A multi-stage growth model leading to high-yield production of carbon nanotubes†

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A novel growth model leading to high-yield production of carbon nanotubes with crystallized $Ni_xMg_{1-x}MoO_4$ as the catalyst is revealed.

Chemical vapor deposition (CVD) is considered one of the most important processes to produce carbon nanotubes (CNTs) on a large scale under mild synthetic conditions. However, the desire to enhance the yield of a single process has led to intense investigation. In CVD systems, root/tip growth models have been commonly accepted to describe CNT growth. Baker[1] and Xie[2] suggested that the growth model usually depends on the contact force between the catalyst and support. CNTs grow through a root growth model with catalyst particles as the root if the interaction is strong; otherwise, CNTs grow according to a tip growth model with catalyst particles as the tip. According to the root/tip growth models, the yield of CNTs depends on the amount of catalyst loaded upon the surface of a host. In order to improve the yield, researchers tried loading more catalyst, but the catalytic component was apt to aggregate and then deactivate when the loading concentration rose above a critical level.[3] A reducing atmosphere such as hydrogen can promote the yield,[4–9] but this can only improve the performance of the catalyst exposed at the surface.

A new catalyst (Ni/Mo/MgO with a mole ratio 1 : 12 : 12) was reported recently,[10] with which one can synthesize multi-walled carbon nanotube bundles, yielding CNTs with a mass of more than 60 times that of the catalyst. The purity of the final product, after removing the catalyst particles by hydrochloric acid treatment, was estimated to be over 95% by thermogravimetric analysis.[11] Although the Ni–Mo catalyst was predicted theoretically to have higher reactivity than other binary metallic catalysts, the catalysis mechanism under such a high loading ratio (mole ratio of Mo to Mg is 1 : 1) is still not well understood, which is significant for designing novel catalysts for higher productivity. In this communication, high-resolution transmission electron microscope (HRTEM) observations were used in combination with dynamic thermal analysis to investigate the growth model leading to high-yield production of CNTs by using $Ni_xMg_{1-x}MoO_4$ as the catalyst and methane as the carbon source. Our results suggest a multi-stage growth model consisting of a multi-stage separation of reduced catalyst layers from the catalyst precursor mother-body and the growth of CNT bundles from both sides of each catalyst layer. This model reasonably explains the high-yield production of CNTs by using this catalyst as well as the microstructure of the final bamboo-like CNT bundles produced.

The Ni/Mo/MgO ($Ni_xMg_{1-x}MoO_4$) catalyst was prepared by a combustion method. The right amounts of $Ni(NO_3)_2\cdot6H_2O$, $(NH_4)_6Mo_7O_{24}\cdot4H_2O$ and $Mg(NO_3)_2\cdot6H_2O$ were dissolved in ethylene glycol to yield a mixture with a molar ratio of Ni : Mo : Mg of around 1 : 12 : 12, then the mixture was heated at 700 °C in air for 25 min to obtain the catalyst. The CNT growth was carried out in the thermal balance unit of the thermal analyzer (STA-499C, NETZSCH) with 0.2–1.0 mg of catalyst in a corundum crucible. Methane was introduced into the thermal analyzer with a flow rate about 20 ml min^{-1}, and argon with a flow rate about 15 ml min^{-1} was used as protection gas. The thermal balance unit was heated from room temperature to 900 °C with a heating rate of 10 °C min^{-1}; after keeping the reaction at 900 °C for 25 min, the system was cooled to room temperature in argon. The changes of weight and heat flow of the whole process were recorded online by a workstation. The TEM investigations were performed on a Tecnai-F20 field emission electron microscope with an accelerating voltage of 200 kV.

The basic crystal structure of the parent catalyst has been measured by X-ray diffraction (XRD).[11] All diffraction peaks in the pattern can be indexed quite well by a monoclinic cell with space group *C*2/*m* with a slight increase of the lattice parameters in comparison with $MgMoO_4$ (PFD 72-2153). This result suggests a possible substitution of Ni^{+2} atoms for Mg^{2+} in the crystal lattice; therefore here we specify the parent catalyst as $Ni_xMg_{1-x}MoO_4$.

