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Synthesis and characterization of high-quality double-walled carbon nanotubes by catalytic decomposition of alcohol

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We report the synthesis of high-quality double-walled carbon nanotubes without defects by catalytic decomposition of alcohol over an Fe–Mo/Al_2O_3 catalyst; the synthesized DWNTs have outer diameters in the range of 1.52–3.54 nm and an average interlayer distance of 0.38 nm between graphene layers.

Double-walled carbon nanotubes (DWNTs), which consist of two concentric cylindrical graphene layers, have many advantages over other types of carbon nanotubes (CNTs) in electrical and mechanical properties.[1,2] Especially, DWNTs can offer excellent field emission properties, which have low threshold voltage for electron emission as single-walled carbon nanotubes (SWNTs) and high emission stability similar to multiwalled carbon nanotubes (MWNTs). There were several reports for the synthesis of DWNTs prepared by different methods such as arc discharge,[3] coalescence of C_{60},[4] and catalytic chemical vapor deposition (CCVD) using methane[5–7] and acetylene.[8] Among several methods, CCVD is an attractive technique because it could promise the controlled growth of nanotubes by adjusting reaction parameters and easily permit large-scale synthesis of nanotubes. Although the synthesis of DWNTs has been studied by several groups,[3–8] it is still difficult to produce high-quality DWNTs without carbonaceous particles or amorphous carbon material. Currently, synthesis of high-quality DWNTs with high yield remains a great challenge. For the synthesis of SWNTs or DWNTs using the CCVD method, various carbon containing molecules (CO, C_2H_2, C_2H_4, CH_4, C_6H_6) were used for carbon feedstock while alcohol was only used to synthesize SWNTs by one group.[9] Moreover, there was no report for the synthesis of DWNTs using alcohol as a carbon source.

In this communication, we report the synthesis and characterization of high-quality DWNTs by catalytic decomposition of alcohol over an Fe–Mo/Al_2O_3 catalyst. Our results demonstrate that alcohol can be used as ideal carbon feedstock to produce high-quality DWNTs.

Fe–Mo/Al_2O_3 catalyst was prepared according to the following procedure.[10] A mixture of $Fe(NO_3)_3{\cdot}9H_2O$ (99%, Aldrich) and Mo solution (Aldrich, ICP/DCP standard solution, 9.8 mg ml^{-1} of Mo in H_2O) was dissolved in DI water for 1 h. The mixed Fe–Mo solution was introduced to the solution of Al_2O_3 powder and DI water followed by sonication for 1 h. In our experiment, the molar ratio of catalyst was Fe : Mo : Al_2O_3 = 1 : 0.1 : 13. After drying, the material was baked in a vacuum at 150 °C for 15 h and then ground in a mortar to break the chunks into fine powder. ~200 mg of supported Fe–Mo catalyst was placed into a quartz boat at the centre of the reactor tube (20 mm i.d., and 500 mm long). The liquid alcohol (ethanol) was placed in a stainless steel bubbler at room temperature. The quartz tube was heated up to 800 °C in an Ar atmosphere. Subsequently, Ar (2000 sccm) passing through alcohol was introduced into the reactor. Alcohol was carried into the reactor maintained at 800 °C for 10 min. The morphologies and microscopic structure of the carbon nanotubes were characterized by scanning electron microscopy (SEM) (Hitachi S-4700), high-resolution transmission electron microscopy (HRTEM) (JEOL, JEM-3011, 300 kV), and Raman spectrometer (Bruker, RFS-100/S, excitation beam wavelength: 1064 nm).

Fig. 1(a) shows the low-magnification SEM image of the as-synthesized product, which indicates large amounts of entangled carbon filaments. These filaments seem to be layer networks, which are similar to purified SWNTs. The overall catalyst surface was perfectly covered with the carbon filaments. Especially, the SEM image shown here is of as-synthesized samples and no purification was conducted before SEM measurement. In this work, the average yield of DWNTs relative to the weight of Fe–Mo metal in Fe–Mo/Al_2O_3 catalyst was over 280% at optimised process conditions. Fig. 1(b) shows the high-magnification SEM image of as-synthesized carbon filaments. The diameters of these carbon filaments are in the range of 20–40 nm and there are no carbonaceous particles on the carbon filaments, showing that the overall as-synthesized carbon filaments have high purity.

