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Effect of Tungsten on the Purification of Few-Walled Carbon Nanotubes Synthesized by Thermal Chemical Vapor Deposition Methods

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Few-walled carbon nanotubes (FWNTs) were synthesized by the methane chemical vapor deposition (CVD) method using binary catalysts Co/Mo and Co/W supported on MgO. It was found that Mo was not only a promoter for FWNT growth but also active in the formation of multiwalled carbon nanotubes (MWNTs) in our CVD process. W was found to be a better promoter since it was much less active in producing MWNT impurities. As a result, the raw FWNT materials prepared from W-containing catalysts were much more easily purified than those from Mo-containing catalysts. Scanning electron microscopy, thermogravimetric analysis, X-ray photoelectron spectroscopy, and transmission electron microscopy were used to characterize both raw materials and purified samples.

Introduction

Carbon nanotubes¹ (CNTs) are known to have unique electrical and mechanical properties. Generally, there exist two kinds of CNTs, single-walled carbon nanotubes^{2,3} (SWNTs) that consist of only a single graphite layer and multiwalled carbon nanotubes⁴ (MWNTs) that consist of multiple sidewall layers. Recently, few-walled carbon nanotubes⁵ (FWNTs), a unique type of MWNTs with generally 2–5 layers of sidewalls and diameters of less than 10 nm have been synthesized in our laboratory by the traditional thermal chemical vapor deposition (CVD) method. It was found that the FWNTs have enhanced electron field emission characteristics compared to other types of nanotubes, with a lower threshold field for emission and improved emission stability because of their high structural perfection resulting from the high growth temperature.⁶ Moreover, unlike SWNTs, even after covalent functionalization, the FWNTs can keep the structural integrity of their inner tubes; thus, the FWNTs are believed to be a better candidate for polymer reinforcement than either SWNTs or the more defective MWNTs.

However, even though FWNTs are unique intermediates that can solve some of the problems of SWNTs and MWNTs, they also introduced their own list of problems that need to be solved before they can be used in bulk applications. Among them, the purity of the sample is one of the major problems. There are carbonaceous impurities, such as graphitic carbon coatings on the surface of the support MgO and short MWNTs and carbon fibers concomitant with FWNTs due to the high growth temperature during the CVD process. Different methods were attempted to remove those impurities. However, no large-scale purification methods have been found to separate or remove carbonaceous impurities from FWNTs efficiently because the FWNTs and the carbonaceous impurities have similar tubular structures and stability against oxidation. Usually many of the FWNTs were lost during purification, resulting in a low purification yield.

In this study, we attempted to change the compositions of

the catalysts to improve the purity of the raw materials. We found that both Mo and W can be used as the promoter to grow FWNTs. However, Mo was active in the formation of short MWNT impurities, while W was much less active in producing tubular carbonaceous impurities during our CVD process. Thus, the raw FWNT materials prepared from W-containing catalysts are of much higher purity and are easier to purify than those from Mo-containing catalysts.

Experimental Methods

Different bimetallic and monometallic catalysts, Co/Mo, Co/W, Co, Mo, and W, supported on a MgO support were prepared by the modified glycine combustion method reported previously.^{5,6} Typically, viscous precursors were made by dissolving desired amounts of $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$, or $(\text{NH}_4)_{10}\text{W}_{12}\text{O}_{40} \cdot 5\text{H}_2\text{O}$ and glycine and citric acid as organic combustion additives in deionized water followed by evaporation at 120 °C. The catalyst powders were obtained by combusting the precursors over 300 °C quickly and annealing at 550 °C for 1 h to remove any organic residues. The optimum molar ratio Co:Mo:MgO among the catalysts used to synthesize FWNTs was 1:1:50.

FWNTs used in this research work were synthesized in a simple CVD setup made of a horizontal tube furnace and gas flow control units.^{7,8} Methane was employed here as the carbon source and hydrogen was also added in a certain ratio to control the methane decomposition rate. In a typical growth experiment, the catalyst was put into a quartz tube and was flushed with hydrogen while the catalyst was heated to 1000 °C. Methane was then introduced. After the reaction proceeded for 10 min, the methane flow was turned off and the system cooled.

The purified FWNTs were obtained by a two-step purification process. The as-synthesized products were first oxidized in Ar-diluted air for 1 h to burn the carbonaceous impurities at certain temperatures that were determined by thermogravimetric analysis (TGA) to selectively etch impurities, followed by refluxing in 6 N HCl aqueous solution to remove the support MgO and the catalyst Co/Mo or Co/W.

