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Low temperature synthesis of carbon nanotubes by direct microwave irradiation

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INTRODUCTION

Carbon nanotubes(CNTs) are materials of increasing interest due to their excellent electronic properties as well as good physical and chemical properties. Various methods for the synthesis of CNTs have been reported : arc-discharge, laser ablation, chemical vapor deposition, flame synthesis, and the high pressure CO(HIPCO) process. However, none of these methods can be used at a low temperature, so the incorporation of CNTs with low melting point materials, such as organic polymers, has been severely limited. Furthermore, expensive vacuum equipment is necessary to lower the temperature of synthesis. Therefore, the strategy frequently used has been to separate the synthesis of CNTs from the fabrication of devices. It is, however, difficult to handle CNTs in the post processing steps, due to their extremely small size. A better strategy is to synthesize CNTs *in situ*, at the exact location of the devices. This strategy has been successful only with high melting point materials.

In our previous study, we reported the CNT synthesis on various supports, even on organic polymer substrates, by microwave heating of the catalysts under atmospheric pressure. The overall objective of this research is to establish a better understanding of the influence of chemical structures and processing conditions on the properties of CNTs which are directly synthesized on polymeric and organic materials through microwave irradiation.

In this study, we report in detail the influence of experimental conditions on the

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morphology and the microstructure in the microwave synthesis of CNTs. The effect of reaction time, flow rate and concentration on carbon yield and the ratio of amorphous carbon to graphitic carbon were studied, and the mechanism for CNT synthesis by microwave heating is proposed based on these observations.

SYNTHESIS OF CARBON NANOTUBES IN A MULTI-MODE CAVITY

Related tasks :

(Task 1.1. Materials selection)

(Task 2.1. Determine the effect of process variables on CNTs and CNTs/polymer properties)

Microwaves are the electromagnetic waves with a frequency range from 300MHz to 300GHz. Compared with conventional heating methods, microwave heating, where the microwave energy is delivered to the materials through molecular interactions with the electromagnetic field, has an advantage of uniform, rapid and volumetric heating. However, some materials can not be easily heated by microwaves.¹⁹⁻²⁴ The power absorbed in a unit volume of the material, $P=2\pi f\epsilon''E^2=\sigma E^2$, is the result of interactions between electromagnetic field and the material. Here, P is the absorbed power per unit volume, f is frequency, ϵ'' is complex permittivity of the material, E is electric field intensity, and σ is conductance. The absorbed power is directly related to the effectiveness of heating. It decreases to 1/e of the original value at the penetration depth, $d_p=c\epsilon_0/2\pi f\epsilon''=1/(\pi f\mu\sigma)^{1/2}$, where d_p is the penetration depth, ϵ_0 is the dielectric constant of free space, and μ is the permeability of the material. It depends on the characteristics of a material since the penetration depth of microwaves is inversely proportional to the conductivity of the material. For microwave heating, the conductivity of a material should not be small and the size of it should not exceed the penetration depth. A conductor, which has high conductivity, has a short penetration depth and it reflects microwaves at its surface. On the other hand, an insulator with low conductivity is transparent to microwaves. Dielectric materials with the medium range of conductivity, absorb microwaves and can be easily heated. Therefore, only the catalyst particles would be heated to the temperature of CNT synthesis, without raising the temperature of the substrate on which the catalysts lie.

At first, we started with the control experiments. Support material, carbon black (microwave absorber) or SiO₂ (microwave insulator), without catalysts was placed in a quartz reactor, with a flowing acetylene (C₂H₂) gas, and irradiated by microwaves. Microwaves didn't stimulate C₂H₂ gas to break down, and there was no evidence of any

CNT formation without catalysts.

Identical experiment was repeated with the carbon blacks loaded with Fe catalysts. The addition of catalysts was essential to the CNT synthesis : CNTs were grown with Fe-loaded C(carbon black). Figs. 1(a) and (b) show the SEM images of the Fe-loaded carbon blacks before and after microwave irradiation. The carbon black supports appear in Fig. 1(a) with no fibrous matters, while tortuous fibrous structures are clearly present in Fig. 1(b) after microwave heating. HR-TEM images in Figs. 1(c) and (d) reveal that the fibrous structure indeed is a multi-walled CNT of approximately 50nm diameter and its fringe structure is well graphitized.

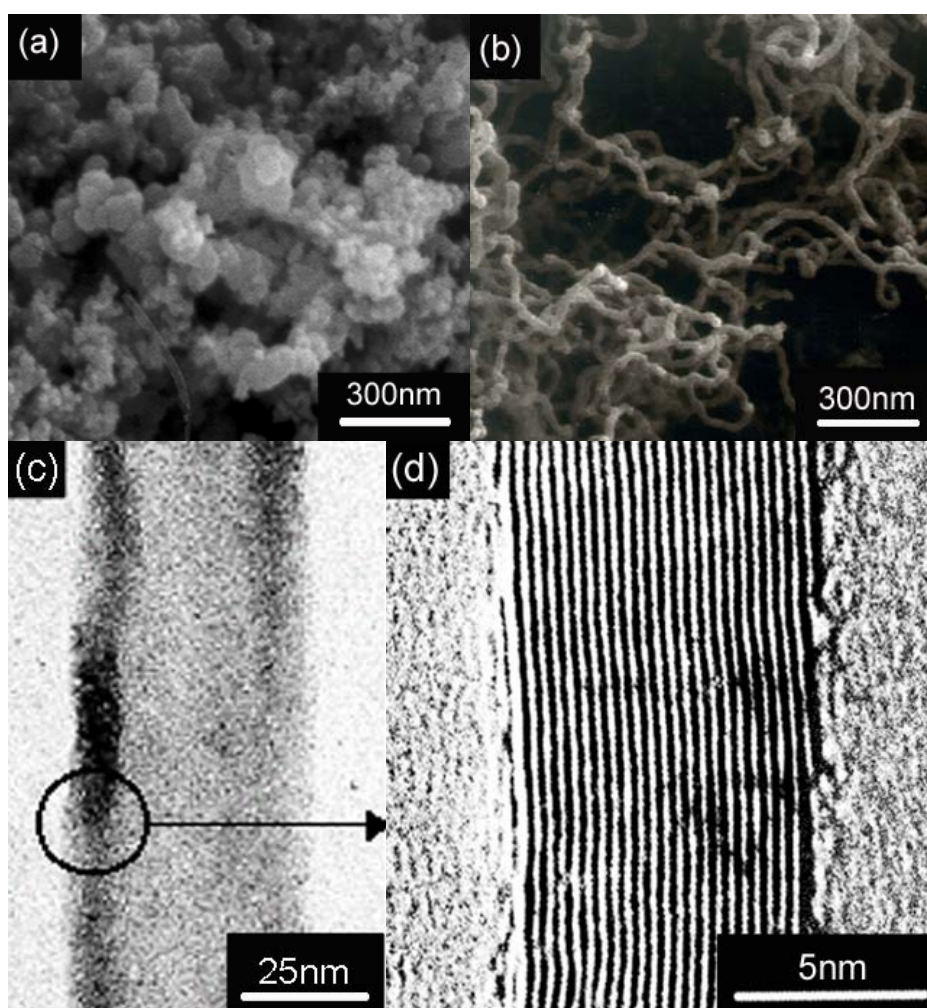


Fig. 1. SEM images of the catalysts loaded on carbon black supports: a) before and b) after microwave irradiation (0.05 g of Fe/C, time = 30 min, $C_2H_2 = 5 \text{ ml min}^{-1}$. c, d) Bright-field image of a CNT and HRTEM image, respectively, showing the graphitized wall structure of the CNT.

It should be checked whether there is a possibility that these CNTs were originated from carbon black supports, not from C_2H_2 gas. Control experiment was performed under the same condition with a flowing inert gas, helium(He), instead of C_2H_2 . No CNT formation was observed in this control experiment, so that CNTs were originated from acetylene gas, not from carbon black supports.

As Co, Ni, and Fe have been known for the efficient 3d transition metal catalysts for CNT synthesis, CNT syntheses with different catalysts were carried out at various experimental conditions. Fig. 2 shows the carbon yield as a function of catalyst type, reaction time and flow rate of C_2H_2 . Here, carbon yield is defined as the equation (1) based on the weight of catalyst.

$$\text{Carbon yield(\%)} = (\text{wt. after reaction} - \text{wt. of catalyst}) \times 100 / \text{wt. of catalyst} \quad (1)$$

Co is thought to be the most effective catalyst for the given synthesis conditions from Fig. 2(a), though Ni and Fe are nearly effective.

Fig. 2(b) shows that carbon yield increases rapidly at the early stage of the synthesis, and then gradually slows down as the synthesis proceeds. Catalyst deactivation might be responsible for this slow-down. The carbon yield increases linearly with the flow rate of C_2H_2 within the range of our experiments (Fig. 2(c)).

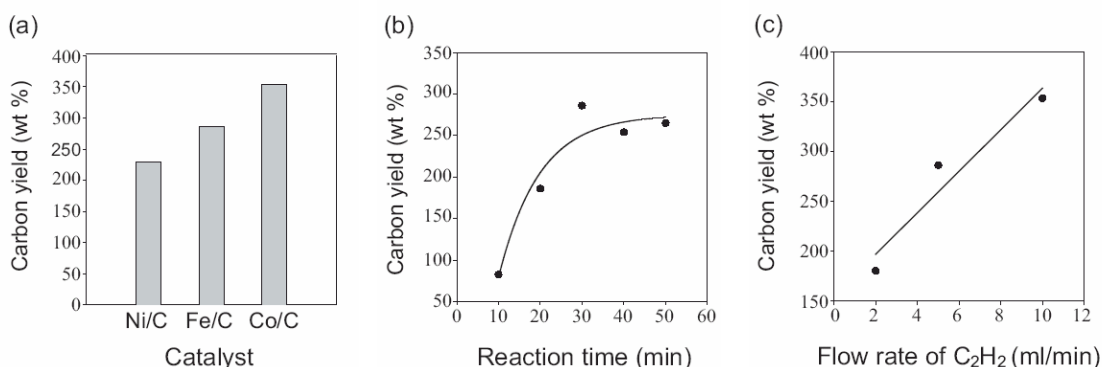


Fig. 2. Effect of reaction parameters on carbon yield. a) Different catalysts: C_2H_2 = 5 ml min⁻¹, time = 30 min. b) Reaction time: catalyst= 0.05 g of Fe/C, C_2H_2 = 5 ml min⁻¹. c) Flow rate of C_2H_2 : catalyst = 0.05 g of Fe/C, time = 30 min.

The main purpose of this research is to achieve selective heating of catalysts. Note that selective heating of catalyst particles cannot be achieved with carbon black supports because carbon black itself is a microwave absorber. Carbon black supports can absorb microwave energy, so they are also heated during microwave irradiation. To achieve true selective heating of catalyst particles, identical experiment was repeated with cobalt catalysts on a SiO_2 support. To our surprise, there was no carbon formation

with flowing C_2H_2 (Fig. 3(a)). Although cobalt catalysts absorb some microwave energy, such a small amount of energy dissipates quickly through the SiO_2 support. Therefore, the temperature of catalyst particles cannot reach the temperature of CNT synthesis.

On the other hand, we reported that CNT synthesis did occur when hydrogen sulfide(H_2S), a co-reactant gas, was introduced with C_2H_2 , or cobalt sulfide was used as a catalyst.²⁵ Confirmation of our previous work is given here with a series of systematic experiments. Details of the reaction conditions appear in Table 1, and the SEM/TEM images of synthesized CNTs are given in Figs. 3 and 4.

