A study on carbon nanotubes prepared from catalytic decomposition of C_2H_2 or CH_4 over the pre-reduced $LaCoO_3$ perovskite precursor

B.C. Liu *, L.Z. Gao, Q. Liang, S.H. Tang, M.Z. Qu and Z.L. Yu **

Chengdu Institute of Organic Chemistry, Chinese Academy of Sciences, Chengdu 610041, PR China
E-mail: lzgao1@hotmail.com

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A large amount of carbon nanotubes with uniform diameter were produced from catalytic decomposition of C_2H_2 or CH_4 over perovskite oxide $LaCoO_3$ catalyst precersor. The result of XRD measurement indicated that after reduction of $LaCoO_3$ at 700 °C cobalt existed chiefly as Co^0 particles supported and separated by La_2O_3. La_2O_3 can prevent Co^0 from agglomeration. The size of Co^0 nanoparticles determined the diameter of carbon nanotubes. The morphologies and microscopic structure of carbon nanotubes were examined by means of scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD) and Raman. Reduction of $LaCoO_3$ in H_2 and thermal oxidation of carbon nanotubes in air were made by thermogravimetric experiments (TG). XPS and Raman results revealed that the carbon nanotubes made from CH_4 are probably more graphitized than those made from C_2H_2.

KEY WORDS: carbon nanotubes; $LaCoO_3$; CH_4; C_2H_2; graphitization

1. Introduction

Carbon nanotubes have attracted much attention in recent years, not only for their small dimension and unique morphologies, but also for their potential of applications in various technologies. The synthesis of carbon nanotubes has become a hot topic [1–7]. Among the current methods employed such as arc discharge, laser vaporization and catalytic methods for carbon nanotubes synthesis, the catalytic method is simple, cheap and productive. In the catalytic method, it is crucial to select and prepare an effective catalyst with appropriate size of active metal particles, usually Fe, Co or Ni. Among them, cobalt was claimed to give rise to the best quality carbon nanotubes [8]. It has been known that if the particle size of the metals is large, carbon filaments or fibers rather than the Iijima-type carbon nanotubes are generally obtained [9,10]. In addition, Dai et al. found that the diameter of carbon nanotubes could be determined by the size of transition metal particles [11]. Therefore, the size of metal particles seems to be very important. In the past decades, perovskite-type oxides have been studied extensively as the catalysts for some catalytic reactions, especially in hydrocarbon activation [12,13]. So far, however, no report is encountered in literature about using perovskite-type oxides as catalyst precursors for the growth of carbon nanotubes. In the present study, by using perovskite-type oxide $LaCoO_3$ as a catalyst precursor, we obtained bulk production of high quality carbon nanotubes and made a comparison on the morphology, structure and graphitic degree between the two kinds of carbon nanotubes generated from CH_4 and C_2H_2 catalytic decomposition, respectively.

* On leave from Nanjing University of Chemical Technology, Nanjing 210009, PR China.
** To whom correspondence should be addressed.

2. Experimental

$LaCoO_3$ was synthesized by the citric acid complexing method. In brief, excess of citric solution was added to a mixed aqueous solution of cobalt and lanthanum nitrates with appropriate stoichiometry. The solution was evaporated with vigorously stirring at 80 °C. When it got dense, the evaporation temperature was increased to 100 °C, and gradually, the slurry burned and turned into a black powder. The black powder obtained was calcined at 600 °C for 1.0 h, subsequently at 800 °C for 3.0 h. Finally, a fluffy black material was obtained. The XRD pattern of the catalyst precursor identified that it is a single phase of $LaCoO_3$ with a cubic ABO_3 perovskite structure.

