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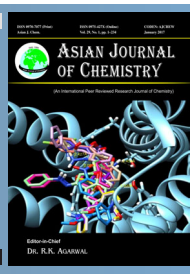

Synthesis of Carbon Nanotubes for Device Applications

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In this work, we report the growth of carbon nanotubes (CNTs) on iron-yttrium (FeY) bimetallic catalyst using thermal chemical vapour deposition technique. The catalysts were prepared by dry impregnation method and characterized by XRD. The XRD analysis shows that the catalyst particle size is < 5 nm with no presence of graphitic structures around the nanoparticles. HRTEM and TGA analyses were used to characterize the as grown CNTs. The TGA analysis shows that the grown CNTs are very stable at high temperature. The HRTEM images show that the CNTs are in bundled form with and of high degree of graphitization. The grown CNTs are very useful for device applications like sensors, filters, capacitors and in batteries.

Keywords: Carbon nanotubes, Chemical vapour deposition, HRTEM, TGA, FeY catalyst.

INTRODUCTION

The production capacity of carbon nanotubes (CNTs) has increased during the past few years besides the CNT related issued patents and publications continues to grow year by year. Today's CNTs find many applications in almost all areas of science and technology because of their excellent mechanical, electrical and optical properties [1]. Some of the applications of CNTs include batteries [2], biomedical applications [3-5], flexible energy storage [6], transistors [7,8], humidity sensors [9], gap waveguide components [10], electrostatic discharging [11], innovative biomaterials [12], high energy capacitor [13], *etc*. However, for many commercial applications of CNTs highly reliable synthesis techniques are needed that should produce high quality of CNTs at large scale. Among the various available CNT synthesis techniques chemical vapour deposition (CVD) is the most employed technique due to the fact that it produces highly pure CNTs in bulk quantity with control over the CNT diameter, length and chirality [1].

In catalyst chemical vapour deposition (CCVD) process the growth of the CNTs involves the decomposition of various hydrocarbons over the catalyst. The popular hydrocarbons employed by the researchers for the synthesis of CNTs includes methane [14-16], ethylene [17] and carbon monoxide [18]. Methane is the most kinetically stable hydrocarbon which is ideal for synthesis of CNTs with less amorphous carbon [19]. On the other hand the most popular catalysts in vague for synthesis of CNTs include Fe, Co and Ni [1]. This is due to the fact that carbon has high solubility and diffusion rate in these metals.

The combinations of two or three metals have also been frequently employed during the past decade and it has been observed that mixture of transition metals offers thermodynamical and chemical benefits [20]. The catalysts are usually supported over solid matrix such as MgO, Al_2O_3 and SiO_2 [21] as they play an important role in growth of CNTs. Among these supports MgO is the best electron donor and it produces high quality CNTs with high degree of graphitization [22]. Furthermore it has been shown that solvents also affect the crystallinity of grown CNTs and the mostly employed solvents for CNTs growth include methanol, ethanol and alcohol [20].

Although there are several reports on the use of yttrium as a catalyst for synthesis of large diameter CNTs by arc-discharge [23-25], however to the best of our knowledge till date no attempt has been made to prepare CNTs on Fe-Y bimetallic catalyst which will be suitable for device applications. Therefore in this study we decided to develop FeY bimetallic catalyst for the growth of CNTs by thermal CVD technique. The results show that the concentration of the catalyst constituents changes the diameter of the grown CNTs, however the quality and crystallization does not change. Therefore, it is expected that the synthesized nanotubes will find number of electronic applications in the near future.

EXPERIMENTAL

Preparation of catalyst: The metal catalyst support mixture was prepared by dry impregnation method as reported earlier [26]. $Fe(NO_3)_3{\cdot}9H_2O$, $Y(NO_3)_3{\cdot}6H_2O$ and $Mg(NO_3)_2{\cdot}6H_2O$ metal salts were received from High Purity Labortary Chemicals (HPLC) Pvt. Ltd. Mumbai. The molar ratios of iron, yttrium and magnesium salts were set as 0.2:0.05:0.9 and 0.2:0.1:0.9. Firstly $Mg(NO_3)_2{\cdot}6H_2O$ was dissolved in methanol, subsequently required amount of $Fe(NO_3)_3{\cdot}9H_2O$ and $Y(NO_3)_3{\cdot}6H_2O$ were added into the MgO solution to get two different types of mixture solutions. All mixture solutions were sonicated for 20 min and subsequently stirred at 90 °C until the solution becomes viscous colloid. Then the catalysts were dried in an oven at 120 °C for 24 h and grinded with pestle and mortar to form a fine powder. Hereafter we refer the two catalysts as $Fe_{0.2}Y_{0.05}$/MgO and $Fe_{0.2}Y_{0.1}$/MgO.

