

# Bulk scale production of carbon nanofibers in an economical way

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**ABSTRACT:** An economical route for the scalable production of carbon nanofibers (CNFs) on a sodium chloride support has been developed. CNFs have been synthesized by chemical vapor deposition (CVD) method by using metal formate as catalyst precursors at 680°C. Products were characterized by SEM, TEM, Raman spectroscopy and XRD method. By thermal analysis, the purity of the as grown products and purified products were determined. This method avoids calcination and reduction process which was employed in commercial catalysts such as metal oxide or nitrate. The problems such as detrimental effect, environmental and even cost have been overcome by using sodium chloride as support. The yield of CNFs up to 7800 wt.% relative to the nickel catalyst has been achieved in the growth time of 15 min. The advantage of this synthesis technique is the simplicity and use of easily available low cost precursors.

**KEYWORDS:** metal formate, carbon nanofiber (CNF), chemical vapor deposition (CVD), high yield, sodium chloride support, environmental friendly route

## 1 Introduction

The interest in the structure and properties of filamentous carbon emerged in the 1970s with the development of transmission electron microscopy with the report of the mechanistic proposals by Oberlin et al. [1] and Endo et al. [2]. Since the discovery of carbon nanotubes (CNTs) by Iijima [3], an intensive research has been carried out on carbon nanofibers (CNFs) and CNTs. These materials have unique mechanical, chemical and electrical properties and hence attracted many researchers. CNTs and CNFs have large number of potential applications which include nanoelectronics [4], energy storage [5], catalyst substrate [6], chemical sensors [7], scanning probe tip [8], electrode material [9], field emission sources [10] and mechanical

reinforcements [11]. However, because of low production capacity and high production costs at present, their applications cannot be extended until large-scale production is realized. Among the many synthetic methods, chemical vapor deposition (CVD) method has advantages of high yield, high selectivity and low cost over traditional physical ones such as laser ablation and arc-discharge. The two major aspects to be focused in CVD technique are: the preparation of uniform catalysts of small size and determination of optimum reaction conditions. We propose a novel approach to grow CNFs at high yield over metal (Ni, Co and Fe) formates on water soluble support using CVD method. This synthetic route is even more efficient than commercial ones employing metal oxide or nitrate as catalyst. The main advantage of use of metal formate as catalyst precursor is that it avoids the lengthy process of reduction and calcination. By using sodium chloride as support, problems such as detrimental effect, environment

and even cost has been overcome. This technique leads to bulk production of CNFs in an economical way. Here we report 7800 wt.% yield of CNFs synthesized over nickel formate/NaCl.

## 2 Experimental

All reagents used were AR-grade and purchased from Sigma Aldrich. Metal formates were prepared by metal acetates and formic acid at 80°C. The microcrystalline precipitates were obtained on cooling which was filtered, dried at 100°C. The formation of metal formates was confirmed by X-ray diffraction (XRD). The supported catalysts were made by dispersing the metal formate catalyst precursors on NaCl powder. The dispersion was done mechanically by using pestle and mortar until homogeneous mixture was formed. The obtained supported catalysts were denoted as Ni/NaCl, Co/NaCl and Fe/NaCl.

The CNFs were grown using the CVD technique. Support with catalyst precursor weighing 0.3 g was loaded into quartz boat. Thermolysis of the catalyst precursor develops metallic nanoparticles when boat is introduced into preheated tube in an argon atmosphere. On introduction of the acetylene gas, the growth of CNFs occurred. The CVD reaction was performed by passing a mixture of 1:10 C<sub>2</sub>H<sub>2</sub> : Ar for 15 min at 680°C. The black product was collected after the reaction was cooled to room temperature in an argon atmosphere. To purify the sample, the raw material was first heated under an air atmosphere at 400°C for 2 h to ensure complete removal of amorphous carbon and then stirred in warm water to remove the catalyst and NaCl support. The sample was finally washed with deionized water and dried in oven. The carbon yields were calculated by Eq. (1):

$$\text{Carbon yield}/\% = \frac{M_{\text{total}} - M_{\text{cat}}}{M_{\text{cat}}} \times 100 \quad (1)$$

where  $M_{\text{total}}$  is the total mass of carbon product and catalyst, and  $M_{\text{cat}}$  is the mass of catalyst.

