Original Research Article **Nanotechnology**

International Journal of Pharma and Bio Sciences

ISSN 0975-6299

HELICAL DOUBLE AND TRIPLE WALLED CARBON NANOTUBES FROM COMBUSTION CATALYST BY CHEMICAL VAPOUR DEPOSITION TECHNIQUES

S. ARULARASI AND T. SOMANATHAN*

Department of Chemistry & Nanoscience, School of Basic Sciences, Vels University, Pallavaram, Chennai – 600 117, India.

ABSTRACT

A simple route for the synthesis of helical double walled carbon nanotubes (DWCNTs) and triple walled carbon nanotubes (TWCNTs) by chemical vapour deposition of acetylene on $Cr_{0.1}Ni_{0.3}Mg_{0.6}O$ catalyst. In this study, high-quality helical double and triple helix carbon nanotubes have been synthesized on combustion catalyst. The morphologies and qualities of the CNTs were characterized by x-ray diffraction scanning electron microscope, transmission electron microscope, and Raman spectroscopy. Structural control over the *h*DWCNTs and *h*TWCNTs was achieved by simply altering the catalyst composition, reaction temperatures and acetylene flow rates. This study demonstrates that Cr can act as an efficient catalyst for the growth of *h*DWCNTs and *h*TWCNTs. This technique opens up the possibility for economically preparing CNTs with controlled coiled structure.

KEYWORDS: **Coiled carbon nanotube, DWCNTs, TWCNTs, Combustion catalyst**

***T.SOMANATHAN**
Department of Chemistry & Nanoscience, School of Basic Sciences, Vels University,Pallavaram, Chennai – 600 117, India.

Received on : 27-08-2016
Revised and Accepted on : 08-11-2016
DOI: http://dx.doi.org/10.22376/ijpbs.2017.8.1. p69-74

INTRODUCTION

Helical or coiled carbon nanostructures research has grown rapidly in properties after the discovery by Iijima,[1-3] owing to their synthesis, structure and attractive unique physical and chemical properties.[4.5] Generally, depending on their structure, carbon nanotubes (CNTs) can be divided into two main types: single-walled nanotubes (SWCNTs) and multi-walled nanotubes (MWCNTs). Recently, helical carbon nanotubes (*h*-CNTs) are more attractive due to their helical or coiled morphology and the fantastic properties of such as large surface area and high peroxidase activity which embrace *h*-CNTs enable them to be used as biosensors and biocatalysts.[6] To date, the predominant methods used for the synthesis of CNTs are arc discharge laser ablation and chemical vapor deposition (CVD). In the case of laser based processing is not suitable for large scale production due to high costs of equipment and energy. Eventhough, arc discharge produce high quality CNTs but it needs high purity graphitic electrode as carbon source which is much expensive. In addition to graphite, there has been promising research into the use of other cheap materials such as hydrocarbon, coal, pitch, oil residue as source materials. According to the previous investigator, synthesis of coiled DWCNTs and TWCNTs can be controlled by arc discharge technique. Among various methods to produce the coiled CNTs, CVD approach is predominant due to the high quality and good controllability. In our previous work, we have demonstrated the helical MWCNTs using combustion catalyst by CVD technique.[7-9] In this study, our work results indicate that helical double walled carbon nanotubes (h-DWCNTs) and triple walled carbon naotubes (h-TWCNTs) can be controlled by optimising synthesis condition using CVD technique.

Experiment

Synthesis of Combustion Catalysts

According to our previous investigation,[7-8] the combustion catalyst were synthesised using the different mole ratio of various metal nitrates such as chromium nitrate [$Cr(NO_3)_2$], nickel nitrate [$Ni(NO_3)_2$] and magnesium nitrate [$Mg(NO_3)_2$] by the general formula $Cr_xNi_yMg_zO$ (Where x= 0.1, y= 0.3 and z = 0.6) in 100ml standard flask. Take 15 ml of the solution in a china dish and add 3g of citric acid which act as a combustion agent or fuels. Mixed the solution well and then kept in muffle furnace at 550 ºC for 5 min. Then the obtained foamy material was crushed with mortar and the finally solid product was used for the growth of carbon nanotubes.

