



Pergamon

Materials Research Bulletin 36 (2001) 471–477

Materials
Research
Bulletin

Carbon nanotubes prepared from CO on pre-reduced La_2NiO_4 perovskite precursor

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(Refereed)

Received 27 March 2000; accepted 17 May 2000

Abstract

A large amount multi-shelled carbon nanotubes with uniform diameter were obtained from catalytic disproportionation of CO using La_2NiO_4 oxides as catalyst precursor, which was prepared by citric acid complexing method. Nickel exists chiefly as Ni^0 particles supported on La_2O_3 after reduction of perovskite-like mixed oxide La_2NiO_4 . These nano-scale Ni^0 particles play a key role for the growth of carbon nanotubes. Transmission electron microscopy, scanning electron microscopy, X-ray diffraction, Raman spectroscopy, and oxidation weight loss analysis were employed to reveal the morphology and microscopic structure of carbon nanotubes. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: A. Nanostructures; B. Chemistry synthesis; C. Raman spectroscopy; C. X-ray diffraction

1. Introduction

Recently, the synthesis of carbon nanotubes has become a hot point in the field of carbon materials after the discover of fullerene [1–5]. As a new allotrope of carbon, carbon nanotubes are provided with many extraordinary properties as a result of their special quasi-one-dimensional structure. Some novel techniques are expected to develop for their potential applications. Among of current methods, the catalytic production of carbon nanotubes is simple and reproducible. With this method, it is crucial to select and prepare an

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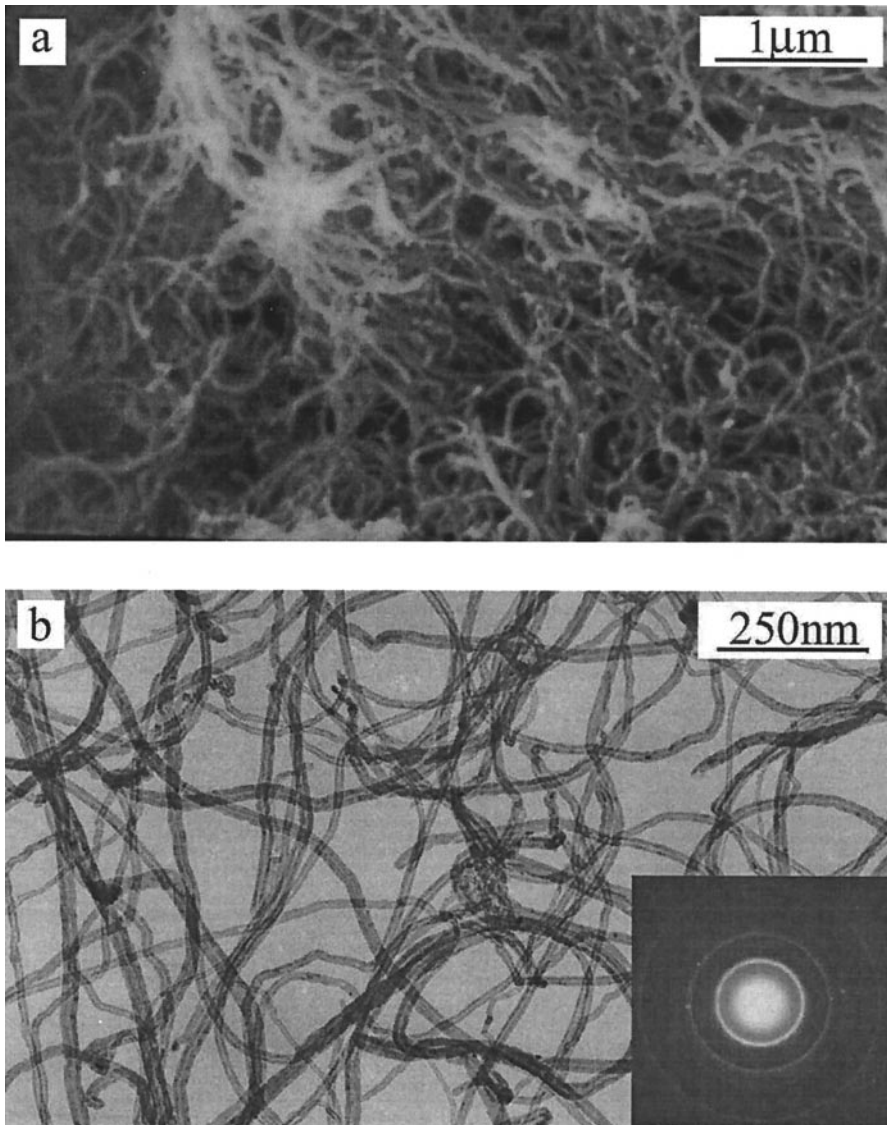