The nanostructure and morphology of CNFs were observed under both scanning electron microscopy

(SEM; SUPRA 40VP Carl Zeiss) and transmission electron microscopy (TEM; CM200, Philips). Thermal gravimetry analysis (TGA) was used to determine the purity and structural stabilities of CNFs. The TGA was performed on SDT Q600 (TA, USA) using dry air as the carrier gas (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 XRD patterns were obtained (JEOL JDX 8P diffractometer with Cu K $\alpha$  radiation,  $\lambda = 1.5418 \text{ \AA}$ ) to determine the crystallinity and purity of CNFs.

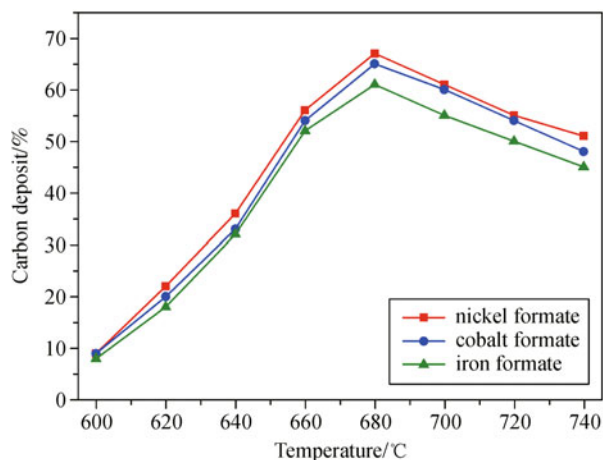
## 3 Results and discussion

Metal formate catalyst precursors decompose directly into catalyst metal nanoparticles without forming the oxide intermediate in a gas flow system [12–13]. Thus this method of synthesizing metal nanoparticles as catalyst for the growth of carbon nanostructures has advantages over other inorganic salts like metal nitrates or oxides. The lengthy process of calcination and reduction is eliminated as metal formate precursors directly yield metal nanoparticles. The support used for catalysts is NaCl, which is easily soluble in water. So the problems such as detrimental effect on CNFs, environment and even cost has been overcome by using water soluble support. Table 1 gives summary of catalyst precursor, metal loading, yield and morphology of CNFs produced.

The melting point of NaCl is 760°C, so all the reactions were performed within this temperature. The metal loading percentage was fixed to 3 wt.% in catalyst support in order to avoid sintering effect of catalyst at high temperatures. A variety of experiments were conducted with 200 sccm argon : 10 sccm acetylene mixture at reaction temperatures between 600°C and 740°C (Fig. 1) for 15 min. Till 680°C, increase in the carbon yield was due to the enhanced diffusion of carbons into metal catalyst and softening of support takes place after 680°C and hence decreases in the carbon yield. The carbon deposit was the maximum at 680°C. Further, the effects of different flow rates on the carbon deposits were studied and the results are presented

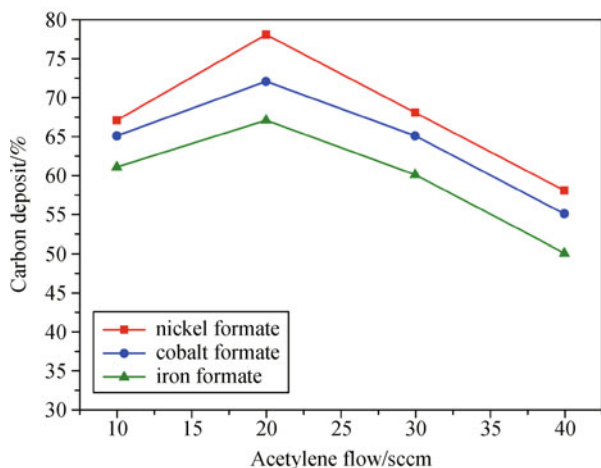
**Table 1** Summary of catalyst precursor, content of metal, CVD parameters, yields and morphology of CNTs produced