Synthesis of helical DWCNTs and TWCNTs

About 100mg of fresh catalyst was placed on a quartz boat located at the middle of the reactor.[8] The $Cr_{0.1}Ni_{0.3}Mg_{0.6}O$ catalyst was loaded into the CVD chamber and to remove the oxidative material that present in the catalyst was done by purging N_2 gas at flow rate of 500 sccm from room temperature to desired temperature (500 – 750 °C) for 10 min. Then at the same temperature, H_2 gas was purged into the reaction chamber at a flow rate of 200 sccm which acts as a reducing gas and finally C_2H_2 gas was purged into CVD chamber at a flow rate of 40 sccm. After the reaction completed, acetylene and hydrogen flow was stopped, whereas nitrogen flow was maintained to cool down the furnace. The pristine CNTs were purified by stirring with Conc. HCl (35%) for 2hr and then washed with distilled water for several times until it becomes neutral.[8,9]

Characterization of carbon nanotubes

X-Ray diffraction (XRD) pattern of CNTs was obtained using a Cu-Kα radiation (λ = 0.154 1 nm). Scanning electron microscopy (SEM) image of the resulting product was measured by using JEOL, JSM6390. High resolution transmission electron microscope (HRTEM) was performed with a Technai T30 300 Kev Brand FEI operating at 200 kV. Further Raman spectroscopy Bruker: RFS27 FT was performed to analysis CNTs.

RESULTS AND DISCUSSION

Production of Helical DWCNTs and TWCNTs

Influence of reaction temperature

CNTs synthesized were studied by varying the reaction temperatures ranging from 500 to 750 ºC (i.e.) 500, 550, 600, 650, 700 and 750 ºC using CVD techniques. The carbon yield of the synthesized CNTs increases almost linearly with increasing the reaction temperature (Fig. 1). The higher carbon yield (525%) is achieved for the reaction temperature of 650 °C. The oxidizing temperature of the CNTs as a function of reaction temperature (Fig. 1) indicates that higher reaction temperatures result in the formation of CNTs with more stable structures. Note that for the reaction temperature below 500 °C, no CNTs formation is achieved (not shown). But comparatively, the low yield of CNTs below 650°C temperature may be related to the non- uniformity from the metal-carbon alloy formation. It is generally accepted that CNTs are formed by carbon atom dissolution, diffusion and precipitation through the catalyst in the CVD process.[10] The dissolution, diffusion and precipitation of the carbon atoms are found to be affected by temperature. It was found from CNTs synthesis was obtained at 650 ºC with high yield is possibly due to optimum decomposition rate of C_2H_2 at the catalytic site. At high temperature, the decomposition of C_2H_2 tends to get increased and consequently the concentrations of carbon atoms increased. In our case at 700 ºC the carbon yield were found to be less. Owing to the higher dissolution rate of carbon, there is a carbon cluster formation over the catalyst particles. This tends to lose their catalytic activity and it retards the growth of CNTs.

Influence of C_2H_2 flow rate

The effect of C_2H_2 gas at different flow (40, 50, 60, 70 and 80 sccm) rate was studied for the catalyst $Cr_{0.1}Ni_{0.3}Mg_{0.6}O$ over the optimized temperature at 650°C for 10 min. When the flow rate of acetylene increased from 40 to 60 sccm, a gradual increase in the carbon yield from 410 to 465 % was observed and clearly seen in Fig. 2. Further, on increasing the flow rate of carbon to 70 and 80 sccm, it started to reduce the CNTs yield significantly to 445 to 395 %, respectively. This may be due to the decrease in the contact time of the hydrocarbon with increase in the flow rate of the gas.

The optimized reaction condition produced the maximum CNTs yield of 529 % using $Cr_{0.1}Ni_{0.3}Mg_{0.6}O$ catalyst at 650 ºC for 10 min with Nitrogen, Hydrogen and acetylene flow rate of 500 sccm, 100 sccm and 60 sccm, respectively.

Characterization of CNTs

The high carbon yield obtained from the decomposition of acetylene over $Cr_{0.1}Ni_{0.3}Mg_{0.6}O$ catalyst was characterized by XRD, SEM, TEM, and Raman spectroscopy.