Fig. 1. (a) SEM image of carbon nanotubes and (b) Low-resolution TEM image and SAED pattern (inset) of carbon nanotubes.

effective catalyst with appropriate size of active metal, usually Fe, Co, Ni. Dai et al. found that the diameter of carbon nanotubes can be determined by the size of transition metal particles [6]. Rodriguez et al. elucidated the impact of the nature of the metal surface during the synthesis of carbon nanotubes [7].

In the past decade, perovskite and perovskite-like mixed metal oxides have been investigated extensively as the catalyst for some chemical reactions, for example, NH_3 oxidation [8]. Up to now, however, no report is seen in the literatures about using perovskite or perovskite-like metal oxides as catalyst precursor for carbon nanotubes growth. In this

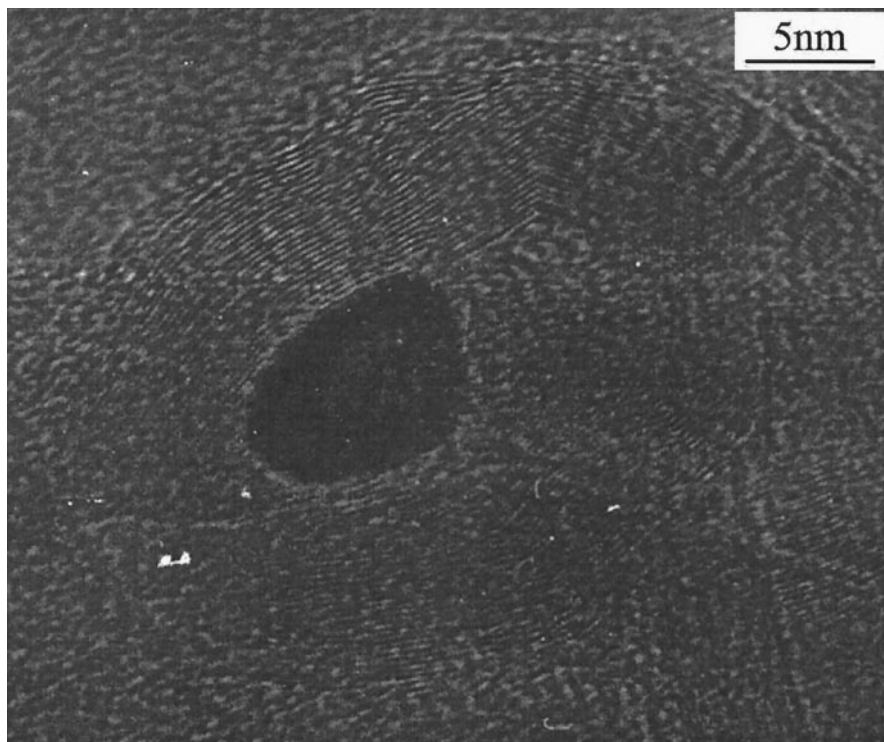


Fig. 2. The Ni particle (about 10nm) encapsulated by nanotubes was shown by HRTEM image of carbon nanotubes.

bulletin, we obtained bulk growth of carbon nanotubes by catalytic disproportionation of CO over Ni nanoparticles prepared by reduction of La_2NiO_4 perovskite precursor.