Catalyst precursor	Content of metal in support /wt.%	Gas flow rate /( $\text{mL} \cdot \text{min}^{-1}$ )		Temperature /°C	Yield /%	Morphology of CNFs
		C <sub>2</sub> H <sub>2</sub>	Ar			
Nickel formate	3	20	200	680	7800	straight, $I_D/I_G = 1.05$
Cobalt formate	3	20	200	680	7200	curved, $I_D/I_G = 1.04$
Iron formate	3	20	200	680	6700	worm-shaped, $I_D/I_G = 1.10$



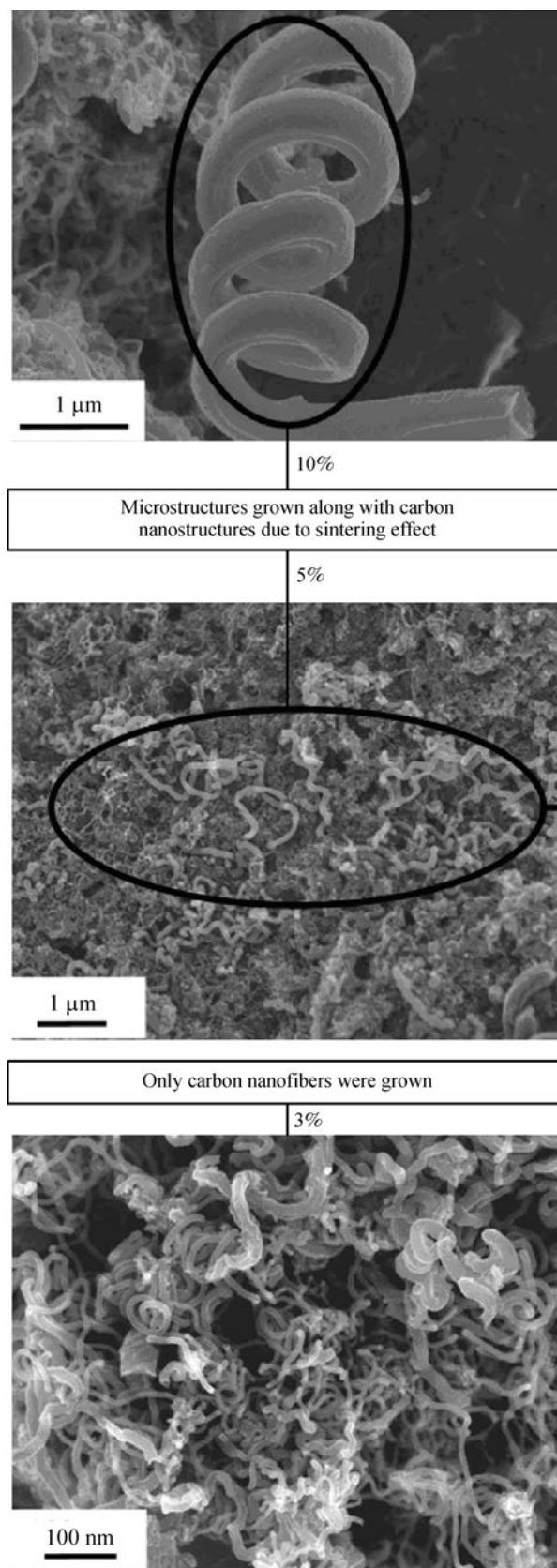
**Fig. 1** Amount of carbon deposit at different temperatures at gas flow (10 sccm C<sub>2</sub>H<sub>2</sub> : 200 sccm Ar).

in Fig. 2. The reactions were performed at various volumes of acetylene for 15 min at optimized temperature. When the flow rate was increased from 10 to 20 sccm, we observed an increased in the yield of carbon deposit; then the yield of carbon deposit was further decreased when the flow rate was increased to 30 sccm. This is because the rate of diffusion of carbon into catalyst particle was slower than that of acetylene decomposition, which would have resulted in the formation of amorphous carbon and deactivates the catalyst. So all the reactions were performed at 680°C with the gas flow of 200 sccm : 20 sccm (Ar : C<sub>2</sub>H<sub>2</sub>) for 15 min.



**Fig. 2** Amount of carbon deposit with different gas flow of acetylene, at constant flow of 200 sccm of argon at 680°C.