Table 1. Reaction conditions for CNTs growth

Entry	Catalyst	$C_2H_2/H_2/H_2S$ (sccm)	Microwave irradiation time (min)	Carbon yield (wt %)
Fig. 4	Co/ SiO_2	10/0/3	30	7.5
Fig. 5(a)	CoS_x/SiO_2	10/0/0	5	31.5
Fig. 5(b)	CoS_x/SiO_2	30/20/0	5	31.5

When hydrogen sulfide (H_2S) was added to the reactant gas stream of C_2H_2 , curved CNTs were grown on Co/ SiO_2 (Fig. 3(b)) after 30 minutes of microwave irradiation with a small carbon yield of 7.5% (Table 1). These CNTs are ranging tens of nanometer thick, and have closed-ends. Various forms of carbons, such as onions and amorphous carbons, were also observed. The HR-TEM image in Fig. 3(c) shows that the fringe structure of the CNT is well ordered though the surface seems to be covered with amorphous carbons. Graphitic nanofibers(GNFs), which have herringbone type fringe structures (Fig. 3(d)), exist as well as CNTs, and they generally have larger diameters than CNTs.

When hydrogen (H_2) or ammonia (NH_3) was introduced with C_2H_2 , instead of H_2S , there was no formation of any carbon. Another control experiment showed that H_2S didn't react with C_2H_2 by microwave irradiation in the absence of catalysts. Based on these observations, we thought that H_2S played a crucial catalytic role together with Co catalysts to induce the growth of CNTs. It has been known that sulfur has an important role in lowering the solidification temperature and in liquefying metal catalysts in CNT synthesis. Sulfur, a surface-active element, has also been known to prevent the deactivation of catalysts by adsorbing on the surface of catalysts and to increase the catalytic activity for CNT synthesis.

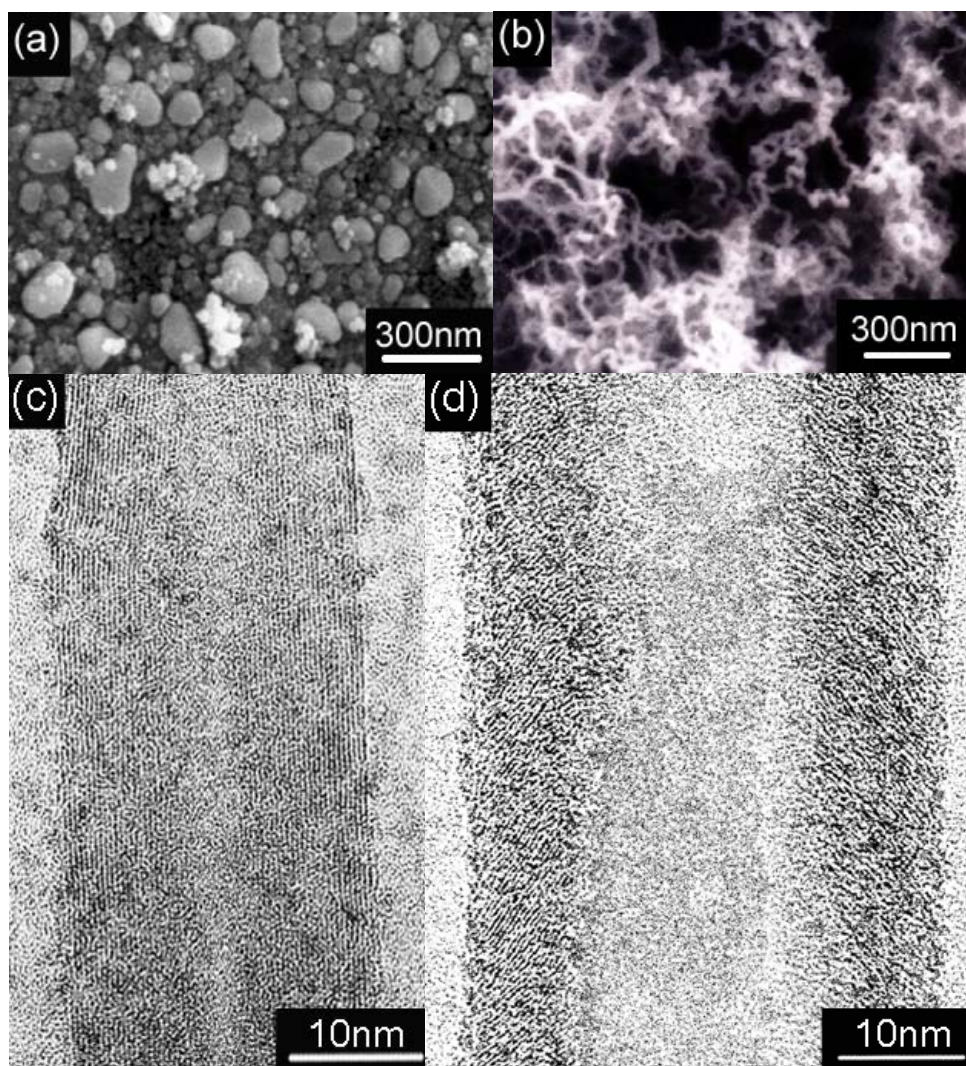


Fig. 3. SEM image of a) Co/SiO₂ after microwave irradiation with flowing C₂H₂ only and b) CNTs grown on Co/SiO₂ with C₂H₂ and H₂S. HRTEM images of c) a CNT and d) a GNF with herringbone structure.

There is an ample possibility that cobalt sulfides (CoS_x) are formed during the reaction with cobalt catalysts and H₂S. Therefore, we adopted CoS_x as catalysts in our later experiments, and their phases were identified as Co₉S₈ by XRD analysis (Fig. 4(b)). Co₉S₈, has a spinel structure and it is a microwave absorber.

CNTs were successfully synthesized with the cobalt sulfide catalysts under flowing C₂H₂ by 5 minutes of microwave heating. As reported in Table 1, carbon yield increases dramatically and the reaction time reduces to as short as 1 min. Cobalt sulfide particles not only possess a high catalytic activity, but also they are easily heated to a high temperature by microwave irradiation, then efficiently transfer the energy to the nearby

acetylene molecules, resulting in the synthesis of CNTs. The catalyst phase was again characterized after reaction using XRD. $\text{Co}_9\text{S}_8/\text{SiO}_2$ was stable during CNT synthesis and there was no change in its phase. (Fig. 4(c))

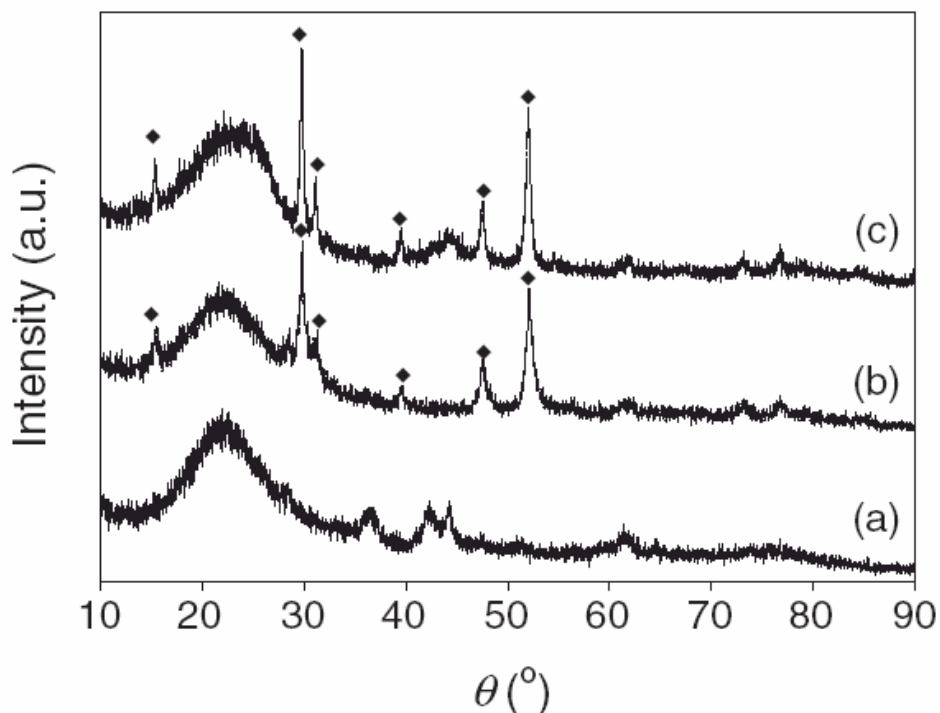


Fig. 4. XRD patterns of the catalyst. a) Co/SiO_2 , b) $\text{Co}_9\text{S}_8/\text{SiO}_2$, and c) $\text{Co}_9\text{S}_8/\text{SiO}_2$ after reaction.

Various forms of nanocarbons were synthesized with cobalt sulfide catalysts on the SiO_2 substrate. Particulate carbons as well as filamentous carbons are observed in Fig. 5(a). The HR-TEM images in Figs. 5(c), (d) and (e) show that these filamentous carbons are either CNTs or GNFs. As in Fig. 5(b), Y-junction or branched CNTs can be seen at certain reaction conditions. It was reported that Y-junction CNTs were synthesized by pyrolysis of hydrocarbons in the presence of sulfur containing compounds such as thiophene, and sulfur was detected as a sulfide phase from the catalyst surface even in micro-contents. In our experiments, Y-junction CNTs were observed in the case of flowing C_2H_2 with H_2 with sulfide catalysts. They have shorter branches than stem CNTs and branching angles are not constant.

The composition of a gas mixture has a large effect on the carbon yield and the ratio of amorphous to graphitic carbons in the microwave-induced reaction. The experiments were carried out (1) by increasing the amount of H_2 with the same amount of C_2H_2 , and

(2) by increasing the concentration of C_2H_2 with a fixed total flow rate. The ratio of amorphous to graphitic carbons, hereafter, named D/G ratio, was quantified by comparing the areas under Raman peaks. We subtracted the baseline from the original peak, and calculated the peak area. It is well known that CNTs have characteristic resonant Raman peaks at a high frequency around 1560cm^{-1} (G -band), while amorphous carbons or fine graphitic particles generally shows a broad peak near 1350cm^{-1} (D-band). Therefore, the position of Raman peaks indirectly indicates the formation of CNTs or amorphous carbons. Previous studies reported that the addition of H_2 during CNTs synthesis made no difference on the formation of CNTs, but H_2 stabilized C-H bonds at the edges of graphite layers, thus prevented the formation of amorphous carbons coated on graphitic tubes.

