Catalytic production of carbon nanotubes by decomposition of CH_4 over the pre-reduced catalysts $LaNiO_3$, $La_4Ni_3O_{10}$, $La_3Ni_2O_7$ and La_2NiO_4

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A large amount of more graphitic carbon nanotubes with a narrow size distribution was produced from catalytic decomposition of CH_4 over pre-reduced $LaNiO_3$, $La_4Ni_3O_{10}$, $La_3Ni_2O_7$ and La_2NiO_4. The structure and component of fresh and reduced $LaNiO_3$, $La_4Ni_3O_{10}$, $La_3Ni_2O_7$ and La_2NiO_4 were determined by X-ray diffraction (XRD). The carbon nanotubes obtained were characterized by means of transmission electron microscopy (TEM) and X-ray photoelectron spectroscopy (XPS). Thermal oxidation of carbon nanotubes in air was made by thermogravimetric experiments (TG). The results revealed that the value of La/Ni in different catalyst precursors influences the diameter distribution and graphitic degree of carbon nanotubes. Lower La/Ni leads to wider diameter and higher graphitic degree of carbon nanotubes.

KEY WORDS: carbon nanotubes; $LaNiO_3$; $La_4Ni_3O_{10}$; $La_3Ni_2O_7$; La_2NiO_4; CH_4

1. Introduction

Carbon nanotubes are attracting much attention because of their novel mechanical and electronic properties. In order to suitably make use of the nanotubes, it is necessary to have them in uniform size, with a narrow size distribution. Therefore, the synthesis of carbon nanotubes has become a hot point [1–7]. To this purpose, most researchers employed metal particles to catalyze the decomposition of hydrocarbons. Compared with other synthesizing methods such as arc discharge and laser vaporization methods, the catalytic method is simple, cheap and productive. It is crucial to select and prepare an effective catalyst containing active metal particles with appropriate size, usually Fe, Co and Ni. It has been known that if the size of the metal particles is large, carbon filaments or fibers rather than Iijima-type carbon nanotubes are generally obtained [8,9]. In addition, Dai *et al.* found that the diameter of carbon nanotubes could be determined by the size of the transition metal particle [10]. Therefore, the size of metal particles seems to be very important. The catalysts reported are often metal or metal oxides supported on SiO_2, zeolite or molecular sieve [11–13]. However, the metal particle size is difficult to control in these kinds of catalysts. On the other hand, it is difficult to purify the carbon nanotubes. In the present study, by employing the citric acid complex method [14], we prepared a series of perovskite-type oxides $LaNiO_3$, $La_4Ni_3O_{10}$, $La_3Ni_2O_7$ and La_2NiO_4 with certain structures and first used them as CH_4 decomposition catalyst precursors to grow carbon nanotubes. Odier [15] revealed that $LaNiO_3$, $La_4Ni_3O_{10}$, $La_3Ni_2O_7$ and La_2NiO_4 are single phase with defined structure. The latter three can be described as $La_{n+1}Ni_nO_{3n+1}$ ($n \geqslant 1$). The catalyst precursors ($LaNiO_3$, $La_4Ni_3O_{10}$, $La_3Ni_2O_7$ and La_2NiO_4) are almost turned into La_2O_3 and active component Ni^0 with different sizes after H_2 reduction. By decomposition of CH_4 over the reduced catalysts, bulk production of high quality carbon nanotubes with dissimilar diameters was obtained. In addition, other advantages can be found employing $LaNiO_3$, $La_4Ni_3O_{10}$, $La_3Ni_2O_7$ and La_2NiO_4 as catalyst precursors: (1) purification is easy, and (2) the catalysts can be recycled. A comparison on the structure and graphitic degree among the four kinds of carbon nanotubes synthesized over the pre-reduced $LaNiO_3$, $La_4Ni_3O_{10}$, $La_3Ni_2O_7$ and La_2NiO_4 was made.

2. Experimental

$LaNiO_3$, $La_4Ni_3O_{10}$, $La_3Ni_2O_7$ and La_2NiO_4 were prepared starting with a stoichiometric mixture of the aqueous solution of nickel and lanthanum nitrates added with little excess of citric solution according to the usual procedure employed in the citric acid complex method. Given La_2NiO_4 as an example, the solution was evaporated by vigorously stirring at 70 °C. When it got very dense, it was put into an oven at 180 °C for 1.0 h. A kind of black powder was then obtained. The black powder was calcined at 500 °C for 2.0 h, subsequently at 800 °C for 4.0 h. Finally, a kind of fluffy black material was obtained.

