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Preparation of Carbon Nanotubes by CVD Process over Nanoparticles of Ni-Ce-Zr Mixed Oxides

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Abstract

Carbon nanotubes (CNTs) were prepared by the catalytic chemical vapor deposition of C_2H_2 at 550°C in 120 minutes using nanoparticles of Ni-Ce-Zr mixed oxides. The CNTs were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), high resolution transmission electron microscopy (HRTEM) and Raman spectroscopy. The results revealed that CNTs with diameter of about 45 nm are obtained. Utilization of Ni-Ce mixed oxides or NiO_2 respectively afforded CNTs with helical and curved morphologies and diameters of about 50 and 90 nm. No CNTs were formed either in the absence of catalyst or exclusion of Ni from Ce-Zr mixed oxides. Details of the catalyst type and its impact on CNTs morphologies will be presented.

Keywords: Nanomaterials; Carbonnanotubes; Catalytic Chemical Vapor Deposition

Introduction

Since the discovery of multiwall carbon nanotubes (MWCNTs) by Ijima in 1991 [1], synthesis of carbon nanotubes for mass production has been achieved by several methods such as flame synthesis [2], laser vaporization [3], arc discharge [4-5], pyrolysis [6], chemical vapor depositions [7-9] and plasma-enhanced chemical vapor deposition (PECVD) [10]. The growth mechanism of the alignment is still far from being clearly understood. Carbon nanotubes have unique mechanical and electrical properties that make them attractive system for wide range of applications including electron field emission sources [11], nanoscale electronic devices [12], chemical filters and storage systems [7]. Compared to other synthesis methods, synthesis of carbon nanotubes by catalytic chemical vapor deposition (CCVD) [13-15] has drawn a lot of research interests since production based on this method leads to large yields of carbon nanotubes at lower cost. In CCVD procedure, CNTs nanotubes are formed by decomposition of a carbon-containing compound (methane, ethane, acetylene) over a catalyst containing nanoparticles of transition metals supported on solid matrices. This method has also the advantage of controlling the diameter, length and morphology of the nanotubes by altering the size and type of the nanoparticles and deposition conditions [16,17].

In this work, we report the synthesis of good quality MWCNTs with significant production rate through acetylene decomposition using different nanoparticles of Ni-Ce-Zr mixed oxides, Ni-Ce oxides and Ni oxides as catalysts.

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2. Experimental

2.1. Materials and Characterization

All materials were obtained from Merck chemical company and used without further purification. Powder X-ray diffraction (XRD) patterns were recorded by a diffractometer (SEIFERT PTS 3003) using a Cu K_α radiation (λ=1.54Å). The morphology was examined by a (Philips XL30) scanning electron microscope (SEM). FTIR spectra were measured on KBr disks with a Bruker-Tensor 27 2002 spectrometer. High resolution transmission electron microscopy (HRTEM) was performed by using TECNAI F20 field emission gun microscope operating at 200 KeV equipped with a Gatan 794 slow scan charge-coupled device camera. The Raman spectra were recorded by using an Almega Dispersive Raman spectrometer Thermo-NICOLET 2003 American.

2.2. Preparation of Catalyst

Nanoparticles of Ni-Ce-Zr mixed oxide were prepared as reported before [18]. Ce $(NO_3)_3$ (1 mmol), Ni $(NO_3)_3$ (1 mmol) and $ZrOCl_2$ (1 mmol) were mixed with distilled water. After stirring for 5 minutes, the pH of the solution was adjusted to 10.5 by addition of KOH (20% W/W). The resultant mixture was refluxed at 80°C for 2 h. The solid product was finally filtered and washed with distilled water until the filtrate solution became neutral. The obtained Ni-Ce-Zr mixture was dried in oven at 120°C for 2 h, followed by calcination at 800°C for 6 h. The same procedure was used for the preparation of Ni-Ce mixed oxide with the exception that no $ZrOCl_2$ was added. The nanoparticles of NiO_2 were prepared as reported previously [18].

2.3. Preparation of CNTs

The C_2H_2 chemical vapor deposition was carried out in a quartz tube equipped with a temperature and gas flow control. The Ar gas was passed for 30 minutes over 0.5 gr of Ni-Ce-Zr mixed oxides catalyst in quartz boat at 550°C. Ar/C_2H_2 (4:1 v/v) mixture was then passed to the system at a flow rate of 120ml/min for 2 h. Passing Ar gas was then continued through the reaction chamber until the temperature of the furnace dropped to 200°C. The prepared CNTs was then modified [19] by emerging into 20% HNO_3 solution and keeping for several hours followed by washing with distilled water and drying in a vacuum oven at 120°C. About 1 g of CNTs was obtained.

