

Design and development of flame reactor unit for carbon nanorods (CNRs) production

Vivek Dhand^a, J S Prasad^a, M Venkateswara Rao^a, K Naga Mahesh^a, L Anupama^a, V Himabindu^{a*},
Y Anjaneyulu^b, V S Raju^c & A A Sukumar^c

^aCenter for Environment, Jawaharlal Nehru Technological University, Kukatpally, Hyderabad 500 085, India

^bDepartment of Chemistry & Environment, TLGVRC, Jackson State University, Jackson, Mississippi 39217, USA

^cNational Centre for Compositional Characterization of Materials, BARC, ECIL Post, Hyderabad 500 062 India

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A pilot scale flame reactor has been designed and developed successfully for producing carbon nanorods by using methane, acetylene as the source of carbon in the oxygen atmosphere under atmospheric conditions without catalyst. The present paper discusses the designing of the flame reactor and the studies carried out on the flame reactor for producing carbon nanorods using methane, acetylene and oxygen gas-system. The carbon nanorods produced using this reactor are in the range of 150-600 nm.

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In 1991 Iijima¹ discovered carbon nanotubes at NEC laboratory Japan, since then other nanotubular structures have been an area of interest along the scientific community across the globe. Nanowires, nanorods and nanobelts constitute an important class of one-dimensional nanostructures, which provide models to study the relationship between electrical transport, optical and other properties with dimensionality and size confinement². This synthesis revolution led to a possible alternative for nanotubes for molecular electronics³. Nanomaterials of carbon⁴⁻⁶ have attracted attention due to their remarkable electronic and mechanical properties⁷⁻⁹. These nanofibers are being evaluated for a host of applications¹⁰ from semiconductor and field emission devices¹¹⁻¹⁵ to structural composites^{16,10}. Carbon based nanorods are produced using different synthesis routes like, vapour-liquid-solid growth, oxide-assisted growth, vapour-solid growth, carbothermal reactions, template-based synthesis, solution-liquid-solid process, solvothermal synthesis² and flame synthesis among others flame synthesis process has many advantages like easy scale-up, *in-situ* catalyst generation, bulk production, continuous process, easier particle size control and the feed gas serves the purpose of both reactant as well as fuel. So, it is highly energy efficient.

Synthesis of nanorods was done in the flame reactor unit using methane, acetylene and oxygen in a diffusion burner purely in the absence of a catalyst. The present paper describes the salient features of flame reactor facility developed for the production of nanorods in our laboratory.

Experimental Procedure

Flame reactor set-up

Flame reactor unit and the flow scheme of the same are given in Figs 1 and 2 respectively. The flame reactor consists of a burner through which the measured flows of methane, acetylene and oxidant (oxygen) enters the reactor chamber. The burner consists of three concentric SS 316 tubes of thickness 1 mm each. The outer diameter of central tube is 4 mm and the spacing between the successive tubes is 2 mm. The hydrocarbon and oxygen mixture can be ignited by an electric spark plug, which can be withdrawn soon after the ignition. Partial combustion reaction takes place in the flame where the soot containing nanorods is produced. The hot effluent gases, solid particles formed pass through an SS filter holder containing filter paper. The soot and carbon nanorods formed in the flame are collected on a glass fiber filter (Axiva, GF/AF) by the aid of vacuum pump. The filter paper is placed in a filter holder, which is made up of SS 304. It is held at 300 mm above the burner face so that the temperature of filter

*For correspondence: (Email: vurimindihimabindu@yahoo.com, drvhimabindu@gmail.com)