The CNTs were grown in the thermal analyzer. Fig. 1 shows the dynamically recorded profiles of CNT growth. As seen from the thermogravimetry curve, CNTs begin to grow after about 80 min, and the total gain is 700% after 25 min. A slight weight loss precedes the rapid weight gain in the derivative thermogravimetry curve. Accompanying the weigh loss, there is a sharp endothermic change in the differential scanning calorimeter curve. As discussed in our previous publication,[12] the weight loss and the endothermic peak appear to be caused by a rapid reduction of $Ni_xMg_{1-x}MoO_4$ to Ni–Mo/MgO. Due to the sudden activation of the catalyst, the CNTs grew discontinuously. To prevent the CNTs from overflowing the

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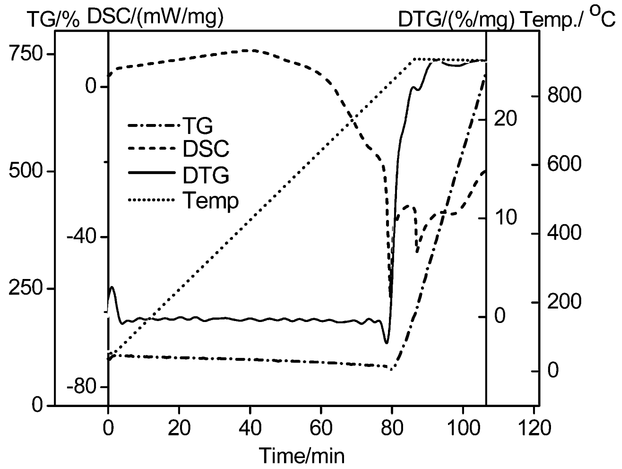

Fig. 1 Typical differential thermal analysis profiles of the CNT growth.

corundum crucible, the experiment with the thermal balance was not continued for a long time.

Microstructural features of the final materials depend essentially on the synthetic process. Fig. 2a–b show scanning electron microscopy (SEM) images illustrating the typical microstructure of the as-synthesized product. Fig. 2a is a low magnification SEM image of an as-synthesized sample, clearly illustrating the morphology of the crystalline CNT product, and it is evident that the product is comprised of clearly aligned CNT bundles. Fig. 2b is a high magnification SEM image. The most interesting features revealed in our SEM observation are the presence of roots (as indicated by arrows in Fig. 2a) and the layered inter-junctions in the middle of bundles (as indicated by arrows in Fig. 2b). The morphology of our product is very different from that obtained by conventional CVD systems, suggesting a new growth model due to the way the catalysts are applied.

In order to understand the detailed structural features of the roots and junctions, we have performed a series of structural analyses by means of electron diffraction and high resolution TEM observation. Fig. 3a shows a typical TEM image of a single root, demonstrating the relationship between CNT bundles and a root-like catalyst particle. It can be clearly seen that the bundles grew from different surfaces of a solid particle. Examining an enlargement of the bundle root, we can see that the surface of the $Ni_xMg_{1-x}MoO_4$ crystal is covered by small particles of less than 10 nm (Fig. 3b). The detailed structure of a single tube of the as-prepared MWNT is revealed in an HRTEM image (Fig. 3c), showing that it consists of graphite fringes that are not perfectly concentric.

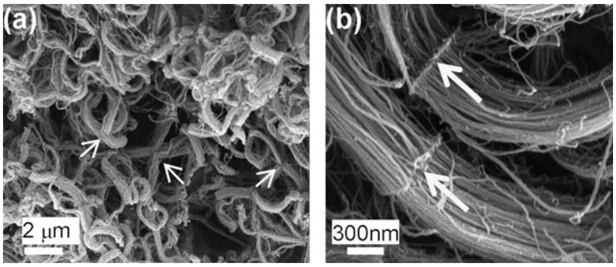

Fig. 2 SEM images showing the microstructure features of the as-made products. (a) A low magnification SEM image; (b) a high magnification SEM image.