Synthesis of carbon nanotubes (CNTs): For each run 0.2 g of catalyst powder was dispersed on a ceramic boat and then placed at a the centre of a horizontal quartz reactor (inner diameter 53 mm) of Thermal CVD System (TechnoS Instruments Model T-TCVD2-M) to grow CNTs. The reactor was heated to 800 °C in Ar atmosphere (99.999 % pure) at a flow rate of 200 sccm and the powder was reduced *in situ* in H_2 (40 sccm) environment for 10 min. Subsequently high purity methane (99.999 % pure) was allowed to pass through the tube and mixed with Ar at a ratio of 1:2 (v/v) at a total flow rate of 150 sccm for 30 min. After the reaction the furnace was cooled to room temperature in Ar atmosphere at a flow rate of 200 sccm so as to avoid burning of grown CNTs at high temperature.

Characterization: XRD measurements of the as prepared catalysts were carried out using Bruker D8 Advanced X-ray diffractometer. The X-ray of wavelength 0.154 nm (CuK_α) was produced using a sealed tube and detected using a fast counting detector based on silicon trip technology (Bruker Lynxlye Detector). The as grown CNTs were characterized by means of Supra 35VP SEM, 300 KV Technai F305 twin HRTEM and TGA study was carried out by using Perkin Elmer STA 6000.

RESULTS AND DISCUSSION

Fig. 1 shows the XRD patterns of the as prepared catalysts. In Fig. 1(a) the peaks at $2\theta \approx 35°$ shows that MgO-Fe forms a strong compound were the peak at $2\theta \approx 29.2°$, 33.8° and 43.8° indicate the presence of yttrium. In Fig. 1(b) an additional peak exists at $2\theta \approx 18°$ which confirms a strong compound formation between catalyst mixtures. Furthermore the peak at $2\theta \approx 26°$ in both XRD patterns (Fig. 1) is missing which shows that multilayer graphite structure do not form around the particles [27]. Scherer formula as well as analytical method revealed that the particle size of the two prepared catalysts is less than 5 nm.

Figs. 2 and 3 shows the micrographs of CNTs grown on the two catalysts $Fe_{0.2}Y_{0.05}$/MgO and $Fe_{0.2}Y_{0.1}$/MgO, respectively. From the HRTEM images it is clear that the grown CNT samples are of good quality with high degree of graphitization. The average diameter of the grown CNTs on the two catalysts $Fe_{0.2}Y_{0.05}$/MgO and $Fe_{0.2}Y_{0.1}$/MgO is 1.86 and 1.51 nm respectively. These results confirm that the both concentrations produce CNTs with distinct properties. Therefore, there exists a strong interaction between the catalyst components which prevents the agglomeration of catalyst particles at high temperature giving rise to good dispersion of particles.

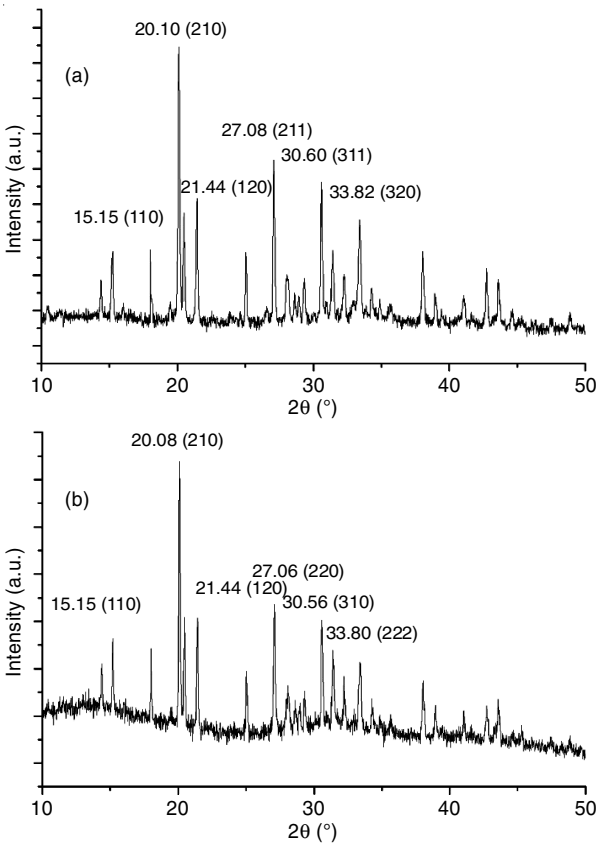

Fig. 1. XRD pattern of (a) $Fe_{0.2}Y_{0.05}$/MgO (b) $Fe_{0.2}Y_{0.1}$/MgO catalysts