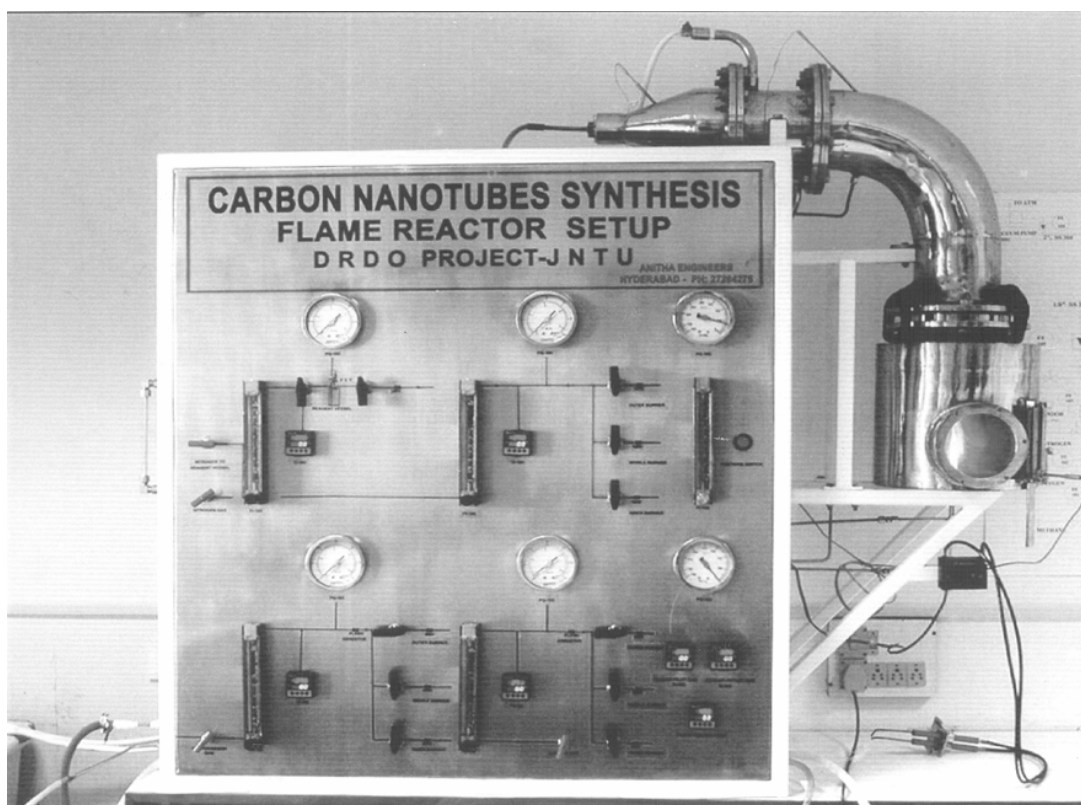


Fig. 1 — Flame reactor unit at JNTU

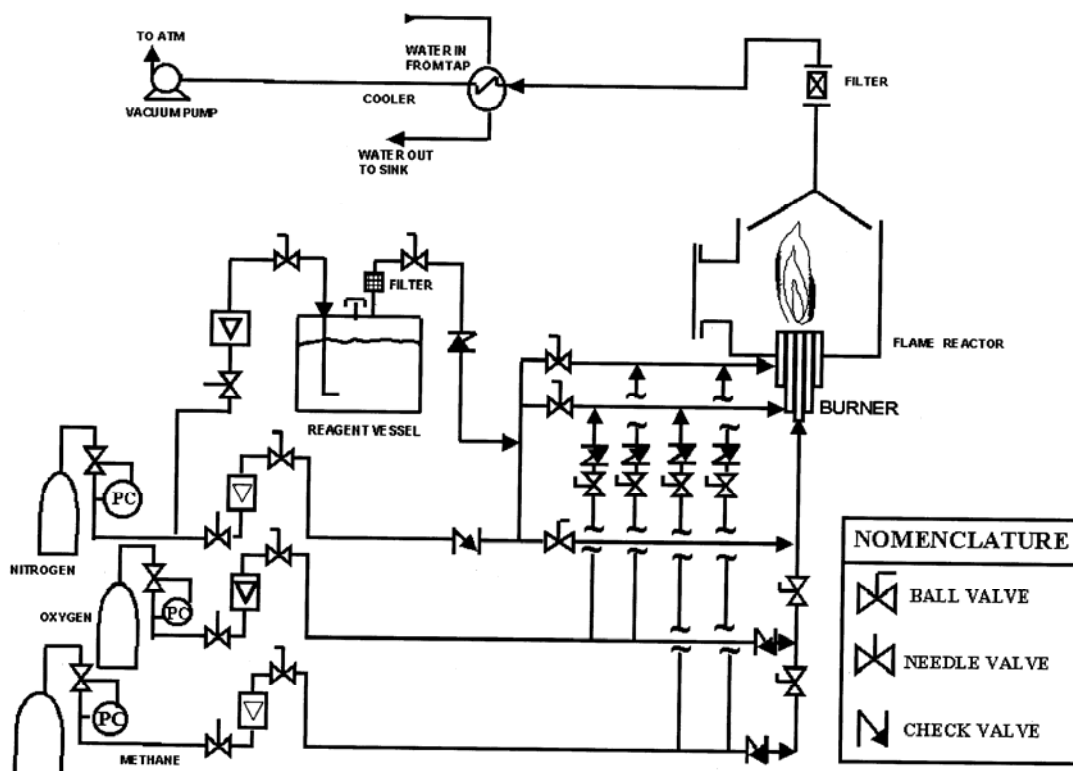


Fig. 2 — Flow scheme of flame reactor unit

would not exceed 300°C so as to prevent the damage of filter and paper. The hot effluent gases are cooled by a water cooler.

Reactor operates under atmospheric pressure. The flame is encased in a top open 300 mm diameter steel chimney to shield the flame over its entire length and to prevent air entrainment from the surroundings. A toughened glass window allows visible monitoring of the combustion process. Check valves are installed right before the burner to avoid backflow of gases. Flame arrestors are provided in oxidant/hydrocarbon lines to avoid explosions. Tubing used for all gases was designed to withstand explosions. Two stage gas regulators are used for reducing the gas pressure to the reaction conditions.

Reactant flows are measured with the help of calibrated rotameters. Temperature and pressure gauges are provided at necessary points to measure the respective readings. Flame temperatures are measured at different axial locations using K-type thermocouple. Flame length is measured using a scale provided on the reactor shell. The control of carbon nanorods growth during flame synthesis depends on various process parameters like reaction gas composition, flame temperature, flame type and gas velocities.

Experimental studies

Studies have been carried out using methane acetylene as carbon source and oxygen as oxidant. The carbon nanorods are formed in the diffusion flame in the absence of catalyst when methane flow rates are varied in between 0.6 to 1.2 slpm and that of acetylene and oxygen are at 0.5 slpm and 0.1 slpm respectively. Passing methane and