XRD

The XRD pattern of the purified CNTs is shown in Fig. 3. The diffraction peak at 26.3°, 43.53° and 61.9° are corresponding to (002), (100) and (101) planes respectively which are indexed to hexagonal graphitic peak of carbon nanotubes. Also the XRD pattern shows low content of amorphous carbon.[11]

SEM image of CNTs grown on $Cr_{0.1}Ni_{0.3}Mg_{0.6}O$ catalyst

The SEM image of the carbon product synthesized from catalyst $Cr_{0.1}Ni_{0.3}Mg_{0.6}O$, by CVD method shows a typical morphology. SEM images show the formation of bundles of CNTs with coiled structure (Fig. 4.a) and also the helical nature with uniform pitches at equal intervals (Fig. 4.b). The coils present various morphologies and diameters, but at the same time they demonstrate certain regularity. The majority of the CNTs were coiled in a regular and tight fashion, and the coil pitch was short. It is worth noting that the CNTs were composed of two or three-coiled nanotubes (*h*-DWCNTs and TWCNTs) connected to a catalyst nanoparticle, and the nozzles of the tubes were clearly visible. From the result, we conclude that the formed CNTs were higher in yield with highly dense helical structure.

HRTEM image of CNTs grown on $Cr_{0.1}Ni_{0.3}Mg_{0.6}O$ catalyst

The HRTEM image shows the typical morphology of the CNTs synthesized from $Cr_{0.1}Ni_{0.3}Mg_{0.6}O$ catalyst. The Fig 5 (a) shows long uniform helically coiled carbon nanotubes with uniform diameter. HRTEM image of the CNTs in Fig. 5 (b) clearly confirms the formations of double helical shaped CNTs. It shows that the synthesized CNTs are double and triple helical and are twisted at right angles almost similar to the structure of a DNA which is clearly seen in insert Figure 4b. The HRTEM image (Figure 5 c & d) shows the formation of DWCNTs and TWCNTs which are free from defects and amorphous carbon coating. The diameters of the coiled nanotubes were in the range of 2-5 nm, roughly the grain size of the catalyst nanoparticle. Moreover, the walls of some tubes were so thick and the inner diameters of those tubes were so small that the tubular structure sometimes cannot be observed clearly.

Raman Spectroscopy

Raman spectroscopy was employed to characterize the crystalline nature of the synthesized CNTs which is shown in Fig. 6. From the RBM signal (134, 150, 164, 180 and 259 cm^{-1} which is shown as insert Fig.6), the diameter of CNTs was estimated to be typically 0.90-1.74 nm. Here the following correlation [10] between diameter '*d*' (nm) and Raman shift '*λ*' (cm−1), $d = 234/\lambda$ was used to calculate the diameter of the CNTs. The detected signal may correspond to the inner tube diameter of DWCNTs and TWCNTs samples since some TWCNTs have tube diameter around 2 nm which is clearly observed in HRTEM observation. The distance between graphite layers, which provides evidence that the sample is DWCNTs according to the related previous report.[12] Raman spectra shows peak at 1592 cm^{-1} corresponding to graphite band (G-band), which was produced from the high degree of symmetry and order of carbon materials. The G-band was generally used to identify well-ordered graphitic nature of CNTs. The peak at 1359 cm^{-1} corresponds to the disorder-induced phonon mode (D-band), which was caused from the disordered components. The 1359 cm^{-1} signal might have come from a symmetry- lowering effect, which had resulted due to the presence of nanoparticles and bending nature of CNTs due to the helical coil formation. [13,14]

Thermogravimetric Analysis

Fig. 7 show the thermogravimetric analysis (TGA) for the CNTs. It is observed that the weight of DWCNTs and TWCNTs shows a slight increase at around 250 °C due to the oxidation of Cr and Ni catalyst. In the temperature range of 400–450 °C, amorphous carbon is considered to be burned since the weight has decreased slowly from the highest point. A sharp decline in the weight is observed for both DWCNTs and TWCNTs at 550–800 °C, demonstrating that nanotubes begin to react with O_2. The finish point for weight decrease is observed at 800 °C, indicating that both kinds of CNTs have the perfect graphitic wall structures.[15,16]

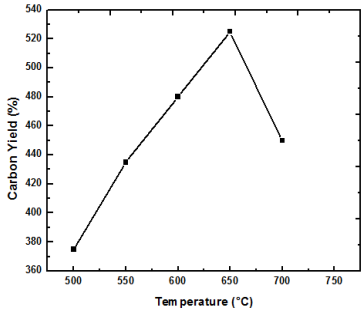

Figure 1
Influence of temperature for carbon yield using $Cr_{0.1}Ni_{0.3}Mg_{0.6}O$ catalyst

