ACCVD Synthesis Conditions Influence on Carbon NanoTubes Structure

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Abstract— **Single (SWNTs), double (DWNTs) and multi (MWNTs) walled carbon nanotubes have been synthesized using Alcohol Catalytic Chemical Vapor Deposition (ACCVD) technique where EtOH vapor and N_2 are used as carbon source and carrier gas, respectively. This low cost method is based on ethanol decomposition over Fe-Co catalyst supported by MgO with and without an increase of temperature occurring before the starting of the synthesis. In this paper, we discussed the influence of EtOH pressure or vapor temperature, N_2 flow rate and synthesis temperature on the CNTs yield and nature. Tube diameters and length range from 1 to 80 nm and 2 µm, respectively. The support/catalyst, purified and non purified CNTs were characterized quantitatively and qualitatively by XRD, TEM, FESEM and EDX.**

Keywords-component; **carbon nanotube, SWNTs, DWNTs, MWNTs, EtOH decomposition, ACCVD synthesis.**

I. INTRODUCTION

Since their discovery in 1991 by Iijima [1], SWNTs, DWNTs and MWNTs have been studied and intense researches are carried out because of their unique structural, chemical and physical properties [2, 3]. Applications of carbon nanotubes (CNTs) range from reinforcement of composites or conductive plastics to electrodes for batteries or flat screens, field effect transistors, chemical or force sensors and electromechanical memory. Thereafter, for these future applications, research on exploring techniques, especially without vacuum equipment [2, 5, 6], for fabrication of CNTs has been very active in hopes of developing a method that is easy and can produce cheap CNTs with high quality and controllable reproducibility of their properties. SWNTs can be either metallic, semi-conducting or semi-metallic depending on their unidimentional microstructures. However, the physical and chemical properties of MWNTs are more complicated due to the interaction or coupling between the constituent layers [4]. For investigating the interaction or coupling behavior between different layers, DWNTs are the ideal and simplest candidates for performing both theoretical and experimental investigation. Despite of the very promising foreseen applications, the use of CNTs (SWNTs, DWNTs and MWNTs) in a wider range is still limited by the high production costs. Although, the synthesis of clean and highly crystalline CNTs is still a great challenge.

Regarding the CNTs synthesis, many previous researches have indicated that the CVD process is one of the most promising ways [7, 8]. Also, they confirm that this CNTs synthesis method, generally, have a wide distribution of diameters [9]. The influence factors on the growth morphology of CNTs, such as hydrocarbon gases, carrier gases, synthesis temperature, reaction time, catalyst, ... were investigated using SEM and TEM analysis [10, 11]. As new approach for high purity generation and at low cost, many research have proposed the use of alcohol, particularly the ethanol and the methanol, as carbon source. The proposed Alcohol CCVD method can product high quality SWNTs and MWNTs when it was combined with appropriate catalysts and experimental process [12-16].

In this paper, we present the ACCVD method based on alcohol carbon source (ethanol: EtOH) and nitrogen (N_2) carrier gas for synthesizing CNTs with narrow diameters distribution. We discuss the effect of some experimental parameters as ACCVD conditions, with and without heating before the starting of the synthesis, such as: EtOH pressure, N_2 flow rate and temperature synthesis. After, the separation of CNTs products from the catalyst/support is also described. In addition, the structure of multi, double and single walled nanotubes is characterized by electron microscopy.

II. EXPERIMENTAL PROCEDURE

In this investigation, our experiments were carried out in a conventional horizontal tube furnace (Carbolite, 1200°C) with a quartz tube of 70 mm outer diameter as reaction chamber. The catalyst used for growing the CNTs is prepared by impregnating MgO powder (VWR international, extrapure, white fine powder) with cobalt acetate (98 %, Sigma Aldrich) and iron acetate (95 %, Acros Organics) in EtOH solution (99.85 %, Sigma Aldrich), as reported in our previous paper [2].

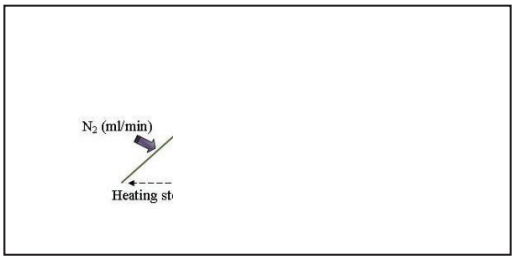

Figure 1. Schematic illustration of the ACCVD process.

TABLE I. CARBON DEPOSIT (WT. %) FROM ETOH DECOMPOSITION OVER FE-CO/MGO AS A FUNCTION OF THE ACCVD PARAMETERS: ETOH VAPOUR TEMPERATURE, N_2 FLOW RATE AND SYNTHESIS TEMPERATURE. LEFT TABLE AT 800 C TEMPERATURE SYNTHESIS AND RIGHT TABLE UNDER 405 MIL/MIN N_2 FLOW RATE: AT TWO PROCESS MODE[(A)].