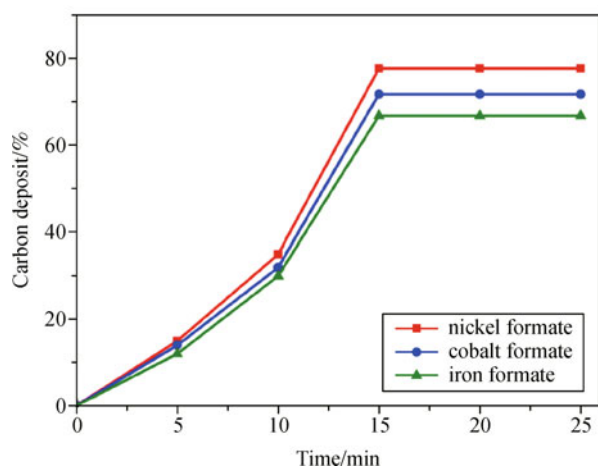
The carbon deposits obtained at different metal concentrations were analyzed by SEM, as shown in Fig. 3. The 10%, 5% and 3% metal concentration in catalyst support was studied at 680°C with gas flow rates of 10 sccm



**Fig. 3** SEM images of carbon deposits obtained at different metal concentrations in support.

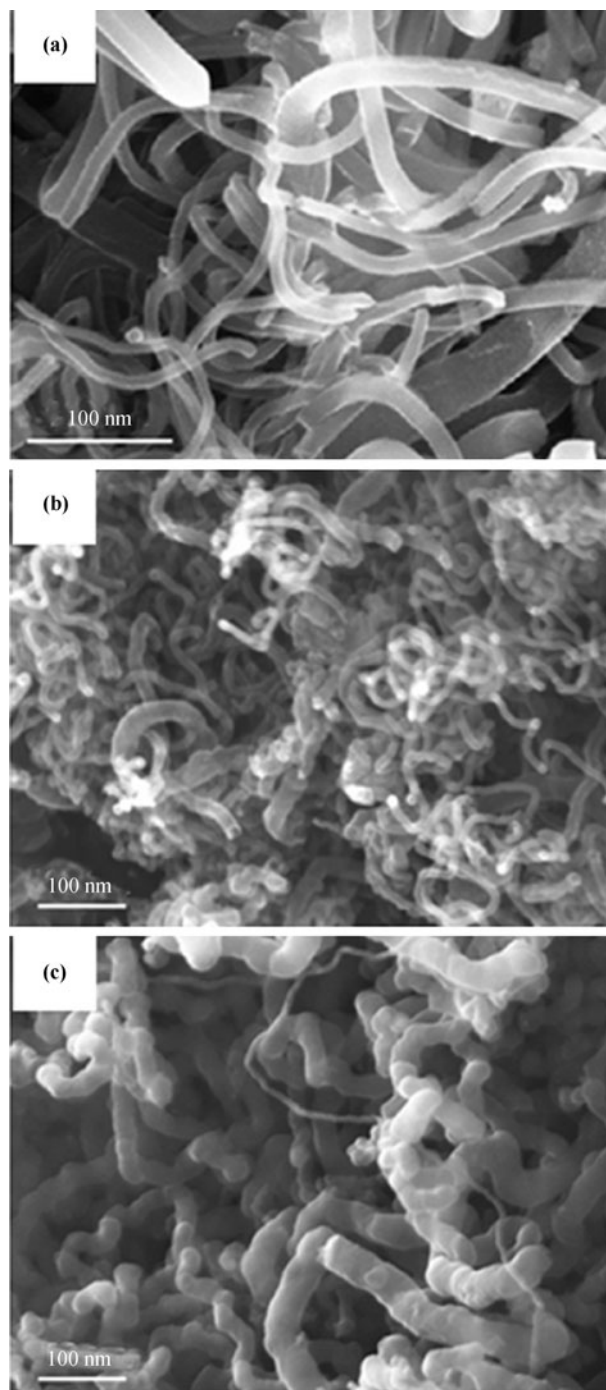
acetylene : 200 sccm argon. From SEM there was a clear evidence for the formation of microstructures for 10% and 5% metal supported catalyst used due to sintering effect of metal catalyst. But for the 3% metal supported catalyst there was no evidence for the formation of microstructures. So this clearly indicates that there was no sintering effect in the 3% supported metal catalyst.

