

Synthesis of Carbon Nanotubes by CCVD Method Using Mesoporous Silica

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Abstract

We have attempted to synthesize carbon nanotubes by catalytic chemical vapor deposition (CCVD) using mesoporous silica SBA-15 as a catalyst supporting material. For CCVD method, it is very important to disperse small metal particles in a supporting material. Therefore we synthesized SBA-15 (diameter of mesopores=6.7 nm) and tried to load catalyst particles into mesopores by two different ways. One is to dip SBA-15 in catalyst-including aqueous solution in vacuum, the other is to disperse Fe atoms on the surface of SBA-15 by alumination and ion-exchange method. Then obtained catalyst-supporting SBA-15 was subjected to CVD treatment using C_2H_2 gas as carbon source at 800°C. As a result, single walled carbon nanotubes and multi-walled carbon nanotubes were prepared. We characterized prepared SBA-15 and catalysts supporting SBA-15 by XRD, TEM and N_2 adsorption-desorption isotherm measurements. Elemental analyses were performed using EDS system equipped with TEM. TEM observation of the CVD treated sample was also carried out.

Key words: carbon nanotubes, CCVD, mesoporous silica

1. Introduction

Since their discovery in the carbon arc by Iijima in 1991 [1], carbon nanotubes (CNTs) have been studied in wide range fields because of their superior mechanical and electrical properties [2-4]. Initially, the product material by carbon arc discharge method included only a small amount of CNTs. In 1996, Thess et al. reported that CNTs can be obtained in a high yield using laser ablation technique [5]. However, it is not easy to scale up the laser ablation system. Therefore, large scale synthesis of CNTs is still a challenge. Another significant problem is how to synthesize the CNTs with desired form. In order to overcome these problems, several methods for the production of CNTs have been tried. Among them, catalytic chemical vapor deposition (CCVD) method is becoming attractive because of its great potential for the large scale production at a low cost. For CCVD method, it is very important to disperse small metal particles in a supporting material. In the present study mesoporous silica was used as a catalyst supporting material.

Mesoporous silica which has periodic aligned uniform mesopores is synthesized by sol-gel process using surfactant micelles as templates. The mesopore size of the mesoporous silica can be tuned from 2 nm to 50 nm by changing ingredients and reaction conditions. It is expected that small, uniform and dispersed catalyst particles for CNT production can be obtained by introducing metal particles into the mesopore of the mesoporous silica. We have tried to make metal catalyst particles in the mesopore of mesoporous silica by two different ways. In this paper, we discuss the yield and the structure of the CNTs obtained by CCVD method using these catalysts.

2. Experimental

2.1 Preparation of mesoporous silica SBA-15

A detailed synthesis procedure for mesoporous silica SBA-15 has been reported elsewhere [6]. In a typical synthesis in this work, 4.0 g of nonionic surfactant P123 ((ethoxy)₂₀-(propoxy)₇₀-(ethoxy)₂₀, BASF) was dissolved in 30 g of water and 120 g of 2 M HCl solution with stirring at 35°C. Then 8.5 g of tetraethoxysilane (TEOS) was added into the solution with stirring for 20 h. The mixture was aged at 100°C overnight without stirring. The solid product was calcinated by slowly increasing the temperature from RT to 600°C in 8 h and keeping at 600°C for 6 h.

2.2 Loading of catalyst nanoparticles into the mesopores of SBA-15 (Method-1)

The prepared SBA-15 in a test tube was heated at 120 °C in vacuum overnight. Then an aqueous solution of iron, cobalt, nickel nitrate/sulfate (2M) was introduced into the test tube. The immersed SBA-15 was taken out from the test tube, washed with distilled water, filtered and dried in Ar at 120 °C for 5 h.