3. Results and Discussion

3.1. SEM and TEM

Figures 1a and 1b show SEM images of CNTs grown at 550°C with Ni-Ce-Zr mixed oxide (sample A). The molar ratio of catalyst was 1/1/1. It was found that CNTs were grown readily at 550°C, below which the growing was not complete.

Further characterization of sample A was carried out using HRTEM. Figures 2a and 2b show the HRTEM images of sample A as curved and Y junction. We checked several CNTs individually and found them all multiwalled. A typical HRTEM image of nanotubes is presented in Figure 2c showing the CNTs well graphitized straight. The distance of inner diameter is about 0.37 nm.

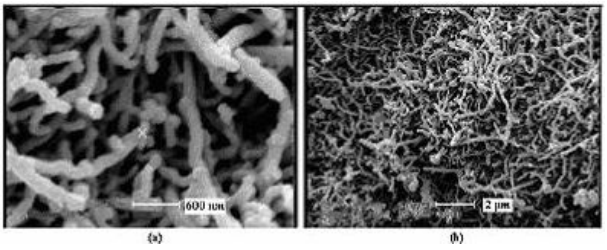

Figure 1. (a,b) SEM images of sample A with different magnifications.

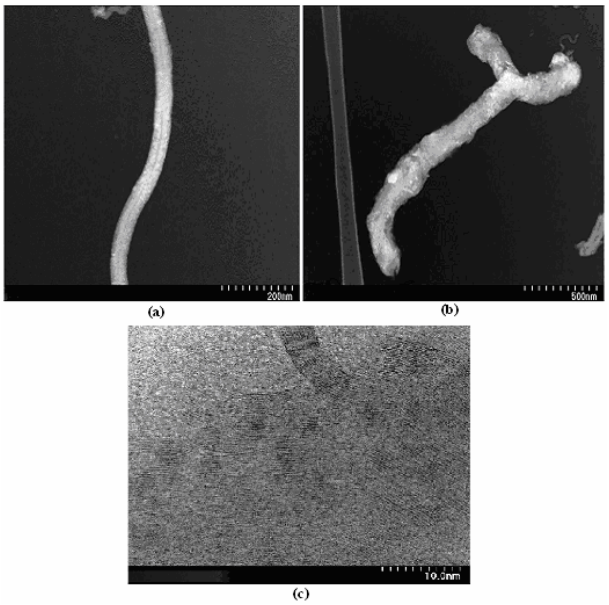

Figure 2. HRTEM image of sample A as mixture of (a) curved, (b) Y junction, and (c) graphitized plane.

Table 1. Carbon nanotube sizes of samples A, B and C

Sample[a]	Morphology	Length (μm)	Diameter (nm)
A	Curved with Y-Junction	6	45[a]
B	Helical	8	55
C	Curved	6	90

[a] This diameter is due to the curved part of sample A.

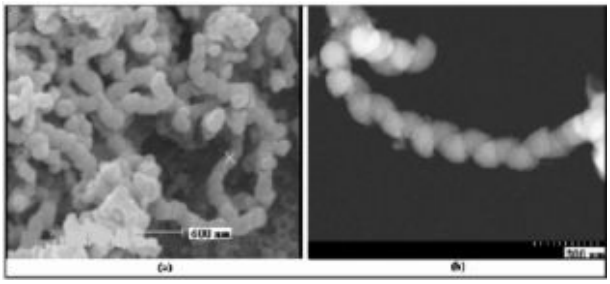

Figure 3. (a) SEM and (b) HRTEM images of sample B.

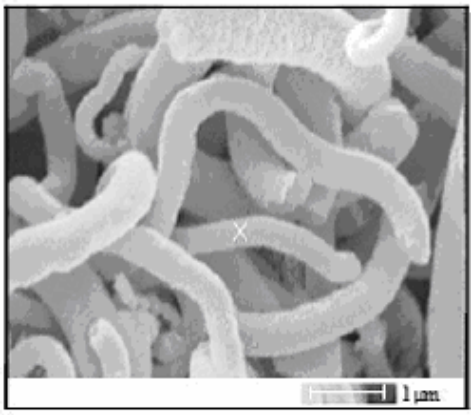

Figure 4. SEM image of sample C.

