Cleandouble-walledcarbonnanotubessynthesizedbyCVD

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Received 3 October 2002; in final form 13 November 2002

Abstract

High quality double-walled carbon nanotubes (DWNTs) were synthesized by decomposition of methane over cobalt (Co) nanoparticles supported on porous MgO nanoparticles. The growth was significantly influenced by catalyst concentration and MgO type. Catalysts with 2.5–5 wt% Co loaded MgO (pore size: ~4 nm) efficiently grow DWNTs with diameters of 2–4 nm, high graphitization, clean surfaces, and clean inside channels. The preliminary separation of DWNTs from MgO, Co and other carbonaceous nanoparticles has been carried out. Energy dispersive X-ray spectroscopy and X-ray diffraction were employed to analyze the chemical composition of the materials before and after purification.©2002ElsevierScienceB.V. Allrightsreserved.

1. Introduction

Carbon nanotubes [1] have attracted a great deal of interest because of their promising properties and potential applications. Single-walled tubes (SWNTs) can be either metallic or semiconducting or semimetallic, depending on their microstructures [2–5]. However, the physical and chemical properties of multi-walled carbon nanotubes (MWNTs) are more complicated due to the interaction or coupling between the constituent layers [6,7]. For investigating the interaction or coupling behavior between different layers, DWNTs are the ideal and simplest candidates for performing both theoretical and experimental investigation. Saito et al. [8] have shown theoretically that the inner and outer layers in a DWNT can be metal–metal, metal–semiconducting, or semiconducting–semiconducting pairs, and that the formation of the DWNTs are determined by the spacing between the two layers rather than by the chiralites. The directions in which easy motion can occur between the inner and outer layers in DWNTs are found to depend on the chiralities of the two layers [6–8], which will affect the mechanical and transport properties of the DWNTs. Experimentally, Flahaut et al. [9] and Bacsa et al. [10] have prepared mixtures of DWNTs and SWNTs by reducing Mg1−xCo xO solid solutions in a H 2–CH 4 atmosphere, the Mg1−xCo xO was synthesized by combustion of metal nitrates and urea. The fraction of DWNTs is about 50% in the mixed product, and the diameter of the DWNTs is about 0.5–5 nm [9]. Hutchison et al. [11] have synthesized

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PII: S0009-2614(02)01862-6
DWNTs by arc discharge between two graphite electrodes in an atmosphere of Ar and H₂, and the graphite anode was drilled a channel and filled with catalyst of Ni, Co, Fe, and S powder. The outer diameter of the DWNTs is in the range of 1.9–5 nm. Bandow et al. [12] have prepared DWNTs by heating peapod (C₆₀ capsulated inside SWNTs) [13,14] at 1200 °C, the C₆₀ chains inside the SWNTs coalesce to form the second (inner) layer resulting in the formation of DWNTs. In this case, the outer diameter of the DWNTs are controlled by the diameter of the original SWNTs. Ci et al. [15] have produced DWNTs by pyrolyzing C₂H₂ on floating iron catalyst at 900–1100 °C, and the growth of the DWNTs is strongly dependent on the sulfur content, which can promote the formation of the DWNTs. Ren et al. [16] have synthesized DWNTs by using CH₄ as carbon source, H₂ as carrier gas, ferrocene ([C₅H₅]₂Fe) as catalyst precursor and thiophene (C₄H₄S) as sulfur source at 1100 °C.

Although DWNTs have been synthesized by a variety of methods, synthesis of clean and highly crystalline DWNTs is still a great challenge. Most of the DWNTs reported previously are either coated on the outside surface or filled inside the inner channel with amorphous carbon, which is a significant drawback for measuring the intrinsic properties of DWNTs. In this Letter, we present a method for synthesizing DWNTs with a clean outer surface and inner channel, and the tubes have a narrow distribution of small diameters. The separation of DWNTs from the catalyst and catalyst support is also described. The structure of the double-walled tubes is characterized by electron microscopy. The extremely clean surface and inside channel together with the high degree of graphitization make our DWNTs ideal both for investigating the interlayer interactions and for exploring the possible applications in of nanotubes in nanoelectronics.

