Experimental Study on synthesis of CNT using Alumina supported catalyst by CVD method

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Abstract

Carbon nanotubes (CNTs) have been a driving force for current advances in nanotechnology, both on an applied and on a fundamental level. CVD is the most effective method for large scale production of CNT at a rate comparatively faster than the other methods used for its production, thus making it the most economical method of CNT production. We have conducted the experiments on synthesis of CNT using alumina supported catalyst having cobalt and iron impregnated on it. Acetylene was used as a source of carbon and Argon was the inert gas used. The aim of conducting the experiment was to identify the effects of various experimental parameters viz. time, temperature, type of gas and its flow rate on the growth of CNT.

Introduction

Carbon nanotubes (CNTs) belong to relatively new nano-materials that have been publically known for almost twenty years, but their history is a little bit longer. Carbon nanotubes (CNTs) were firstly observed and described in 1952 by Radushkevich and Lukyanovich [1] and later in 1976 the single (or double) walled carbon nanotubes were observed by Oberlin et al[2]. In more recent history the discovery of CNTs is attributed to Iijima as the first scientist who described the multi-walled carbon nanotubes (MWNTs) preparation process after a random event during the test of a new arc evaporation method for C60 carbon molecule fabrication in 1991[3].Carbon nanotubes (CNTs) are a new form of carbon molecules with many outstanding properties which makes them potentially useful in various applications such as electronic, mechanical, composite, medical, etc. In most cases, the production of nanotube emitters is based on catalytic decomposition of carbon-bearing gases on nanoparticles dispersed on a support. Obviously, such approach involves tedious and timeconsuming preparation of supported catalyst nanoparticles. Thus it is particularly attractive to grow carbon nanotubes directly on the surface of catalytically active transition metals such as iron, nickel and cobalt. CVD technique is very useful for producing such structures. Various CVD methods have been developed for synthesizing SWCNTs as well as MWCNT, such as, catalytic CVD or thermal CVD, plasma enhanced CVD (PECVD) (Cheng et al. 1998) and floating catalyst CVD method (Ago et al. 2005; Chen et al. 2006). In the CVD process, organic compounds are decomposed in the presence of catalyst. In the catalytic CVD and PECVD, CNTs growth takes place on the substrate. But in the floating catalyst technique, large quantity of CNTs is generated without use of any substrate. Therefore, the floating catalyst technique is very competitive for producing CNT on large scale for industrial applications. But, controlling the size and composition of the catalyst nanoparticles is a major issue for this technique.

Fig. 1 Methods of CNT synthesis. [4]

Experimental work

Methods of Preparation of Catalyst There are so many methods of preparation of catalysts and so many different types of catalysts available for the synthesis of CNT. Here we are focusing on the co precipitation, impregnation methods both dry and wet for the preparation of catalyst using Cobalt and Iron with Alumina as the support. Al(OH)3 was obtained from different sources. The support was impregnated with nitrate salt solutions of either Fe or Co or a mixture of Fe and Co so as to get 2.5 wt.% of the metal on the support. Further details of the methods of preparation of all the support–metal mixtures are reported elsewhere [5,6,7].

Wet impregnation method [7] About 17.0 g of aluminium nitrate was mixed well with 5 ml of distilled water. To the paste so obtained, a mixture containing 1.23 g of Fe(NO3)3.9H2O and 0.83 g of Co(NO3)2.6H2O was added and homogenised. The semisolid thus resulted was dried in an air oven at 120°C. A light brown solid obtained was powdered.

Dry impregnation method [7] 1.23 g of Fe(NO3)3.9H2O was thoroughly mixed with 0.83 g of Co(NO3)2. 6H2O and 1ml of water. 9.5g of commercial Al(OH)3 powder was added and mixed well to get a homogeneous mixture. The solid thus obtained was dried at 120°C in a hot air oven cooled and powdered. A dark brown solid was obtained.

Co-precipitation method [7] 30.5 g of aluminium nitrate, 1.23 g of Fe(NO3)3 .9H2O and 0.83 g of Co(NO3)2 .6H2O were added one after the other while stirring vigorously to 800 ml of hot distilled water and continued stirring for 2 h. A light brown turbid solution was obtained (pH 4). Ammonia solution (1:1) was added drop wise with vigorous stirring until the pH rose to 8. The reddish brown precipitate formed was digested on a water bath for 1h, washed by decantation and finally filtered through a Buckner funnel using Whatmann no. 1 filter paper. The precipitate was dried in an air oven at 120 °C. A hard solid obtained was ground into a fine powder. A very dark brown powder was got.

