Large Scale Synthesis of Carbon Nanofibres on Sodium Chloride Support

Regular Paper

Ravindra Rajarao and Badekai Ramachandra Bhat[*]

Catalysis and Materials Laboratory, Department of Chemistry, National Institute of Technology Karnataka, India
* Corresponding author: chandpoorna@yahoo.com

Abstract Large scale synthesis of carbon nanofibres (CNFs) on a sodium chloride support has been achieved. CNFs have been synthesized using metal oxalate (Ni, Co and Fe) as catalyst precursors at 680 °C by chemical vapour deposition method. Upon pyrolysis, this catalyst precursors yield catalyst nanoparticles directly. The sodium chloride was used as a catalyst support, it was chosen because of its non-toxic and water soluble nature. Problems, such as the detrimental effect of CNFs, the detrimental effects on the environment and even cost, have been avoided by using a water soluble support. The structure of products was characterized by scanning electron microscopy, transmission electron microscopy and Raman spectroscopy. The purity of the grown products and purified products were determined by the thermal analysis and X-ray diffraction method. Here we report the 7600, 7000 and 6500 wt% yield of CNFs synthesized over nickel, cobalt and iron oxalate. The long, curved and worm shaped CNFs were obtained on Ni, Co and Fe catalysts respectively. The lengthy process of calcination and reduction for the preparation of catalysts is avoided in this method. This synthesis route is simple and economical, hence, it can be used for CNF synthesis in industries.

Keywords Carbon nanofibres, chemical vapour deposition, sodium chloride support, metal oxalate

1. Introduction

Since the discovery of CNTs by Iijima in 1991 [1], carbon nanofibres (CNFs) and carbon nanotubes (CNTs) have attracted much attention due to their exciting physico-chemical, electrical and mechanical properties. Various potential applications in the area of nanoelectronics [2], catalysis [3], polymer composites [4], energy storage [5] and sensors [6] have been reported by researchers. CNFs are usually obtained by the chemical vapour deposition [7] (CVD) method from the decomposition of gaseous hydrocarbon over metal catalyst particles. Other methods such as flame synthesis [8], arc discharge [9] and laser ablation [10] have also been used to synthesize CNFs and CNTs, but they are energy intensive, expensive and yield less when compared to CVD. The catalytic growth of CNFs mechanism is well established and contains several steps as follows: (i) a carbon source is decomposed on the surface of transition metal nanoparticles, (ii) liquidised metal carbide is formed by diffusion of carbon atoms into the nanoparticles, (iii) after over saturation or due to cooling down of the particles, the carbon precipitates to form polyaromatic layers (graphenes). The choice of the supporting material and catalyst has been found to be an important factor to synthesize CNFs by the CVD method. The support materials such as silica, alumina or magnesia

are widely studied [11-13]. But these supports are soluble in acids and hence an acid wash is required to separate these supports from carbon structures after growth. The wash with acid cause's detrimental effects on the CNFs and acid is even released into the environment. So water soluble supports, such as sodium chloride [14], potassium chloride [15] and calcium chloride [16], have also been used to synthesize CNFs in order to avoid the use of acid. The basic idea behind using a water soluble support returns to Steigerwalt and Lukehart [17] who employed silicate or carbonate. Metal catalysts, such as Fe [18-21], Ni [22, 23], Cu [24], Co [25, 26] and their alloys [27], have been investigated widely. However, until now, the reported catalysts require the lengthy process of reduction and calcination for their preparation [11, 13]. So in order to avoid the above mentioned problems, in this work we have used metal oxalate as catalyst precursors. The main advantage of use of metal oxalate as catalyst precursors is that it avoids the lengthy process of reduction and calcination. Our recent studies conclude that sodium chloride is a better water soluble support when compared to potassium chloride in terms of yield [28]. Hence in this study we have used sodium chloride as a support and metal oxalates as catalyst precursors. The yield and morphology of CNFs obtained on different catalyst has been investigated. The effects of temperature and gas flow rate on the carbon deposit were also investigated. Here we report the 7600, 7000 and 6500 wt% yield of CNFs synthesized over Ni, Co and Fe oxalate as catalyst precursor and long, curved and worm shaped CNFs over Ni, Co and Fe catalyst on NaCl support.

2. Experimental

2.1 Preparation of supported catalysts

All chemicals were of analytical grade and were purchased from Merck and Sigma Aldrich, and used as received without any further purification. Argon (99.95 % purity) and acetylene gases (99.99 % purity) were procured from Buruka agencies, Bangalore, and of highest possible purity. Metal oxalates were prepared by metal salts and ammonium oxalate. The formation of metal oxalates was confirmed by the X-ray diffraction method. The supported catalysts were made by dispersing the metal oxalate catalyst precursors on sodium chloride support. The obtained supported catalysts were denoted as Ni/NaCl, Co/NaCl and Fe/NaCl.