The TGA measurement was done in 15% air in Ar with a heating rate of 5 °C/min from room temperature to 900 °C with

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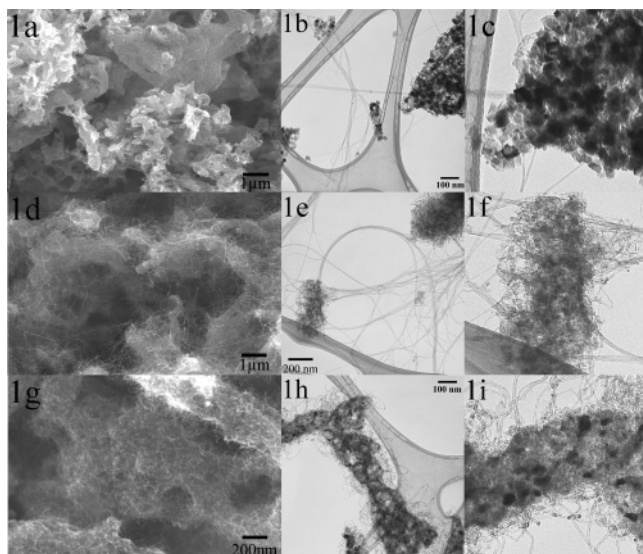


Figure 1. SEM and TEM images of as-grown samples from catalysts Co/MgO (a–c), Co/Mo/MgO (d–f), and Mo/MgO (g–i).

a TA instrument SDT2960. The sample morphology was characterized with a Hitachi HF-2000 scanning electron microscope (SEM) and a Philips 301 transmission electron microscope (TEM) operated at 80 kV. X-ray photoelectron spectroscopy (XPS) data were recorded on a Kratos Axis Ultra system with monochromatic Al K α X-rays (1486.6 eV). Sample charging during the measurements was compensated for by an electron flood gun.

Results and Discussion

Parts a and d of Figure 1 show the SEM pictures of as-prepared materials from catalysts Co/MgO and Co/Mo/MgO, respectively. There were very small amounts of CNTs grown from the Co/MgO catalysts, while the CNT yield was greatly improved by using Co/Mo/MgO, which indicates that Mo is a very good promoter to grow FWNTs due to the similar synergistic effect of Co and Mo observed in the synthesis of SWNTs.^{7,9,10} Parts b and e of Figure 1 are the TEM images of the raw CNT materials from Co/MgO and Co/Mo/MgO catalysts that also confirm the increased yield by Mo addition. However, a lot of short MWNTs were found close to the surface of the support, which is more clearly shown in Figure 1f. Since we cannot find such tubular carbonaceous impurities in Figure 1c, which shows the surface of the raw materials from Co/MgO catalysts, it was highly possible that such short MWNTs resulted from the Mo addition. Parts g and h of Figure 1 show that only short MWNTs were grown from the Mo/MgO catalyst. The length and the morphology of the short MWNTs in Figure 1f are very similar to those in Figure 1i. Moreover, the XPS data show that the binding energies of the Mo 3d orbital are identical in the reduced catalysts Co/Mo/MgO and Mo/MgO, which indicates that the Mo species in these two catalysts are in the same chemical environments (Supporting Information). These results show that Mo is not only a promoter to grow FWNTs but also an active catalyst to form tubular carbonaceous impurities in our CVD process.

Figure 2 shows the differential thermogravimetric (DTG) curves of the as-grown samples from Co/Mo/MgO and Mo/MgO in a diluted air atmosphere. The peaks are centered at 635 and 640 °C for the products from Co/Mo/MgO and Mo/MgO, respectively, which means that the burning temperature of the short MWNTs grown from Mo/MgO is around 640 °C

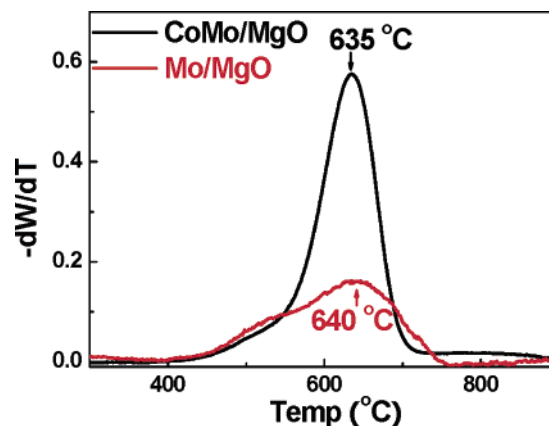


Figure 2. DTG plots of as-grown samples from catalysts Co/Mo/MgO and Mo/MgO.

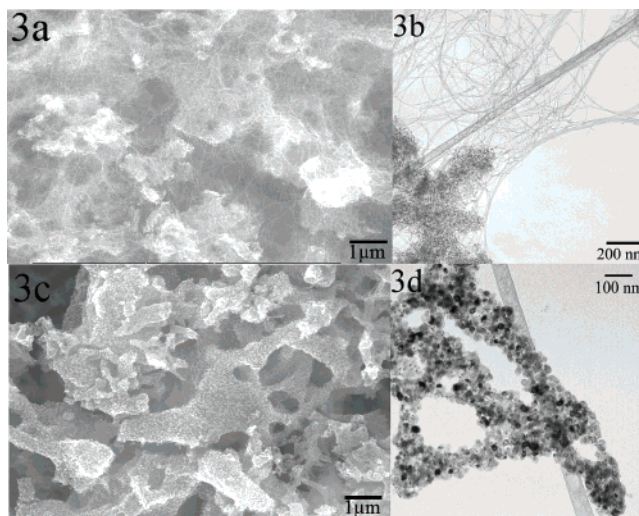


Figure 3. SEM and TEM images of as-grown samples from catalysts Co/W/MgO (a, b) and W/MgO (c, d) and the DTG plots (e) of those samples.

while the average burning temperature of the mixture of FWNTs and carbonaceous impurities from Co/Mo/MgO is about 635 °C. This result indicates that the thermal stability of FWNTs should be similar to those of carbonaceous impurities in dilute air, making it very difficult to remove the MWNT impurities from the as-grown FWNT samples. HRTEM images (Supporting Information) clearly show that the diameters of FWNTs are in the same range as those of short MWNT impurities, which confirms there should be no significant difference between their burning temperatures.