acetylene through the inner ring and oxygen through the middle burner produced a diffusion type of flame. The temperature of the flame has been recorded by the thermocouple. The system was run for about 30 min at different flow rates of methane and the soot was collected on the filter paper. The soot formed on the filter paper was scrapped out carefully and weighed. The sample was heat-treated in a furnace under atmospheric conditions to remove the amorphous carbon at 500°C for one hour. Most of the amorphous carbon was oxidized below 500°C¹⁷. The heat-treated sample is then cooled and weighed again to know the percentage loss of amorphous carbon gravimetrically. The carbon left after heat treatment was weighed to know the yield of nanorods. The percentage carbon yield is defined as:

$$\text{Carbon Yield (\%)} = (W_1 - W_2)/W_1 \times 100.$$

where, W_1 is the initial weight of carbon collected. W_2 is the carbon remained after the heat treatment. The total % carbon yield corresponds to the amount of nanorods obtained after heat treatment. It is then characterized for the presence of carbon nanorods using XL 30 Series Philips Scanning Electron Microscope (SEM) and PW1830 Phillips X-ray diffractometer (XRD) and Hitachi H7500 transmission electron microscope (TEM).

Results and Discussion

SEM picture of Fig. 3 at a magnification of 5102× shows good growth of elongated nanorods of lengths in order of 5 micron with the internal diameter varying from 250 nm to 500 nm at flow rates of 0.8 slpm of methane, 0.5 slpm acetylene and 0.1 slpm of oxygen. Figure 4 at the magnification of 5102× shows the nanorods with varying diameter ranging from 200 nm to 600 nm and lengths up to 5 micron at a flow rate of 0.6 slpm of methane, 0.5 slpm acetylene