2.3 Loading of catalyst nanoparticles into the mesopores of SBA-15 (Method-2)

Alumination and ion exchange were carried out as follows [7]: 0.5 g of SBA-15 was combined with 50 ml of dry ethanol containing 0.111 g of $AlCl_3$ (for Si/Al mole ratio = 10) with stirring at RT for 12 h. The obtained material was then filtered, washed with ethanol, and dried at 80°C in air. After the alumination, Fe(III) was ion exchanged into the aluminated SBA-15 by stirring in 0.5 M $Fe_2(SO_4)_3$ aqueous solution for 1 h with gentle boiling. The resultant solid was then filtered and washed with hot distilled water to remove physically adhered Fe(III) ions. For convenience, the obtained materials after the alumination and the ion-exchange treatments are abbreviated as AlSBA-15 and AlSBA-15(Fe), respectively.

2.4 CVD treatment

Catalysts supported by mesoporous silica prepared by above mentioned Method-1 and Method-2 were evacuated in a SiO₂ tube and the temperature of the reactor was increased from RT to 800°C in 3 h. Then C₂H₂ and Ar gases were flowed for 2 h at flow rates of 5 cm³/min and 250 cm³/min, respectively.

2.5 Characterization

The as-prepared SBA-15, AlSBA-15, AlSBA-15(Fe) were characterized by XRD, TEM and N₂ adsorption-desorption isotherm measurements. Elemental analyses were performed using EDS system equipped with TEM. TEM observation of the CVD treated sample was also carried out.

3. Results and discussion

The observed N₂ adsorption-desorption isotherm at 77 K and pore size distribution for the prepared SBA-15 are shown in Fig. 1. A type IV adsorption with a hysteresis loop, as defined by IUPAC, is clearly seen. We determined the pore size distribution from the adsorption branch of the isotherm by Barrett-Joyner-Halenda (BJH) method. The very sharp peak in the pore size distribution diagram (Fig. 1(b)) indicates that the SBA-15 has well-defined uniform pore dimensions and that the mean pore size is about 6.7 nm. Fig. 2 shows the TEM images of the SBA-15. The hexagonal array of uniform channels is directly visible.

The catalyst particles loaded by Method-1 are shown in Fig. 3. As shown in Fig. 3(a), a lot of catalyst nanoparticles deposited in the mesopores of the SBA-15. However, the larger metal particles were also observed on the outer surface of the SBA-15 (Fig. 3b).

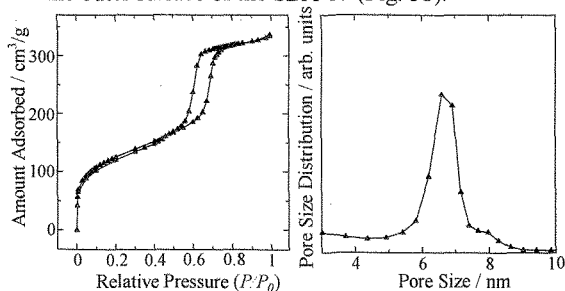


Fig. 1 N₂ adsorption-desorption isotherm at 77 K and pore size distribution for the prepared SBA-15.

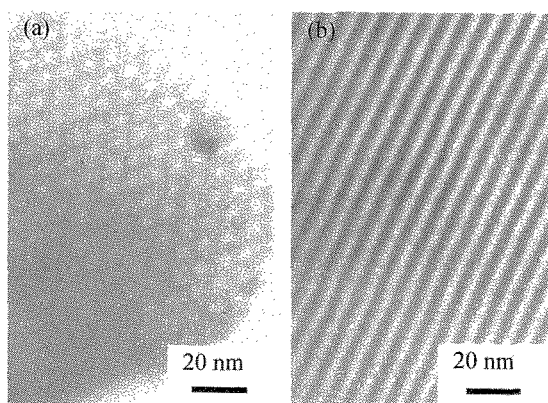


Fig. 2 TEM images of the prepared SBA-15.