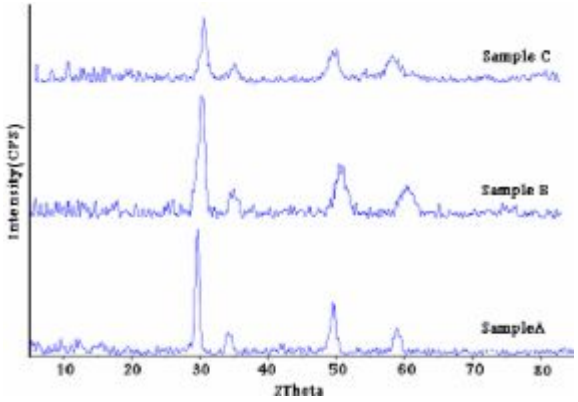

Figure 5. XRD patterns of samples A, B, and C.

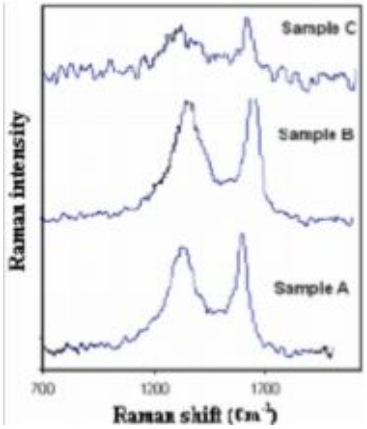

Figure 6. Raman spectra of samples A, B, and C.

The SEM and HRTEM images of CNTs grown at 550°C with Ni-Ce mixed oxides (sample B) are shown in Figures 3a and 3b respectively. The diameters and lengths of prepared CNTs are given in Table 1.

Figure 4 shows the SEM images of CNTs prepared on NiO_2 catalyst (sample C). It can be observed that the tube diameters with nanoparticles of NiO as catalyst is bigger than the others. The diameters and morphologies of obtained CNTs under similar conditions depend on the type of mixed oxides as catalyst.

3.2. XRD Patterns

Figure 5 shows the XRD patterns of samples A, B and C of CNTs. the intensity of peaks is increased and is relatively sharpened in sample A relative to others (B and C). The XRD pattern of sample A is consistent with high oriented pyrolytic graphite (HOPG).The peaks at scattering angles (2θ) correspond to the reflection from (002), (100) and (101) crystal planes respectively [18]. The XRD pattern of sample B is similar to A, and the reflection intensity for C is lower relative to others.

3.3. Raman Spectroscopy

Figure 6 shows Raman spectra of samples A, B, C. The Raman bands appearing at 1580 and 1350 cm^{-1} are known as G (Graphite) and D (Disorder) bands respectively. The G band is related to the C-C carbon material frequency with a sp^2 orbital structure and the D band is attributed to the disorder-induced vibration of C-C band [20-22]. In general, the D/G peak ratio heights below one implies the formation of good quality nanotubes [23]. The intensity of D and G peaks are stronger for A and B relative to sample C. However, all three samples exhibit ratios below one.

Based on the obtained results, it is observed that the morphologies of samples A, B and C are different. The trend in sample diameters are as A<B<C and some Y junction is seen in sample A (Figures 1b and 2b). Sample B has helical structure. These results indicate that in the case of mass production of CNTs with nanoparticles of mixed oxides, the type of nanoparticles mixed oxides has essential role in morphologies of CNTs. The observed CNTs morphology change could be due to the position of Ni atoms in mixed oxides. In fact, C_2H_2 decomposition is strongly dependent on the interaction between C_2H_2 and nickel particles in mixed oxides.

It is generally accepted that the CNT growth processes involve the adsorption and decomposition of gases (C_2H_2) containing carbon on catalyst surface, the dissolution and diffusion of the released carbon atoms dissolved in catalyst particles and the precipitation of the graphite-like layers [16]. However, in this work curved and Y junction tubes were formed with Ni-Ce-Zr. By using Ni-Ce and NiO, the CNTs were formed with helical and longer length with bigger diameters respectively. The precipitation region of the carbon atoms and the growth rate along the circumference seems to depend on the type of catalyst composition [16,17]. Based on the results obtained by others and us in this work, we speculate that the type of mixed oxide and position of Ni in mixed oxides have important effects on CNT growth. Although such explanation has been supported by others, it is a hypothesis [9], because little knowledge has been accumulated about the growth mechanism.

Conclusions

In this study, it was found that the grown of CNTs and morphology of the obtained CNTs depend on the nanoparticles mixed oxides type. Without using catalyst, and at 550-650°C, no decomposition of C_2H_2 is observed. It was also found that, with no nickel oxide present in mixed oxides, no CNTs are formed. The CVD process with Ni-Ce-Zr as catalyst is a good procedure for mass production of CNTs. By using only NiO nanoparticles as catalyst, CNTs with bigger diameter are obtained.

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