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The carbon nanotubes were produced by catalytic decomposition of CH_4 in a fluidized-bed catalytic reactor. The catalyst precursor (0.1000 g) was packed into the reactor, and then heated in a flow of N_2 (flow rate = 30 ml/min) from room temperature to 750 °C. Then H_2 was fed into the reactor kept at a temperature of 750 °C for 1.0 h to reduce the catalyst precursor. After reduction, feed gas CH_4 (flow rate = 450 ml/min) was conducted through the reactor at the temperature of 750 °C for 30, 60 or 90 min. Then the reactor was cooled down to room temperature in an N_2 atmosphere. Thus, raw carbon nanotubes were prepared. Then the raw carbon nanotubes were purified by nitric acid.

The structure and component of fresh and reduced $LaNiO_3$, $La_4Ni_3O_{10}$, $La_3Ni_2O_7$ and La_2NiO_4 were determined by X-ray diffraction (XRD, D-MAX, Rigaku, Cu K_α radiation). The carbon nanotubes obtained were characterized by transmission electron microscopy (TEM) (Jeol IEM-100CX) and X-ray photoelectron spectroscopy (XPS) (VG ESCA MARK II). The oxidation of carbon nanotubes in air was performed through thermogravimetry (TG) (Perkin–Elmer TGA7).

3. Results and discussion

XRD results indicate that $LaNiO_3$, $La_4Ni_3O_{10}$, $La_3Ni_2O_7$ and La_2NiO_4 are single phase. After reduction in H_2 at 750 °C, they decomposed to La_2O_3 and Ni^0. A high yield of carbon nanotubes was obtained at 750 °C in the fluidized-bed reactor over the 750 °C reduced $LaNiO_3$, $La_4Ni_3O_{10}$, $La_3Ni_2O_7$ and La_2NiO_4. Correlation between reaction time and carbon nanotubes yield is also discussed. The yields of carbon nanotubes over different catalyst precursors, using 0.1000 g catalyst precursor in different reaction time, are given in table 1. Clearly, with the increase of the content of Ni in catalyst precursors from La_2NiO_4 to $LaNiO_3$, the yields of carbon nanotubes also increase. With the reaction time extended, more amount of carbon nanotubes was obtained from 30 to 60 min, but there was only little increase from 60 to 90 min. After 60 min, some active components (Ni^0) were encapsulated by carbon nanotubes, resulting in the growing speed decrease. Accordingly, 60 min is taken as a typical reaction time.

Figure 1 shows the typical TEM images of as-synthesized carbon nanotubes over different catalyst precursors of nickel composite oxides. As the TEM images show, there lies some distinctness among the four kinds of carbon nanotubes. The ranges of diameter and the average diameters of different carbon nanotubes are listed in table 2. A trend can be drawn from table 2: if the ratio of La/Ni in catalyst precursor is bigger, the outer-diameter is smaller and the inner-diameter is also smaller. The catalyst precursors ($LaNiO_3$, $La_4Ni_3O_{10}$, $La_3Ni_2O_7$ and La_2NiO_4) were almost turned into La_2O_3 and

Table 1
Yields of carbon nanotubes obtained from dissimilar catalysts with different reaction time.

Catalyst precursor	Ni	Carbon nanotubes yield (g)		
(100 mg)	(%)	30 min	60 min	90 min
La_2NiO_4	14.66	0.2026	0.342	0.3095
$La_3Ni_2O_7$	18.17	0.3479	0.5068	0.5254
$La_4Ni_3O_{10}$	19.76	0.4026	0.5983	0.6112
$LaNiO_3$	23.90	0.4513	0.6494	0.6552