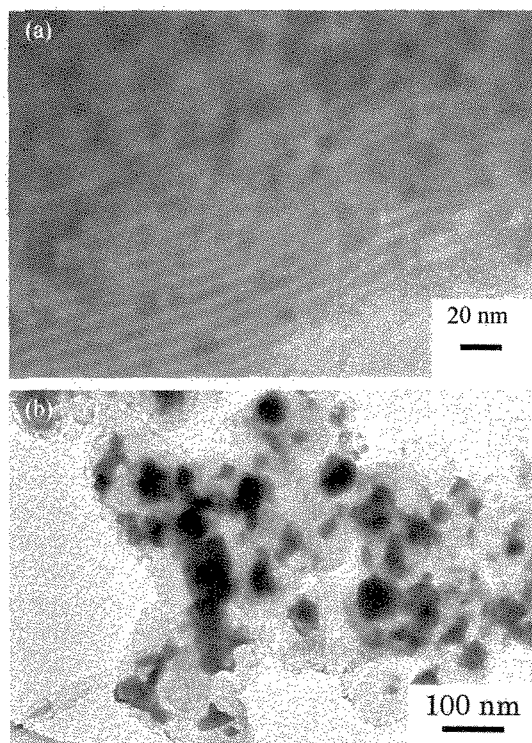


Fig. 3 (a) The catalyst particles loaded into SBA-15 by Method-1, (b) The larger metal particles were also on the outer surface of the SBA-15.

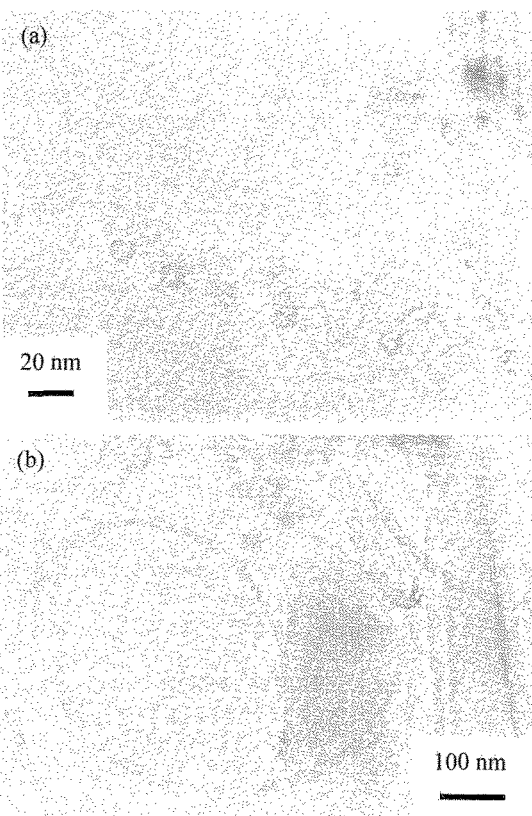


Fig. 4 TEM images of the MWNTs obtained by the CVD treatment using the Method-1 catalysts.

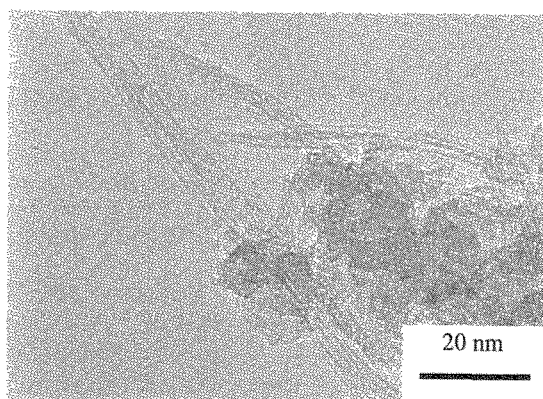


Fig. 5 TEM image of the prepared SWNTs using $\text{Fe}_2(\text{SO}_4)_3$ catalyst.