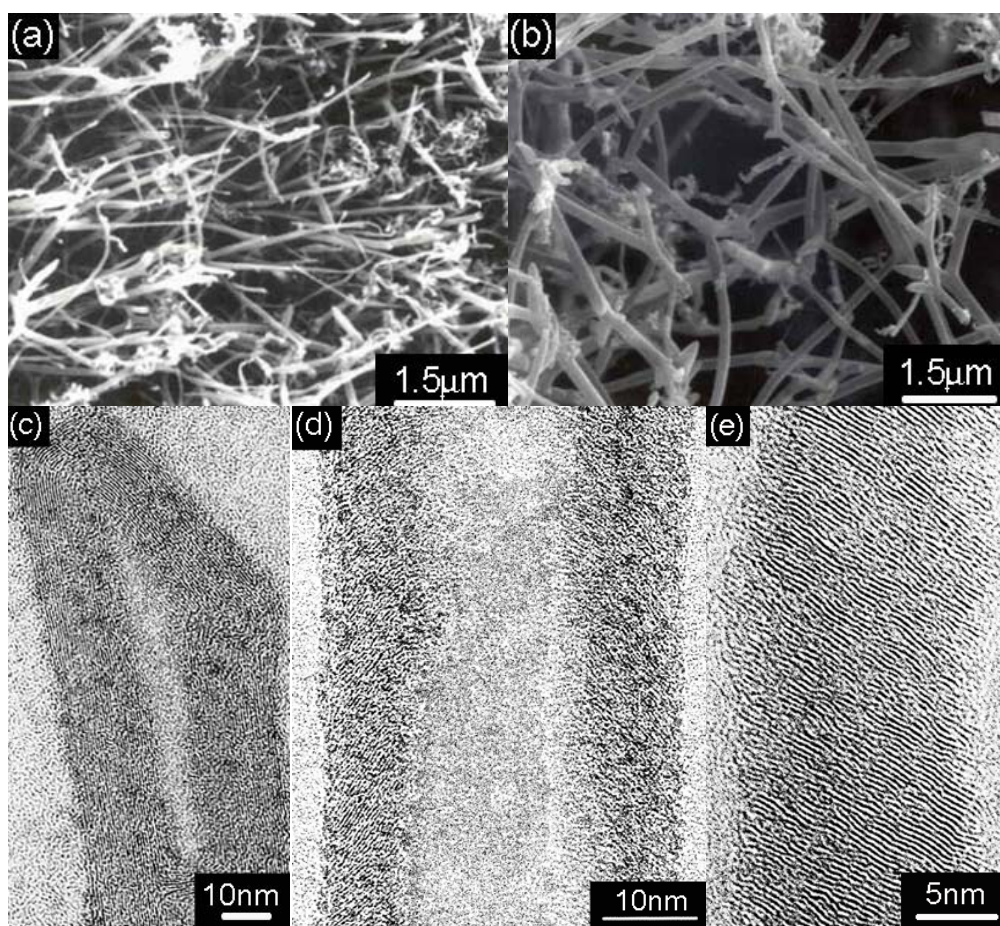


Fig. 5. SEM images of a) CNTs grown on CoS_x/SiO_2 and b) Y-Junction CNTs. c) HRTEM images, respectively, of a GNF with herringbone structure.

Fig. 6(a) shows that carbon yield decreases with the addition of H_2 at a fixed C_2H_2 flow rate. However, the amount of added H_2 seems to have little effect on the amorphous to graphitic ratio, though the data were scattered a lot. Similar trend is again observed in Fig. 6(b). Carbon yield increases with the increase of C_2H_2 concentration at a constant total flow rate. The amorphous to graphitic ratio changes more sensitively in this Figure.

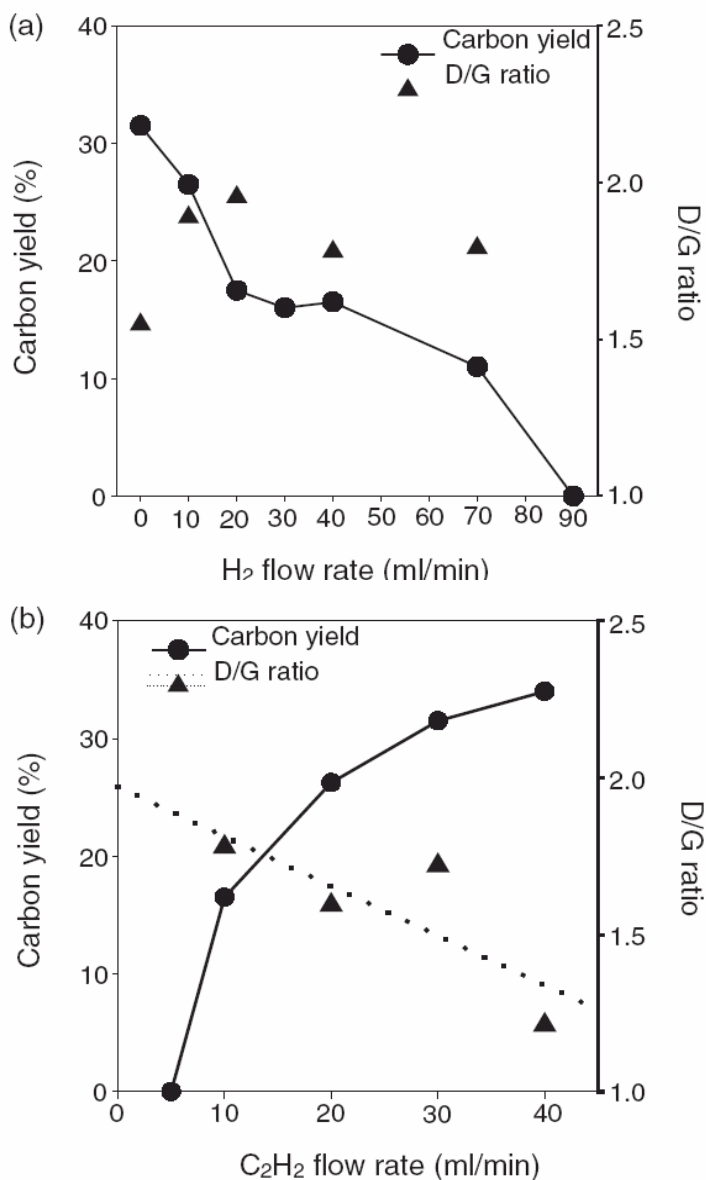


Fig. 6. Effect of gas composition on carbon yield and the ratio of amorphous carbon to graphitic carbon (D/G ration). a) H_2 flow rate added to 10 mL min^{-1} of C_2H_2 , b) C_2H_2 flow rate in a constant total flow rate of 50 mL min^{-1} : 0.2 g of CoS_x/SiO_2 , time = 5 min .

With the knowledge obtained so far, CNTs were directly synthesized on organic polymer substrates by using microwaves. Cobalt naphthenate solution was painted on Teflon or polycarbonate substrates. Also prepared were the Teflon substrates loaded with cobalt sulfide. In the case of cobalt naphthenate, microwaves were irradiated directly onto the substrates with a gas mixture of C_2H_2 , H_2S and H_2 . Temporary arcing occurred during the synthesis and the substrate was covered with black powders. SEM photograph in Fig. 7(a) shows that these black powders are fibrous carbons with some bends and entanglements.

In the case of cobalt sulfide catalysts, reaction time was reduced to as little as 30 seconds. Arcing also occurred during microwave irradiation, but the Teflon substrates appeared not damaged. Figs. 7(b) and (c) show the morphology of CNTs synthesized with cobalt sulfide catalysts. The morphology of fibrous carbons changes from short and straight to long and curved depending upon the reaction conditions. Parametric study about the effect of reaction conditions on the morphology is ongoing. Fig. 7(d) is the HR-TEM image of one CNT appeared in Fig. 7(b). This figure reveals that this CNT has a small hollow core, thick walls and a closed-end. The fringe structure is well ordered and amorphous carbons cover the outer skin of the CNT. The formation of bud-like carbons on the surface of CNTs was also observed in Fig. 7(e). It implies that the synthesized CNTs may play some role in the formation of these nanocarbons.

An explanation is attempted here for the mechanism of the synthesis of CNTs by microwave irradiation. The incoming microwaves are absorbed by catalysts and/or substrates, depending upon the dielectric property of the material. A material is heated by absorbing microwave energy. Penetration depth is an important concept, where the absorbed power decreases to $1/e$ of the original value. It is inversely proportional to the conductance of the material. Dielectric materials with large penetration depths can be easily heated by microwave irradiation. Materials with high conductance such as metals, however, have small penetration depths. Therefore, heating is mainly confined to the thin surface layer.

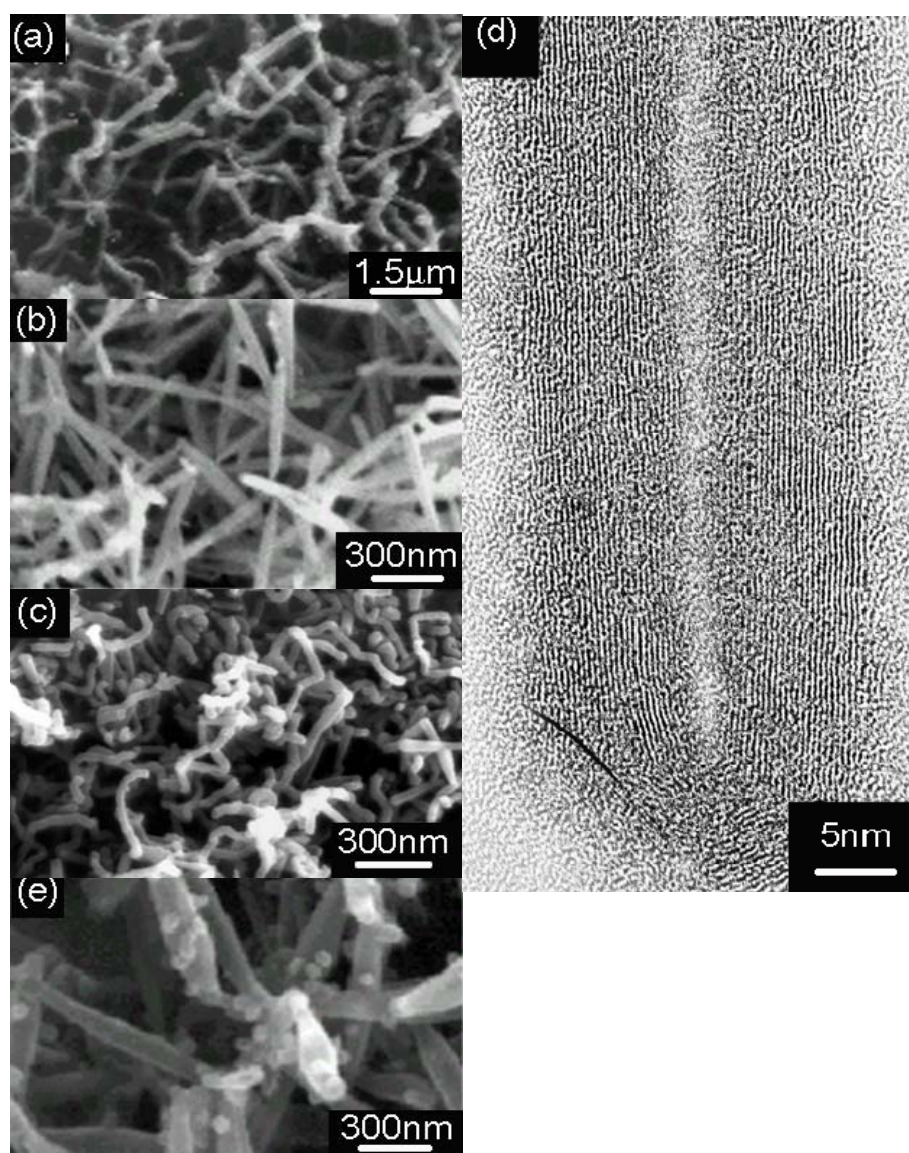


Fig. 7. SEM and HRTEM images of CNTs grown on organic polymer substrates. a) Cobalt naphthenate/polycarbonate, b,c) CoS_x/Teflon, d) wall structure of a CNT of Fig. 7b,e) bud-like carbons on CNTs.