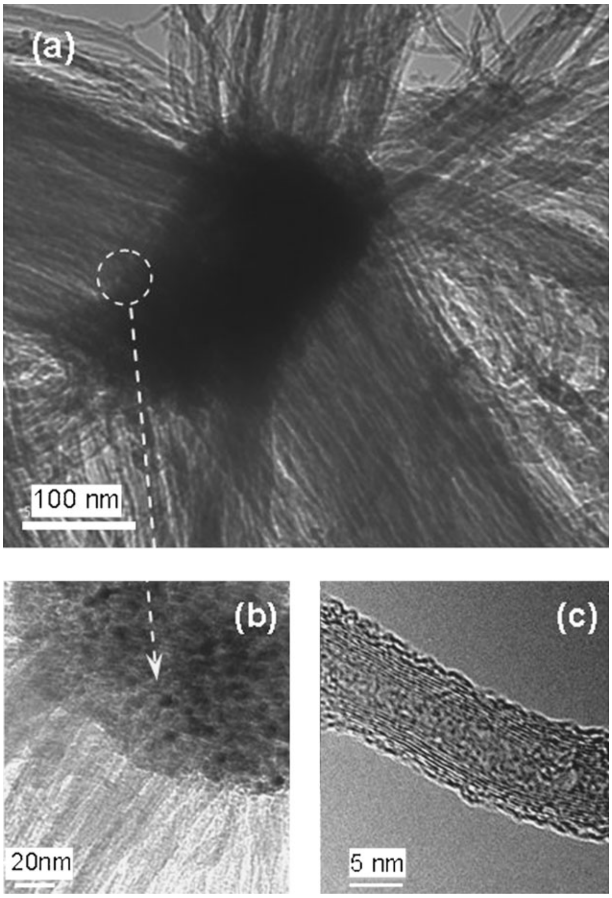

Fig. 3 (a) TEM morphology of CNT bundles developing from a solid particle. (b) Enlargement of the root of a CNT bundle. (c) HRTEM image of a single tube.

In order to obtain an aligned CNT array, a plane-like template with well dispersed nano-size catalyst particles is always needed;[2] otherwise the CNTs will grow in random directions. From the SEM image of a catalyst parent (Supplementary Fig. 1†), we can see many faceted surfaces that can serve as the initial growth planes for CNT bundles. An SAED pattern taken from the center of the root suggests it is still well crystallized (Supplementary Fig. 2†), and further detailed analysis demonstrates that the root particle is $Mg_2Mo_3O_8$ with a hexagonal symmetry, which is an intermediate phase following a phase transformation procedure from $MgMoO_4$ to $Mg_2Mo_3O_8$ then to $Mo_{0.84}Ni_{0.16}$ as reported in a previous publication.[13]

Besides the large root, thin flakes perpendicular to bundles can be frequently observed along the growth direction of the CNT bundles, as shown in Fig. 4a. The image from an appropriate angle (Fig. 4b) clearly reveals that the shape of the interpolated flakes is the shape of the bundle section, indicating that the CNTs developed from both sides of a layered junction as can be seen in the SEM image in Fig. 2b. This special TEM morphology of CNT bundles is very similar to stems of bamboo. Energy dispersive X-ray (EDX)