	EtOH (torr)		
N_2 (ml/min)	0 C (12)	16 C (34)	25 C (59)
205	- (0.05)	0.7 (3.11)	-
300	1.67 (3.59)	12.97 (13.01)	-
405	3.06 (6.94)	**13.98 (26.80)**	12.16

	EtOH (°C)	
T_{syn} (C)	16	25
800	13.98 (26.80)	12.16
900	6.63 (6.88)	3.49
1000	-	1.79

[(A)] Values given in the parentheses refer to the wt% of carbon deposit obtained with calcinated catalyst (mode 1= Fig 1a) and those figures without parentheses refer to the wt% of carbon deposit obtained with maintained synthesis temperature (mode 2= Fig 1b)

The ACCVD growth was carried out, in this experiments, at different EtOH pressure (different EtOH reservoir temperatures), with different N_2 flow rate and synthesis temperature, with and without reactor heating before the synthesis step (see table. 1). At the end, the product was weighted and characterized with and without EtOH precursor.

To date, it is noteworthy that the MgO support is easily removed by a mild non oxidative washing with an HCl aqueous solution comparing with other supports like Al_2O_3, zéolite, … promising various applications with high purity CNTs [2]. Consequently, all obtained ACCVD products have submitted hydrochloric acid treatment (HCl, 30 %, Aldrich) at room temperature in order to purify the ACCVD synthesized CNTs by removing the MgO support and some Fe-Co catalyst particles.

Finally, JEOL JSM 7500 F field emission scanning electron microscope (FESEM) was employed to examine the morphology and the purity of products. Philips Tecnai transmission electron microscope (TEM) was used to characterize the structure, the diameter and the length of the CNTs. Energy dispersive X-ray spectroscopy (EDX) attached to the FESEM examination was carried out on the samples before, after ACCVD synthesis and after acid treatment to analyze the compositions. Selected CNTs specimens were studied by high magnification TEM (JEOL JEM 2100 F field emission electron microscope, FETEM, operated at 200 kV) and the Raman spectra were recorded using a Microraman RENISHAW spectrometer (RAMASCOPE 2000, He-Ne laser 632,8 nm = 1,96 eV excitation with spot size 1 μm^2 and 1 cm^{-1} resolution) (with an He-Ne laser, 632,8 nm = 1,96 eV excitation, in order to confirm the few walled CNTs formation. The specimens for TEM and FESEM analysis were prepared by making a few drops of the suspension (sonicated EtOH with synthesized CNTs) onto a microgrid covered with a holey carbon thin film and a Al pastille, respectively.

III. RESULTS AND DISCUSSION

Many parameters control the ACCVD growth of CNTs such as carbon source kind, carrier gas kind, gas flow, temperature synthesis, time synthesis, catalyst kind, catalyst percentage, … Among these, gas flow inside the growth chamber and synthesis temperature are one of the important factors in determining the growth and structure of the obtained CNTs. Fig. 2 is a typical FESEM image of the as-synthesized and purified carbon products. It shows that abundant carbon filaments have been produced by catalytic decomposition of EtOH over Fe-Co/MgO catalyst. Using TEM analysis, the illustrated morphology indicates that these carbon filaments are SWNTs, DWNTs or MWNTs. They are connected to MgO particles in form of bridges (Fig. 2b and 2 c). In addition, EDX characterization of focalized point of the sample, shows the absence of the MgO support after the HCl purification step with presence of few catalyst particles (Fe-Co = 5.18 %, wt%).

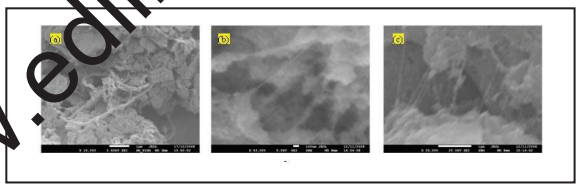

Figure 2. FESEM pictures of CNTs obtained by EtOH-CCVD technique :
- 800 C : (a) 16 C/300 ml/min and (b) 16 C/405 ml/min, purified.
- 900 C : (c) 16 C/405 ml/min, purified.

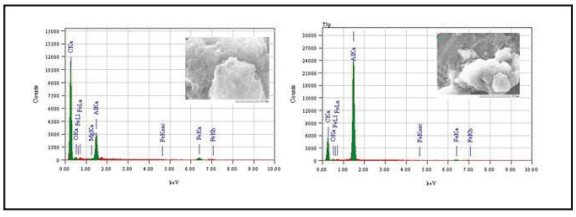

Figure 3. EDX analysis of EtOH/N_2: 16 C/405 ml/min at 900 C (product condition): crude ACCVD-CNTs (left) and purified ACCVD-CNTs (right).