In our experiments, metal or metal sulfide catalysts were used. Because 3d transition metals such as Fe, Co, Ni are good conductors, they reflect microwaves at the surface. However, the catalyst particles are as small as their penetration depths - about 50nm (Fe), 130nm (Co), and 230nm (Ni) - , volume heating of the catalyst particles are possible. Metal sulfides are also microwave absorbers and they can be heated up to 500-1000°C. SiO₂, a microwave insulator, doesn't absorb microwave energy. To make things worse, it dissipates the energy absorbed by the catalyst particles, so that CNTs cannot be synthesized with Co/SiO₂ (Fig. 8(a)). On the contrary, carbon is a microwave absorber

and it can be heated up to 1000°C.²⁰ Therefore, the catalyst particles are easily heated with carbon supports (Fig. 8(b)).

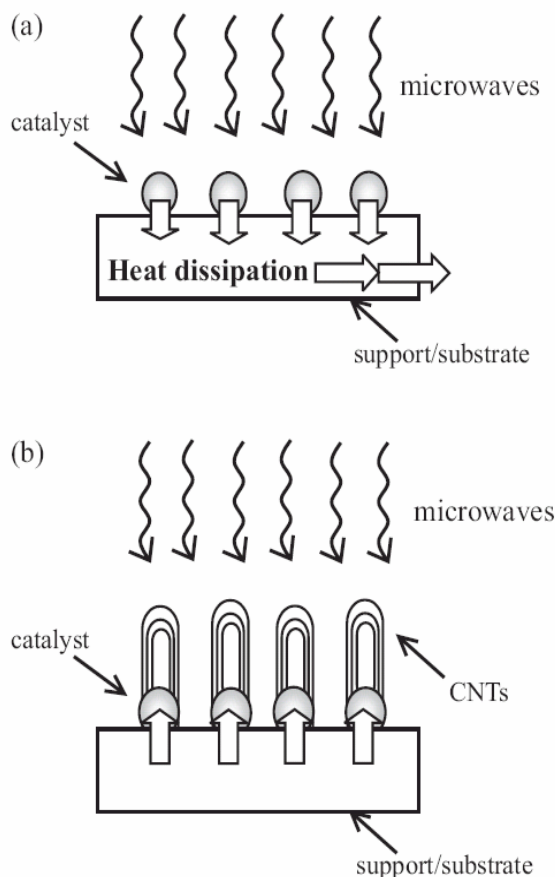


Fig. 8. Mechanism of CNT synthesis by microwave heating a) Microwave-insulating substrate, b) microwave-absorbing substrate.

The decomposition of acetylene is initiated on the heated catalysts. Once the reaction occurs, the formation of carbons continues due to the continuous supply of energy from the exothermic reaction and from the synthesized carbons which can absorb additional microwave energy. Therefore, selection of catalyst and substrate materials is of paramount importance in the synthesis of CNTs with microwaves. The addition of hydrogen sulfide raises the activity of catalysts for the decomposition of acetylene. CNT synthesis proceeds until catalyst particles are deactivated.

ASSEMBLE A SINGLE-MODE MICROWAVE EQUIPMENT

Related tasks :

(Task 1.2. Building a new equipment)

Selective heating of catalyst particles by direct irradiation of microwaves was first reported by the present investigators using the multi-mode microwave device. Multi-mode microwave device is designed to distribute the microwave energy evenly throughout the cavity. This objective is usually achieved by using a metal diffuser. As a result, close control over the desired location and reproducible heating are difficult to be achieved even with a well-designed cavity. Furthermore, spatial variation in the strength of electromagnetic field results in a position-sensitive synthesis of CNTs. Therefore, we have assembled a new equipment, with which microwaves are delivered to the single-mode chamber by a waveguide for the efficient and uniform heating. This equipment is in operation now, and has been generating many interesting results. Fig. 9 shows the photograph of actual equipment. Major parts of this equipment include a magnetron, an autotuner, a circulator, a directional coupler, a reactor with a sliding short, a power meter, 9 mass flow controllers, and 3 controllers. Fig. 10 schematically shows the engineering details of this new equipment, and the specifications of the parts are given in Table 2.

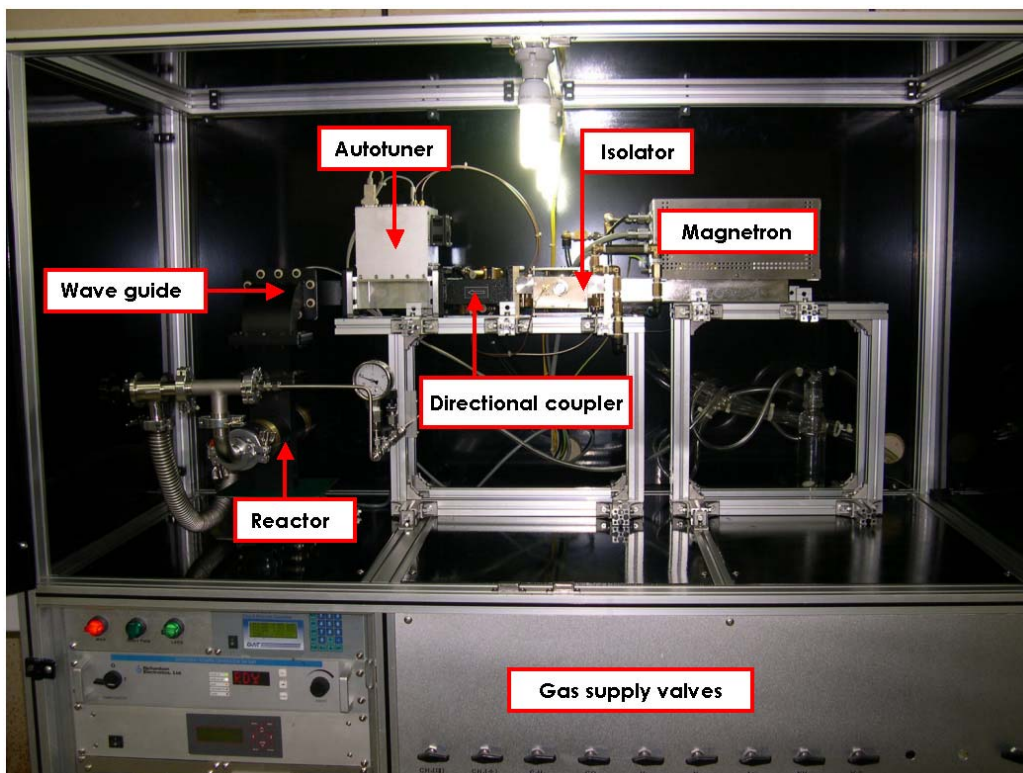


Fig. 9. Photograph of the actual equipment

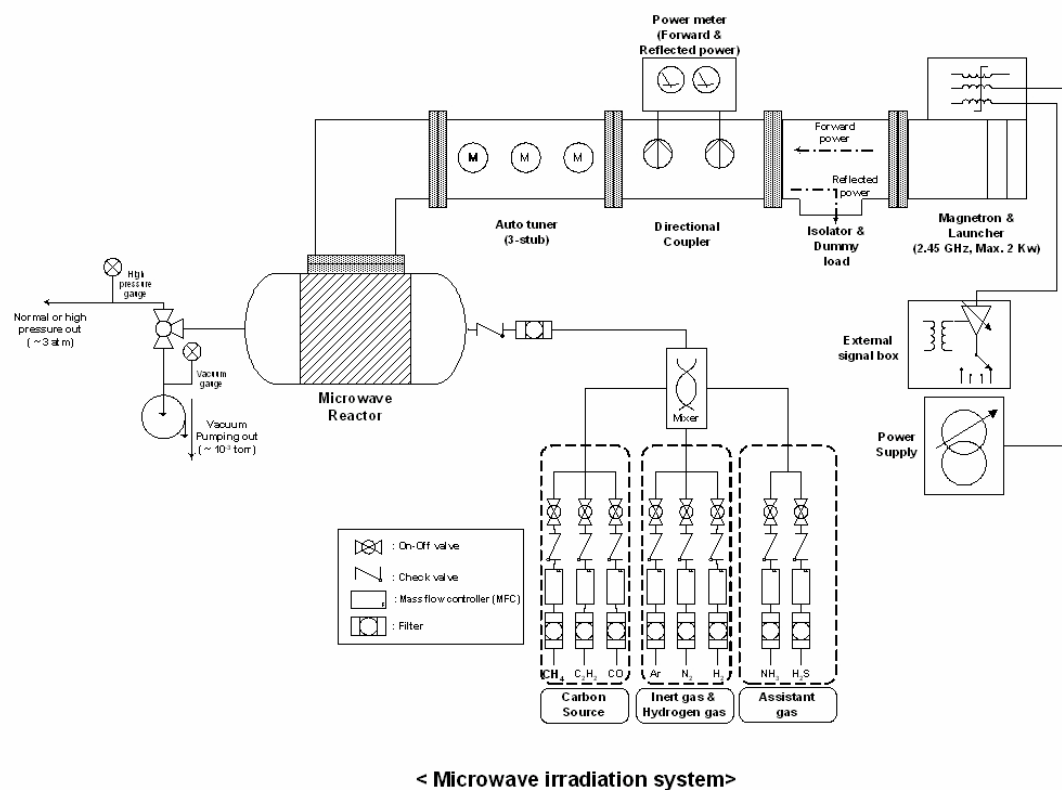


Fig. 10. Schematic diagram of the single-mode microwave heating system.

Table 2. Specifications of the parts of the microwave equipment

Generals	Max. 2 Kw
	Single & multimode operation
	10^{-3} Torr ~ 3 atm
Power supply	SM-840E, Richardson Elec. Ltd.
	Max. 3.0 kW
Magnetron & launcher	MH-2.0W-S1, National Electronics
	2.45 GHz, Max. 2 kW
	Include 2M130/NL 10250 magnetron
	Continuous wave
Isolator	2722-162-11171, National Electronics
	Max. 3.0 kW
	Include circulator & dummy load
Directional coupler	WRDDCB2.0, SAIREM S.A.
	Max. 2.0 Kw
Tuner	WR340Autotune3A, IBF Electronics
	Max. 6.0 kW
	3-stub, motorized autotuner
Reactor	1. 7610 downstream applicator
	ASTEX (modified by FEEL)
	2. SPCFV mode converter
	ASTEX (modified by FEEL)
Available gas	CH ₄ , CO, C ₂ H ₂ ,
	Ar, N ₂ , H ₂ ,
	NH ₃ , H ₂ S
Mass flow controller (MFC)	Brooks 5850E (Input 0~5 V) x 9ea
	CH ₄ (8000 sccm), CH ₄ (500 sccm), CO (1500 sccm), C ₂ H ₂ , (500 sccm),
	Ar (500 sccm), N ₂ (500 sccm),
	H ₂ (500 sccm), NH ₃ (500 sccm),
	H ₂ S (50 sccm)
MFC controller	GMC – 1000, GAT

SYNTHESIS OF CARBON NANOTUBES IN A SINGLE-MODE CAVITY

(Task 1.1. Materials selection)

(Task 2.1. Determine the effect of process variables on CNTs and CNTs/polymer properties)

(Task 2.2. Grow pure CNTs and SWNTs on polymer substrates)

A single-mode cavity has a fixed profile of electromagnetic wave. Therefore, we can generate reproducible results for the synthesis of CNTs using microwaves in this cavity, at least in principle. The most important task in our work is to elucidate whether microwaves are able to synthesize SWNTs as well as MTNTs. To achieve this goal, we changed the catalysts to the well-known catalysts for SWNTs, because the discovery of new catalysts is outside of the scope of this work. Our choice of the catalysts for SWNTs synthesis was that of professor Dai of Stanford University. This is partly because of the proven reputation of this catalyst, and partly because of the availability inside POSTECH. Professor Hee-Chul Choi of Chemistry department used to be a postdoctor of professor Dai, and willingly provided the recipe for the catalysts. Fig. 11 shows the procedure to prepare the catalysts in this work.

