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In situ synthesis of carbon nanotubes through combustion technique

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Abstract: Nanostructured carbon materials offer unique advantage in several areas owing to their exceptional properties like chemical stability, strong mechanical strength and high electrical conductivity. In this present work, we have prepared carbon nanotubes (CNTs) in a single step (in situ) through combustion method using chemical vapour deposition technique (CVD). By varying the combustion fuels, we have obtained high yield CNTs. The synthesized CNTs were characterized by various techniques like X-Ray diffraction (XRD), Field Emission Scanning Electron Microscope (FESEM), High Resolution Electron Microscope (HRTEM) and Raman Spectroscopy. HRTEM images clearly reveals that the obtained CNTs are multiwalled carbon nanotubes (MWCNTs) with inner diameter of 4-5nm. Raman Spectrum supports the information about good graphitisation of MWCNTs. The as synthesized CNTs owing to its typical morphology can be utilized as nanocomposite material and the work is under process.
Key words: Multiwalled carbon nanotubes, Combustion catalyst, Insitu, CVD and HRTEM.

Introduction

The fundamental interest on carbon nanotubes (CNTs) has raised due to its exceptional properties like large surface area, small size, high thermal stability, electrical conductivity and their ability to involve in variety of chemical transformations[1-4] CNTs are been prepared by different techniques out of those catalytic chemical vapour deposition (CCVD)[5-7] is found to be the most renown method than other methods. Synthesis of CNTs in CCVD includes various stages like preparation of catalyst and carrying out CVD process. Also while synthesizing catalyst key factors like reproducibility, uniform catalyst size is also very important. Solution combustion synthesis (SCS) technique[8] for the preparation of CNTs is known to be the simplest of all methods because the time required for synthesizing is very less as well as the reproducibility is high. Combustion fuel plays a vital role in acquiring uniform sized catalyst along with more active site. In this present work we have synthesized CNTs in single step (in-situ) using combustion catalyst through SCS technique. The combustion fuel effects were also optimized.

Experimental Details

Synthesis of CNTs

According to our previous report[9], we have synthesised catalyst and CNTs in the same CCVD system.

First the required catalytic metal oxides ($Fe_{0.20}$ $Co_{0.10}$/$Mg_{0.70}O$) were prepared by taking the stoichiometric ratio of their metal nitrates aqueous solution. To it 250 mg of combustion fuel like citric acid(C), oxalic acid(O), urea(U) and citric acid:urea(C:U) was added separately for different fuel study and then sonicated. Then the sonicated solution of about 30ml was taken in a Silica boat and placed in the centre of the CCVD and heated upto 550°C for 10 min. The reaction was further carried out like in our earlier reports[8]. The pristine CNTs were characterized without any further purification using Scanning electron microscopy (SEM) image JEOL, JSM6390. High resolution transmission electron microscope (HRTEM) with Technai T30 300 Kev Brand FEI. X-ray diffraction (XRD) was carried out CuKα, λ=0.1541 nm on G.E Inspection Technologies, model no XRD 3003 TT. Raman spectroscopy through Bruker: RFS27 FT.

Result and discussion

Efficiency of combustion fuels:

The effect of various combustion fuels were studied over the catalyst $Fe_{0.20}Co_{0.10}Mg_{0.70}O$. In this study catalytic metals were kept constant and varied the combustion fuels like O, U, C and C:U to synthesized CNTs in a single step. From Table. 1 It clearly indicates that CNTs prepared from combustion fuel mixture C:U have higher deposition of carbon product. The reason is due to the highly oxidising nature of the fuel[10] and very short period when compared with other fuels. The result obtained by this technique which gives fine catalytic particles with high surface area probably used to decompose acetylene to get high yield of CNTs.