A. *EtOH flow effect*

The effect of EtOH pressure or EtOH vapor temperature on the structure and yield of CNTs has been systematically investigated in the ACCVD method.

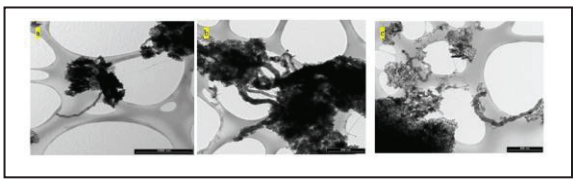

Figure 4. TEM pictures of CNTs products obtained at 800 C with heating-up (Fig. 1a) depending to EtOH vapor temperature and to N_2 flow rate: (a) 0 C/405 ml/min, (c) 25 C/405 ml/min, (e) 16 C/300 ml/min.

Typical low magnification TEM studies give further information on the morphology and microstructure of the prepared CNTs. At low EtOH concentrations (0 °C), a few of MWNTs (thin[(b)] and thick[(c)] with 300 ml/min and 405 ml/min N_2, respectively) are formed with extremely low density, as shown in figures 4 a and 4 d. Though, with high concentration (16 °C and 25 °C) at N_2 all flow rate, we can observe the presence of dominant thick MWNTs with different diameters. Besides, due to the some big particles containing our support, some giant carbon nano-fibers «CNFs» are also formed with varied length ranged between 1 nm and 8 nm, as reported in figures 4 d and 5 e. The CNFs length decreases and increases with increasing N_2 flow rate and EtOH or process changing from mode 1 to mode 2, respectively. The yield of CNTs increases significantly with increasing the N_2 gas flow. Also, it increase with increasing EtOH vapor temperature to attend the maximum at 16 °C then decrease with higher EtOH concentration. As a result, the CNTs yield reaches 14 % and 27 % for mode 1 and mode 2, respectively at 16 °C EtOH and 400 ml/min N_2, as optimized condition for best product of this ACCVD process.

In addition, this observation revealed that more than 80 % of the CNTs were made up of MWNTs. At low reacting gas flow, the CNTs have completely hollow cores, whereas at high flow the CNTs have a bamboo structure (see figures 4 e, 4 g and 4 h). Consequently, growth of MWNTs accompanied with presence of amorphous carbon and catalyst particles has been well observed with all EtOH and N_2 flow concentrations. However, the yield and the uniformity of the NTs are significantly affected by these parameters with and without heating mode, as shown in figure 4 and 5, respectively. With all N_2 flow carrier gas used, CNTs can grow because their using to help the ACCVD reaction.

B. Temperature synthesis effect

We have confirmed, as reported in the previous works using hydrocarbon precursor [16-18], that the reaction temperature affects significantly the type and the yield of produced CNTs. So, in our experiment, CNTs can grow in temperature range from 800 to 1000 °C. However, it is found that the yield is the highest at 900 °C in two process modes. Figure 5 illustrates the influence of ACCVD temperature on the product showing the mainly of them are bundles with no MWNTs observed at high EtOH (16 and 25 °C) and at high temperature (900 and 1000 °C) using 405 ml/min of N_2.

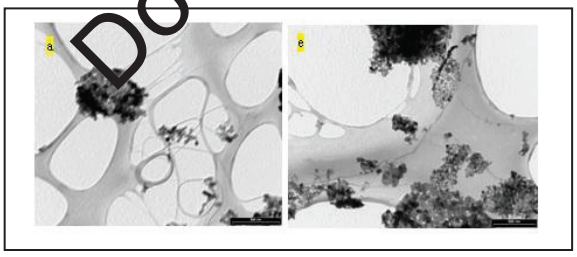

Figure 5. TEM pictures illustrating the synthesis temperature influence with heating step (Fig. 1a), for EtOH/N_2 at 900 C : (a) 16 C/405 ml/min and (b) 25 C/405 ml/min.

Further, TEM observations revealed that more than 93 % of the CNTs in bundle form were made up of SWNTs or DWNTs bundles arrangement and 10 % of individual one (Figure 6).

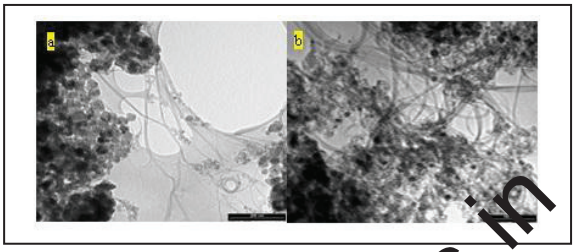

Figure 6. TEM pictures illustrating the synthesis temperature influence under EtOH/N_2:16 C/405 ml/min and without heating step (Fig. 1b) at 900 C : (b) without and (c) with HCl purification.

