International Journal of Innovation and Applied Studies
ISSN 2028-9324 Vol. 3 No. 1 May 2013, pp. 1-5

http://www.issr-journals.org/ijias/

Flame Synthesis of Carbon Nanorods with / without catalyst

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ABSTRACT: The carbon nanorods (CNR's) were synthesized using flame reactor with diffusion burner. The growth of carbon nanorods in presence and absence of catalyst has been studied. The role of ferrocene as catalyst in the synthesis of carbon nanorods was investigated using a Flame Reactor at different oxygen to fuel ratios. The fuel used over here is acetylene. The fuel i.e., acetylene to oxygen ratio is also optimized to produce the carbon nanorods in presence of cataylst. The carbon nanorods showed a very good result with increasing yield and decreasing diameter with the use of catalyst. The morphology, purity and crystal structural characterization of CNR's was carried out using scanning electron microscopy, transmission electron microscopy and X-ray diffraction. From the analysis it was observed that in the presence of ferrocene, the density of CNR's increased with variable lengths between 10 – 50 micrometers (µm) with an average tube diameter range of 150 – 300 nanometers (nm), when compared to a non-catalytic synthesis which yielded CNR's with lengths and diameter ranging from 10 -180 micrometers (µm) and 3-10 micrometers (µm) respectively. These carbon nanorods can be widely used in various applications such as electronic devices, semi-conducting materials, electrodes, hydrogen storage and composites for its outstanding properties.

KEYWORDS: Flame synthesis, Nanomaterials, Acetylene, Ferrocene.

1 INTRODUCTION

Carbon nanomaterials have attracted great interest from past few decades owing to their promising physical and chemical properties. Till date different carbon nanomaterials have been reported such as carbon nanoparticles [1], nanotubes [2], onions [3], nanowires [4], nanofibers [5] and carbon nanorods [6]. These nano meter carbon material are expected to have relatively large band gap and are expected to behave like a semiconductor. More interestingly carbon nano rods have been largely applied as anodic materials in batteries apart from their applications like fillers [7] and high-performance electrode materials in batteries [8]. Upto now, various methods have been proposed for thier synthesis like ball milling [9, 10] chemical vapor deposition [11], laser ablation, chemical reduction and co-precipitation [12-15]. More recently, new synthetic methods like flame synthesis, sol-gel, microwave plasma and low energy cluster beam deposition [16] have been developed.

We have earlier reported the synthesis of carbon nanorods using the flame reactor. Here in this article we report the synthesis of carbon nanorods using a diffusion burner with acetylene as a sole carbon source and oxygen as an oxidant in the presence of catalyst, ferrocene. We have aimed to study the difference between the growth of CNM's with and without catalyst with respect to the (oxidant to fuel) O/F ratio in the range of 0.6 – 1.2 v/v. The samples were characterized using SEM, TEM and XRD.

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2 EXPERMENTAL

The experimental design & procedure for the synthesis of carbon nanorods has been reported [17]. Basically the flame reactor consists of a burner through which measured flows of oxygen and acetylene in various ratios enters the reactor chamber controlled by the calibrated rotameters. On spark ignition soot is produced which is collected over a glass fiber filter paper (GF/A Whatmann). The experiments were carried out using 0.5g of catalyst (ferrocene) in the range of 0.6 to 1.2 v/v. The same experiment was repeated without catalyst to study the difference in with and without catalyst.

3 RESULTS AND DISCUSSIONS

The SEM micrograph of the CNM (Fig. 1a) synthesized at O/F ratio of 0.6v/v in the absence of catalyst yielded microrods with lengths up to 10µm and their diameters ranging around 3µm. Fig. 1b represents the SEM image of two microrods synthesized at 0.8 v/v, these rods were found to be extremely lengthy and measured up to 150 µm each with their diameters up to 5 µm. At O/F ratio of 1.0 v/v (Fig. 1c) and 1.2 v/v (Fig. 1d) showed similar results with some mass of amorphous carbon around. The average diameter of a microrod in Fig. 1c was found to be 8 µm where as the lengths greater than 120 µm. The SEM image at 1.2 v/v (Fig. 1d) showed little lengthy wire like rods with lengths in the ranging 50-180 µm and diameter around 10µm respectively.