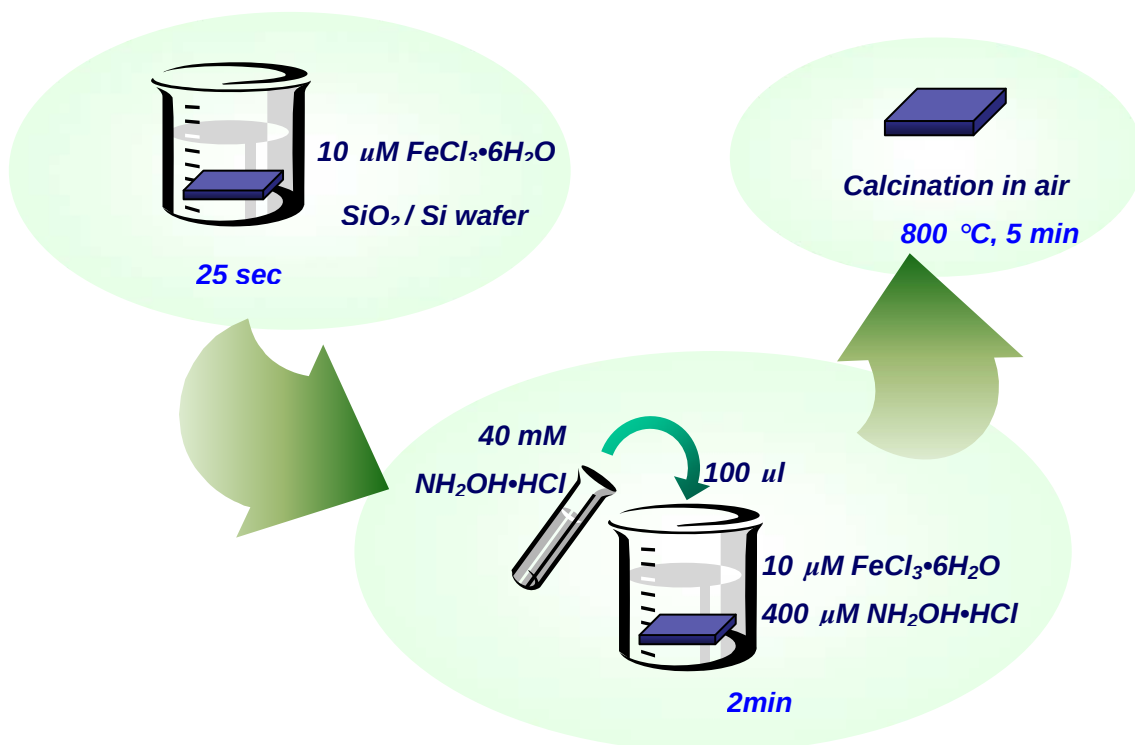


Fig. 11. Procedure for the preparation of catalysts for SWNTs.

Since this catalyst has a form of a solution, it is convenient to apply onto a

substrate. We used Si wafer as the substrate, because the calcination step required a high temperature of 800°C. The solution containing iron ions was transformed to the iron particles of a few nanometer diameter on the surface of the substrate with the function of reducing agent. Calcination removes the impurities and improves the crystal lattice of the iron particles. Fig. 12 shows the AFM images of the Si substrate before and after calcinations.

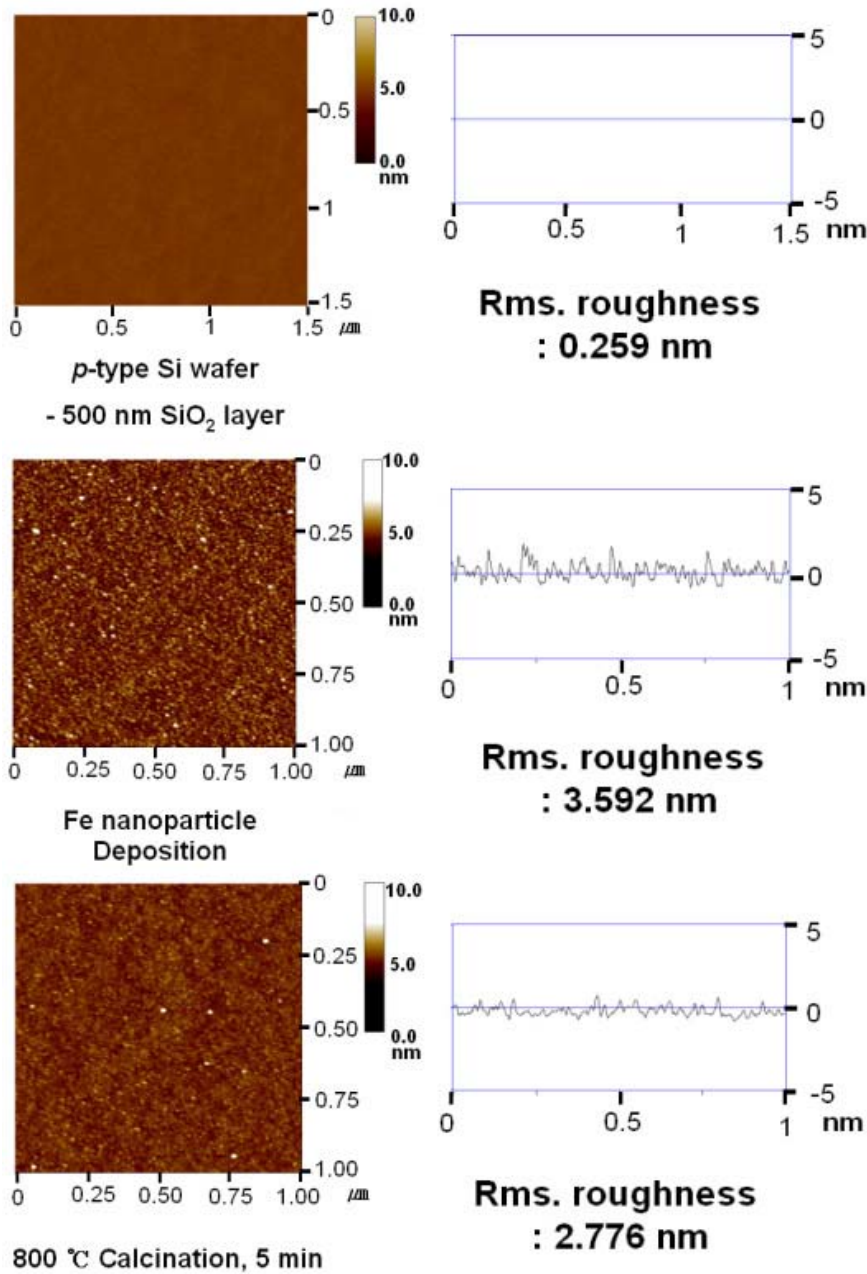
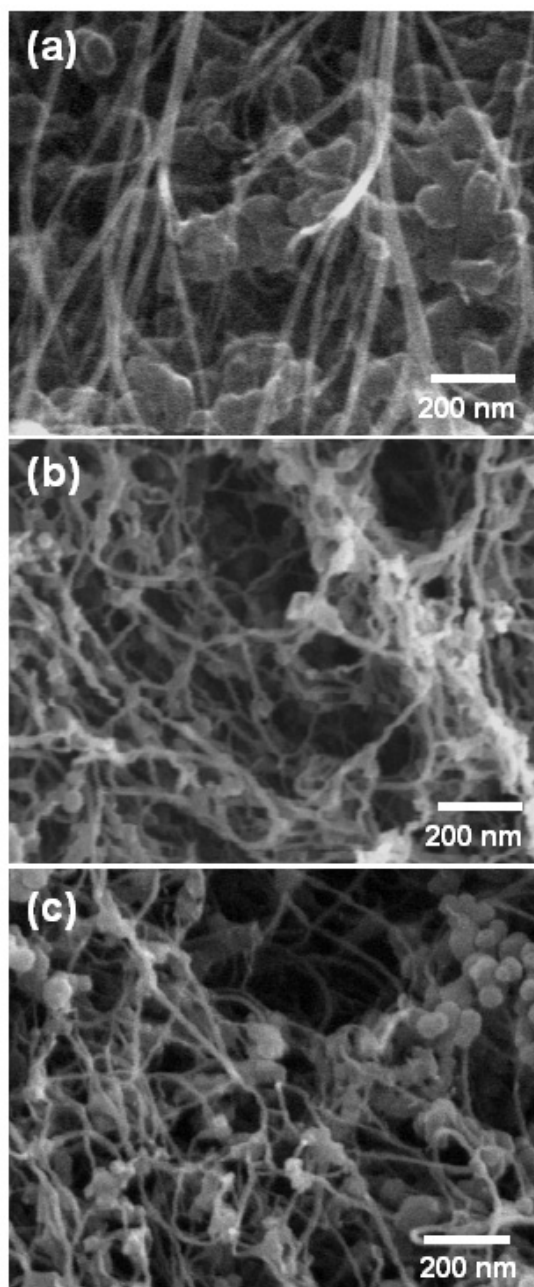


Fig. 12. Surface morphology of the Si substrate

Microwaves deliver energy to the catalyst particles very efficiently. The

reaction time was quite short, usually less than one minute. Fig. 13 is the result of microwave synthesis of SWNTs. Carbon particles as well as fiber-like carbons were synthesized. This is because of the large concentration of hydrocarbons in the reactant



gas mixture.

Fig. 13. Carbons synthesized in the single-mode cavity. (a) 10 sec, (b) 20 sec, and (c) 30 sec. Reactant gas mixture : methane (1000sccm), hydrogen (500 sccm), and acetylene (20 sccm)). Microwave power : Forward (800W), Reflected (<50W).

Concentration of hydrocarbons were reduced in the reactant gas mixture to

reduce the formation of carbon particles. Fig. 14 shows that the reduction of carbon particles with increasing reaction time. We do not have a clear explanation for these results, but the trend is obvious.

