

## A Study on Production of Carbon Nanotubes by CH<sub>4</sub> Decomposition over LaNiO<sub>3</sub>, La<sub>4</sub>Ni<sub>3</sub>O<sub>10</sub>, La<sub>3</sub>Ni<sub>2</sub>O<sub>7</sub> and La<sub>2</sub>NiO<sub>4</sub>

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**Abstract:** Carbon nanotubes (CNTs) of narrow size distribution can be abundantly produced in the catalytic decomposition of CH<sub>4</sub> over pre-reduced LaNiO<sub>3</sub>, La<sub>4</sub>Ni<sub>3</sub>O<sub>10</sub>, La<sub>3</sub>Ni<sub>2</sub>O<sub>7</sub> and La<sub>2</sub>NiO<sub>4</sub>. The CNTs obtained were characterized by means of transmission electron microscopy (TEM). Thermal oxidation of CNTs in air was monitored thermogravimetrically (TG). The results revealed that a lower La/Ni ratio of the catalysts would lead to a wider diameter distribution and a higher degree of graphitic nature.

**Keywords:** Carbon nanotubes, LaNiO<sub>3</sub>, La<sub>2</sub>NiO<sub>4</sub>, La<sub>3</sub>Ni<sub>2</sub>O<sub>7</sub>, La<sub>4</sub>Ni<sub>3</sub>O<sub>10</sub>, CH<sub>4</sub>.

### Introduction

In the present study, by employing the citric acid complex method<sup>1</sup>, we prepared a series of perovskite-type oxides, viz. LaNiO<sub>3</sub>, La<sub>4</sub>Ni<sub>3</sub>O<sub>10</sub>, La<sub>3</sub>Ni<sub>2</sub>O<sub>7</sub> and La<sub>2</sub>NiO<sub>4</sub> for the growth of CNTs. After H<sub>2</sub> reduction, the catalysts turn into La<sub>2</sub>O<sub>3</sub> and active component Ni<sup>0</sup> of various sizes. By means of CH<sub>4</sub> decomposition over the reduced catalysts, high quality CNTs with dissimilar diameters can be generated in mass amount. In this paper, we attempt to make a comparison on the structure, graphitic nature among the four kinds of CNTs synthesized over the pre-reduced LaNiO<sub>3</sub>, La<sub>4</sub>Ni<sub>3</sub>O<sub>10</sub>, La<sub>3</sub>Ni<sub>2</sub>O<sub>7</sub> and La<sub>2</sub>NiO<sub>4</sub> materials, respectively.