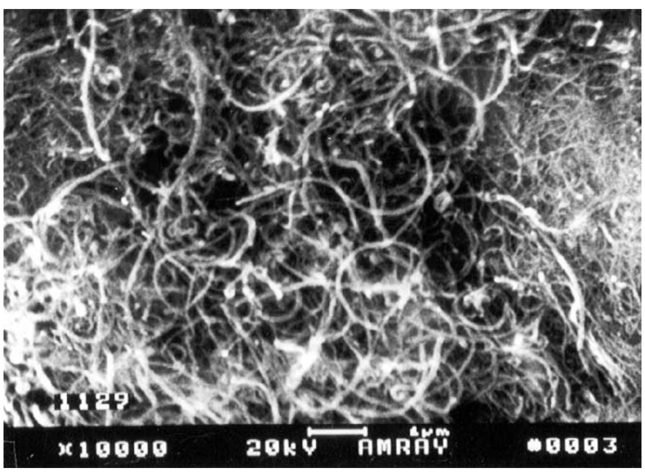
The carbon nanotubes were synthesized by using a fluidized-bed catalytic reactor. The $LaCoO_3$ catalyst precursor (100 mg) was packed into the reactor, and then was heated in a flow of N_2 (flow rate 25 ml/min) from room temperature to 700 °C. Then H_2 was conducted into the reactor at the same temperature for 1.0 h to reduce $LaCoO_3$. After reduction, feed gas C_2H_2 ($C_2H_2/N_2 = 1/9$, v/v, flow rate 700 ml/min) or CH_4 (flow rate 460 ml/min) was introduced through the reactor at the temperature of 700 °C for 30 min. After the scheduled time, the reactor was cooled down to room temperature by the passage of nitrogen gas. Thus, we have synthesized carbon nanotubes without purification. The carbon nanotubes were then washed in nitric acid for purification.

The morphologies and microscopic structure of carbon nanotubes were characterized by scanning electron microscopy (SEM) (KYKY-AMRAY-1000B), transmission electron microscopy (TEM) (Jeol JEM-100CX), X-ray diffraction (XRD) (D/max-rA), X-ray photoelectron spectroscopy (XPS) (VG ESCA MARK II) and Raman spectroscopy (Dilor XY 800 1 cm^{-1}). The reduction of $LaCoO_3$ in H_2 (H_2/He = 1/9, v/v, flow rate 30 ml/min) and oxidation of carbon nanotubes in air were performed over thermogravimetry (TG) (Perkin–Elmer TGA7) (scanning rate 10 °C/min, 4.040 mg of samples).

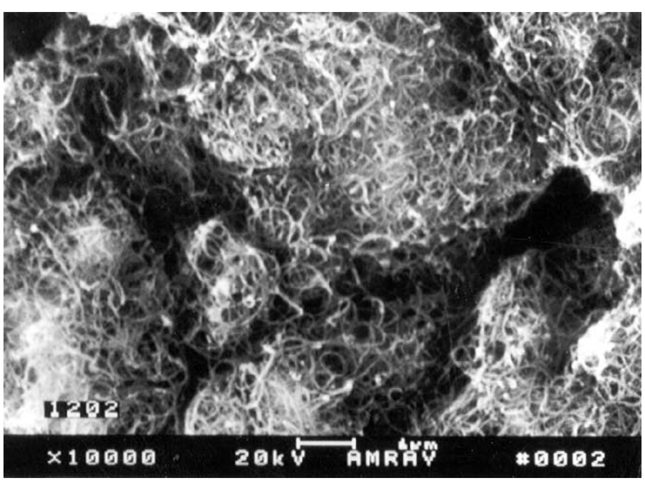
3. Results and discussion

In our reactor scale, we obtained a high yield of carbon nanotubes at 700 °C. We synthesized 27.9 g of carbon nanotubes over 1 g catalyst in 1 h by decomposition of CH_4. Over 1 g catalyst, in 1 h, using C_2H_2 as carbon source we could produce 22.0 g carbon nanotubes. Using C_2H_2 as carbon source, C_2H_2 has to be diluted, whereas using CH_4 as carbon source, it need not. Figure 1 shows the typical SEM images of as-synthesized carbon nanotubes showing the presence of a large number of carbon nanotubes with entangled shape. It clearly illustrates the homogeneity of the tubes. The lengths of carbon nanotubes are up to ~20 μm. The carbon nanotubes were contaminated slightly by the amorphous carbon. Figure 2 shows the typical TEM images of as-synthesized carbon nanotubes. The TEM observations reveal that the diameters of carbon nanotubes are ca. 10–30 and ca. 10–40 nm made from CH_4 and C_2H_2, respectively. In general, the diameters of carbon nanotubes produced over the $LaCoO_3$ precursor are even, comparatively, the carbon nanotubes from CH_4 are more regular than those from C_2H_2. We observed helix-shaped carbon nanotubes in the carbon nanotubes from C_2H_2 (figure 2(b)). This is consistent with the literature [14]. However, helix-shaped carbon nanotubes could not be produced by CH_4.