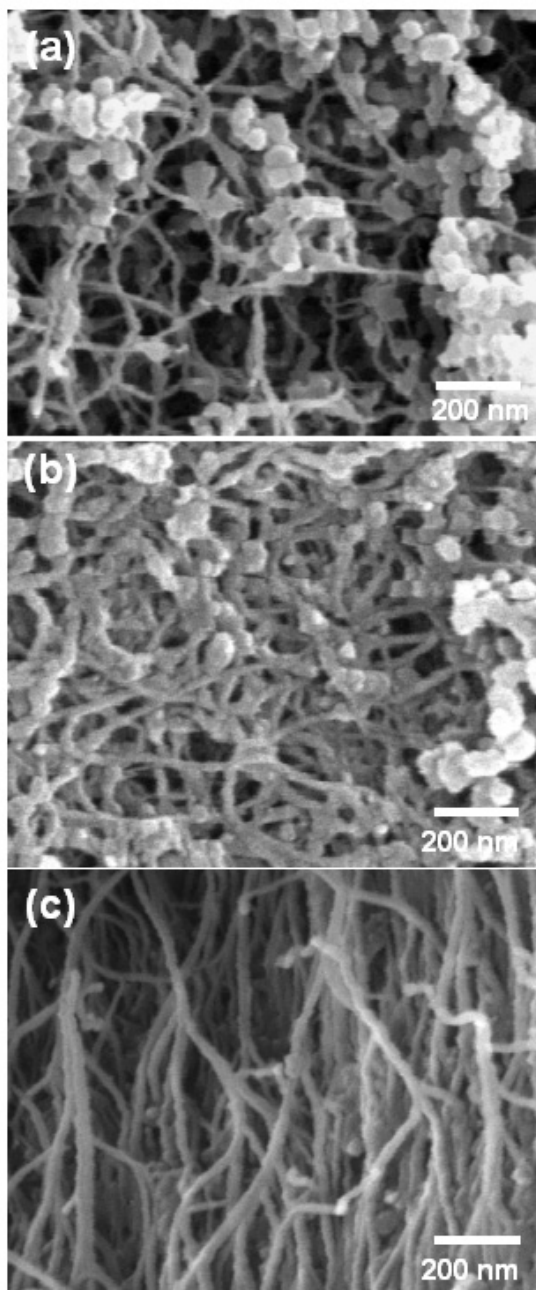


Fig. 14. Carbons synthesized in the single-mode cavity. (a) 10 sec, (b) 20 sec, and (c) 30 sec. Reactant gas mixture : hydrogen (80 sccm), and acetylene (80 sccm)). Microwave power : Forward (800W), Reflected (<50W).

HR-TEM study, together with Raman study, revealed that these fibrous carbons

are in fact bundles of SWNTs. Fig. 15 show the Raman spectra of the samples shown in Figs. 13 and 14. D-bands (around 1300 cm^{-1}) are still noticeable due to the presence of amorphous carbons, though the amount is relatively small compared with that of crystalline carbons. Note that sharp peaks are observed around 200 cm^{-1} , which is the characteristic of the breathing mode of SWNTs. Interestingly enough, RBM peaks are very sharp and there is only one peak for each sample. This fact indicates that the diameters of synthesized SWNTs have very narrow distribution. Extensive investigation is necessary for the important implication to the advancement of nanotube technology.

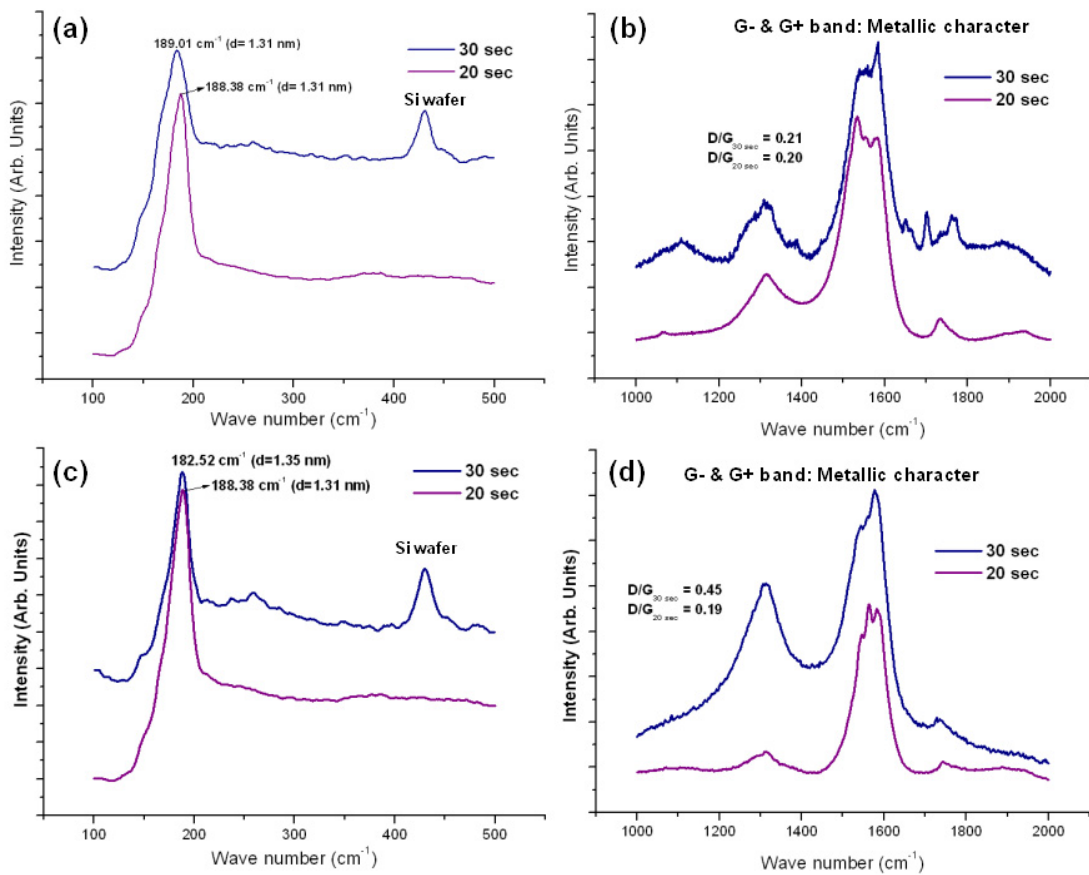


Fig. 15. Raman Spectroscopy of CNTs; (a) and (b) is synthesized in the CH_4 (1000 sccm) + H_2 (500 sccm) + C_2H_2 (20 sccm) gas flow. (c) and (d) is synthesized in the C_2H_2 (80 sccm) + H_2 (80 sccm) gas flow. Diameter is calculated by Kuzmany equations ($d(\text{nm}) = \frac{235}{(\nu(\text{cm}^{-1}) - 9)}$)

A decisive evidence of the presence of SWNTs was obtained from HR-TEM

data. Fig. 16 clearly shows the presence of SWNT bundles, though the quality of the photographs is poor. The photographs on the left were obtained from the sample (c) in Fig. 13, the photograph on the right came from the sample (c) in Fig. 14. We are now looking for cooperation with SAMSUNG for better quality photographs.

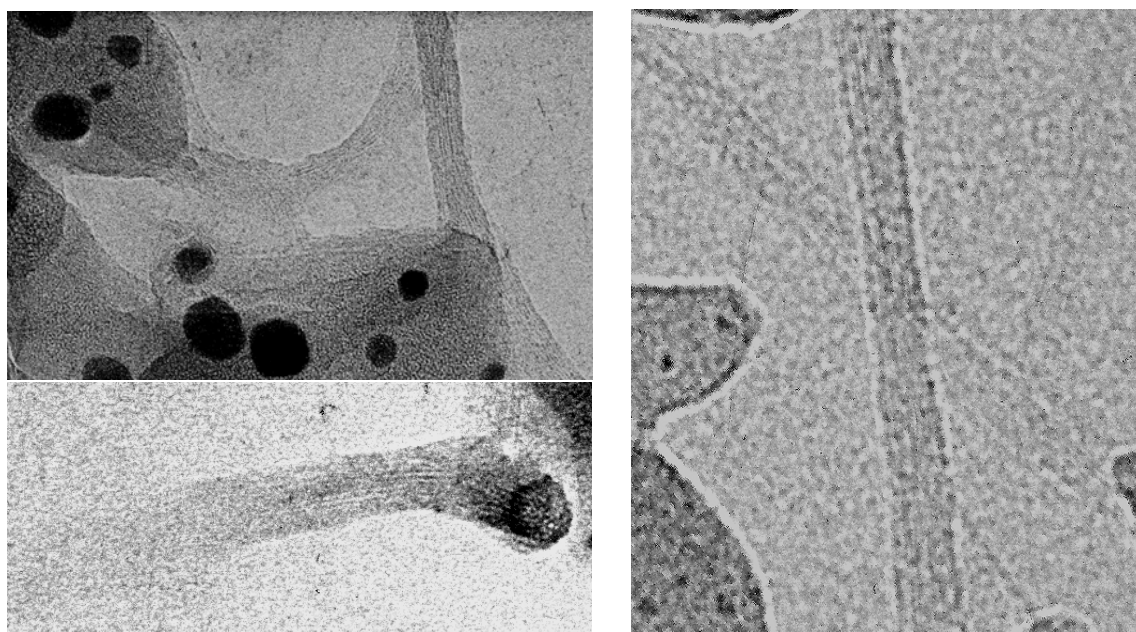


Fig. 16. HR-TEM image of the SWNT bundles.

One of the goals of this work is to investigate the possibility of synthesizing pure SWNTs using microwave technique. The knowledge obtained up to now strongly suggests that a low concentration of hydrocarbon is beneficial to the synthesis of highly pure SWNTs. We repeated our experiment with a low concentration of hydrocarbons in the gas mixture. Fig. 17 show the results : SWNT bundles with almost no particles. Since we obtained this result a few days ago, we need more experiments to ensure the reproducibility. Such experiments are on-going now in my laboratory.

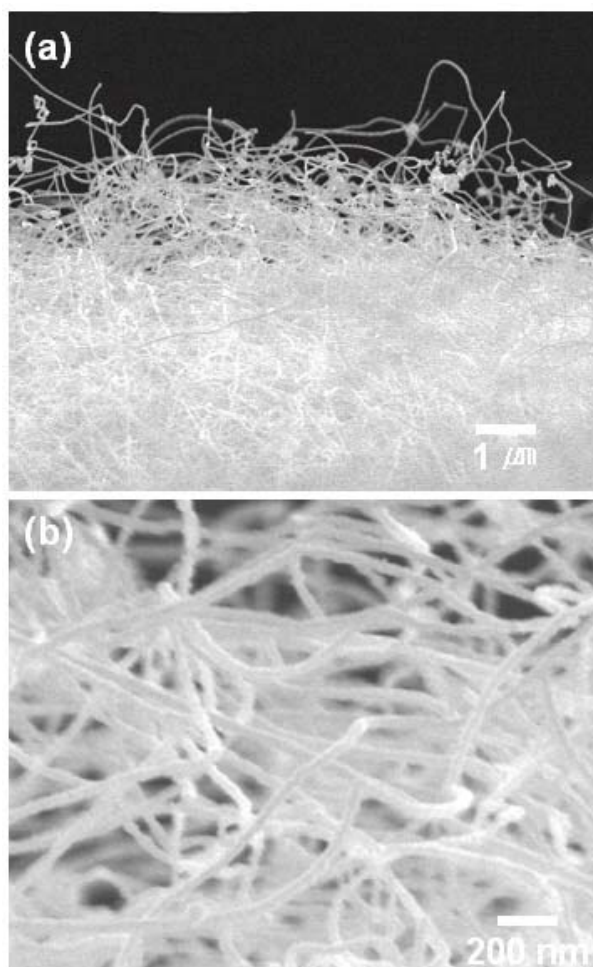


Fig. 16. SWNT bundles synthesized in the single-mode cavity. There is virtually no carbon particles in the reaction product. Reaction time : 1 min. Reactant gas mixture : Argon (80 sccm), and acetylene (20 sccm)). Microwave power : Forward (800W), Reflected (<50W).

We are now in a position to investigate our final goal : Synthesis of SWNTs on polymeric substrates. To make long story short, we are not sure to achieve this goal yet. We do have many interesting results concerning this goal, but more investigations are necessary to make a definite conclusion. Here, we just present the data we have obtained up to now.