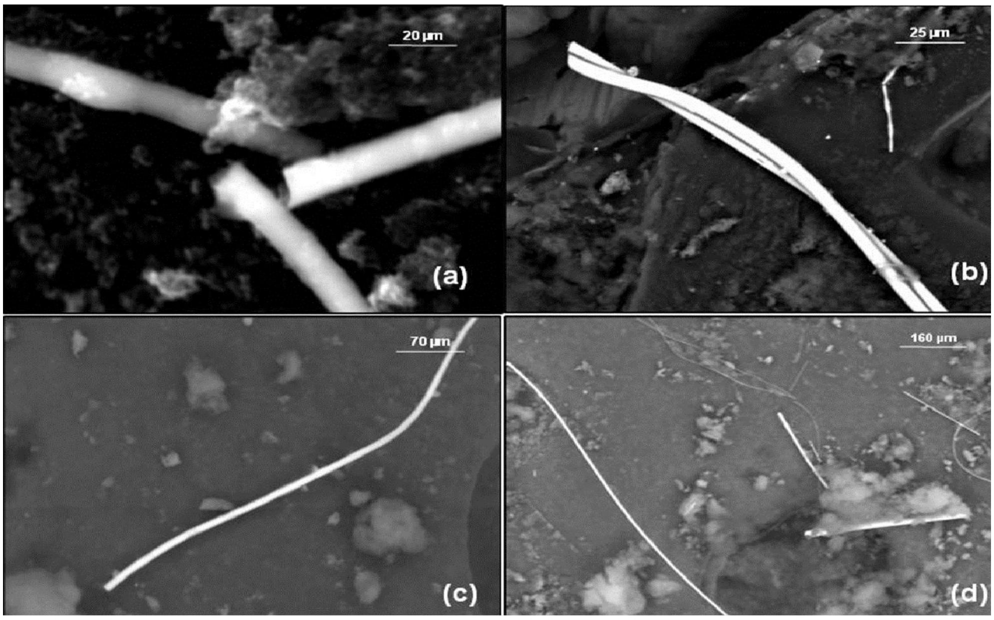

Fig. 1. SEM Images of microrods produced using acetylene and oxygen in the absence of catalyst.
(a) Microrods produced at O/F ratio of 0.6 v/v. (b) Microrods produced at O/F ratio of 0.8 v/v.
(c) Microrods produced at O/F ratio of 1.0 v/v. (d) Microrods produced at O/F ratio of 1.2 v/v.

Upon introduction of catalyst (ferrocene), growth of nanomaterials was dense in the O/F range of 0.6v/v to 1.2v/v as shown in the SEM images. Fig. 2a shows a SEM image of a nanorod synthesized at 0.6v/v with an average length of 30 – 40 µm and diameter around 210nm. Fig. 2b shows SEM image of densely entangled mass of nanorods at 0.8v/v with an average diameters in the range of 150 nm and lengths stretching up to 50 µm respectively. At 1.0v/v many equi-sized rods joined together to form a rope like structure as shown in Fig. 2c. The average diameter of the individual equi-sized rod was around 300nm, a very few thin rods with the average diameter and lengths of 140nm and 5-10µm respectively were also. Fig. 2d shows less dense nanorods at 1.2v/v. The figure shows two different sized nanorods: The thicker rods measure up to 700nm in diameter whereas the thinner rods measure nearly 200nm. The average length of all the nanorods was found to be 15µm.