2. Experimental

The La_2NiO_4 oxide was synthesized by decomposing the amorphous precursors [8]. In brief, to a mixed aqueous solution of nickel and lanthanum nitrates with appropriate stoichiometry, excess of citric solution was added. The resulting gel was evaporated to dryness with stirring. The obtained residue was calcined in air at 773K for 4h and then pelleted prior to calcination at 1073K for 6h. The pulverized samples (ca. 60–80 mesh) was used as catalyst precursor to prepare carbon nanotubes.

The production of carbon nanotubes was carried out with a horizontal quartz glass reactor, 30mm in diameter and 1000mm in length. The constant temperature zone is 400mm in length in the middle segment of the tube. Schleppling the catalyst precursor, the quartz boat was placed in the reactor. The amount of catalyst in oxidation state used for all experiments was 100mg. In all experiments, the reaction pressure was maintained at ambient pressure. After the La_2NiO_4 oxide were reduced in a flow of H_2 at 1073K, the reactor was controlled to 873K and CO was introduced into the reactor, passing over the catalyst with 30ml/min for 60 minutes. After cooled to the room temperature in a flow of Ar, the products were collected.

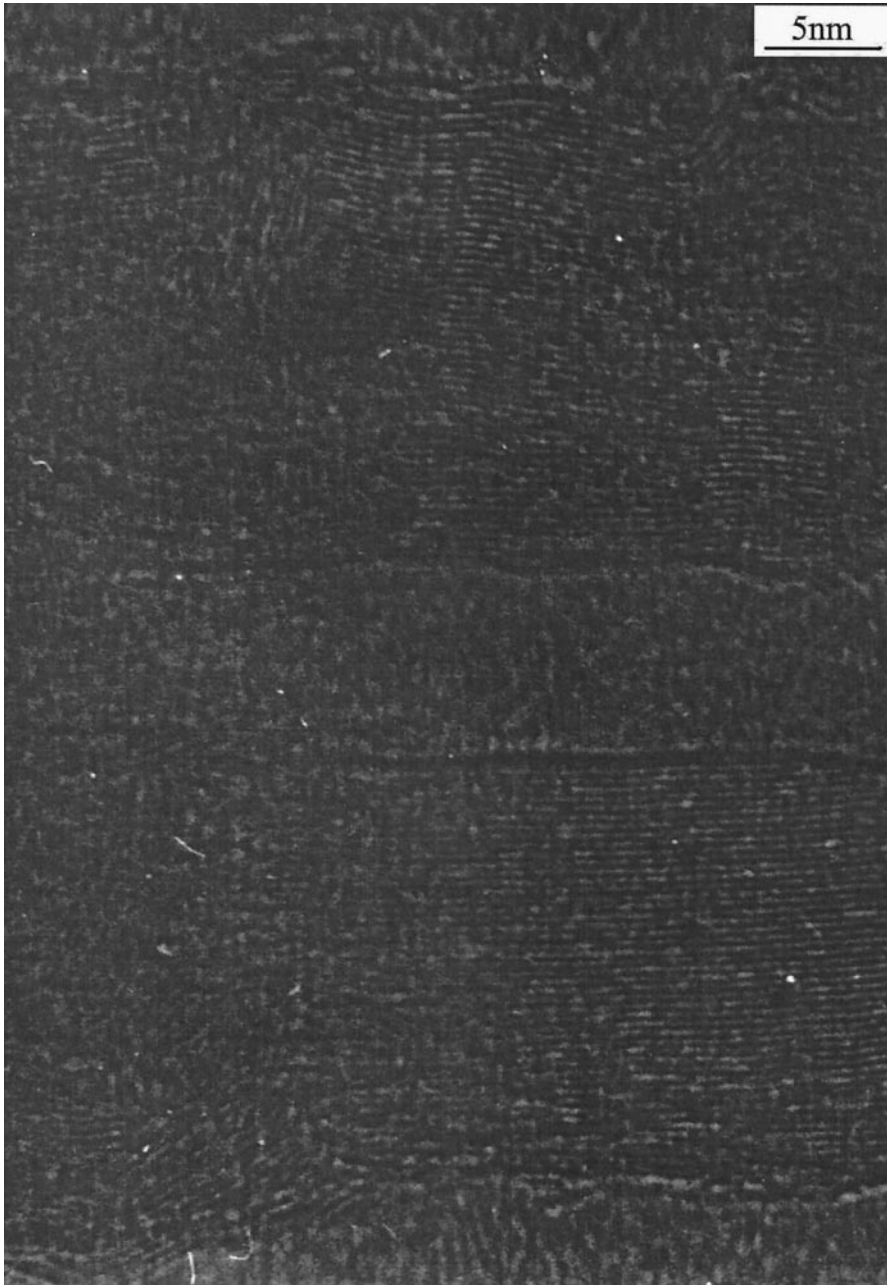


Fig. 3. The walls of a typical carbon nanotube was shown by HRTEM image.

The product was sonicated and dispersed onto a copper grid for microscopic observation. The microstructure of obtained carbon nanotubes were observed by means of scanning electron microscopy (JOEL JXA-840), low-resolution transmission electron microscopy (JOEL JEM-100CX) and high-resolution transmission electron microscopy (Hitachi 8100,

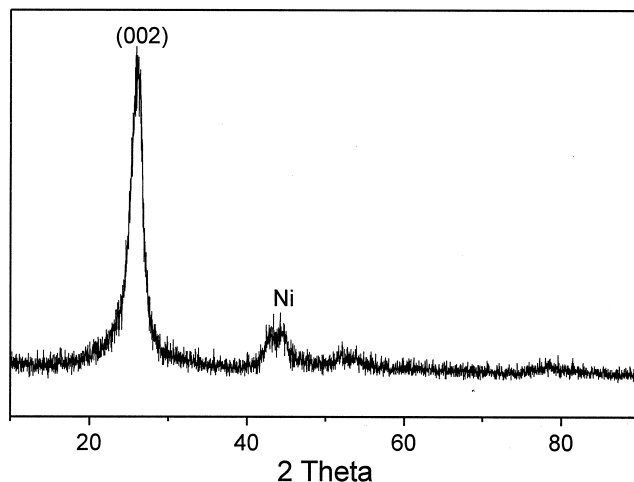


Fig. 4. X-ray diffraction pattern of synthesized carbon nanotubes.