Table. 1. Carbon weight from $Fe_{0.20}$ $Co_{0.10}Mg_{0.70}O$ using various combustion catalyst

Catalyst	Combustion fuel	Temp (°C)	C_2H_2 Flow ml/min	Reaction time(min)	Carbon weight (mg)
$Fe_{0.20}$ $Co_{0.10}Mg_{0.70}O$	Citric acid	650°C	100	10	352
	Oxalic acid				210
	Urea				290
	Citric acid: Urea				383

XRD pattern of MWCNTs

The X-ray diffraction patterns of CNTs synthesized by in-situ method using combustion fuel C:U (for $Fe_{0.20}$ $Co_{0.10}Mg_{0.70}O$ catalyst) is shown in Fig. 1. The pattern shows an intense peak at 26.03 and 42.98 which are assigned to (002) and (001) reflections of typical graphite, this evidently proves the absence of amorphous carbon. Also we can find a peak at 44.31 corresponds to (110) plane of crystalline Fe-Co alloy (JCPDS 49-1567)[11] respectively. Comparatively a high intense peak is seen for CNTs obtained from C:U combustion fuel. The intense peak gives a clear picture that the CNTs obtained are having good crystalline nature.

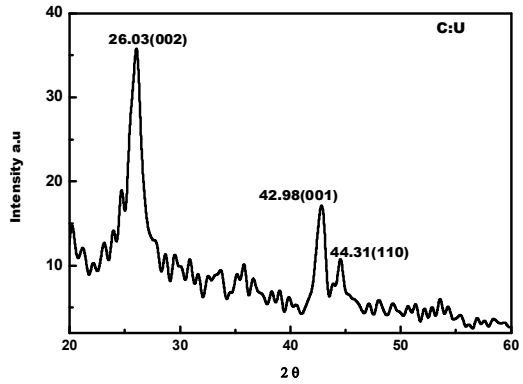

Fig. 1. XRD of synthesized CNTs using C:U combustion fuel

SEM image of MWCNTS

The FE-SEM image of the synthesized CNTs using $Fe_{0.20}$ $Co_{0.10}Mg_{0.70}O$ (C:U) catalyst was shown in Fig 2. The SEM image corresponding to Fig. 2a shows the presence of bundle of CNTs and in Fig. 2b we can demonstrate that the formed CNTs are having helical morphology. Also we can infer that the obtained CNTs

are long uniform and without much structural destruction, the presence of nanoparticles at the tip of the CNTs in (Fig. 2b) suggests the tip growth mechanism.

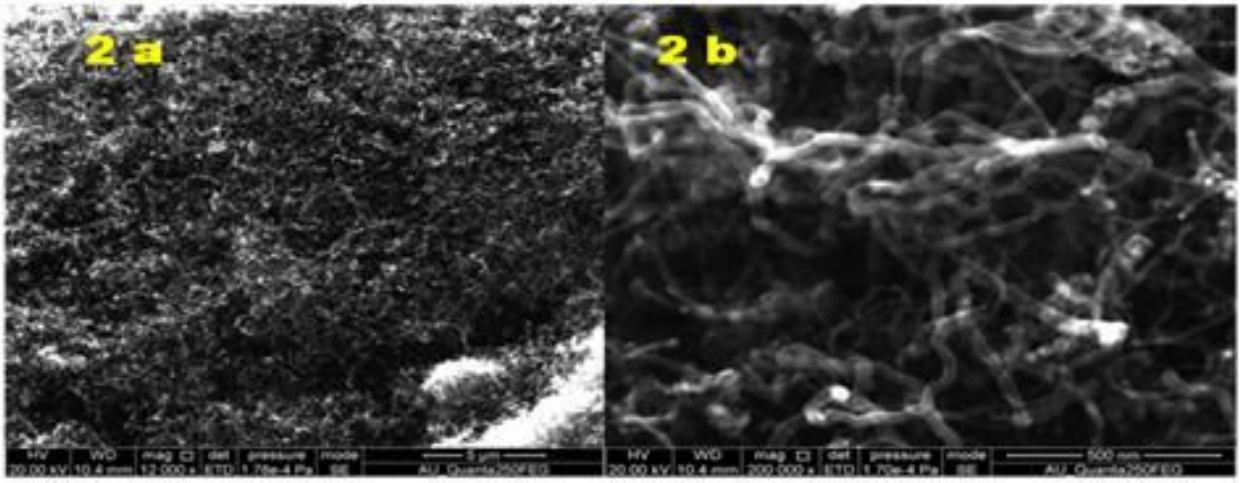

Fig. 2 SEM images of CNTs a) bundle of CNTs b) CNTs with helical shape

HRTEM image of h-MWCNTS

The morphology of the assynthesized CNTs were studied through HRTEM analysis. The HRTEM image shown in Fig.3a clearly indicates that the obtained CNTs are having helical morphology that too double helical nature. In Fig. 3b the image is from the curly region which shows parallel wall structure in it [12, 13] with an internal diameter of about 4-5nm. The results obtained were coinciding with our previous report [9].