Reaction time was fixed to 15 min after performing various experiments. Figure 4 shows the effect of reaction time on carbon yield under the constant reaction temperature of 680°C and C<sub>2</sub>H<sub>2</sub> : Ar flow rate ratio of 20/200 sccm and 3% metal supported catalyst, indicating that carbon yield increases up to 15 min. After 15 min, the yield remains constant, implying that the catalyst became inactive after 15 min. So hence the optimized reaction conditions were 20 sccm acetylene : 200 sccm argon gas flow rate, temperature at 680°C, 3 wt.% metal in support and the reaction time was 15 min for all the catalysts.



**Fig. 4** Effect of reaction time on the carbon yield over metal formats.

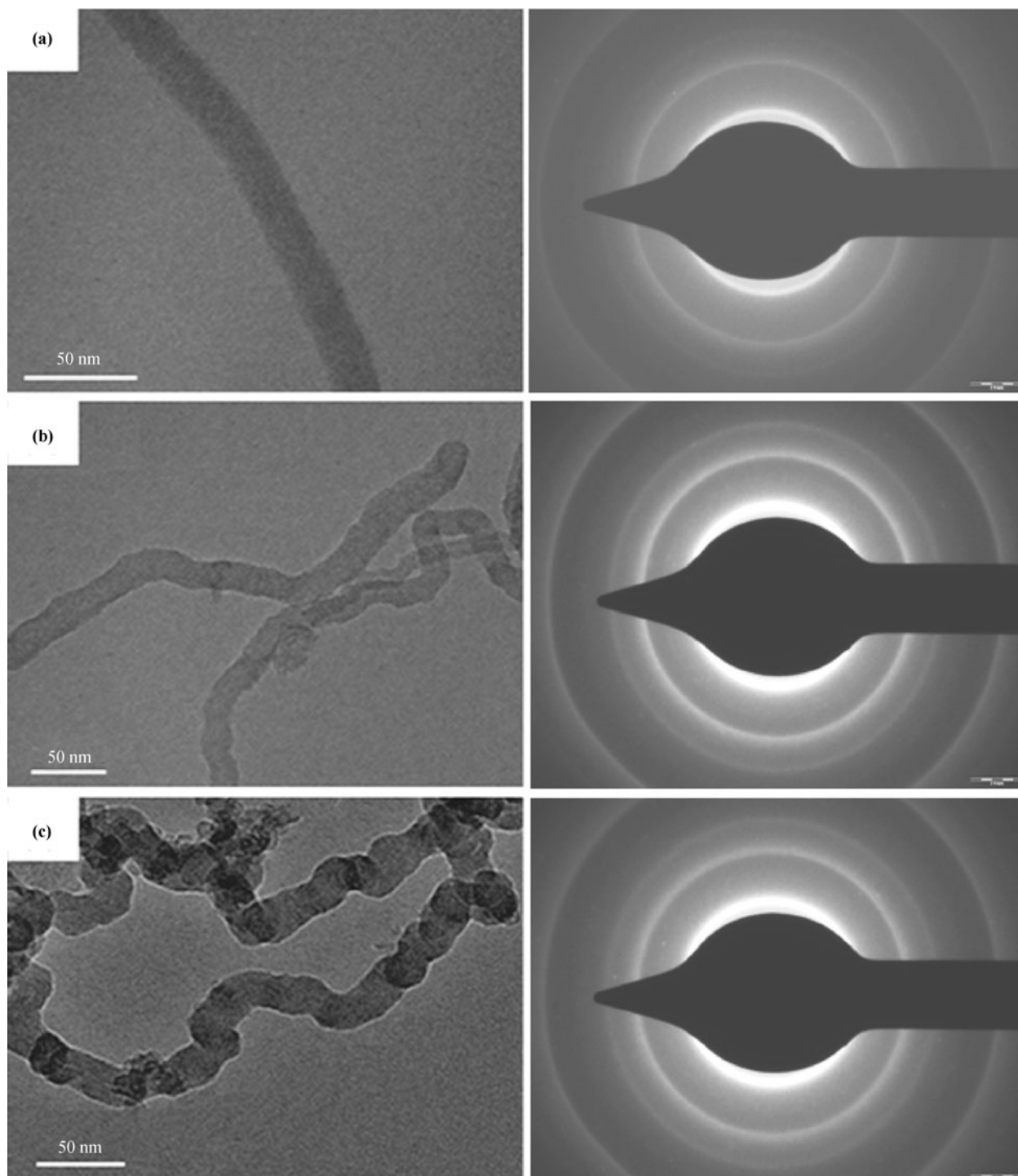
The SEM and TEM images of purified CNFs synthesized by the catalyst Ni/NaCl, Co/NaCl and Fe/NaCl are shown in Figs. 5 and 6. Most of CNFs synthesized on Ni/NaCl are straight; however some helical and twisted ones are also present. The diameter distribution is in the range of 10–40 nm. Curved nanofibers were synthesized on Co/NaCl and the diameters of these nanofibers were found to be 10–30 nm. The nanofibers synthesized by catalyst Fe/NaCl show helical morphology, with diameters ranging from 20 to 50 nm. The selected area electron diffraction (SAED) patterns taken from the synthesized CNTs show the presence of sharp graphitic (002) and (004) reflections. However, the yield of nanofibers with respect to the nickel/