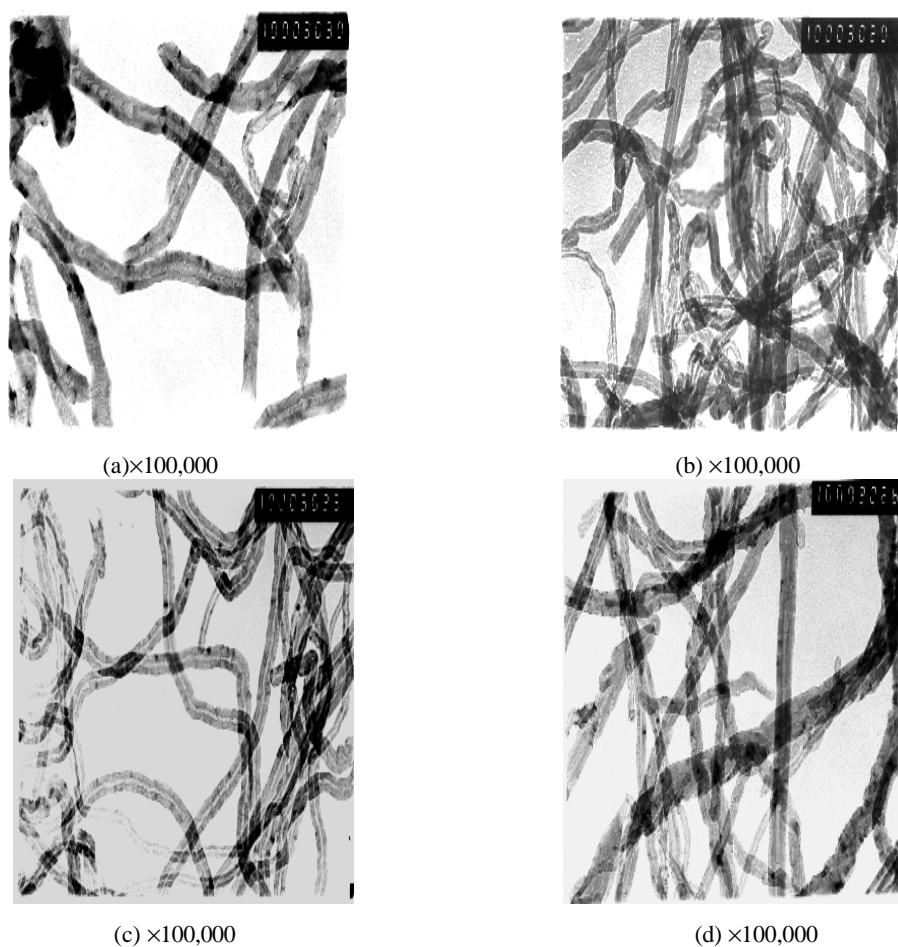
### Experimental

The LaNiO<sub>3</sub>, La<sub>4</sub>Ni<sub>3</sub>O<sub>10</sub>, La<sub>3</sub>Ni<sub>2</sub>O<sub>7</sub> and La<sub>2</sub>NiO<sub>4</sub> catalysts were prepared by complex method. The CNTs were generated by catalytic decomposition of CH<sub>4</sub> over LaNiO<sub>3</sub>, La<sub>4</sub>Ni<sub>3</sub>O<sub>10</sub>, La<sub>3</sub>Ni<sub>2</sub>O<sub>7</sub> and La<sub>2</sub>NiO<sub>4</sub> in a fluidized-bed catalytic reactor at 750°C for 60 min. The raw CNTs were then treated in nitric acid for purification. The CNTs obtained were characterized by transmission electron microscopy (TEM) (JEOL IEM-100CX). The TGA study of the oxidation of CNTs was performed in air (Perkin-Elmer TGA7).

## Results and discussion

**Figure 1** shows the typical TEM images of as-synthesized CNTs obtained over different catalysts of nickel composite oxides. One can observe that there are clear differences between the four kinds of CNTs. The range of diameter and the average diameters of

**Figure 1** TEM images of CNTs produced over (a)  $\text{LaNiO}_3$ , (b)  $\text{La}_4\text{Ni}_3\text{O}_{10}$ , (c)  $\text{La}_3\text{Ni}_2\text{O}_7$  and (d)  $\text{La}_2\text{NiO}_4$



the CNTs are listed in **Table 1**. With the increase in La/Ni ratio of the catalysts, the CNTs outer- and inner-diameters become smaller.

With the variation of the La/Ni ratio in  $\text{La}_x\text{Ni}_y\text{O}_z$ , the amount of  $\text{La}_2\text{O}_3$  generated after reduction varied, so the effect of  $\text{La}_2\text{O}_3$  in preventing  $\text{Ni}^0$  from agglomerating varied. According to the XRD results of  $\text{La}_x\text{Ni}_y\text{O}_z$  reduction in  $\text{H}_2$  at  $750^\circ\text{C}$ , the estimated size of the  $\text{Ni}^0$  particles shows a declining order of  $\text{LaNiO}_3 > \text{La}_4\text{Ni}_3\text{O}_{10} > \text{La}_3\text{Ni}_2\text{O}_7 > \text{La}_2\text{NiO}_4$ . The diameters of CNTs synthesized over  $\text{LaNiO}_3$ ,  $\text{La}_4\text{Ni}_3\text{O}_{10}$ ,  $\text{La}_3\text{Ni}_2\text{O}_7$ ,  $\text{La}_2\text{NiO}_4$  decline in the same order. The present method appears to be promising in the synthesis of