The typical example of the TEM images of the carbon materials obtained by the CVD treatment using the Method-1 catalysts is shown in Fig. 4. It was found that multi-walled carbon nanotubes (MWNTs) as shown in Fig. 4 can be produced by this procedure, independent of the kind of the catalyst metal. On the other hand, the yield of MWNTs obtained by this procedure highly depends on the catalyst source material. In the case of $\text{Fe}_2(\text{SO}_4)_3$ and $\text{Ni}(\text{NO}_3)_2$, the largest amount of MWNTs was obtained. It is noted that single-walled carbon nanotubes (SWNTs) were also observed in the case of $\text{Fe}_2(\text{SO}_4)_3$ (Fig. 5). However, most of the CVD products was amorphous carbon and the yield of MWNTs and SWNTs is estimated to be less than 0.1 wt% of the total amount of the deposited carbon. Therefore, this procedure is not very suitable for CNT production.

Fig. 6 shows EDS pattern of AISBA-15. Al K α peak is clearly seen in this spectrum and no metal particle was observed by TEM. Therefore Al atoms were incorporated into the SBA-15 by substitutionally replacing the Si atoms of silanol groups in the wall surface of SBA-15.

TEM images of AISBA-15(Fe) are shown in Fig. 7. It is noted that part of the SBA-15 particles was transformed into the aggregation of tubular structure after the ion-exchange treatment (Fig. 7(b)). Strong Fe peaks were detected only from the transformed part by EDS measurement. However, no metal particle was observed in this part. Therefore, Fe atoms were incorporated into the framework of SBA-15 and this led to the transformation.

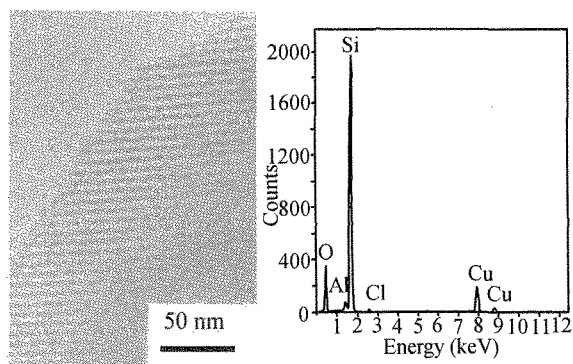


Fig. 6 TEM image and EDS pattern of AISBA-15.

MWNTs were obtained by the CVD treatment using the AISBA-15(Fe) (Fig. 8). The yield of MWNTs is much greater than that obtained using Method-1 catalysts. As shown in Fig. 8, the average outer and inner diameters of the obtained MWNTs are about 40 nm and 10 nm, respectively. The distribution of the outer diameter is estimated from 20 nm to 100 nm. The length of the most of the MWNTs was greater than 1 μm . The yield of MWNTs is estimated to be about 10 wt% of the total amount of the deposited carbon. It was confirmed by high resolution TEM observation that the walls of the MWNTs are well graphitized and that the MWNTs are grown from metal catalyst particles having 10-40 nm size. The metal particles were not observed before the CVD treatment. Therefore, it is thought that the aggregation of the incorporated Fe atoms occurred