2.2 Synthesis of CNFs

The CNFs were grown using the CVD technique. The length and diameter of the quartz tube were 900 mm and 25 mm, respectively. The catalyst with support weighing 0.3 g was taken in the quartz boat. The boat was placed in the centre of the quartz tube after the reactor reached 680 °C in an argon atmosphere, where the fresh nanoparticles are formed upon thermal decomposition. On introduction of the acetylene gas, the growth of CNFs occurred. The CVD reaction was performed by passing a mixture of 20 sccm C_2H_2 : 200 sccm Ar for 15 min at 680 °C. The reactor was cooled in an argon atmosphere and then carbon deposits were collected. The carbon yield is calculated by equation 1:

$$\frac{M_{Total} - M_{Cat}}{M_{Cat}} \; 100 = Carbon\; yield\, \% \qquad (1)$$

2.3 Purification of CNFs

To purify the sample, the as grown product was first heated under an air atmosphere at 400 °C for 2 h and then stirred in warm water to remove the catalyst and support. The sample was finally washed with deionized water and dried in an oven.

2.4 Characterisation of CNFs

The nanostructure and morphology of CNFs were observed under both scanning electron microscope (SEM, SUPRA 40VP Carl Zeiss) and transmission electron microscope (TEM, CM200 Philips). Thermal gravimetry analysis (TGA) was used to determine the purity and structural stabilities of the CNFs. The TGA was performed on SDT Q600, TA, USA (flow rate: 50 mL/min). The heating rate was 10 °C/min. A Raman spectrum was obtained (Renishaw, RM 1000, He-Ne laser excitation line at 633.0 nm) to understand the relative intensity of G-band and D-band at ambient condition. The X-ray diffraction (XRD) patterns were obtained (JEOL JDX 8P diffractometer with Cu Kα radiation, λ=1.5418 A°) to determine the purity and crystallinity of CNFs.

3. Results and discussion

Metal carboxylate catalyst precursors decompose directly into catalyst nanoparticles without forming the oxide intermediate in a gas flow system [29, 30]. The TG analysis of cobalt oxalate was carried out in an inert atmosphere. The TG profile of cobalt oxalate confirms the formation of metal without forming metal oxide (Fig. 1). Thus this method of synthesizing nanoparticles as catalyst for the growth of CNFs has advantages over other inorganic salts like metal nitrates or oxides. Metal oxalate precursors directly yield nanoparticles hence the lengthy process of calcination and reduction is eliminated. The support used for catalysts is sodium chloride, which is easily soluble in water. So the problem of the detrimental effect on CNFs has been overcome by using a water soluble support. Table 1 gives the summary of catalyst precursor, yield and morphology of the CNFs produced.
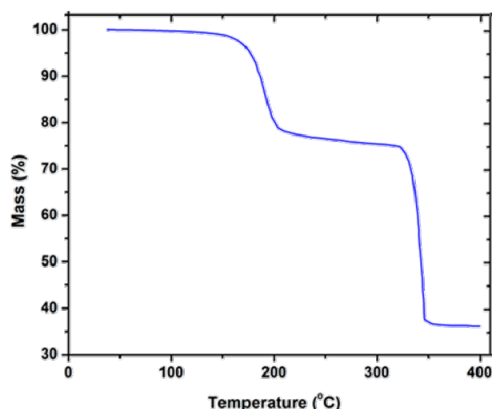
Figure 1. TGA profile of cobalt oxalate

The melting point of NaCl is 800 °C, so all the reactions were performed within this temperature. A variety of experiments were conducted with argon-acetylene mixture (200 sccm : 10 sccm) at reaction temperatures between 600 °C to 740 °C (Fig. 2). The carbon deposit was maximum at 680 °C. Further, the effects of different flow rates on the carbon deposits were studied over the optimized condition, at 680 °C for 15 min. When the flow rate was increased from 10 sccm to 20 sccm, we observed a maximum carbon deposit; then the percentage of carbon deposit was further decreased, when the flow rate was increased to 30 sccm, respectively (Fig. 3). So all the reactions were performed at 680 °C with a gas flow of 200 sccm: 20 sccm (Ar:C_2H_2) for 15 minutes. The metal loading percentage was fixed to 3 wt% in the catalyst support in order to avoid the sintering effect of the catalyst at high temperatures.