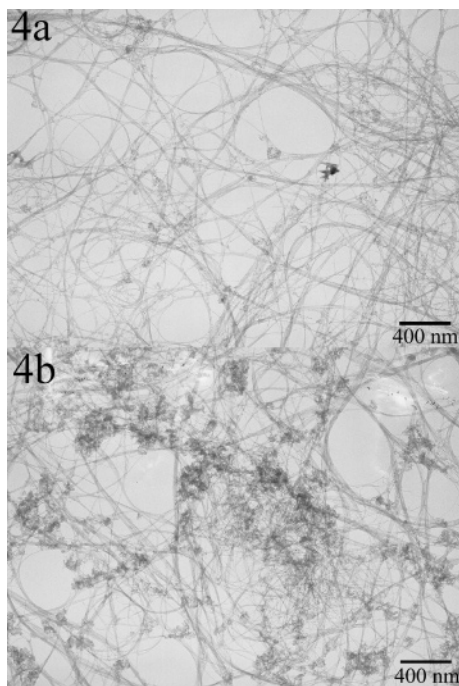


Figure 4. TEM images of purified samples from catalysts Co/W/MgO (a) and Co/Mo/MgO (b).

Due to the strong chemical similarities to Mo, tungsten has been investigated as a catalyst component and a Co/W bimetallic catalyst was studied¹¹ for the growth of SWNTs. Moreover, according to the vapor–liquid–solid mechanism, which is generally used to explain CNT growth, W might be less active to grow CNTs than Mo due to the fact that the eutectic point of C/W is approximately 500 °C higher than that of C/Mo from the phase diagrams (Supporting Information).

We studied the growth of FWNTs using catalysts to which W was added instead of Mo. Parts a and b of Figure 3 show that we also obtained a high FWNT yield from a Co/W/MgO catalyst similar to the Co/Mo/MgO catalyst, which indicates that W can indeed be used as the promoter to grow FWNTs with a high yield. Furthermore, as expected, there were no thick tubular structures found in the products from W/MgO catalyst as shown in Figure 3c,d, which proves that W is truly less active than Mo for the formation of CNTs. XPS measurements confirm that similar W species existed after reduction of Co/W/MgO and W/MgO in a H₂ atmosphere (Supporting Information), which supports that W species in the Co/W/MgO catalyst would be inactive to grow any tubular carbonaceous structure. Figure 3e shows the DTG curves of the as-grown samples from Co/W/MgO and W/MgO. The peak centered at 544 °C indicates the burning temperature of the carbon products from W/MgO, which are composed of nontubular carbonaceous impurities. This burning temperature is lower than 605 °C, which is the average burning temperature of the raw materials from Co/W/MgO. Thus, it was expected that the raw materials from Co/W/MgO might be purified by burning away the nontubular carbonaceous impurities between 544 and 605 °C.

We performed a purification procedure for as-grown samples from both Co/Mo/MgO and Co/W/MgO at 600 °C in 15% air in Ar atmosphere for 1 h. After refluxing in 6 N HCl and washing with DI water, we obtained purified samples, and the TEM images are shown in Figure 4. Figure 4a shows very pure FWNT samples obtained from Co/W/MgO with only a few impurities, while there are still a lot of impurities left after purification for those samples obtained from Co/Mo/MgO shown in Figure 4b. We also performed similar sets of experiments using Fe/Mo/MgO and Fe/W/MgO catalysts and found similar results (Supporting Information). Therefore, the raw materials from W-containing catalysts were more easily purified than those from Mo-containing catalysts since W was indeed less active in growing tubular carbonaceous structures than Mo in our methane CVD process.

Conclusions

In summary, FWNTs were synthesized with a high yield using a binary catalyst of Co/Mo or Co/W supported on MgO during our high-temperature methane CVD process. Both Mo and W can work as promoters to improve the FWNT yield. However, Mo is very active in growing short MWNTs, the parts of the impurities concomitant with FWNTs in the as-grown samples. In contrast, W is only active in growing nontubular carbonaceous impurities, which are much more easily burned away during the purification step. As a result, the raw materials from W-containing catalysts were more easily purified than those from Mo-containing catalysts.

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Supporting Information Available: XPS spectra of the Mo 3d and Co 2p orbitals from reduced catalysts Co/Mo/MgO, Mo/MgO, and Co/MgO, HRTEM images of typical FWNTs and MWNTs, phase diagrams of C/Mo and C/W, and the detailed results obtained from catalysts of Fe/Mo/MgO and Fe/W/MgO. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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