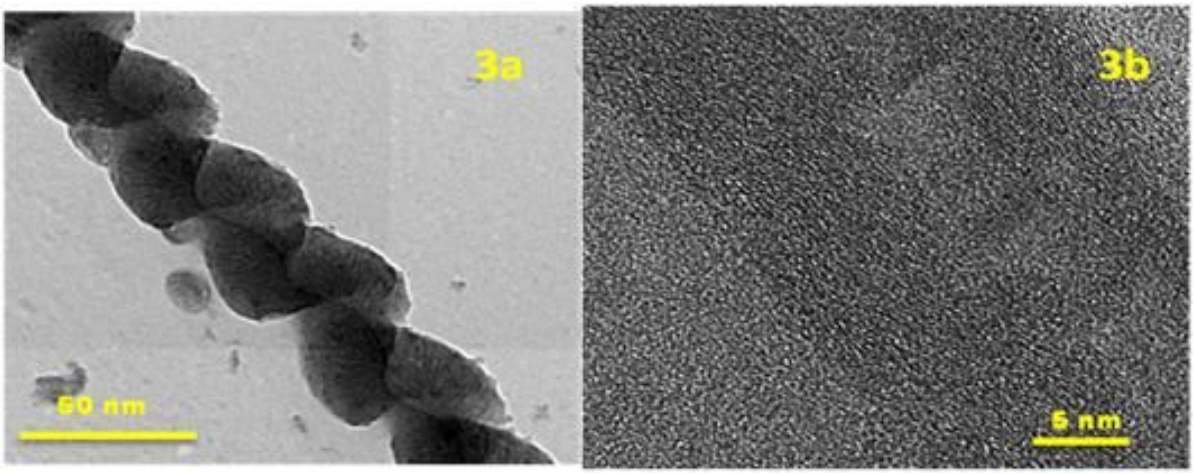

Fig. 3 HRTEM images of CNTs a) helical CNTs b)high magnification of h-MWCNTS

Raman Spectroscopy

The graphitic nature of the CNTs was studied through disordered band (D- band) and Graphitic band (G- band) from Raman Spectroscopy[14]. In Fig. 4, Raman spectroscopy shows peaks at 1285cm^{-1} and 1605 cm^{-1} named D- band associated for the disordered graphite raised due to the defects on the surface of carbon nanotubes and G-band corresponds to the E_2g vibration mode of graphite which is usually used as an identiy for well- ordered carbon nanotubes, respectively. The absence of peak in the lower frequency region confirms the nature of CNTs as MWCNTs which is also a proved evident from HRTEM images[8,15]. The increase in the intensity of the D-band has come due to the symmetry-lowering effect raised from the presence of nanoparticles and helical shaped CNTs. The (I_G/I_D) intensity ratio of the two band are found to be (0.99) which shows a very good graphitic nature of the CNTs[9,16,17].

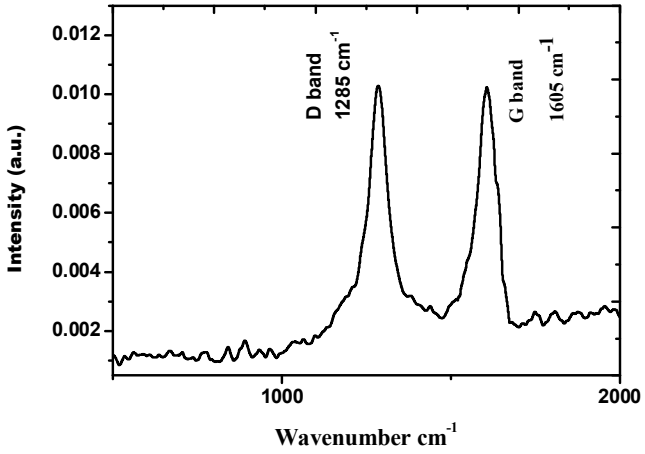

Fig .4 Raman spectrum of h-MWCNTs

Conclusion

In this present work we have synthesized h-MWCNTs by in-situ method which reduces the time and highly expensive chemicals. The XRD result shows a good crystalinity of the pristine CNTs with C:U combustion fuel which is evident for the absence of amorphous carbon. SEM and HRTEM images also confirm the helical nature of CNTs without any structural destruction. The CNTs synthesized by this in-situ method have unique property which can be potentially used in various application as nanocomposite material.

