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Synthesis of Carbon Nanotubes from Polypropylene in the Presence of Ni/Mo/MgO Catalysts via Combustion

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We demonstrated an efficient improvement of activity of Ni catalysts by combining with Mo and Mg elements, by which massive growth of multiwalled carbon nanotubes (MWNTs) with straight and double helical structures have been achieved from polypropylene (PP) by means of a one-step combustion method. Scanning electron microscopy (SEM), transmission electron microscopy (TEM), and thermogravimetric analysis (TGA) are applied to characterize the morphology and the purity of products.

Carbon nanotubes (CNTs) exhibit a series of unique properties that make them promising for many applications, such as in structural materials and electronic and optical devices.[1] Continuous, low-cost production and easy purification of CNTs have long been much desired. A variety of synthetic methods including arc discharge,[2] laser vaporization,[3] and chemical vapor deposition (CVD)[4] have been explored. Among all the synthetic approaches, catalytic decomposition of carbon-containing feedstock is a promising method for the production of CNTs on a large scale. Numerous carbon-containing chemicals, such as CH_4, C_2H_2, and C_6H_6, were used as carbon sources to produce CNTs by catalysis.[5] Synthesis of CNTs using polymers as the carbon source is recently emerging, which offers the advantage of resource saving and environmental protection due to potential application of a large amount of virtually nondegradable polymers as carbon source instead of incineration and landfilling. A further advantage of carbonization is the release of hydrogen gas. In some previous works,[6] CNTs have been produced, respectively, from polyethylene, poly(vinyl alcohol), blends of poly(methyl methacrylate)/polyacrylonitrile, and poly(tetrafluoroethene) under inert atmosphere. These methods, however, usually require complicated setups and inert gas protection.

More recently, our group has proposed a simple one-step combustion method, heating the charring catalysts mixed in polymer matrix in a forced flame condition.[7] However, polymers as carbon sources often lead to the lower yield of conversion because the temperature for pyrolysis of carbon sources to synthesize CNTs is higher than that for degradation of polymers, thus, most of the degradation products escape as gaseous components. Balancing the pyrolysis rate of polymers with the activity and lifetime of the catalysts is crucial to massive growth of CNTs. Our previous results show that organically modified montmorillonite (OMMT) and solid acid can effectively enhance the yield of CNTs during combustion of PP in the presence of Ni catalyst.[8] Generally the activity of Ni catalyst is the highest among Fe group elements while its lifetime is very short due to easy coating with amorphous carbon on its surface during CNTs synthesis; therefore, H_2 is often introduced together with carbon source to remove the amorphous carbon and increase the lifetime of Ni catalyst.[9] In a recent report, Hata et al. found that water could act in promoting and preserving catalytic activity as a result of selectively removing amorphous carbon at the growth temperature.[10] Similar to H_2 and water, the OMMT and solid acid blended in PP/Ni composites can effectively assist the activity of Ni catalyst during combustion and result in high-yield formation of CNTs. However, OMMT and solid acid induce more impurities (amorphous carbon, MMT, or solid acid) and must be removed through purification steps. Thus, we want to synthesize a metal catalyst with higher activity to be adapted to a one-step polymer combustion method that can effectively catalyze CNTs formation from polymer in situ during combustion.

In this work, we chose Ni as main charring activity sites and Mo and Mg as the synergy constituent to promote and preserve the activity of catalysts. Ni/Mo/MgO catalysts have been applied in ethylene CVD to produce multiwalled cabon nanotubes (MWNTs) in work by Li et al.[11] However, it does not adapt to our polymer combusion systems and little amount of CNTs grow from it, so we must prepare a novel Ni/Mo/MgO catalyst (Nmm-cat) with a new constituent which has a higher acitivity and lifetime in our experimental conditions.

The Nmm-cats were prepared by a combustion method reported by Li et al.[11] In this work, the right amounts of $Mg(NO_3)_2 \cdot 6H_2O$, $(NH_3)_6Mo_7O_{24} \cdot 0.4H_2O$, and $Ni(NO_3)_2 \cdot 0.6H_2O$ were dissolved in PEG200. The solution was subsequently placed in a muffle furnace heated at 650 °C. It immediately ignited, and the fire lasted for 5 min. The formed material was kept at 650 °C for an additional 5 min. Finally, foamy materials were obtained and ground to fine powders. The obtained Nmm-cats were mixed with PP (melt flow index of 0.8 $g\,min^{-1}$) in a Brabendermixer at 100 rpm and 190 °C for 10 min.