According to the XRD calculations, we found that the diameters of carbon nanotubes were frequently close to the size of the Co nanoparticles. TEM observation indicated that the particle size of the reduced catalyst is near to 20 nm.

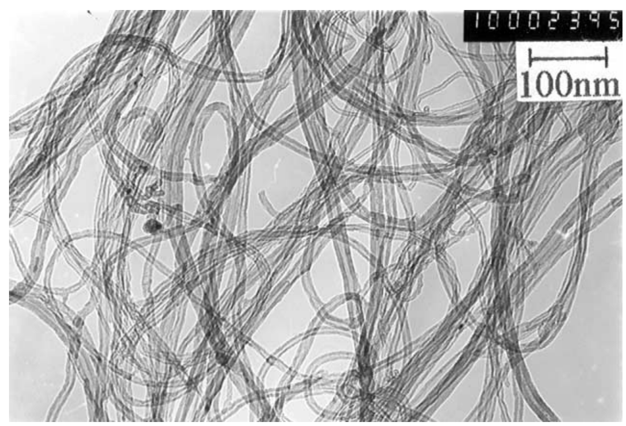


(a)

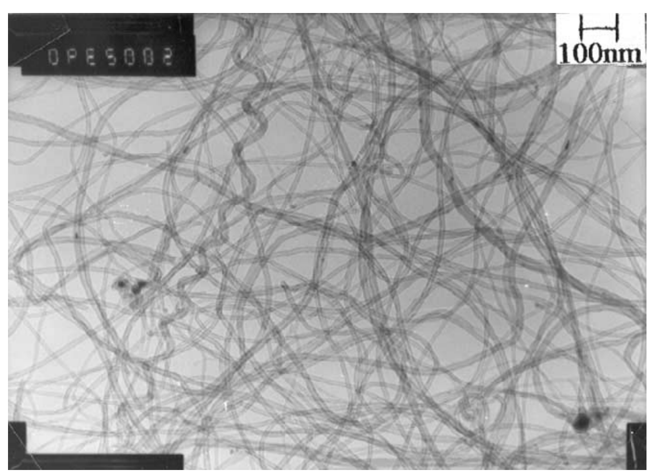


(b)

Figure 1. SEM images of carbon nanotubes obtained from decomposition of (a) CH_4 and (b) C_2H_2.



(a)



(b)

Figure 2. TEM images of carbon nanotubes obtained from decomposition of (a) CH_4 and (b) C_2H_2.

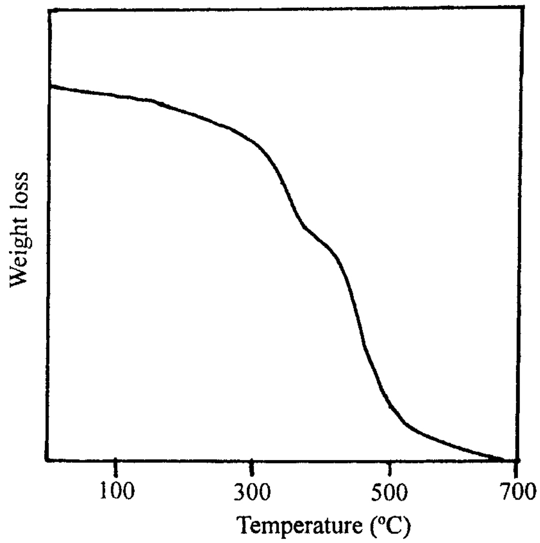


Figure 3. The TG plot during reduction of $LaCoO_3$ in H_2.

In ABO_3 perovskite lattice, the Co^{3+} and La^{3+} ions were evenly distributed each other. Figure 3 shows the TG plot of $LaCoO_3$ in H_2. We found that it was reduced through two steps, at 320 and 442 °C. At 700 °C, it had completely been reduced. According to the weight loss, we estimated that most of Co^{3+} has been reduced to metallic cobalt. XRD results confirmed that after reduction at 700 °C, the perovskite structure of $LaCoO_3$ has been collapsed and transformed into Co^0 and La_2O_3; cobalt exists chiefly as Co^0 and La_2O_3 prevents Co^0 particles from agglomeration. Well-dispersed Co^0 nanoparticles are very advantageous for the growth of carbon nanotubes, resulting in relatively well graphitized hollow nanotubes of more uniform size. Comparing with arc discharge and laser vaporization methods, we found obviously other advantages using this kind of catalyst precursor: (i) the reaction temperature is milder, and (ii) purification and separation of carbon nanotubes are convenient due to freely soluble catalyst in acid.