operated at 200keV). Carbon nanotubes were also characterized by X-ray diffraction with Cu $K\alpha$ radiation. Raman spectra (Dilor LABRAM-I instrument) of carbon nanotubes were measured with the Ar^+ wave length of 514.5 nm. The oxidation weight loss of carbon nanotubes was analyzed by Perkin-Elmer (7th series system).

3. Results and discussion

The carbon nanotubes were prepared by disproportionation of CO at 873K on pre-reduced La_2NiO_4 , the Boudouard reaction $2CO = CO_2 + C$. A bulk growth of well-turbostratic carbon nanotubes was obtained. Fig. 1a is a characteristic SEM image of carbon nanotubes. We can observe innumerable carbon nanotubes with entangled and interlaced shapes. Most of them are up to several 10 μm . In Fig. 1b, many rope-like carbon nanotubes were shown by a typical TEM image. The diameter of them is mostly ca. 20nm, which is frequently close to the size of Ni particles. Some Ni particles are found to be encapsulated by carbonaceous tubes (Fig. 2). In our experiment, the metal particles play a key role in the formation of carbon nanotubes. By XRD, we know that the catalyst precursor La_2NiO_4 is formed as single phase with a tetragonal structure. Ni^{2+} and La^{3+} ions were evenly distributed. After reduction, La_2O_3 prevents Ni^0 particles from agglomerating, and nickel exists chiefly as nano-scale Ni^0 particles. Well-dispersed Ni crystallites are very advantageous for carbon nanotubes growth. Using this kind of catalyst precursor, other advantages of preparing nanotubes are also shown obviously. The yield of product is higher and the reaction temperature is milder comparing with arc discharge method. The purification and separation of carbon nanotubes is convenient due to freely soluble catalyst.