Consequently, this SWNTs or DWNTs diameters are difficult to resolve from this TEM images and need the high resolution TEM analysis as well as a mode RBM control of Raman analysis. However, the bundles diameters appear to be between [4 – 38 nm] and [2 – 7 nm] at 900 °C with 16 °C and 25 °C of EtOH. We can observed that this bundles are clean and almost no amorphous carbon found on their outer walls, which indicates that there was no alcohol thermal decomposition on the surfaces of this kind of NTs. This examination revealed also that the outer diameters CNTs obtained with 1000 °C are lower than 5 nm indicating a very narrow distribution of diameters. For this reason, our high resolution results have confirmed the presence of few walled CNTs (FWNTs). Figure 7 shows the high magnification TEM micrographs of the purified CNTs synthesized at high temperatures (800 and 900 °C). This high resolution micrographs show that each CNT product consists of not only bundles of aligned FWNTs and especially of SWNTs (with diameter ranging between 1.8 nm and 3.3 nm) but confirms also the presence of isolated SWNTs and DWNTs sometimes. Based on this deepen results, it can be proposed that the obtained RBM peaks with diameters up to 2 nm (as reported relationship in [12]) correspond to bundled SWNTs or DWNTs. Figure 8 shows their complete Raman spectra. This latter will well indicate the high quality and selectivity of Alcohol-CCVD products by strong G band peak (~ 1580 cm^{-1}) and weak D band peak (~ 1300 cm^{-1}) with G/D intensity ratio of 0,27.

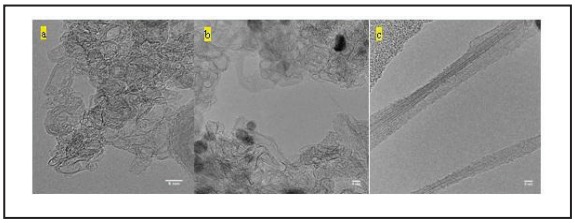

Figure 7. High magnification TEM pictures illustrating the synthesis temperature influence under EtOH/N_2:16 C/405 ml/min (in mode 1): (a) 800 C, (b) and (c) 900 C.

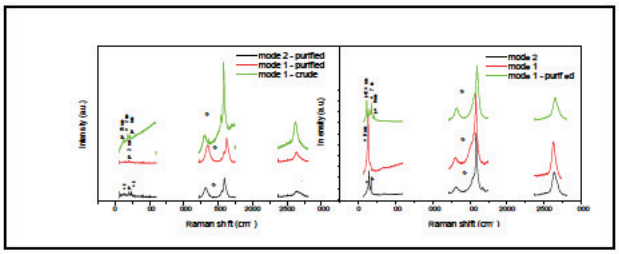

Figure 8. Raman spectra for crude and purified products in optimised condition (EtOH/N_2:16 C/405 ml/min (in mode 1 and 2): (left) 800 C and (right) 900 C.

IV. CONCLUSION

Here, we report a simple, high purity and low cost SWNTs, DWNTs and MWNTs synthesis by using a new carbon precursor molecule, alcohol specially EtOH with heating up the catalyst before the synthesis step (calcinated catalyst), as original work. Decomposition of EtOH over Fe-Co catalysts supported with MgO in different important ACCVD conditions (EtOH vapor temperature, N_2 flow rate, temperature synthesis and catalyst calcination) were carried out. This investigation shows that the structure and yield of CNTs with a narrow diameters distribution and not more than 2 µm of length are strongly affected by the previously given parameters. Fortunately, our experimental result indicates that homogenise catalyst-support with fine particle are efficient for growing uniform fine CNTs and the big particles are not favorable for the CNTs growth but for carbon fiber formation. We have found better yield with 34 torr of EtOH (16 °C) and 405 ml/min of N_2. The outer and inner diameters of the obtained MWNTs (56 % thin MWNTs) at 800 °C, in mode 1 or mode 2, are in the range of 1 – 80 nm and 3 – 10 nm, respectively. In addition, we have succeeded to synthesis individual and bundles of SWNTs or DWNTs as soon as few walled CNTs at synthesis temperature higher than 900 °C. Therefore, the EtOH-CCVD atmospheric process with growth temperature (> 900 °C) and with EtOH vapor temperature (16 °C) are recommended for the SWNTs synthesis and found in agreement with other references using hydrocarbon source. Our results have confirmed that high purity and quality features of this alcohol CCVD technique guarantee easy scale-up production at a lower cost and with safe. So, the ACCVD products with low cost producing method would be very useful in many applications and in the measurement of properties of this kind of carbon.

ACKNOWLEDGMENT *(HEADING 5)*

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