Fig. 2 shows the high-resolution TEM (HRTEM) image of as-synthesized carbon filaments. In Fig. 2(a) and 2(b), the carbon filaments observed in the SEM can be seen as DWNT bundles, which have two concentric graphene sheets. DWNTs have larger diameters than those of SWNTs and also have different diameters in a bundle unlike SWNTs. From HRTEM observation, the outer diameter and the interlayer spacing of DWNTs are in the range of 1.52–3.54 nm and 0.34–0.41 nm, respectively. The as-synthesized DWNTs have clearly resolved walls and no amorphous carbon materials overcoated on the surface of nanotubes, which indicates the synthesis of high-quality DWNTs. Beside DWNT bundles, sometimes we could find some isolated DWNTs in the TEM observation. Generally the diameter of an isolated DWNT is much larger than that of an individual DWNT in a bundle. Fig. 2(c) shows an HRTEM

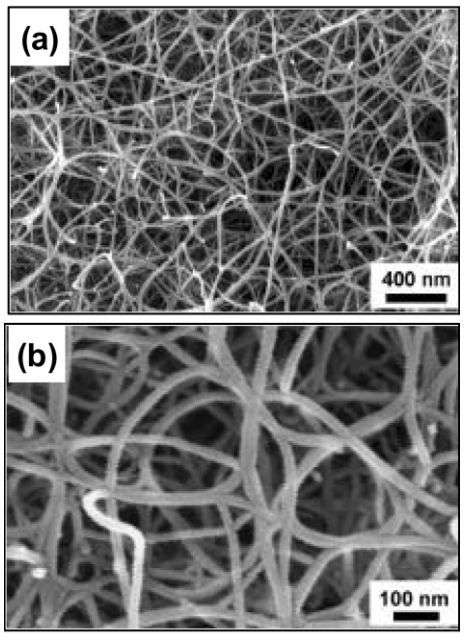

Fig. 1 SEM images of the as-synthesized carbon filament material by catalytic decomposition of alcohol. (a) low magnification SEM image, (b) high magnification SEM image.

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image of a typical isolated DWNT, which indicates a clear graphene layer. The isolated DWNTs have a large outer diameter of 3.75 nm and an interlayer distance of about 0.41 nm between graphene layers.

We could find a little amorphous carbon materials partly in the carbon products even though the synthesized carbon materials generally indicate high-purity DWNTs. Moreover, carbon shells and SWNTs appeared in our products but the approximate proportion of DWNTs was over 95% from HRTEM observation.

Fig. 3 shows the Raman spectrum of the as-synthesized nanotube materials, which indicates the appearance of a weak D-band at 1273.4 cm^{-1} and a strong G-band at 1587.2 cm^{-1}. The small ratio of I(D)/I(G) displayed in Fig. 3 demonstrates that the defect level in the atomic carbon structure is low, indicating that high-quality DWNTs can be synthesized using our method. In Fig. 3, there are several peaks in radial breathing mode (RBM), resulting from various diameters of nanotubes. In previous works, the diameters of SWNTs were calculated by the expression $w = 6.5 + 223.75/d$.[11,12] It was suggested that the same formula as that used in a SWNT bundle could be used to calculate the diameter of DWNTs in a DWNT bundle.[6] In this work, we adopted the expression: $w = 6.5 + 223.75/d$, to calculate the diameter of DWNT. The spectrum obtained in the RBM frequency domain shows seven components at 89.1, 100.8, 109.1, 150.5, 166.2, 173.9, and 263.5 cm^{-1}. The diameters of nanotubes calculated from the RBM frequency are 2.71, 2.37, 2.18, 1.55, 1.40, 1.34 and 0.87 nm, respectively. It is well known that nanotubes with large diameter (> 3 nm) exhibit a weak Raman cross-section; as a result, their RBM frequency cannot be detected. But we can deduce that the outer tube diameter of DWNTs with an inner tube diameter of 2.71 nm is about 3.47 nm according to the mean interlayer spacing of DWNTs (0.38 nm). With the calculated diameters from the RBM frequency, we can confirm that the outer diameter and inner diameter of DWNTs are in the range of 1.55–3.47 nm and 0.87–2.71 nm, respectively. The diameters of DWNTs calculated from Raman analysis are in good agreement with HRTEM observation.