References

1. Salvetat JP, Bonard JM, Thomson NH, Kulik AJ, Forro L, Benoit W, Zuppiroli L. Mechanical properties of carbon nanotubes. Appl. Phys. A, 1999, 69; 255-260.
2. Tan DZW, Chang H, Nguyen ST, Duong HM. Controlled synthesis of MnO_2/CNT nanocomposites for super capacitor application. Materials Technology: Advance functional materials, 2014, 29; 107.
3. Kim P, Shi L, Majumdar A, McEuen P. Thermal transport measurements of individual multiwalled nanotubes. Phys. Rev.Lett., 2001, 87; 1-4.
4. Zhao D, Yang X, Chen C, Wang X. Enhanced photocatalytic degradation of methylene blue on multiwalled carbon nanotubes–TiO2. J. Colloid Interface Sci., 2013, 398; 234-239.
5. Somanathan T, Pandurangan A. Direct synthesis of vanadium substituted mesoporous MCM-41 molecular sieves: a systematic study for the growth of SWNTs. J Porous Mater., 2009, 16: 657–665.
6. Qi X, Chan Qin, Zhong W, Chaktong Au, Ye X, Du Y. Large-scale synthesis of carbon nanomaterials by catalytic chemical vapor deposition: a review of the effects of synthesis parameters and magnetic properties. Materials., 2010, 3; 4142-4174.
7. Mohana Krishna V, Abilarasu A, Somanathan T, Gokulakrishnan N. Effective synthesis of well graphitized high yield bamboo-likemulti-walled carbon nanotubes on copper loaded α-alumina nanoparticles. Diamond Relat. Mater., 2014, 50; 20-25.
8. Somanathan T, Pandurangan A. Helical multiwalled carbon nanotubes (h-MWCNTs) synthesized by catalytic chemical vapour deposition. New carbon materials, 2010, 25; 175-180.
9. Saravanan A, Karthika Prasad, Gokulakrishnan N, Kalaivani RA, Somanathan T. Efficiency of transition metals in combustion catalyst for high yield helical multiwalled carbon nanotubes. Adv. Sci. Eng. Med., 2014, 6; 1-5.
10. Toniolo JC, Takimi AS, Bergmann CP. Nanostructured cobalt oxides (Co_3O_4 and CoO) and metallic Co powders synthesized by the solution combustion method. Mat. Res. Bul., 2010, 45; 672-676.
11. Yue GH, Wang LS, Wang X, Chen YZ, Peng DL. Characterization and magnetic properties of $Fe_{70}Co_{30}$ alloy nanowire arrays. J. Appl. Phys, 2009, 105; 074312, 1-5.
12. Gao R, Wang ZL, Fan S. Kinetically controlled growth of helical and zigzag shapes of carbon nanotubes. J. Phys. Chem. B., 2000, 104; 1227-1234.)
13. Rao Surisetty V, Kozinski J, Ajay Kumar Dalai. Novel Ni-Co-Mo-K catalysts supported on multi walled carbon nanotubes for higher alcohols synthesis. Journal of catalyst, 2013, 1-8.

14. Dresselhaus MS, Dresselhaus G, Saito R, Jorio A. Raman spectroscopy of carbon nanotubes. Phys. Rep, 2005, 409; 47-99.
15. Somanathan T, Pandurangan A. Towards the low temperature growth of uniform diameter multi walled carbon nanotubes by catalytic chemical vapour deposition technique. Nano-Micro Lett., 2010, 2, 204-212.
16. Gokulakrishnan N, Kania N, Bastien Leger, Lancelot C, Grosso D, Monflier E, Ponchel A. An ordered hydrophobic P6mm mesoporous carbon with graphitic pore walls and its application in aqueous catalysis. Carbon, 2011, 49; 1290-1298.
17. Kim TW, Park IS, Ryoo R. A synthetic route to ordered mesoporous carbon with graphitic pore walls. Angew Chem. Int. Ed., 2003, 42: 4375-4379.

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