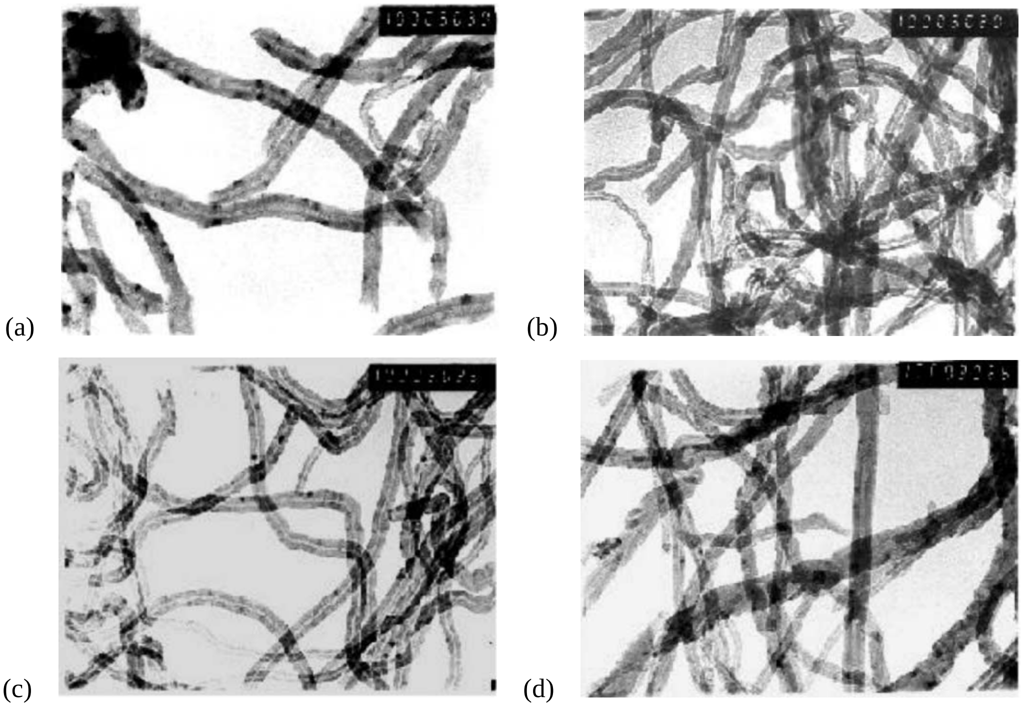

Figure 1. TEM images (×100 000) of CNTs produced from catalytic decomposition of CH_4 over the pre-reduced (a) $LaNiO_3$, (b) $La_4Ni_3O_{10}$, (c) $La_3Ni_2O_7$ and (d) La_2NiO_4 at 750 °C .

Ni^0 by reduction at 750 °C, and La_2O_3 can prevent Ni^0 from agglomeration. With the variation of the ratio of La/Ni in $La_xNi_yO_z$, the amount of La_2O_3 varies after reduction, so the degree of the effect of preventing Ni^0 from agglomerating by La_2O_3 varies. According to the XRD results of $La_xNi_yO_z$ being reduced in H_2 at 750 °C, one can estimate the particle size of nickel based on the correlation

$$L = 0.89\lambda/\beta\cos\theta,$$

where L is the average particle size, λ is the wavelength of Cu K_α radiation (0.154 nm), β is the half-height width of diffraction peaks, θ is the Bragg angle. The estimated sizes of the Ni^0 particles showed a declining order of $LaNiO_3$ (12.5 nm) > $La_4Ni_3O_{10}$ (9.6 nm) > $La_3Ni_2O_7$ (8.2 nm) > La_2NiO_4 (6.8 nm). The diameters of carbon nanotubes synthesized by $LaNiO_3$, $La_4Ni_3O_{10}$, $La_3Ni_2O_7$ and La_2NiO_4 revealed the same order. It can be drawn that the diameter of carbon nanotubes depends on the particle size of Ni^0. This is consistent with the literature [10]. Viewing on the structure, we can formulate $La_4Ni_3O_{10}$, $La_3Ni_2O_7$ and La_2NiO_4 as $La_{n+1}Ni_nO_{3n+1}$ ($n \geqslant 1$). La_2NiO_4 can be described as $LaNiO_3$/LaO, $La_3Ni_2O_7$ as $2LaNiO_3$/LaO and $La_4Ni_3O_{10}$ as $3LaNiO_3$/LaO. $LaNiO_3$ is a perovskite unit, LaO is a rock salt layer. After being reduced, LaO can prevent nickel particles from agglomerating. The higher the LaO unit concentration in the catalysts is, the smaller the size of nickel particles will be after reduction. No LaO rock salt in $LaNiO_3$, so after reduction there are the biggest nickel particles in it. Then on the reduced $LaNiO_3$ catalyst, the widest CNTs were generated. In contrast, in La_2NiO_4, the ratio of LaO rock salt layer and $LaNiO_3$ perovskite unit is 1 : 1, highest among $LaNiO_3$, $La_4Ni_3O_{10}$, $La_3Ni_2O_7$ and La_2NiO_4, the smallest nickel particles would be formed after La_2NiO_4 was H_2 reduced. Thus, over the reduced La_2NiO_4, the narrowest CNTs were obtained. With the development of the application of carbon nanotubes, a more exacting diameter is required. From the above observation, the present method may be promising to synthesize diameter-controllable carbon nanotubes in certain array. Figure 1(a) shows that the carbon nanotubes include non-cylindrical layer-by-layer tubes, especially similar to boron–carbon nanotubes from the pyrolysis of C_2H_2–B_2H_2 mixture [16].