A better degree of average graphitization of carbon nanotubes was exhibited by selected area electron diffraction (SAED) pattern (inset to Fig. 1b). Details of the structure of carbon nanotubes were opened out by HRTEM image (Fig. 3), which confirmed that multi-walled

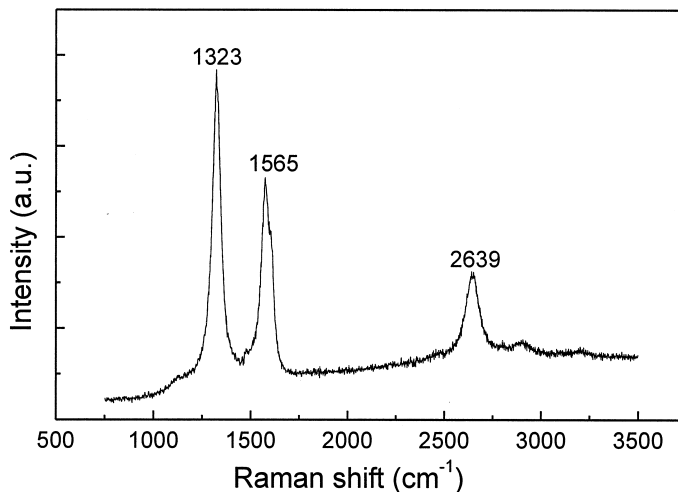


Fig. 5. Raman spectrum of obtained carbon nanotubes.

were obtained. Many cylindrical graphite layers were arranged regularly in the inner wall. But some amorphous carbon layers can be observed to cover the outer periphery of carbon nanotubes. Unlike our results, single-walled carbon nanotubes were produced with CVD method utilizing CO and supported MoO_x catalyst [6].

The X-ray diffraction was performed for carbon nanotubes (Fig. 4). A strongest peak at 26° corresponds approximately to that of graphite. The interlayer spacing (d_{002}) within multi-walled carbon nanotubes is 0.342nm, which is slightly wider than that of ideal graphite. At ca. 44° , 54° Ni crystallite peaks can also be found. At room temperature with frequency 700–3500 cm^{-1} , Raman shift spectrum of carbon nanotubes was analyzed (Fig. 5). Two sharp peaks present at about 1565 and 1323 cm^{-1} , which are characteristic G-line and

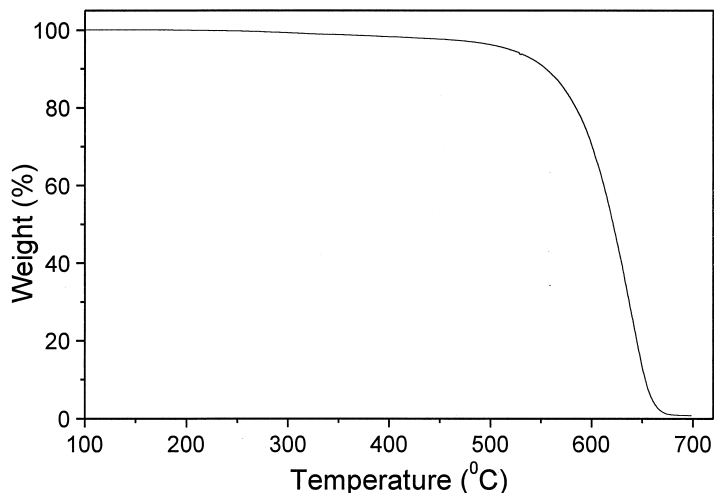


Fig. 6. Weight loss curve of carbon nanotubes in the air.

D-line. They are correspondingly characteristic peak of graphite. These features are close to that of multi-walled carbon nanotubes.

The oxidation behavior of obtained carbon nanotubes was studied by thermogravimetric instrument with increasing temperature rate 10°C/min (Fig. 6). In the air, the onset of oxidation was at a temperature of 588°C, which is lower than results of Ajayan (over 700°C) [9], but higher than that of Kukovitskii (ca. 420°C) [10]. The initial weight loss can be ascribed to the exist of amorphous carbon on the outer wall of nanotubes and some surface structure defects. In addition, the terminal of carbon tubes are usually active for oxidation reaction.

Acknowledgments

The authors gratefully acknowledge the financial support from the Chinese Academy of Sciences.

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