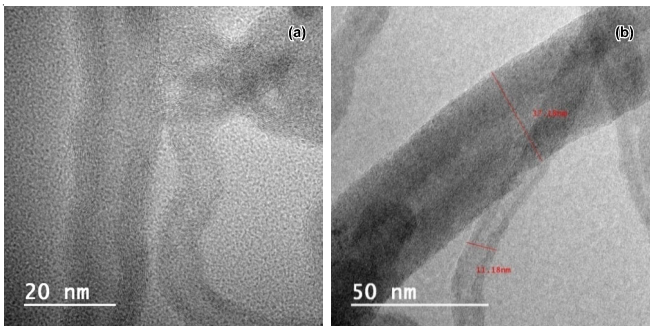

Fig. 2. HRTEM images of as grown CNTs on $Fe_{0.2}Y_{0.05}$/MgO catalyst

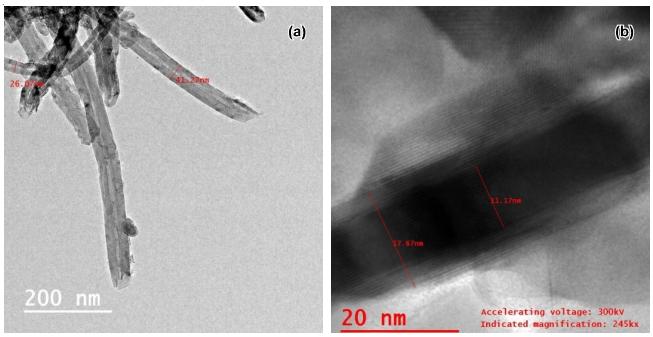

Fig. 3. HRTEM images of as grown CNTs on $Fe_{0.2}Y_{0.1}$/MgO catalyst

In order to examine the thermal stability of the two grown CNT samples we have performed TGA analysis as shown in Fig. 4. The plots of the two prepared CNT samples are almost flat with a small amount of weight loss around 4 % which is the proof of their high thermal stability, the synthesised nanotubes will find applications in various electronic devices.

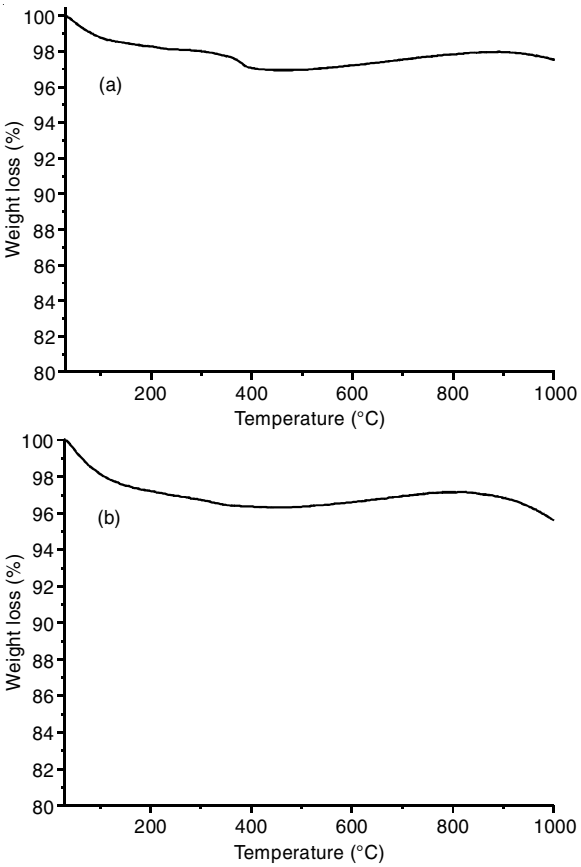

Fig. 4. TGA plots of the as grown CNTs on (a) $Fe_{0.2}Y_{0.05}$/MgO (b) $Fe_{0.2}Y_{0.1}$/MgO catalysts

Conclusion

In this study a new bimetallic catalyst (FeY) was developed to grow CNTs of high degree of crystallization and purity as revealed by HRTEM images and TGA analysis. The CVD reaction was carried out at 800 °C. The concentration of yttrium was changed to observe the changes in the morphology of grown CNTs. HRTEM analysis indicated that the synthesized CNTs are in bundled form with less defects and high degree of graphitization. The study is very important from both scientific and applied point of view.

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