Table 2
The ranges of diameter and the average diameter of different carbon nanotubes synthesized by dissimilar catalysts.

Catalyst	Diameter (nm)		Average diameter (nm)	
	Outer	Inner	Outer	Inner
$LaNiO_3$	20–45	10–20	35	12
$La_4Ni_3O_{10}$	20–40	6–10	30	10
$La_3Ni_2O_7$	10–30	5–15	25	8
La_2NiO_4	10–40	5–15	20	6

The oxidation of obtained carbon nanotubes in air has been studied over thermogravimetry. The results are shown in figure 2. In figure 2, it is clear that the oxidation of carbon nanotubes obtained over the pre-reduced $LaNiO_3$, $La_4Ni_3O_{10}$, $La_3Ni_2O_7$ and La_2NiO_4 samples occurred at *ca.* 653.00, 645.45, 640.09 and 636.05 °C, respectively, which were higher than that reported by Kukovitsku (*ca.* 420 °C) [17]. It has been reported that graphite could be oxidized at *ca.* 520 °C [17]. The higher the oxidation temperature is, the more graphitic the carbon nanotubes will be. The more graphitic carbon nanotubes will be utilized widely. Probably, rare earth metals such as La added in catalysts may influence the graphitic degree of the carbon nanotubes obtained. It is evident that carbon nanotubes with good quality can be prepared from $La_xNi_yO_z$ precursors.

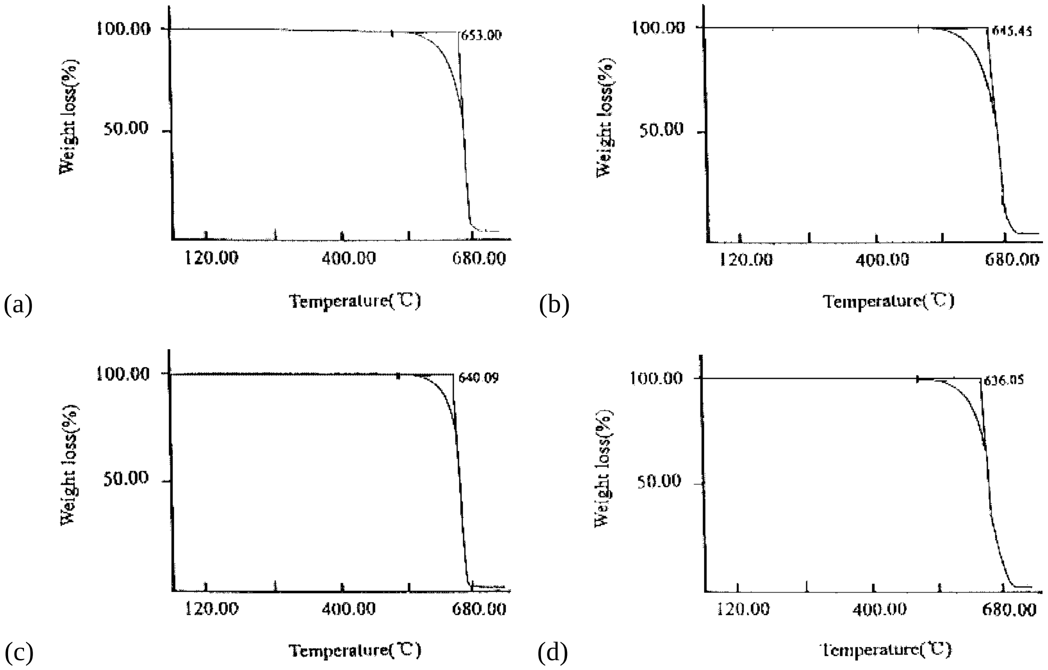

Figure 2. The TG plot during oxidation of CNTs prepared over the pre-reduced (a) $LaNiO_3$, (b) $La_4Ni_3O_{10}$, (c) $La_3Ni_2O_7$ and (d) La_2NiO_4.