2. Experimental

The experiments were carried out in a conventional horizontal tube furnace with a quartz tube (of 46 mm inner diameter) as the reaction chamber. The catalyst used for growing the DWNTs is prepared by impregnating MgO powder with cobalt nitrate ethyl alcohol solution. MgO powders (Nantek) used as catalyst support have a specific surface area (BET) of ~400 m²/g and a crystallite size of 3–4 nm and an average pore diameter of 3 nm. For loading the Co catalyst onto the MgO powder, a certain amount of cobalt nitrate hexahydrate (Co(NO₃)₂·6H₂O, 98%, Aldrich) was dissolved in 40 ml ethyl alcohol (Aldrich, denatured with 5% isopropyl alcohol and 5% methyl alcohol) by sonicating for 5 min, then MgO powder was immersed in the solution with sonication for 50 min. After drying, the material was baked at 130 °C for 14 h followed by grinding in mortar to break the chunks into powder. Catalysts with compositions of Co/MgO = 0.5, 1.5, 2.5, 5, 7, 9, 12, 15, 20 wt% have been prepared.

For carbon nanotube growth, the catalyst (50 mg) loaded onto a Mo boat was reduced at 900–1000 °C for 1 h in flowing gases of H₂ (40 sccm) and N₂ (100 sccm) at a pressure of 200 Torr, then the N₂ was replaced with CH₄ (10 sccm) to start carbon nanotube growth. The growth period typically lasts for 1 h. As reported in the previous work, the reaction temperature affects significantly the type and the yield of nanotubes [17]. In our experiment, nanotubes can grow in the temperature range from 900 to 1000 °C, however, it is found that the yield is the highest at 1000 °C. Therefore, we chose the temperature of 1000 °C for catalyst reduction and nanotube growth. Hydrochloric acid (HCl, 38%, Aldrich) treatment at room temperature and oxidation in air at elevated temperature (400–750 °C) have been performed in order to purify the DWNTs by removing the MgO substrate and Co catalyst particles and any amorphous carbon.

The morphology of the DWNTs was examined by scanning electron microscopy (SEM, JEOL JSM-6340F), and structural analysis was carried out using transmission electron microscopy (TEM, JEOL 2010). Energy dispersive X-ray spectroscopy (EDX) attached to the SEM and X-ray (D8 Discover, Bruker Axs) examination was carried out on the samples before and after acid treatment to analyze the compositions. The specimens for TEM analysis were prepared by dispersing the samples...
in ethanol. A few drops of the suspension were dripped onto a microgrid covered with a holey carbon thin film.

3. Results and discussion

Growth of nanotubes has been observed with all the different Co concentrations, however, the yield and the uniformity of the nanotubes are significantly affected by the Co concentration, as shown in Fig. 1. At Co concentrations \( \leq 1.5 \) and \( \geq 7 \) wt\%, a few of very fine carbon nanotubes are formed and the density is extremely low, as shown in Figs. 1a and d. But the reasons for low nanotube yields at low and high Co concentrations are different. It is found that, after growth, low Co concentration catalysts (\( \leq 1.5 \) wt\%) change their original color of slightly green to slightly gray, indicating a rare and insufficient growth of carbon nanotubes which is in consistent with the SEM examination. The low yield growth is attributed to the low density of Co catalyst particles loaded on the MgO substrates. In contrast, the high Co concentration (\( \geq 7 \) wt\%) catalysts turn black after growth, indicating the deposition of carbon on the catalyst. SEM analysis shows that lots of carbon particles are formed on these high Co concentration catalysts, and the amount of carbon particles increases with the Co concentration. It is speculated that the high concentration of Co will promote the formation of big Co particles, which will result in the growth of carbon particles \cite{18}. Besides the big particles, some giant fibers are also formed from high Co concentration catalysts. These results show that catalysts with both low and high concentrations of Co are not favorable for the carbon nanotube growth. Fortunately, our experimental result indicates that catalysts with intermediate Co concentrations of 2.5–5 wt\% are efficient for growing uniform fine carbon nanotubes as shown in Figs. 1b and c, and these carbon nanotubes are DWNTs as proven by TEM analysis (see next part). The DWNTs form a web-like network which connect or bridge MgO particles. The uniformity of the DWNTs growth is affected by the dispersion of the catalyst powders. If the catalyst layer is too thick nanotubes can only grow.