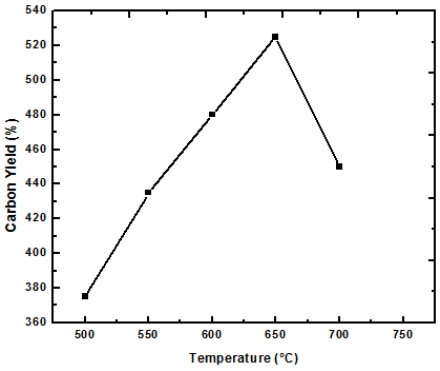

Figure 2
Influence of C_2H_2 flow rate for carbon yield using $Cr_{0.1}Ni_{0.3}Mg_{0.6}O$ catalyst

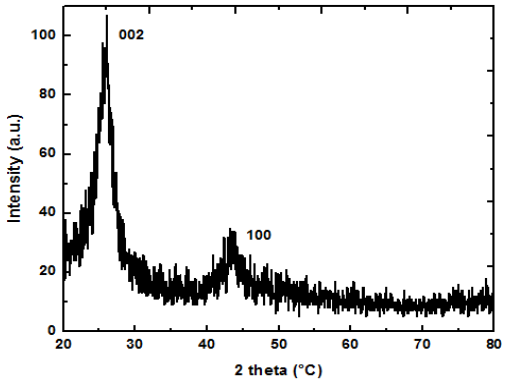

Figure 3
XRD of purified CNTs

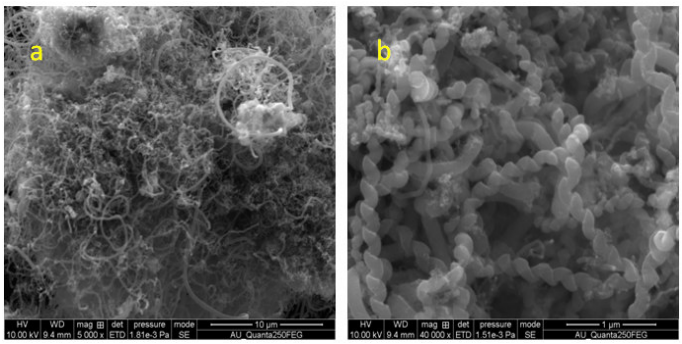

Figure 4
SEM images of CNTs synthesized by $Cr_{0.1}Ni_{0.3}Mg_{0.6}O$ catalyst

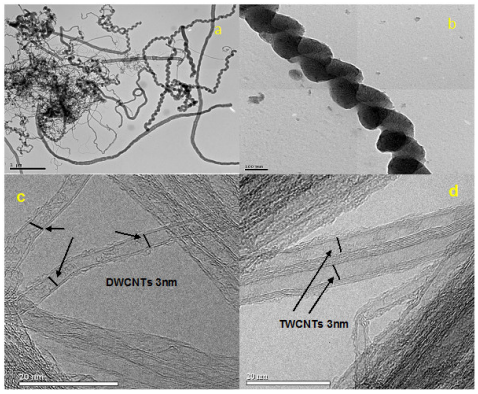

Figure 5
TEM image of helical DWCNTs and TWCNTs

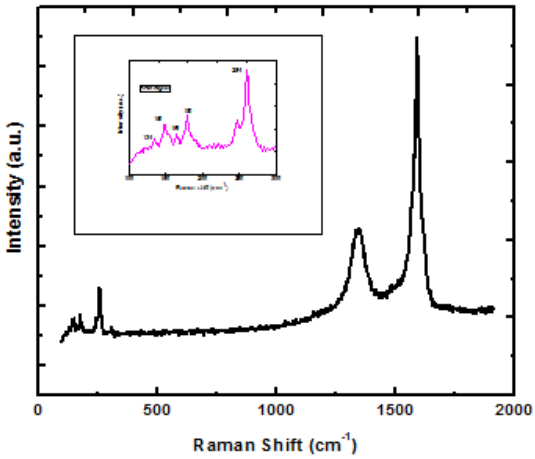

Figure 6
Raman Spectrum of CNTs

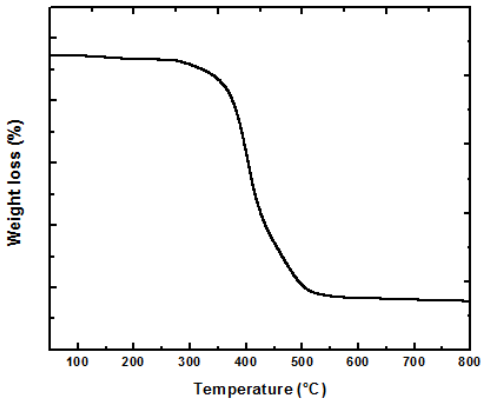

Figure 7
TGA of CNTs

CONCLUSION

In conclusion, high quality DWCNTs and TWCNTs were successfully synthesised using $Cr_{0.1}Ni_{0.3}Mg_{0.6}O$ catalyst. The structure and morphology were confirmed by XRD, SEM, HRTEM, Raman spectroscopy and TGA. The diameters of DWCNTs and TWCNTs were distributed in the range of 0.90 – 1.74 nm, which were well coincided with the tube diameter value obtained by HRTEM observation. This simplest technique opens up the possibility of the cost effective method which attributed to synthesize well graphitized DWCNTs and TWCNTs at high yield and can also control the shape and size of the CNTs at low temperature.

ACKNOWLEDGEMENTS

One of the authors, T. Somanathan would like to thank the Department of Science and Technology (DST) for the award of Fast Track Young Scientist Award and also for providing financial support (SR/FT/CS-111/2011).

CONFLICT OF INTEREST

Conflict of interest declared none.

REFERENCES

1. Iijima S. Helical microtubules of graphitic carbon. Nature 1991; 354: 56-8.
2. Raduchkevich LB, Luk'yanovitch VM. The structure of carbon forming in thermal decomposition of carbon monoxide on an iron catalyst. Soviet Journal of Chemical Physics. 1952; 26: 88–95.
3. Oberlin A, Endo M, Koyama T. Filamentous growth of carbon through benzene decomposition. J. Cryst. Growth. 1976; 32: 335-49
4. Hanus MJ, Harris AI. Synthesis, characterisation and applications of coiled carbon nanotubes. J Nanosci Nanotechnol 2010;10: 2261–83.
5. Zhang M, Li J. Carbon nanotube in different shapes. Mater Today 2009;12:12–18.