The fabrication procedure of CNTs by polymer combustion is as follows. A piece of the mixed composite (about 10 g) was placed in a crucible and put in the muffle furnace heated at 850 °C for 10 min. The crucible was then allowed to cool to room temperature, and obtained black powder, henceforth called the as-synthesized product, was investigated without further purification.

For investigating the effect of the mole ratio of Mo and Mg in Nmm-cat on the yield of CNTs, we disslove a constant quantity of $Ni(NO_3)_2$ in PEG200 and then systematically alter the mole ratio of Mo and Mg in PEG200 to prepare the Nmm-cats. Table 1 lists the composition of Nmm-cats and presents the corresponding yield of CNTs. Results show that only Ni in the catalyst gives a lowest yield of CNTs which is similar with our previous results. Addition of Mo to the catalysts has proven to be favorable to enhance the yield of CNTs. The yield of CNTs increases with the increase of Mo mole fraction in catalyst. At

Table 1. Effect of the mole fraction of Mo and Mg in Nmm-cat on the yield of CNTs

	$Ni(NO_3)_2/(NH_4)_6Mo_7O_{24}\cdot 4H_2O/Mg(NO_3)_2$ (mole ratio)	Yield of CNTs[a] /%
Nmm-01	5/0/0	5
Nmm-02	5/0.05/0	18
Nmm-03	5/0.1/0	34
Nmm-04	5/0.15/0	16
Nmm-05	5/0.2/0	8
Nmm-06	5/0.1/0.25	41
Nmm-07	5/0.1/0.5	49
Nmm-08	5/0.1/1.0	58
Nmm-09	5/0.1/1.25	51
Nmm-10	5/0.1/1.5	48

[a] The yield of the CNTs (y) is calculated by amount of the as-synthesized product (M) divided by amount of PP in the used sample, i.e., $y = (M/M_{PP}) \times 100\%$. The weight ratio of PP/Nmm-cat is 97/3.

higher mole fraction, however, the yield of CNTs experiences a sharp drop. This phenomenon indicates that incorporation of the Mo element into the catalyst promotes the activity of Ni catalysts and that an optimum value of Ni/Mo mole ratio is about 5/0.1. Based on the above results, the influence of the mole fraction of Mg in Nmm-cat on the yield of CNTs was investigated in the presence of Ni and Mo. Interestingly enough, the yield of CNTs was substantially increased by the addition of Mg in the catalyst. By varying the Mg mole fraction in the catalyst, we demonstrated a highest activity of Ni/Mo/MgO catalyst with the $Ni(NO_3)_2/(NH_4)_6Mo_7O_{24}\cdot 4H_2O/Mg(NO_3)_2$ ratio of 5/0.1/1 (mole), which indicated that Mo and Mg as the synergy constituents in a Ni catalyst could effectively promote and preserve the activity of catalysts in our polymer combustion conditions. The Nmm-cat with the $Ni(NO_3)_2/(NH_4)_6Mo_7O_{24}\cdot 4H_2O/Mg(NO_3)_2$ ratio of 5/0.1/1 (mole ratio) was used for the remainder of the work.

Figure 1 presents the XRD profiles of Nmm-cat prepared freshly by a combustion method. The appearance of the diffraction peaks of $MgNiO_2$, $NiMoO_4$, and MoO_3 phases in the curve demonstrates that the phase structure of the Nmm-cats is uniform and that it belongs to a kind of polymetallic oxide alloy.

A typical SEM image of the product synthesized on the above catalyst by combustion is shown in Figure 2a, which shows that extremely abundant CNTs have been formed. More interestingly, about 5% CNTs obtained belong to the helical CNTs with several hundreds of micrometers in length along with about 95% straight CNTs in the as-synthesized product. High-resolution SEM (Figure 2b) studies of the CNTs reveal that the helical CNTs have a double helical structure with a diameter of about 60 nm, more than two times that of the straight CNTs. Low-resolution transmission electron microscopy (TEM) studies (Figure 2c) of the synthesized product illustrate that the CNTs belong to the MWNTs with straight and helical structures, in agreement with those measured by SEM. High-resolution TEM studies in Figure 2d show that the CNTs are clean MWNTs free from amorphous carbon. Furthermore, from Figure 2d we observed some bamboo-shaped structures in the MWNTs with the same curvature of the compartment layer, while the graphitic layers in the wall are parallel and the interlayer spacing of MWNTs is about 0.34 nm, consistent with the (002) plane lattice parameter of graphite carbon. It is noteworthy that the SEM and TEM characterizations are carried out on the as-synthesized carbon material without purification.