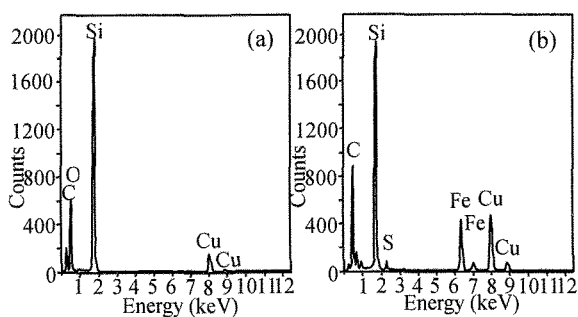
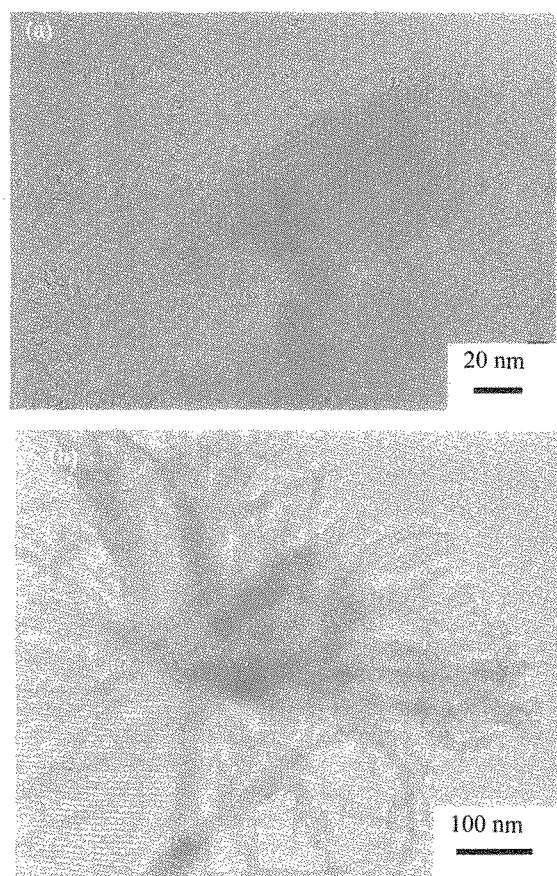


Fig. 7 TEM images and EDS patterns of AISBA-15(Fe). (a) is a usual periodic aligned uniform mesopores and (b) is a part of the SBA-15 particles transformed into the aggregation of tubular structure.

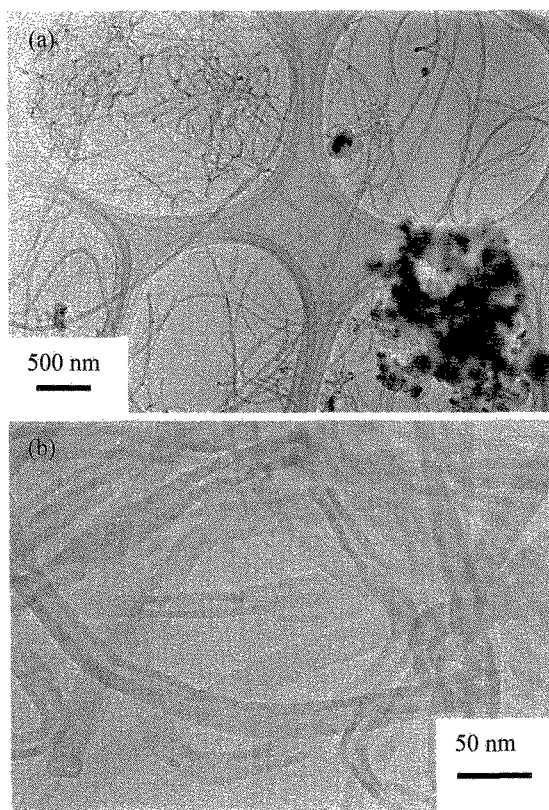


Fig. 8 TEM images of MWNTs were obtained by the CVD treatment using the AISBA-15(Fe).

during the CVD process. If the mechanism of the aggregation is revealed and the rate of the aggregation is able to be controlled, it will be possible to tune the diameter of CNTs and the yield of CNTs will be improved.

4. Conclusion

It was found that SWNT and MWNT can be produced by the present procedure using the catalyst particles prepared by two methods, Methods I and II. However, in the case of Method I, the amount of the produced CNTs was very small irrespective of the kind of the catalyst metals. In Method I, catalyst particles are formed not only in the mesopores of the SBA-15 but also on the outer surface of the SBA-15. Since the large catalyst particles on the outer surface promote the production of amorphous carbon, it is difficult to improve the yield of CNTs. On the other hand, in the case of Method II, since fine metal particles are selectively produced, MWNTs can be synthesized on a large scale.

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