**Fig. 5** SEM images of purified CNFs grown on (a) nickel formate, (b) cobalt formate, and (c) iron formate.

NaCl catalyst has been considerably higher.

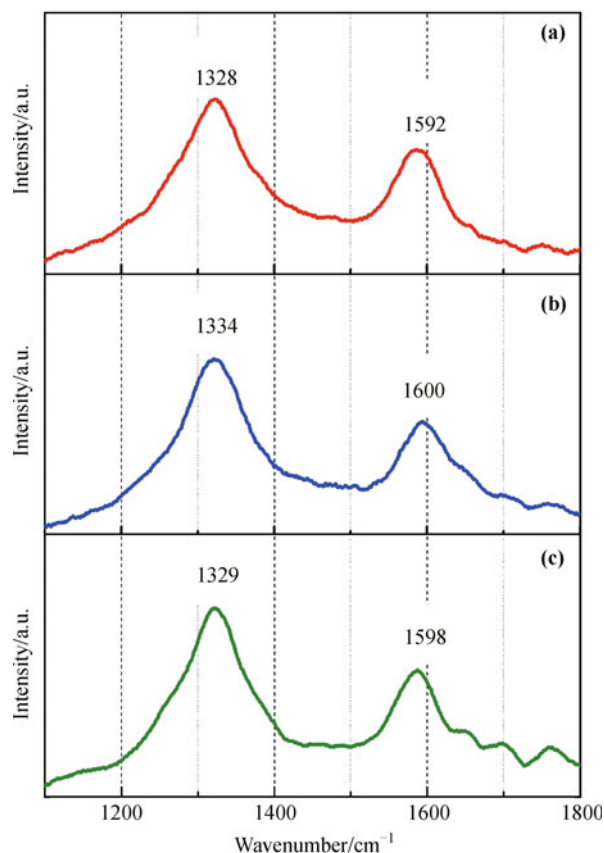
Raman spectroscopy is a useful technique to analyze the degree of graphitization of CNFs. It provides information about the crystal structure and the presence of the disorder and defects [14]. The Raman spectra of the purified CNF samples are shown in Fig. 7. The D-band, observed around 1330 cm<sup>-1</sup> for CNFs grown on catalyst Ni/NaCl, Co/NaCl



**Fig. 6** TEM images and corresponding SAED patterns of purified CNFs grown on (a) nickel formate, (b) cobalt formate, and (c) iron formate.

and Fe/NaCl is due to either the wall disorder or the presence of amorphous carbon deposited on the outer surface of nanofibers. The G-band, around  $1595\text{ cm}^{-1}$  for CNFs grown on catalyst Ni/NaCl, Co/NaCl and Fe/NaCl indicates the presence of crystalline graphitic carbon in the

CNFs. The ratio  $I_D/I_G$  of intensities of the D- and G-bands is regarded as an index for the crystalline order of CNFs. A lower  $I_D/I_G$  value indicates a higher degree of graphitization [15]. The  $I_D/I_G$  value for purified CNFs grown on Ni/NaCl, Co/NaCl and Fe/NaCl is almost unity, indicating