Catalyst precursor	Actual yield after purification (for 300 mg of supported catalyst)	Yield %	Morphology of CNFs, I_D/I_G
Nickel oxalate	~ 0.700 g	7600	Long Curved CNFs, I_D/I_G=1.28
Cobalt oxalate	~ 0.635 g	7000	Curved CNFs, I_D/I_G=1.30
Iron oxalate	~ 0.595 g	6500	Helical CNFs, I_D/I_G=1.23

Table 1. Summary of catalyst precursor, yield, morphology and I_D/I_G value of CNFs produced.
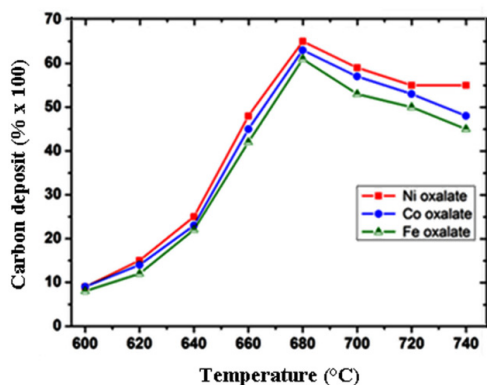

Figure 2. Chart of the amount of carbon deposit with different temperature at gas flow (10 sccm C_2H_2: 200 sccm Ar)
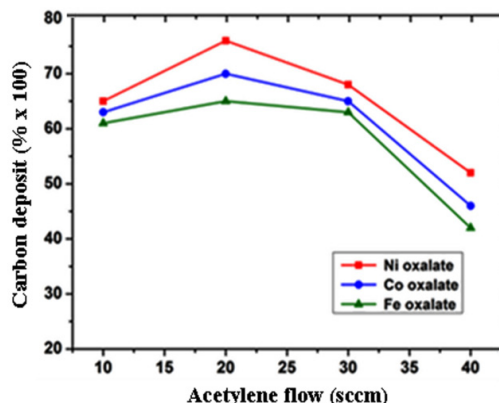

Figure 3. Chart of amount of carbon deposit with different gas flow of acetylene (sccm), at a constant flow of 200 sccm of argon at 680°C

The SEM morphology of purified CNFs synthesized is shown in Fig. 4. Most of CNFs synthesized on Ni/NaCl are long curved. The diameter distribution is in the range 10-60 nm. Curved nanofibres were synthesized on Co/NaCl and the diameters of these nanofibres were found to be 20-30 nm. The nanofibres synthesized by catalyst Fe/NaCl show worm-like morphology with diameters ranging from 20-50 nm. The worm shaped CNFs have their own applications in the field of composites, hydrogen storage and as nano springs. However, the yield of nanofibres with respect to the Ni/NaCl catalyst has been considerably higher when compared to Co/NaCl and Fe/NaCl catalysts. Structural details of products were further investigated by TEM. Fig. 5 shows the TEM images of the purified CNFs. There is clear evidence from the TEM micrograph for the formation of CNFs.
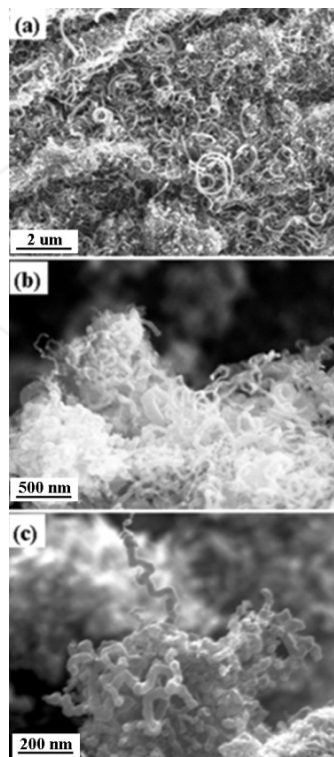

Figure 4. SEM images of purified carbon nanofibres grown on (a) nickel oxalate (b) cobalt oxalate (c) iron oxalate

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The samples were analysed by Raman spectroscopy in order to understand the structure perfection (Fig. 6). It can be seen that spectra of all samples consist of 2 peaks: the peak of C-C stretching mode (G-band) appeared at around 1590 cm^{-1}, which indicates the presence of graphene layers in CNFs. D-band at around 1330 cm^{-1} indicates the existence of defective graphene layers [31, 32].

Thermal analyses for the samples were carried out from room temperature to 700 °C with a rate of 10 °C/min in an air atmosphere. TGA analysis of the as grown products showed no weight loss in air until 490 °C (Fig. 7); this indicates the absence of amorphous carbon or the presence of minimal amounts of amorphous carbon [33]. The main loss at ~520 °C indicates that CNFs are stable until 500 °C. The analysis revealed that after the purification, the purity of the CNF product was better than 98.5 %.