Carbon Nanotube's Production

For the synthesis of carbon nanotubes acetylene gas was used as the source of carbon. The synthesis reactions were conducted in a horizontal tubular furnace, at a very low pressure. Pyrolysis of the hydrocarbon was conducted in the temperature range of 500-800°C.In a typical experiment, about 0.5 g of accurately weighed catalyst was spread over a ceramic plate as a thin layer and placed inside the quartz tube. After purging with argon gas, the acetylene gas stream was opened for about an hour. The flowrates of Argon and Acetylene was 100-500 sccm for Ar and 520 sccm for C2H2.The reaction unit was cooled to room temperature and the weight of the carbon deposit along with the catalyst was found out. The percentage of carbon deposit was calculated taking into account the weight loss of the catalyst at the reaction temperature.

Observation and results

SEM and Raman analysis of carbon deposit Raman analysis of the as synthesized carbon deposit was carried out to know the nature of the distribution of nanotubes in the carbon deposit. The density and the characteristics of the CNTs in the as produced carbon were analysed using SEM analysis. The images below

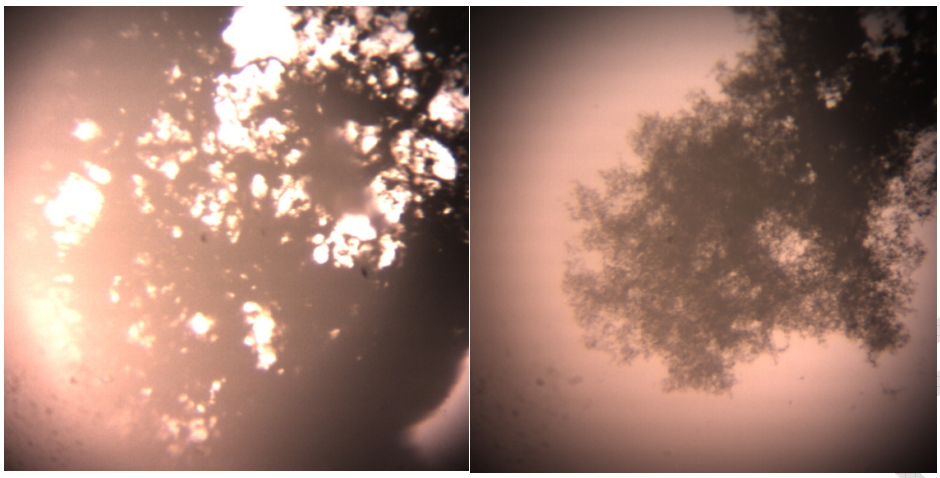

Fig 2 : Images of CNTs under a optical microscope

The major observation was that the powdered catalyst was converted into a cotton like mass . A distinct colour change was observed in the catalyst which changed from light brown to carbon black. This sample was analysed using SEM and Raman Spectroscopy. The diameters of the nanotubes were varying between 17-45nm. This variation in diameter is due to parameters like temperature, flow rate and duration of the experiment.

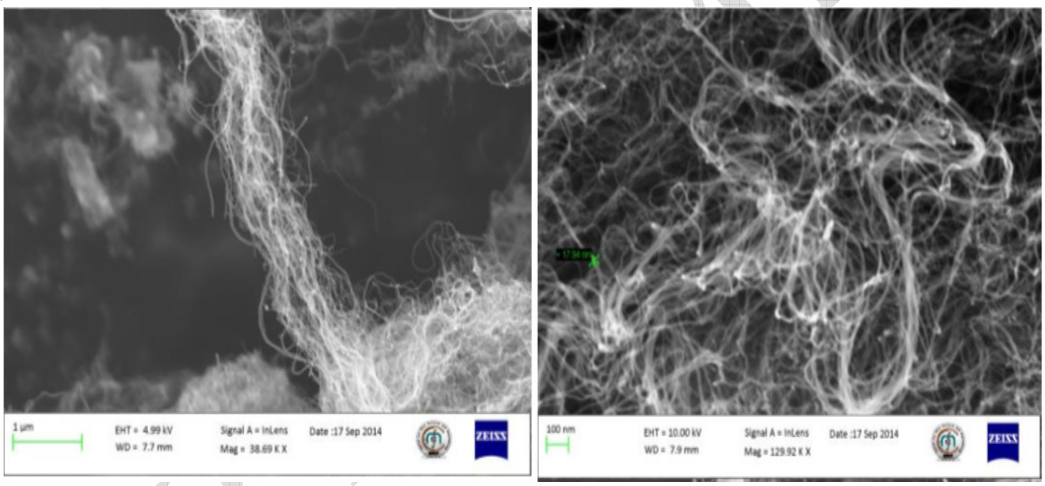

Fig 3- Scanning electron micrographs (SEM) of the CNTs produced

Conclusion

We have investigated the previously observed narrow temperature window for CVD growth of CNTs on Co using a Fe catalyst. A minimum growth temperature of 700 °C is required for observation of CNTs, although carbon deposition can be detected at lower growth temperatures. From the experimental analysis we can conclude that the quality and growth of CNT is improved with the increase in temperature and optimization of flow rates.

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