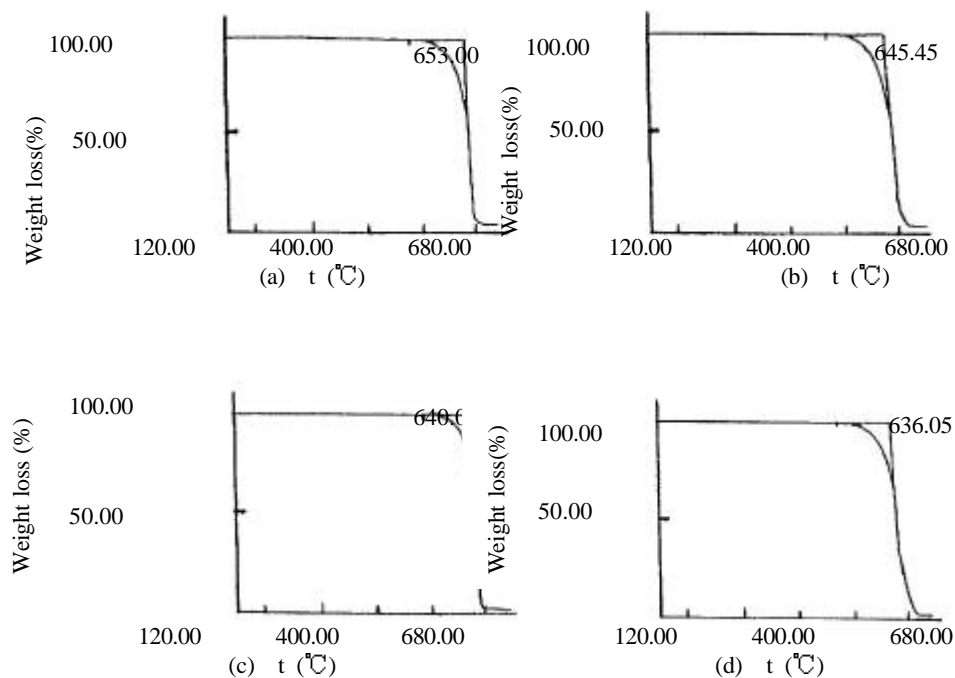
carbon nanotubes in a diameter-controlled manner.

**Table 1** The range and average diameter of the CNTs synthesized over the catalysts

Catalyst	Diameter range (nm)		Average Diameter (nm)	
	outer-	inner-	outer-	inner-
LaNiO <sub>3</sub>	20~45	10~20	35	12
La <sub>4</sub> Ni <sub>3</sub> O <sub>10</sub>	20~40	6~10	30	10
La <sub>3</sub> Ni <sub>2</sub> O <sub>7</sub>	10~30	5~15	25	8
La <sub>2</sub> NiO <sub>4</sub>	10~40	5~15	20	6

The oxidation of the obtained CNTs has been studied in air by means of thermogravimetry (**Figure 2**). It is clear that the threshold temperatures for the oxidation of the CNTs obtained over the LaNiO<sub>3</sub>, La<sub>4</sub>Ni<sub>3</sub>O<sub>10</sub>, La<sub>3</sub>Ni<sub>2</sub>O<sub>7</sub> and La<sub>2</sub>NiO<sub>4</sub> samples were *ca* 653.00°C, 645.45°C, 640.09°C and 636.05°C, respectively, about 220°C higher than that reported by Kukovitskii (*ca* 420°C)<sup>2</sup>. It has been reported that graphite could be oxidized in air at *ca* 520°C<sup>2</sup>. For the CNTs, which are more graphitic in nature, threshold temperature for oxidation should be higher.

**Figure 2** The TG plot during oxidation of CNTs prepared over (a) LaNiO<sub>3</sub>, (b) La<sub>4</sub>Ni<sub>3</sub>O<sub>10</sub>, (c) La<sub>3</sub>Ni<sub>2</sub>O<sub>7</sub> and (d) La<sub>2</sub>NiO<sub>4</sub>



Probably, the increase of La content in the catalysts influences the degree of graphitic

nature and quality of the CNTs produced. We observed that the lower the La/Ni ratio is, the higher is the graphitic nature and thermal resistance in air.

### Conclusion

The reduced  $\text{LaNiO}_3$ ,  $\text{La}_4\text{Ni}_3\text{O}_{10}$ ,  $\text{La}_3\text{Ni}_2\text{O}_7$  and  $\text{La}_2\text{NiO}_4$  are good catalysts for the mass production of CNTs with enhanced graphitic nature. The diameter of the CNTs can be confined to a narrow range through the variation of the La/Ni ratio.

### Acknowledgment

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### References

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