}_4)_3/\text{SnCl}_2$ catalyst.

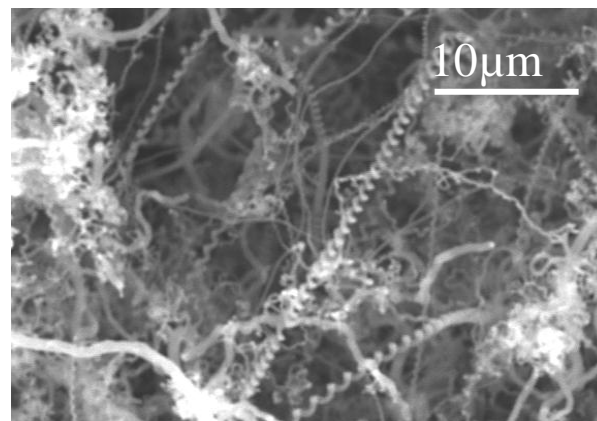


Fig 4. SEM image of carbon nanocoils grown on SiO_2 substrate synthesized by $\text{Fe}_2(\text{SO}_4)_3/\text{SnCl}_2$

The coil diameter and line diameter of these coils are differed from each other, ranging from 500 to 1000 nm and 100 to 200 nm, respectively. However, the coil length can reach up to several tens to several hundreds of micrometers. This result indicates that the catalyst prepared by the solution methods is highly efficient for synthesis of carbon nanocoils. However, Using $\text{Fe}_2(\text{SO}_4)_3$ only as a catalyst only obtains some disordered carbon fibers whose diameter are about 100-200nm. For comparison, $\text{FeCl}_3/\text{SnCl}_2$ and $\text{Fe}(\text{NO}_3)_3/\text{SnCl}_2$ solutions were prepared as the catalyst precursors. Carrying out deposition under the same conditions, we obtain a low yield of carbon nanocoils with varied morphology. However, most of the depositions are disordered carbon fibers. Based on existing researches, Fe-Sn-O is very important catalyst in the growth of carbon nanocoils [4, 9, 14]. It is found that Fe-additions lead to the growth of carbon nanotubes, while Sn induces their helical growth [4]. At the same time, the addition of a small amount of S has a promoting effect on the growth of carbon nanocoils. Motojima *et. al.* found that carbon microcoils could be prepared by pyrolysis of acetylene activated using a Ni catalyst and a small amount of H_2S or thiophene impurities, and sulfur was very crucial for the high efficient synthesis of carbon microcoils [12]. It is due to the addition of sulfur that enhances the catalytic activity and selectivity. A similar effect may occur in our system, in addition to the porous morphology of the catalyst film formed in the calcine process, which enhances the activity of catalysts. Therefore, carbon nanocoils are synthesized in high yield and large quantity. This would be the reason why the $\text{Fe}_2(\text{SO}_4)_3/\text{SnCl}_2$ catalyst precursor is very efficient for the synthesis of carbon nanocoils. The reaction mechanism of S impurity is still not clearly understood, which needs a further study.

For the further optimization of $\text{Fe}_2(\text{SO}_4)_3/\text{SnCl}_2$ solution, molar ratios of 3:0.1 to 3:1 (molar ratio of Fe/Sn was 6:0.1 to 6:1), were selected. Experimental evidence points out that the optimum molar ratio of Fe/Sn is 60:1. This result is consistent with Okazaki's research [14], in which they have used Fe-In-Sn-O fine particle catalysts for synthesizing CNCs and the optimum composition of In and Sn was found to be between 10 and 33% and below 3.3% (but not zero) relative to Fe composition, respectively. Using Sn as an addition catalyst has advantages in a large quantity system, because Sn is indispensable and the amount of addition of Sn is small for the growth of carbon nanocoils.

Summary

We synthesized carbon nanocoils by thermal CVD with the catalysts prepared by a solution method. $\text{Fe}_2(\text{SO}_4)_3/\text{SnCl}_2$ solution has been proved to be an effective catalyst precursor combination, which exhibits a high efficiency for synthesis of carbon nanocoils. It is found that Sn is required for the growth of carbon nanocoils. The porous morphology of $\text{Fe}_2(\text{SO}_4)_3/\text{SnCl}_2$ calcined catalyst film in addition to a little sulfur impurity would be beneficial to enhance the catalytic activity, which induce the mass synthesis of carbon nanocoils.

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