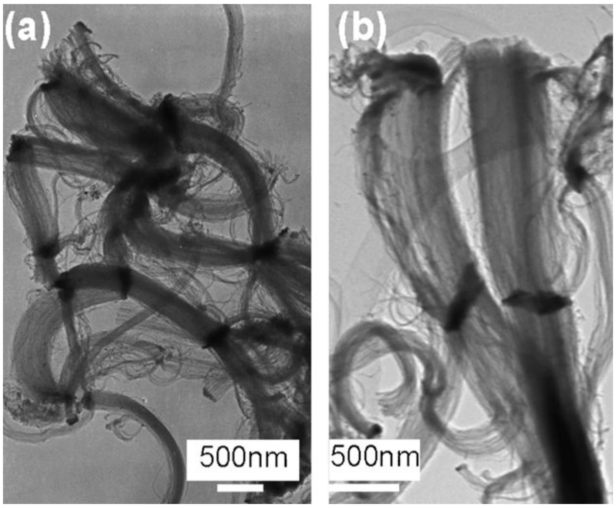

Fig. 4 (a) TEM images of bamboo-liked CNT bundles with several inter-junctions. (b) Enlargement of an inter-layer.

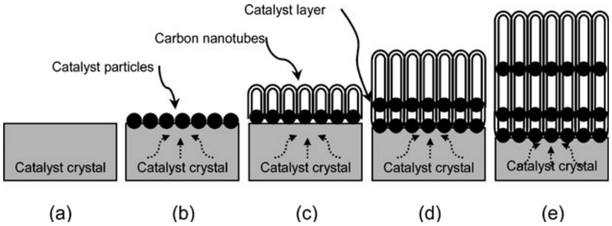

Fig. 5 Diagrammatic sketch of multi-stage growth model. With $Ni_xMg_{1-x}MoO_4$ crystal (a) as the catalyst precursor, the metallic catalyst particles precipitate over the faceted surface and form a catalyst layer (b), upon which CNT bundles then develop (c). As the CNTs grow, a new layer of catalyst forms and the earlier layer is peeled off the parent body by the force of CNTs growing between two layers (d). Repeating the steps from (b) to (d), bamboo-like CNT bundles develop.

microanalysis is also employed to determine the chemical composition of the thin flakes. An EDX spectrum (Supplementary Fig. 3†) of a thin flake clearly demonstrates that the product is composed of Mo, Ni, C and O elements. No Mg was detected in this layer. It is obvious that the thin flake junction is composed of material from the parent catalyst. The absence of Mg suggests a weak interaction between active (Ni–Mo) alloy phase and MgO. In order to explain the existence of several junction layers along the length of one bundle as illustrated in Fig. 4a, we suggest a multi-stage growth model as schematically illustrated in Fig. 5. In this model the different junction layers in a single bundle were generated at different times, and were peeled off of the parent crystal one by one as the CNTs continued to grow.

Based on both the differential thermal analysis and the TEM characterization, the growth process is conceived as follows. When the surface of each particle of the $Ni_xMg_{1-x}MoO_4$ precursor is reduced, a layer of active (Ni–Mo) catalyst forms over the faceted surfaces of the precursor crystal, and then CNTs grow suddenly as described by the root growth model. The well crystallized parent catalyst with faceted surfaces has a hidden potential to guide the formation of aligned CNT bundles. As the CNT bundles continue to grow, newly $Ni_xMg_{1-x}MoO_4$ catalyst precursor is reduced, precipitating a new active (Ni–Mo) catalyst layer and allowing the CNT bundles to grow connecting this new layer and the last layer. Probably due to a weak interaction force between the catalyst layer and the MgO host, the old layer separates from the parent body and is then pushed away by the force of CNT growth. With the successive generation of fresh catalyst layers from the parent body, a bamboo-like CNT bundle with several junctions develops.

In this work, a high yield of CNT bundles was obtained by using $Ni_xMg_{1-x}MoO_4$ as the catalyst precursor, with the effective catalyst elements embedded in its crystal lattices, rather than loading the catalyst on the surface of a support as in the established processes. This new method improves the loading concentration of the catalyst in one single process without being restricted by the surface area of the support; therefore, high-yield production of CNTs was achieved by a multi-stage growth model suggested by our high-resolution TEM observations and dynamic thermal analysis. This idea shows a path to design new catalysts for further enhancing CNT yield, and it suggests that very similar methods could be applied to other catalytic reactions.

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