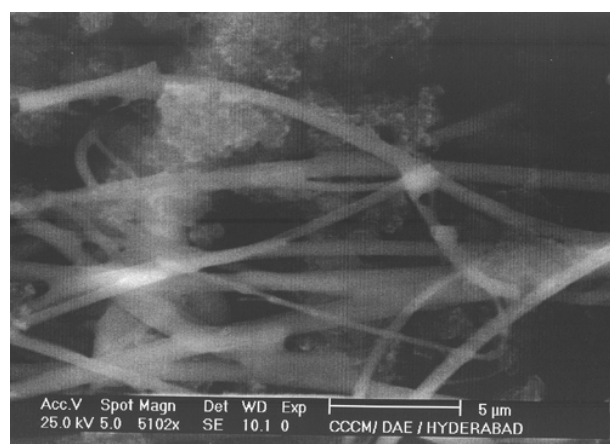


Fig. 3 — SEM image of methane-acetylene and oxygen at 0.8 slpm of methane



Fig. 4 — SEM image of methane acetylene-oxygen at 0.6 slpm of methane

and 0.1 slpm of oxygen respectively. In Fig. 5 at a magnification of 10000 $\times$ the SEM picture shows the most abundant growth of carbon nanorods with an average length of 2 microns with the diameter ranges from 150 nm to 600 nm at flow rate of 1.2 slpm of methane, 0.5 slpm acetylene and 0.1 slpm of oxygen, similar SEM results were obtained by Liming Yuan and his co-workers using methane¹⁸ flames and by Randall Vanderwal *et al.*¹⁹ who experimented using acetylene flames.

Plot (Fig. 6) drawn between flow rates of methane and the carbon yield (%) shows the highest carbon nanorods yield at a flow rate of 1.2 slpm. Also it may be observed from the above plot that the nanorods yield increases with increase in methane flow rate this is because of the increase in the gravimetric mass of methane thereby resulting in production of large quantities of carbon soot containing nanorods and smaller fullerenes. XRD investigations were carried out using CuK α 1 type of radiation with a wavelength (λ) of 1.54060 $\text{\AA}$ (Fig. 7) to assess out for the presence of nanorods, from the International Centre For Diffraction Database (ICDD) PCPDF-2 Release-2003, we find that the XRD pattern of sample at 0.6 slpm of

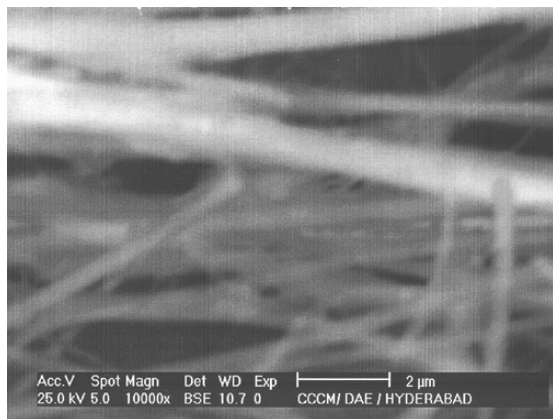


Fig.5 — SEM image of methane acetylene-oxygen at 1.2 slpm of methane

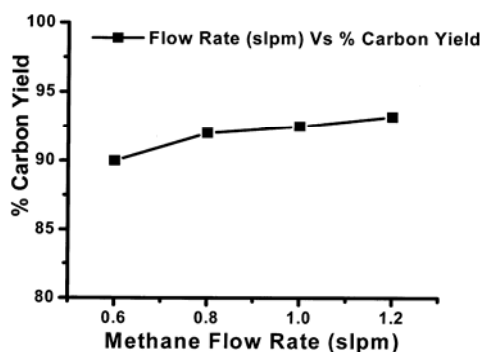


Fig.6 — Methane flow rate versus % carbon yield

methane, 0.5 slpm acetylene and 0.1 slpm of oxygen shows two peaks with an orientation of 002 at 2θ value of 25.73° which corresponds to presence of carbon nanorods and 0030 at 2θ value of 64.60° confirming the presence of carbon. XRD plot of sample at 0.8 slpm of methane shows three peaks with an orientation of 110 at peak 2θ value of 8.66° showing the presence of carbon in the form of C_{70} , the second peak with an orientation of 111 at 2θ value of 12.71° showing presence of C_{60} and the third peak with an orientation of 111 at 2θ value of 26.71° showing the presence of graphitic carbon respectively. The investigation of SEM and XRD indicates the formation of nanorods in the flammable mixture of gases. Smoothing of the above XRD was done using polynomial type quintic method at the convolution of 25 data points. The TEM image (Figs 8 and 9) of an isolated nanorod grown at 0.6 slpm shows that it is