Fig. 1. SEM images of as-grown DWNTs on catalysts with Co concentrations of: (a) 1.5 wt\%, (b) 2.5 wt\%, (c) 5 wt\% and (d) 7 wt\%.
on the surface of the catalyst layer. In order to get a uniform growth across the catalyst particles, it is necessary to disperse the catalyst layer as thin as possible. In order to obtain the mass increase of the catalyst after growth, 50 mg sample grown from catalyst with optimal loading of Co at 2.5 wt% was oxidized at 700 °C in air for 30 min. After oxidation, the originally black samples turn into milk white, and the weight loss is 12.1 mg. This result indicates that the weight increase due to DWNTs and carbonaceous materials after growth is 32%. High-magnification SEM image (Fig. 2) shows that the DWNTs grow in the form of small bundles consisting of several to several tens of individual small tubes as indicated by arrowheads in Fig. 2. It is commonly observable that a bundle of DWNTs branches many times to form smaller bundles, therefore it is still difficult to tell an individual DWNT from a bundle by SEM. The tendency of DWNTs to grow in bundles is very similar to the reports in [15,16]. The formation of DWNT bundles is due to the van der Waals force between the small diameter DWNTs. The length of the carbon nanotube bundles is about 20 μm, meaning that the growth rate of DWNTs is about 20 μm/h.

To examine the role of the MgO support particles in the growth of DWNTs, we have tried to use Nanomyte™ MgO nanoparticles (Nanopowder Enterprises) as catalyst support to grow carbon nanotubes at the same conditions described above. These MgO particles have crystallite size of 25 nm, surface area of 50 m²/g, particle size of 50 nm and are non-porous. It is found that there are no small nanotubes grown from this type of MgO particle, but only a few big diameter nanotubes. It is noticeable that the surface area of the Nanomyte™ MgO is much smaller than that of Nantek MgO particles, and the Nanomyte™ MgO is non-porous and Nantek MgO particles have uniform nanopores. It is speculated that the high surface area and nanopores of the Nantek MgO facilitates the growth of the carbon nanotubes [19]. In addition, Nantek MgO particles have nanopores with diameter ~3 nm compatible with the diameter of the DWNTs (see next TEM images). It is most likely that the Co particles seated inside the nanopores promote the nucleation of DWNTs and the nanopores confine the diameter of the DWNTs [20].

For investigating the structure and quality of the nanotubes, TEM examination was carried out on the as-grown carbon nanotubes. Fig. 3 shows TEM images of DWNTs grown from catalyst with Co concentration of 2.5 wt%. The DWNTs exist in bundles (Fig. 3a) which are consistent with SEM

![Fig. 2. High-magnification SEM images of DWNTs grown from catalyst with Co concentration of 2.5 wt%, revealing the bundling nature of DWNTs.](image-url)
examination (Fig. 2). Although the as-grown samples contain some particles, the DWNTs are extremely clean. There are no impurities or amorphous carbon inside and outside the tubes, as shown in high-magnification TEM images in Figs. 3b–d. These clean DWNTs are obviously ideal materials for investigating unambiguously the electronic transport properties and interaction behavior between the double layers. Fig. 3c shows a bundle of bent DWNTs, indicating that the nanotubes are very flexible and strong. Fig. 3d shows a single DWNT of about 3 nm in outer diameter. TEM examination shows that the diameters of DWNTs distribute in a very narrow range of 2–4 nm. Occasionally, some single-walled, triple-walled and multi-walled carbon nanotubes have also been observed by TEM, but the amount is very low.