The difference made here is the change of the substrate. We deposited a thin layer of chromium on Teflon substrates, then deposit catalysts. The chromium layer was necessary to guarantee good adhesion of catalyst particles on Teflon. However, chromium also absorbs microwave energy during SWNTs synthesis, so that the reaction time greatly reduced. Fig. 17s-21 shows the results.

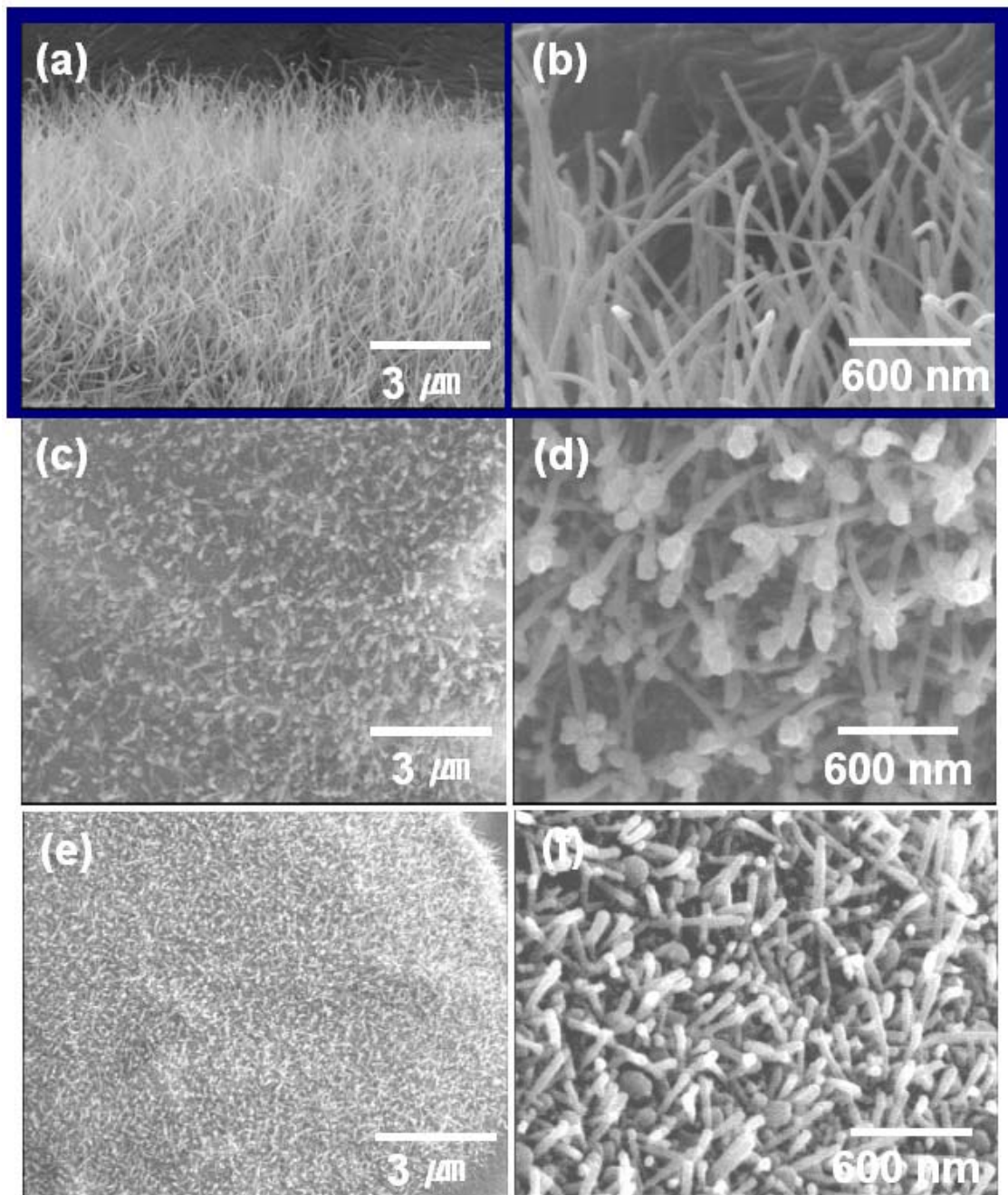


Fig 17. SWNTs synthesized on polymer substrates. (a) and (b) : 5 sec, (c) and (d) : 3 sec, and (e) and (f) : 1 sec. Reactant gas mixture : Argon (80 sccm), and acetylene (80 sccm)). Microwave power : Forward (300W), Reflected (0W). Chromium adhesion layer was 500 nm.

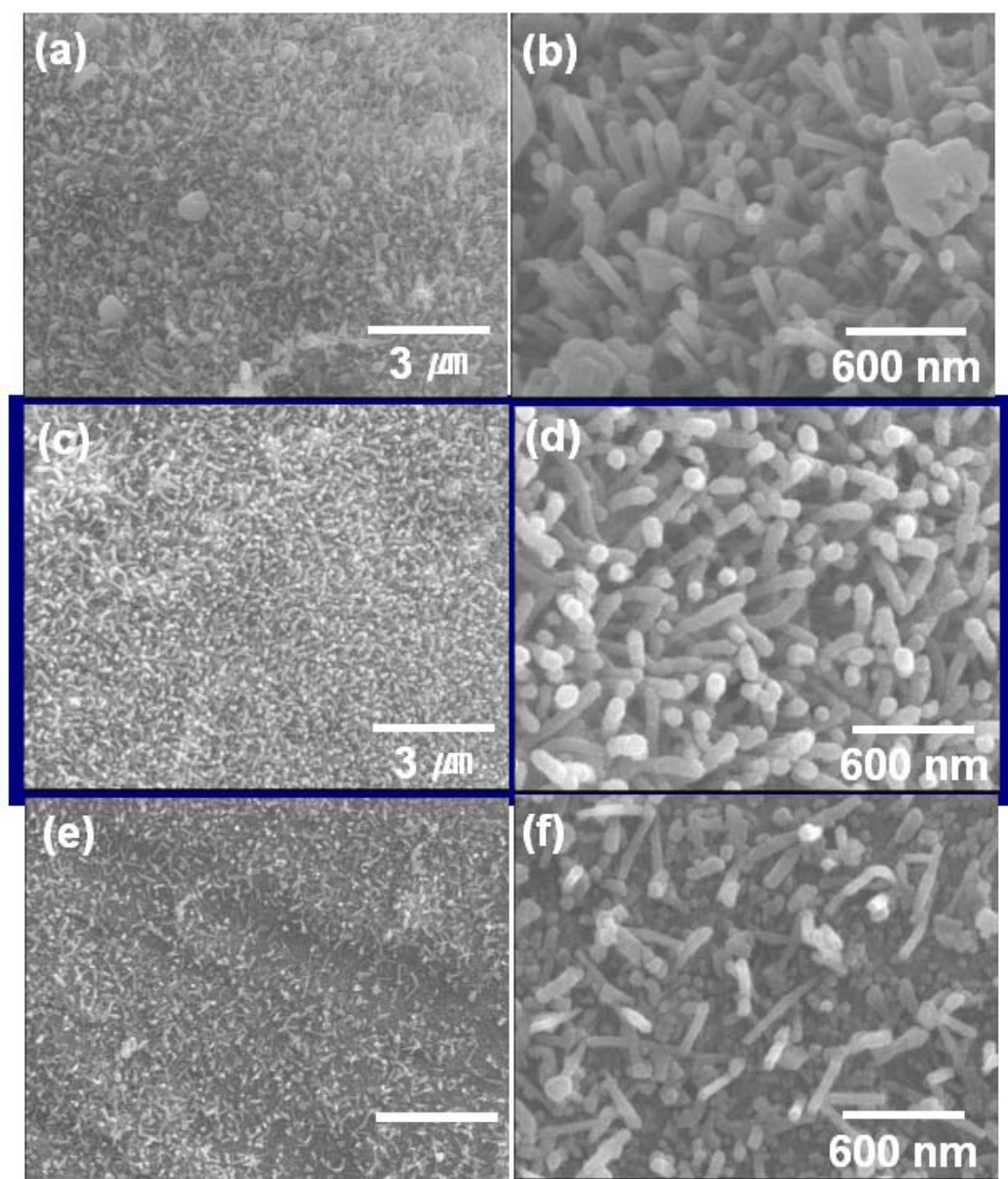


Fig 18. SWNTs synthesized on polymer substrates. (a) and (b) : 5 sec, (c) and (d) : 3 sec, and (e) and (f) : 1 sec. Reactant gas mixture : Argon (80 sccm), and acetylene (80 sccm)). Microwave power : Forward (400W), Reflected (0W). Chromium adhesion layer was 500 nm.

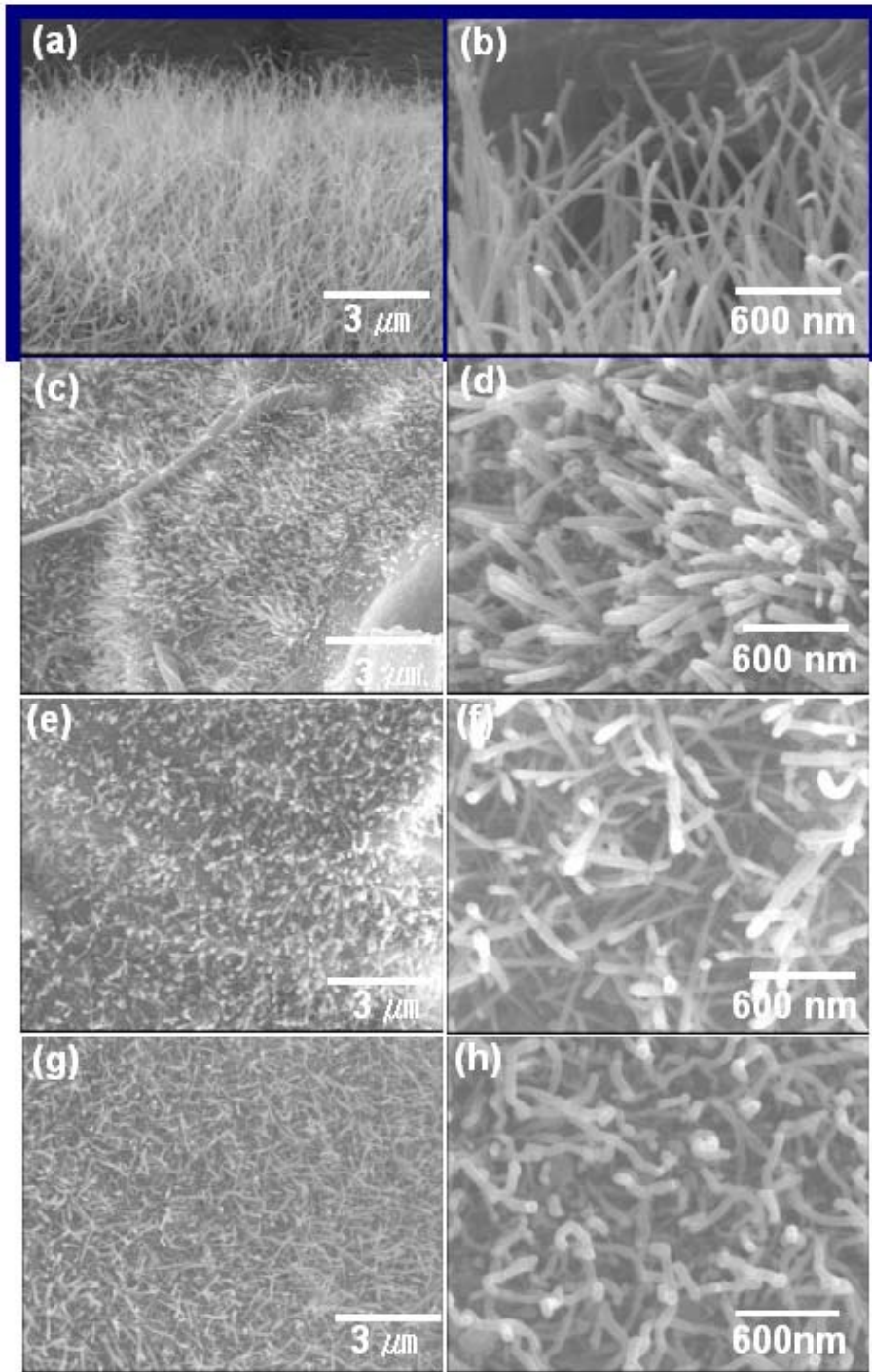


Fig 19. SWNTs synthesized on polymer substrates. (a) and (b) : 5 sec, Argon (80 sccm), and acetylene (80 sccm) (c) and (d) : 5 sec, Argon (80 sccm), and acetylene (20 sccm) and (e) and (f) : 3 sec, Argon (80 sccm), and acetylene (80 sccm), (g) and (h) : 3sec, Argon (80 sccm), and acetylene (20 sccm). Microwave power : Forward (300W), Reflected (0W). Chromium adhesion layer was 500 nm.