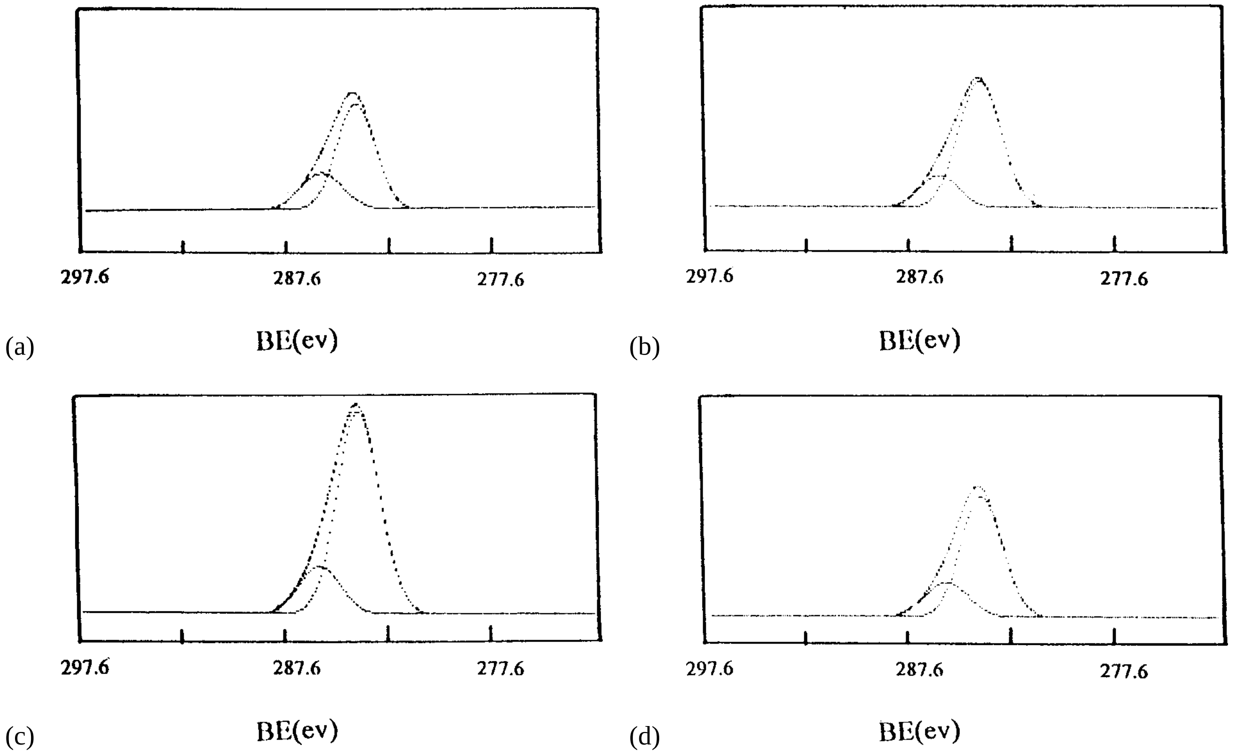

Figure 3. XPS spectra of carbon nanotubes synthesized over the pre-reduced (a) $LaNiO_3$, (b) $La_4Ni_3O_{10}$, (c) $La_3Ni_2O_7$ and (d) La_2NiO_4.

Besides, the sequence of the initializing oxidation temperature of different carbon nanotubes is related to the ratio of La/Ni in $La_xNi_yO_z$. The lower the ratio of La/Ni is, the more graphitic carbon nanotubes will be obtained. Considering the size of carbon nanotubes, we concluded that the narrower tubes are easier to be oxidized.

The XPS spectra for carbon nanotubes shown in figure 3 revealed that the electron binding energy (C $1s_{1/2}$) of carbon nanotubes synthesized by $LaNiO_3$, $La_4Ni_3O_{10}$, $La_3Ni_2O_7$ and La_2NiO_4 are 284.11, 284.04, 283.94 and 283.92 eV, respectively. The results imply that the carbon nanotubes obtained are more graphitic and also suggest that the value of La/Ni may influence the graphitic degree of carbon nanotubes.

4. Conclusion

The reduced La–Ni mixed oxides $LaNiO_3$, $La_4Ni_3O_{10}$, $La_3Ni_2O_7$ and La_2NiO_4 are good catalyst precursors to grow a large amount of regular and more graphitic carbon nanotubes. In a certain range, the diameter of carbon nanotubes can be controlled through varying the ratio of La/Ni.

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