Figure 4 shows the X-ray diffraction patterns of carbon nanotubes. We can observe the maximum position of a strongest (002) diffraction peak of carbon nanotubes which coincides approximately with that of graphite. The interlayer spacing (d_{002}) within multi-walled carbon nanotubes from decomposition of C_2H_2 is 0.3455 nm, whereas that from decomposition of CH_4 is 0.3442 nm, wider by a few percent than that of an ideal graphite crystal (0.3354 nm). This fact was ascribed to a combination of tubular curvature and *van der Waals* force interactions between successive graphene layers. The wide interplanar spacing is characteristic of the turbostratic carbon.

The oxidation of obtained carbon nanotubes in air has been studied over thermogravimetry. The results are shown in figure 5. From figure 5, it is clear that the oxidation of the carbon nanotubes made from C_2H_2 occurred at a temperature of ca. 552.7 °C and the oxidation of carbon nanotubes made from CH_4 occurred at the temperature of ca. 526.4 °C, which were higher than those reported by Kukovitsku

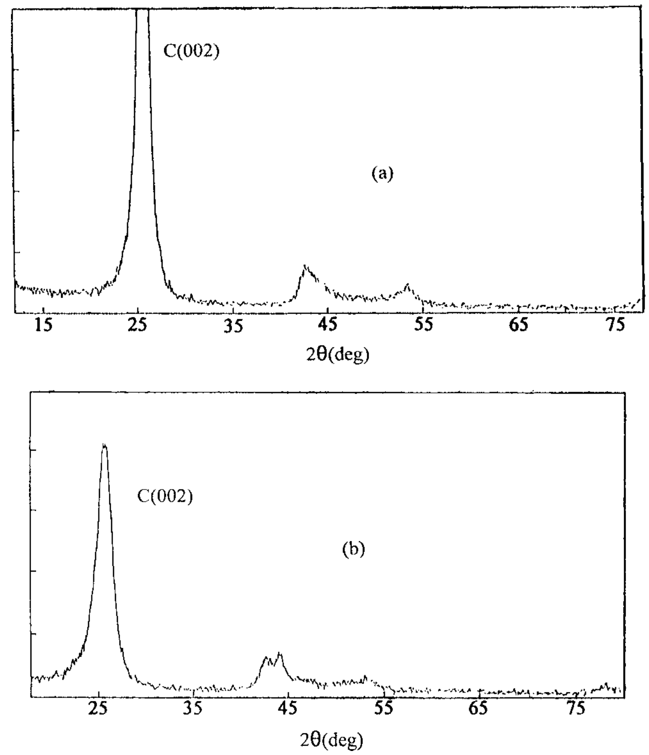


Figure 4. XRD patterns of carbon nanotubes obtained from decomposition of (a) CH_4 and (b) C_2H_2.

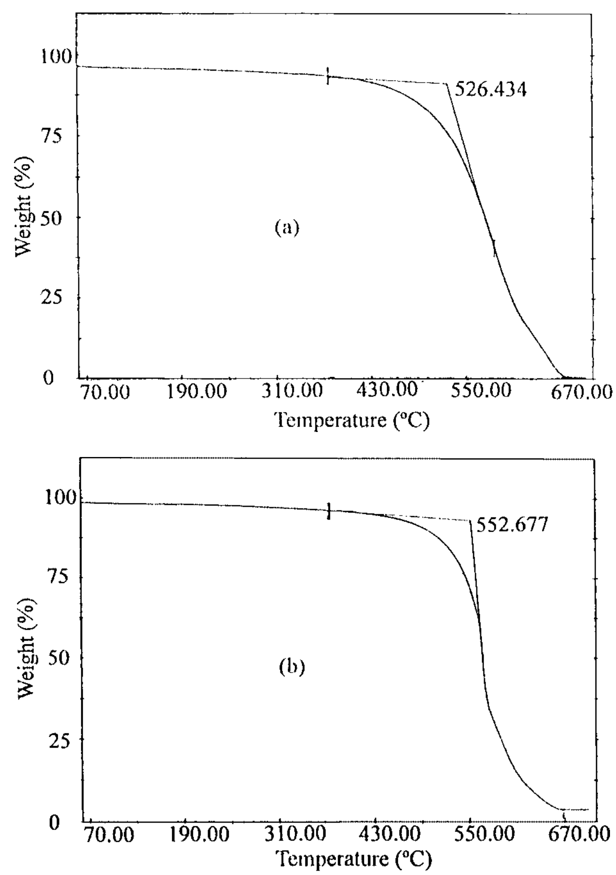


Figure 5. The TG plots during oxidation of carbon nanotubes obtained from decomposition of (a) CH_4 and (b) C_2H_2.