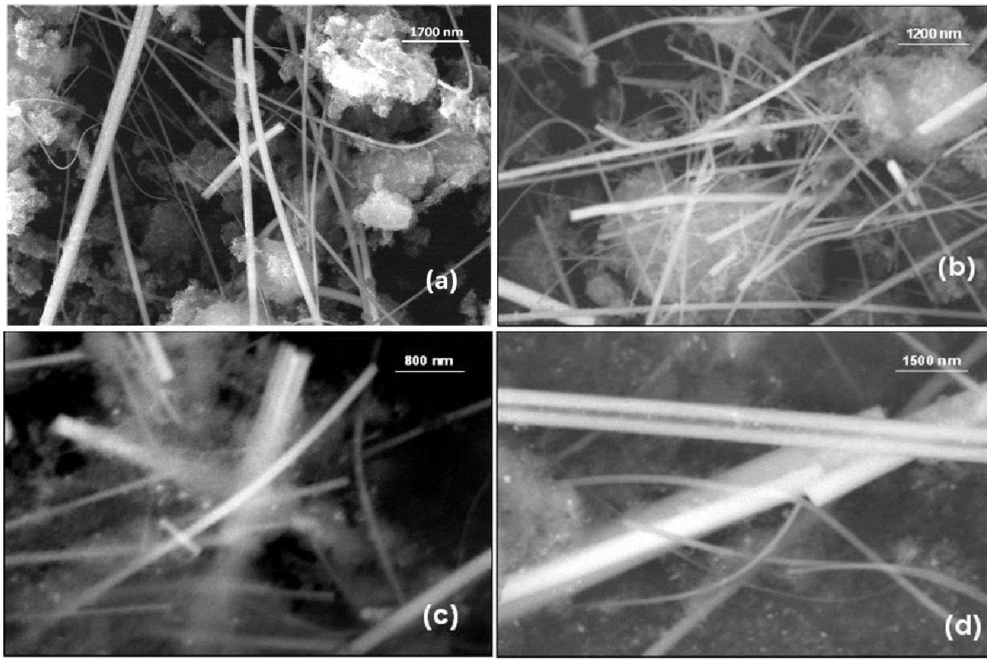

Fig. 2. SEM Images of nanorods produced using acetylene and oxygen in the presence of ferrocene as catalyst. (a) Nanorods produced at O/F ratio of 0.6 v/v. (b) Nanorods produced at O/F ratio of 0.8 v/v. (c) Nanorods produced at O/F ratio of 1.0 v/v. (d) Nanorods produced at O/F ratio of 1.2 v/v.

Thus from the SEM analysis it was found that the synthesis of CNRs catalyzed by the catalyst(ferrocene) had better crystal structures and smaller diameters compared to those synthesized without catalyst [18,19,20]. Furthermore, the CNRs synthesized using catalyst had smoother and cleaner the topologies compared to that synthesized in absence of catalyst. It is well accounted in the literature that the diameters of the nanorods were mainly determined by the size of the catalysts [18, 19, 20]. Higher temperatures enhanced the decomposition of ferrocene to produce fine Fe clusters increasing the possibility for the growth of CNR's with smaller diameters.

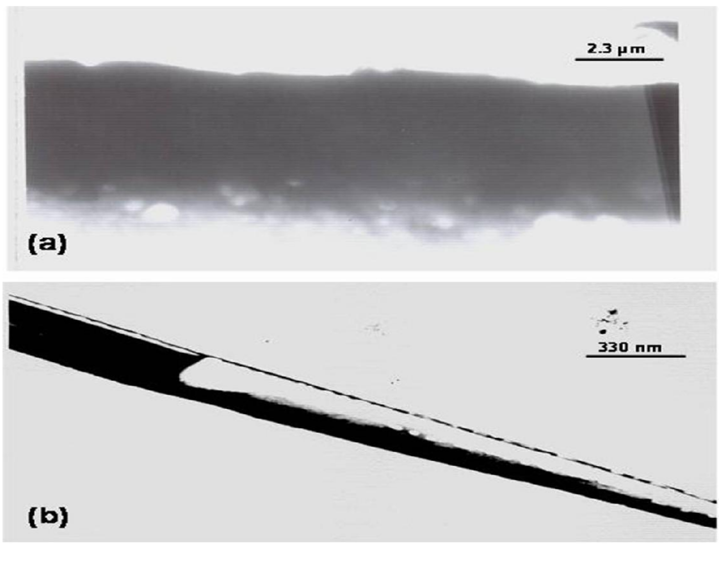

Fig. 3. TEM image of nanorods using (a) In the absence of catalyst (b) In the presence of catalyst.

The TEM image (Fig. 3a) shows the typical microrod of 15µm in length with a diameter around 5µm obtained at O/F 0.8V/V grown without catalyst. In case of catalysed reactions the diameter of the nanorods increase with increasing catalyst concentration [21, 22, 23, 24, 25] as shown in TEM image (Fig. 3b). The O/F of 0.8v/v with catalyst showed the best result as per TEM analysis but the total yield was found to be low. The length of the rods measured nearly 10µm with a variable diameter distribution along its axis. Fig. 3b explains the basal growth of CNR's from the catalyst which is well documented in the literature [21, 22, 23, 24, 25].