**Fig. 7** Raman spectra of purified CNFs grown on (a) nickel formate, (b) cobalt formate, and (c) iron formate.

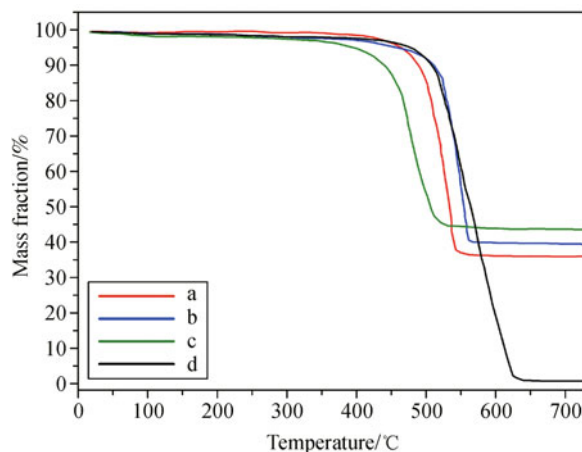
presence of defects in the CNFs.

Thermogravimetric analysis (TGA) is a useful technique to estimate the purity of CNFs [16]. The weight loss profile in Fig. 8 was obtained by heating the as grown and purified CNFs from room temperature to 700°C at a rate of 10°C/min in air atmosphere. The TGA curves indicate a significant mass drop around 500°C, which corresponds to the weight loss in the combustion of CNFs. The quantitative analysis revealed that after the single-step purification, the purity of CNF products was up to 99%.

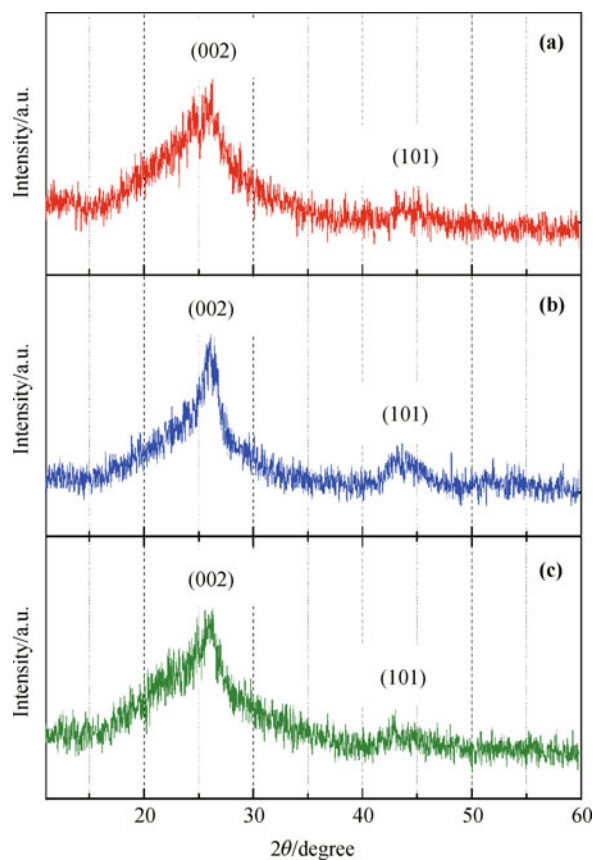
Figure 9 shows the powder XRD pattern of the purified CNF samples. The high and low peaks at 26.0° and 43.5° can be indexed to (002) and (101) diffraction planes of hexagonal graphite (JCPDS card files, no. 41-1487), respectively. The patterns clearly show that the CNFs are well graphitized and free from catalyst and support.

## 4 Conclusions

We have successfully synthesized the CNFs on large scale by using metal formate as catalysts on water soluble



**Fig. 8** TGA curves of carbon products grown on nickel formate (a), cobalt formate (b), iron formate (c), and purified product grown on cobalt formate (d).



**Fig. 9** XRD patterns of purified CNFs grown on (a) nickel formate, (b) cobalt formate, and (c) iron formate.

support. The advantage of the present synthesis technique is the simplicity and use of easily available low cost precursors. The toxic or corrosive reagents have been completely avoided. Because of the simplicity and high yield of this route, there is a raise in hope for a large scale

and low-cost synthesis of CNFs suitable for industrial application.

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