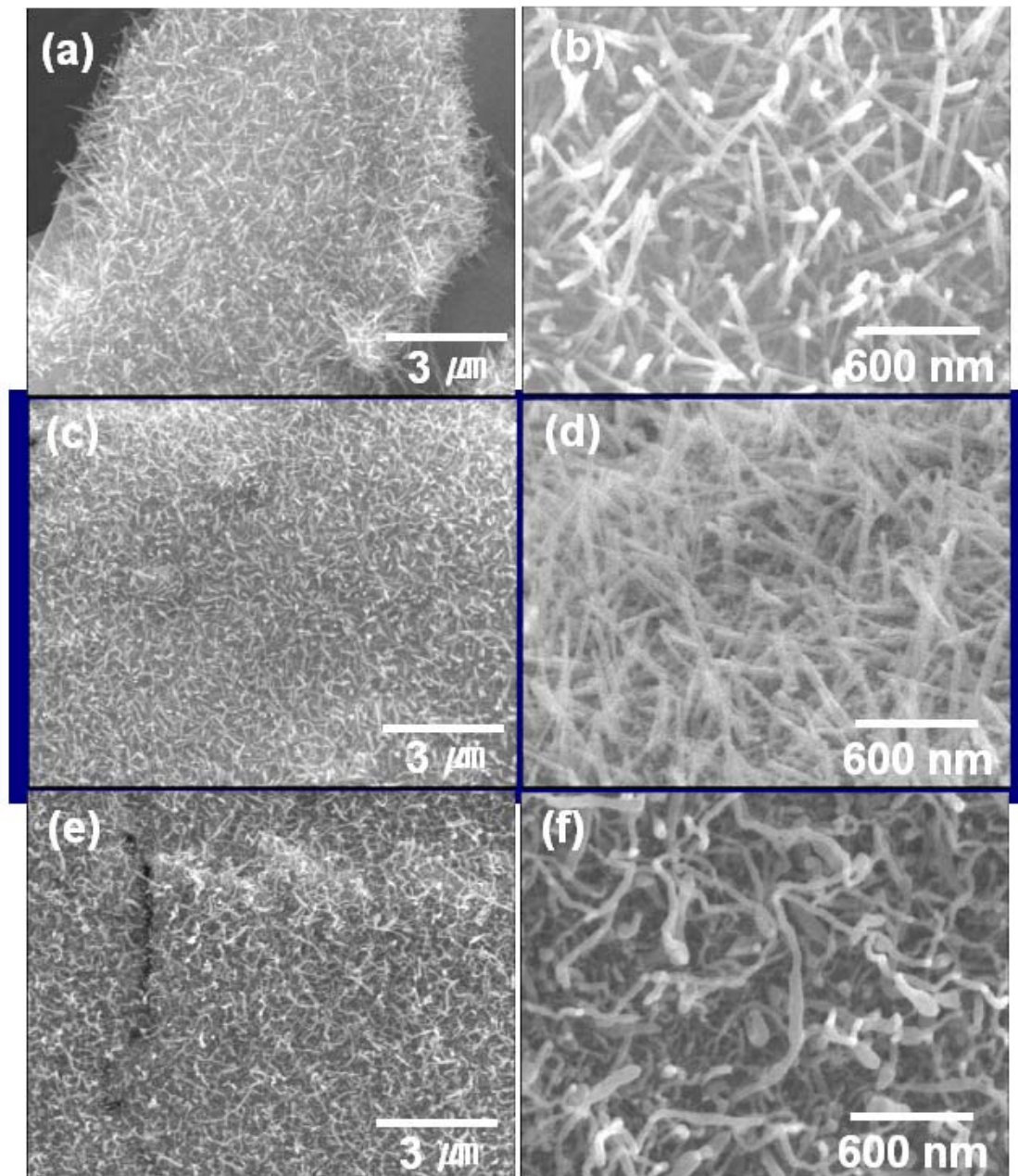


Fig 20. SWNTs synthesized on polymer substrates. (a) and (b) : 5 sec, (c) and (d) : 3 sec, and (e) and (f) : 1 sec. Reactant gas mixture : Argon (80 sccm), and acetylene (80 sccm)). Microwave power : Forward (300W), Reflected (0W). Chromium adhesion layer was 100 nm.

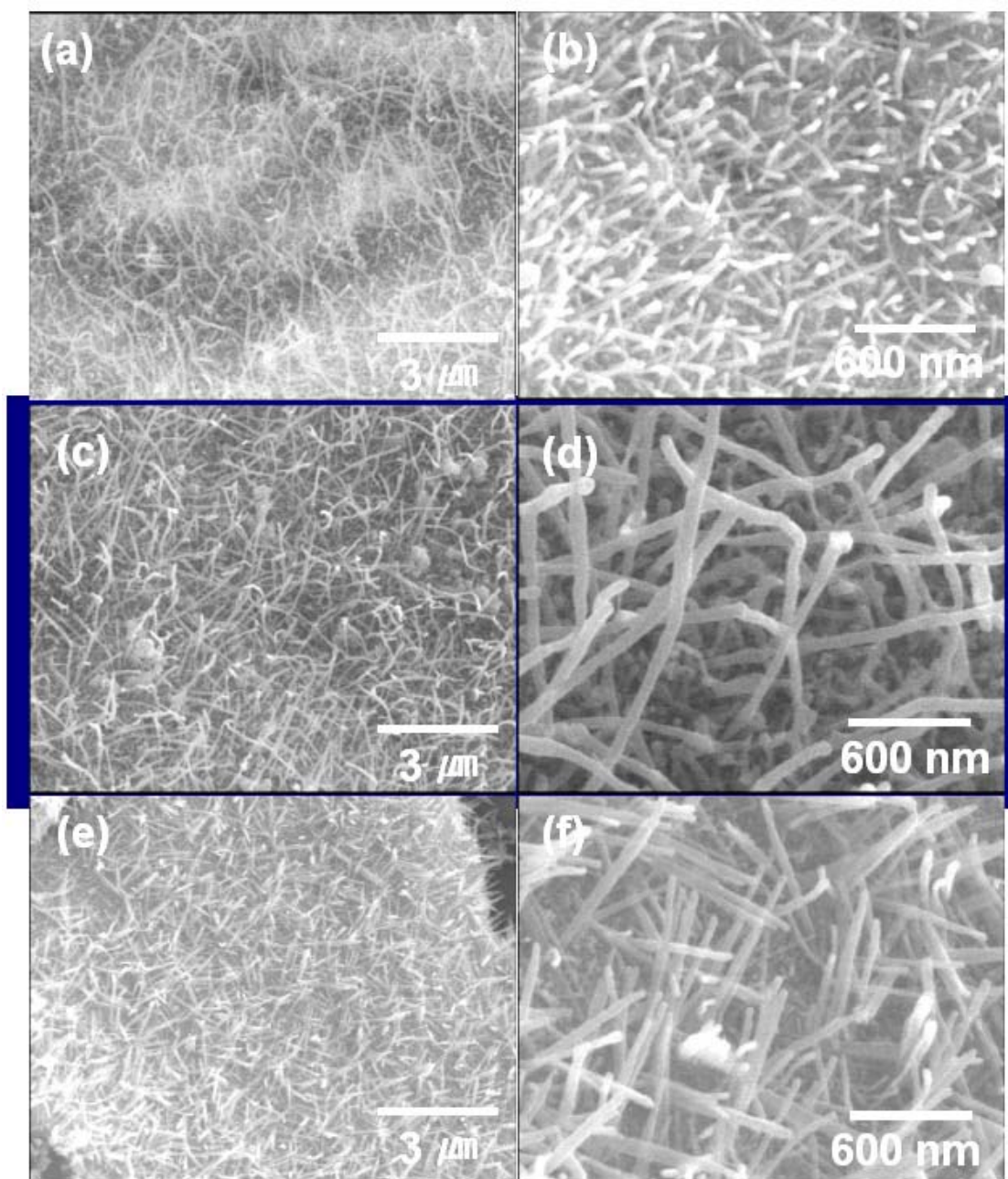


Fig 21. SWNTs synthesized on polymer substrates. (a) and (b) : 5 sec, (c) and (d) : 3 sec, and (e) and (f) : 1 sec. Reactant gas mixture : Argon (80 sccm), and acetylene (80 sccm)). Microwave power : Forward (400W), Reflected (0W). Chromium adhesion layer was 100 nm.

The conclusion from all these data is quite obvious. Microwave heating is a very efficient method to heat catalyst particles, decompose hydrocarbons, and finally synthesize CNTs. However, we have to reserve our conclusion until we finish the analysis of synthesized CNTs.

PRESENTATIONS RELATED WITH THIS WORK

- 1. Kun-Hong Lee, “In situ synthesis of carbon nanotubes on organic polymer substrates”, Proceedings of the 3rd US-KOREA workshop on nanostructured materials and nanomanufacturing, Seoul, Korea (2004, 5/10-11)**
- 2. Kun-Hong lee, “Microwave synthesis of carbon nanotubes on organic polymer substrates”, Air Force Research Laboratory, Dayton, U.S.A. (2004, 7/13-14)**
- 3. Eun-Hwa Hong, Beom-Jin Yoon, Dae-Sup Shim and Kun-Hong Lee, “Direct synthesis of carbon nanotubes on organic polymer substrates”, Proceedings of the international symposium on microwave science and its application to related fields, Takamatsu, Japan (2004, 7/27-30)**
- 4. Kun-Hong Lee, Eun-Hwa Hong, Beom-Jin Yoon, and Dae-Sup Shim, “Direct synthesis of carbon nanotubes on organic polymer substrate”, Proceedings of the annual meeting of the American Institute of Chemical Engineers, Austin, U.S.A. (2004, 11/7-12)**
- 5. Dae-Sup Shim, Eun-Hwa Hong, Beom-Jin Yoon, Dong-Myung Yoon, Kun-Hong Lee, Sang-Ho Oh and Chan-Gyung park, “Synthesis of carbon nanotubes on polymer surface by microwave irradiation”, Proceedings of the 6th cross straits symposium on materials, energy and environmental engineering, Pohang, Korea (2004, 11/18-19)**