For purifying the samples, the as-grown material was oxidized with hydrochloric acid (HCl, 38%) at room temperature for half an hour. Then, the suspension was filtered through a membrane with a pore size of 0.22 μm (Millipore) and washed with distilled water followed by drying at 150 °C. After the above purification, the materials aggregated to form thin black film or ribbon deposits as shown in Fig. 4a. It is clearly shown that after the above purification steps, the DWNTs are tangled.
highly curled and mixed with nanoparticles. However, the DWNTs buried inside the black deposit can be aligned by stretching the deposit (Fig. 4b). Although, after stretching, the diameter of the straightened DWNTs (Fig. 4b) are smaller than that before stretching (Fig. 4a), the straightened DWNTs are still bundles rather than individual DWNTs, as indicated in Fig. 4c. The phenomena of alignment of DWNTs under elongation may be useful for further study and potential applications.

Figs. 5a and b show the EDX analysis of the samples before and after acid treatment, respectively. It clearly shows that the as-grown material (Fig. 5a) contains Mg, Ca, Co, O and C. Mg and O are from MgO nanoparticles, and Ca is from the impurities of the starting materials. After acid treatment, Mg is not detected, but C and Co are dominant components in the samples (Fig. 5b). The weight ratio of C to Co in the purified sample is 56:35, as derived from the EDX data. This result indicates that HCl acid has removed all the MgO nanoparticles, but not the Co catalyst particles. TEM examination reveals that some cobalt particles of 50 nm in diameter are wrapped with carbon layers, similar to that reported in [11]. These graphitic layers will protect the Co particles from acid attack, therefore the remaining Co in the acid treated sample is ascribed to the Co particles covered with graphitic layers. X-ray diffraction on the acid treated samples indicates that the Co particles encapsulated with carbon have fcc structure. This observation may imply that the Co particles facilitating DWNT growth also have fcc structure.

The above experimental result elucidates that acid treatment of the as-grown samples is very efficient for removing the MgO particles but not for removing the Co particles. Oxidation in air at elevated temperature [21] has been carried out on our DWNTs to attempt to open the carbon shells covering on the Co particles and to remove the amorphous carbon particles. At temperatures of 400–650 °C, the oxidation of carbon particles does not occur; at temperatures of 650–750 °C, the DWNTs are oxidized simultaneously with the carbon particles due to the small diameter and few layers of DWNTs [22,23]. Therefore, the harsh oxidation process cannot be applied to the
DWNTs. It has been reported that single-walled carbon nanotubes can be successfully purified by centrifuge [24] or microfiltration [25] or size exclusion chromatography [26], these methods might be employed to purify the DWNTs.

4. Conclusions

In summary, we have successfully produced very uniform and clean DWNTs from Co particles dispersed on porous MgO nanoparticles. Both the surface area and pore size of the MgO nanoparticles affect the growth of DWNTs. Very uniform DWNTs have been prepared by using catalyst of Co 2.5–5 wt% loaded on MgO nanoparticles with pore size of 3 nm. The DWNTs have a very narrow diameter distribution of 2–4 nm. These high-quality DWNTs will facilitate the fundamental research on their properties and applications in nanoelectronics. A preliminary purification process has been performed through acid treatment and oxygen oxidation to remove the MgO, Co and amorphous carbon particles. Acid treatment is very efficient for removing MgO particles but not Co particles covered with graphitic shells. Oxidation in air, a proven effective method for MWNTs purification, cannot be used for purifying DWNTs due to the destructive attack of oxygen on DWNTs. Some of the methods for purifying SWNTs may be employed to purify the DWNTs, which are under investigation.

Acknowledgements

This work is partly supported by The US Army Natick Soldier Systems Center under grants DAAD16-00-C-9227 and DAAD16-02-C-0037, partly by DoE under a grant DE-FG02-00ER45805, and partly by NSF under a grant ECS-0103012.

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