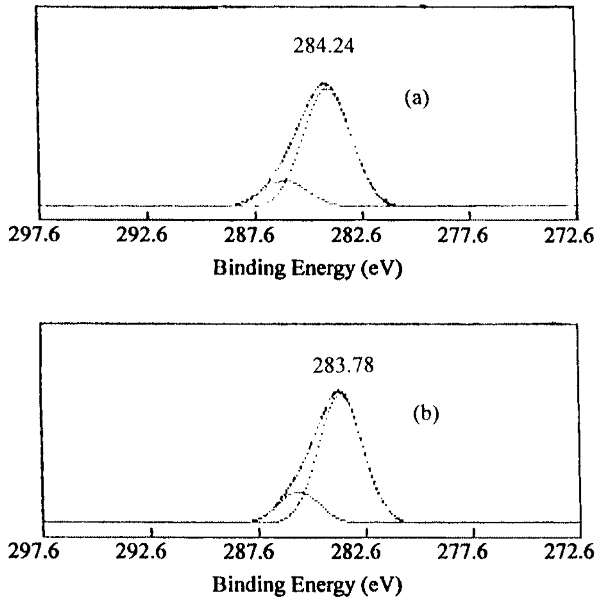


Figure 6. XPS spectra of carbon nanotubes obtained from decomposition of (a) CH_4 and (b) C_2H_2.

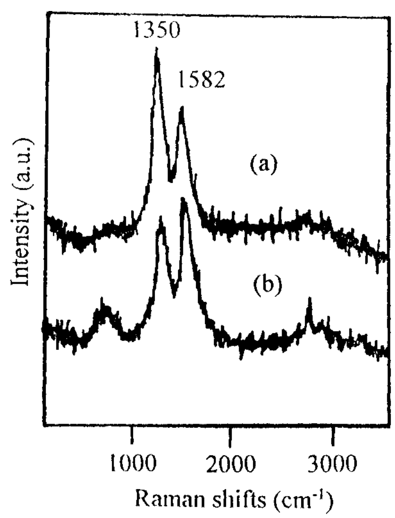


Figure 7. Raman spectra of carbon nanotubes obtained from decomposition of (a) CH_4 and (b) C_2H_2.

(ca. 420 °C) [15]. It has been reported that graphite could be oxidized at ca. 520 °C [15]. We suggest that the carbon nanotubes made from C_2H_2 and CH_4 are highly graphitic. It has been reported that the CNTs made from arc discharge were oxidized over 700 °C [16]. We deduced that the arc discharge could make higher graphitized CNTs than the present catalytic method. SEM (figure 1) photos also indicated that a little amorphous carbon existed in the carbon nanotubes.

The XPS spectra for carbon nanotubes shown in figure 6 revealed that the electron binding energy (C $1s_{1/2}$) of carbon nanotubes from decomposition of C_2H_2 was 283.78 eV, and that from decomposition of CH_4 was 284.24 eV. The C $1s_{1/2}$ of graphite is 284.3 eV. The results implied that the carbon nanotubes from CH_4 are possibly more graphitized.

Figure 7 shows the Raman scattering spectra of carbon nanotubes made from CH_4 and C_2H_2. In figure 7, one can observe peaks at 1350 cm^{-1} (D band) and 1582 cm^{-1} (G band). These indicate that the carbon nanotubes are higher graphitized and exhibit less lattice distortion. We also observed that the intensity of band at 1350 cm^{-1} in figure 7(a) is stronger than that in figure 7(b), also meaning that the carbon nanotubes from CH_4 might be of higher graphitic degree than those from C_2H_2.

4. Conclusion

Reduced $LaCoO_3$ was a good catalyst to grow a large amount of carbon nanotubes with uniform diameter by using CH_4 or C_2H_2 as carbon source. The carbon nanotubes made from CH_4 might be more graphitic than those made from C_2H_2.

Acknowledgement

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