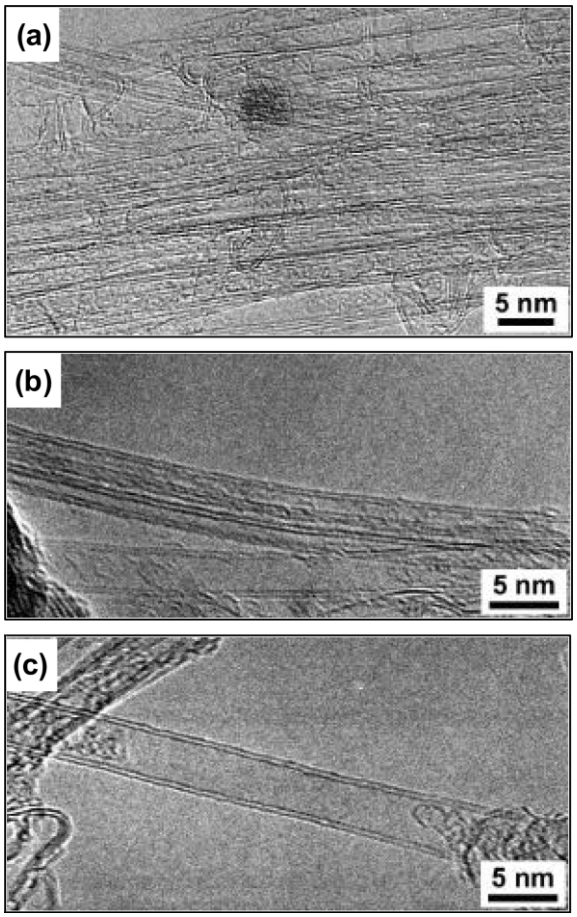

Fig. 2 HRTEM images of the as-synthesized DWNTs by catalytic decomposition of alcohol. (a), (b) DWNTs in a bundle have two concentric graphene sheets, (c) A typical isolated DWNT with large diameter of 3.75 nm.

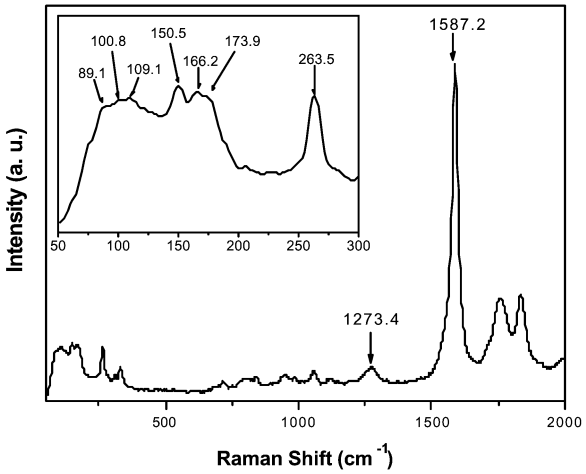

Fig. 3 Raman spectrum of the as-synthesized DWNTs by catalytic decomposition of alcohol.

In summary, high-quality DWNTs have been synthesized by catalytic decomposition of alcohol over Fe–Mo/Al_2O_3 catalyst. The synthesized DWNTs have outer diameters in the range of 1.52–3.54 nm and an average interlayer distance of 0.38 nm between graphene layers. Our results demonstrate that alcohol can be used as a very ideal carbon feedstock to produce DWNTs over alumina supported Fe–Mo catalyst.

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