XRD (Fig.4a) of microrods produced using acetylene and oxygen without catalyst at an O/F ratio of 0.8 v/v showed one strong peak. Using the PDF-2 database the first peak at 2θ angle of 43.545^o was found with (110) orientation of atoms along its plane with peak corresponding to graphite with a rhombohedral type of system and a rhombocentred lattice. The peak broadening also confirms the presence of abundant amorphous state of carbon.

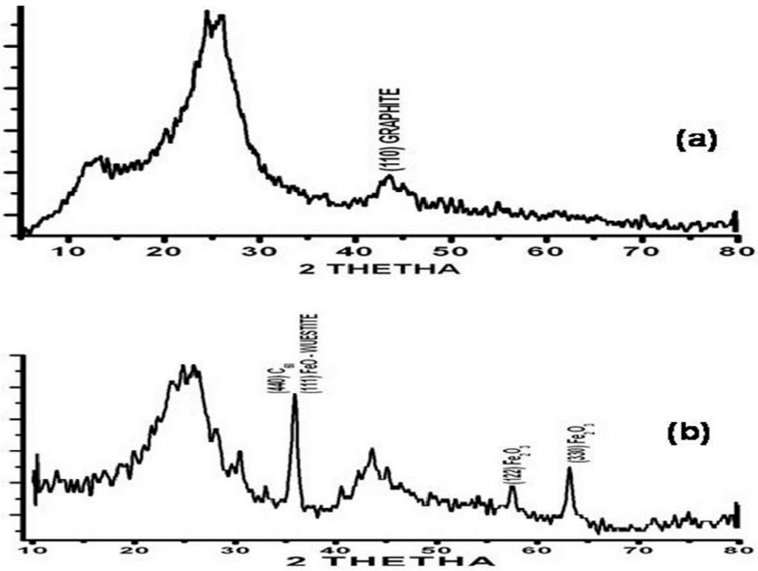

Fig. 4. XRD of carbon material produced using acetylene and oxygen.
(a) O/F of 0.8 v/v in the absence catalyst. (b) O/F of 0.8 v/v in the presence of catalyst.

XRD (Fig. 4b) of nanorods at 0.8 v/v in the presence of catalyst resulted in heterogeneous crystallinity in the sample. The raw scan detected three strong peaks. The first peak at 2θ angle of 35.932^O was found with (111) orientation of atoms along its plane with peak corresponding to FeO in the form of wuestite mineral with a cubic type of system and an FCC lattice. The same peak was also detected for the presence of C_{60} with (440) as its orientation of atoms with a cubic system and a Face centered cubic (FCC) lattice. The second peak at 2θ angle of 57.504^O was found with (122) orientation of atoms along its plane with peak corresponding to Fe_2O_3 with a rhombohedral type of system and a rhombocentred lattice. The third peak at 2θ angle of 63.226^O was found with (330) orientation of atoms along its plane with peak corresponding to Fe_2O_3 with an orthorhombic type of system and a primitive type lattice respectively. The average crystalline size at 2θ = 35.0^O of the ferrocene catalyzed samples was calculated as 30 nm which is evident in the SEM images which shows highly dispersed bright spots in the SEM scans of Fig. (2a - 2d) respectively.

4 CONCLUSION

In the present investigation, we have successfully grown a CNR's using catalyst in acetylene – oxygen system with a diffusion type of burner. The CNR's morphology and catalyst concentration were closely examined. The CNRs shows a good result with increasing yield and decreasing diameter using catalyst. CNRs in the form of nanorods of 150 – 400 nm diameters were synthesized in good quantities. These nanorods with decrease in their diameters to the nearest minimum for their use in many applications like hydrogen storage, semi-conducting materials, electrodes, medicine applications and composites.

ACKNOWLEDGEMENT

The authors acknowledge the financial support given by Defence Research Development Organization (DRDO), Govt. of India and also thank National Centre for Compositional Characterization of Materials (NCCCM), Hyderabad for providing SEM data of all samples.

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