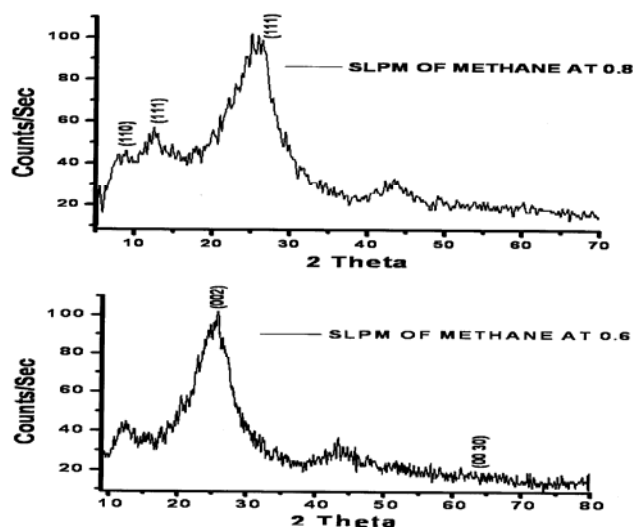


Fig. 7 — XRD pattern of Figs 3 and 4

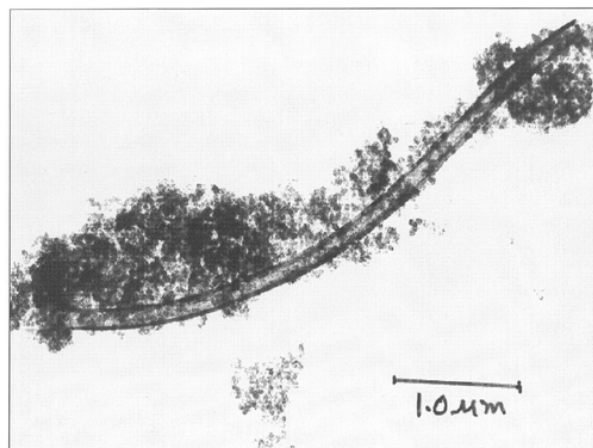


Fig. 8 — TEM image of methane acetylene-oxygen at 0.6 slpm of Methane- low magnification of 17900 $\times$

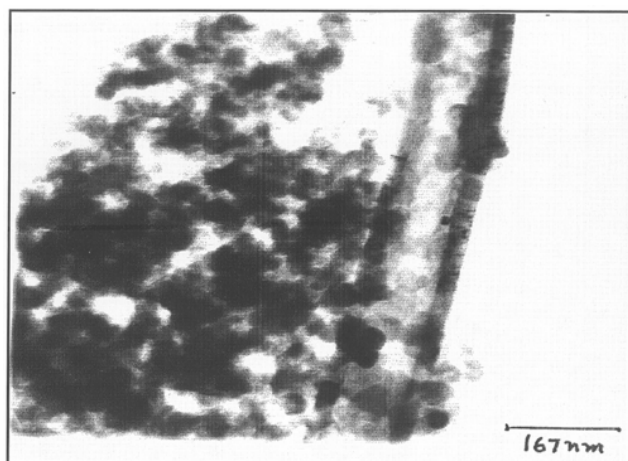


Fig. 9 — TEM image of methane acetylene-oxygen at 0.6 slpm of methane-high magnification of 107400 $\times$

hollow and lengthier in appearance. The approximate diameter of the CNR was found to be around 167-170 nm and length up to 3 microns.

Conclusions

Nanorods are widely used in electronics and various other electrical devices. A pilot scale flame reactor was designed for producing carbon nanorods using methane, acetylene as carbon source and oxygen as oxidant under atmospheric conditions without any catalyst using flame synthesis process. The TEM, SEM and XRD investigations confirm the presence of carbon nanorods with their diameter varying from 150 nm to 600 nm and lengths ranging 2-5 microns. From the % carbon yield plot we infer that as we increase the flow rate of methane from 0.6 slpm to 1.2 slpm the nanorods yield also increases gradually with increase in good growth of nanorods.

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