6. Cui R, Han Z, Zhu J. Helical Carbon Nanotubes: Intrinsic Peroxidase Catalytic Activity and Its Application for Biocatalysis and Biosensing, Chem. Eur. J. 2011, 17; 34: 9377-84.
7. Saravanan A, Karthika Prasad, Gokulakrishnan N, Kalaivani RA, Somanathan T. Efficiency of transition metals in combustion catalyst for high yield and well graphitised helical multiwalled carbon nanotubes. Adv. Sci. Eng. Med. 2014; 6: 809-813

8. Somanathan T, Pandurangan A. Helical shaped multiwalled carbon nanotubes (*h*-MWNTs) synthesized by catalytic chemical vapour deposition (CCVD) technique. New Carbon Materials. 2010; 25: 175-180
9. Somanathan T, Pandurangan A. Helical shaped multiwalled carbon nanotubes synthesized by catalytic chemical vapour deposition (CCVD) technique. Carbon. 2010; 48: 3974
10. Qiu H, Shi Z, Gu Z, Qiu J. Controllable preparation of triple-walled carbon nanotube and their growth mechanism. Chem. Commun. 2007; 1092–1094
11. Saravanan A, Abilarasu A, Somanathan T. Single step synthesis of h-MWCNTs and its application as visible light driven photocatalyst in dye degradation studies, Int J Pharm Bio Sci., 2015; 6(3): 518 – 529
12. Sugai T, Yoshida H, Shimada T. Okazaki T, Shinohara H. New synthesis of high-quality double-walled carbon nanotubes by high-temperature pulsed arc discharge. Nano Lett. 2003; 3: 769–773.
13. Qiu H, Shi Z, Guan L, You L, Gao M, Zhang S, Qiu J, Gu Z. High-efficient synthesis of double-walled carbon nanotubes by arc discharge method using chloride as a promoter. Carbon. 2006; 44: 516-521
14. Kim H, Kang J, Kim Y, Hong BH, Choi J, Iijima S. Synthesis of Ultra-Long Super-Aligned Double-Walled Carbon Nanotube Forests, J. Nanosci. Nanotechnol. 2011; 11: 470-473
15. Huang HJ, Kajiura H, Tsutsui S, Murakami Y, Ata M. High quality double-walled carbon nanotube super bundles grown in a hydrogen-free atmosphere. J Phys Chem B 2003; 107: 8794–8.
16. Zhang H, Sun CH, Li F, Li HX, Cheng HM. Purification of multiwalled carbon nanotubes by annealing and extraction based on the difference in van der Waals potential. J Phys Chem B 2006;110: 9477–81.