Figure 6. Raman spectra of purified carbon nanofibres grown on (a) nickel oxalate (b) cobalt oxalate (c) iron oxalate

Figure 7. TGA analysis of carbon products grown on (a) nickel oxalate (b) cobalt oxalate (c) iron oxalate and purified product grown on (d) cobalt oxalate
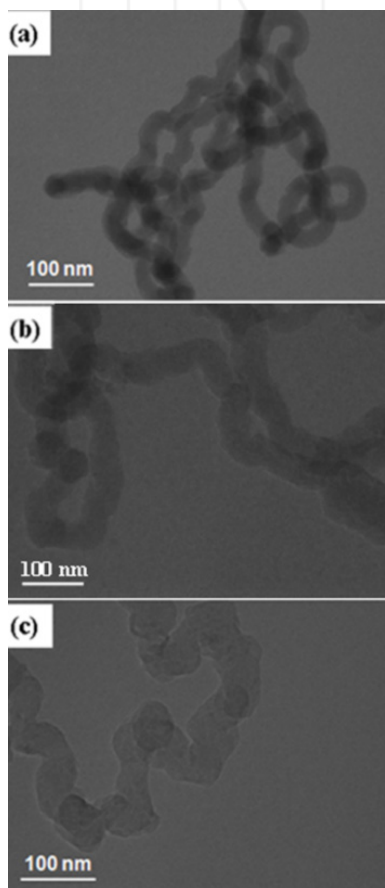

Figure 5. TEM images of purified carbon nanofibres grown on (a) nickel oxalate (b) cobalt oxalate (c) iron oxalate

The purified samples were also characterized by using XRD diffraction. The XRD pattern (Fig. 8) also shows the structural feature of CNFs. The spectra contains two characteristic peaks at 26.0° and 43.5°, indexed with (002) and (101) diffraction planes of hexagonal graphite (JCPDS card files, no 41-1487), respectively. No other noticeable peaks induced by catalyst or support can be observed in the XRD pattern.
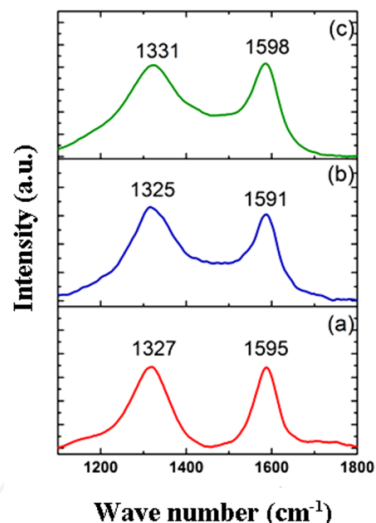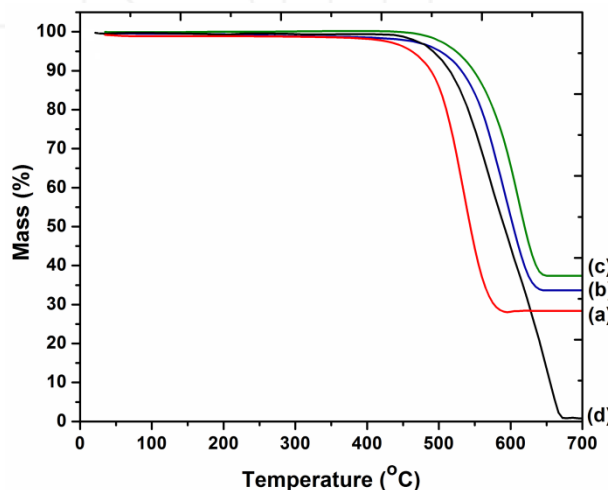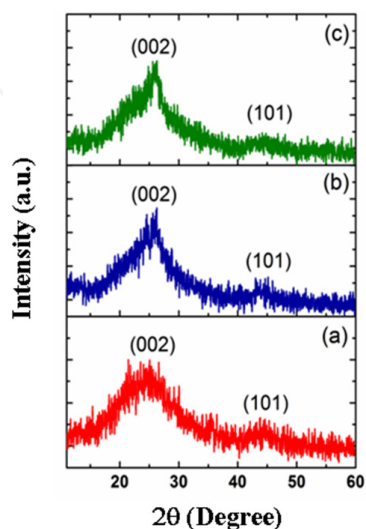

Figure 8. XRD pattern of purified carbon nanofibres grown on (a) nickel oxalate (b) cobalt oxalate (c) iron oxalate

4. Conclusions

We have successfully synthesized the carbon nanofibres on a large scale by using metal oxalate as catalyst precursors on a sodium chloride support. Metal oxalates directly yield metal nanoparticles on pyrolysis, thereby eliminating the lengthy process of calcination and reduction. Sodium chloride was used as a support because of its water soluble and non-toxic nature. The purity of the purified product was up to 98.5 %. In particular, the yield of the CNFs obtained by nickel oxalate has found to be high when compared to cobalt oxalate and iron oxalate. The long straight, curved and worm shaped CNFs were obtained over Ni, Co and Fe catalyst. This synthesis method can be applied in industries for the large scale synthesis of CNFs in an economical and environmentally friendly way.

5. Acknowledgements

6. References

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