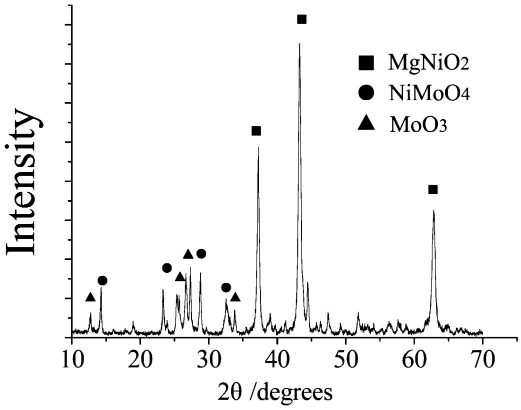

Figure 1. The XRD results of the Ni/Mo/Mg catalyst.

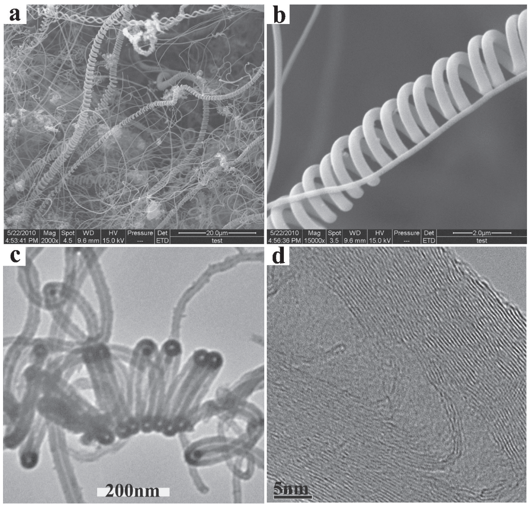

Figure 2. Microstructure of the as-synthesized carbon material from PP/Nmm-cat.

Thermogravimetric analyses (TGA) are often used to investigate the distribution and species of the carbon phases present in carbon nanotubes. Here the TGA measurement was implemented on 10 mg of the as-synthesized carbon material (Figure 3). Only 0.3% residue remained after heating above 800 °C, indicating very high purity. The combustion range of the MWNTs was 600 to 800 °C, with the peak weight reduction occurring at 730 °C.

The representative Raman spectrum of the sample shows the typical features of MWNTs. The spectrum demonstrates the peak frequencies of the graphite (G) mode at $1575\,cm^{-1}$ and contains disorder modes at $1343\,cm^{-1}$ (D). The line at $2922\,cm^{-1}$ is assigned to a combination of graphitic and disorder modes (G + D).[13]

According to above results, combination of the Mo and Mg elements into the Ni catalysts not only results in massive growth of the clean, high-quality MWNTs but also induces some helical

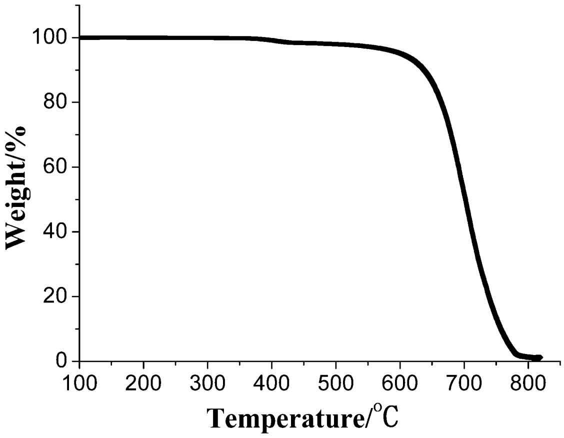

Figure 3. Thermogravimetric data (ramp rate, 10 °C min^{-1}) of a 10-mg sample of the as-synthesized carbon material in air.

structures during combustion of the PP/Nmm-cat composites. In contrast with MWNT synthesis by C_2H_2 CVD using Nmm-cat,[11] where high-quality MWNT bundles are synthesized, the present system has a much higher utilization efficiency of carbon source, and the manufactured MWNTs possess the special morphology, while both MWNT materials have similar purity according to the TGA results. In the case of helical MWNTs, we found that five kinds of Ni/Mo/MgO catalysts and five kinds of Ni/Mo catalysts all can result in the formation of the helical and straight CNTs in this catalytic system. However, as for single Ni catalysts, only straight CNTs appear in the residue. On the other hand, several reports have claimed to produce helical MWNTs in the presence of Mo-containing catalysts.[12] Thus, we tentatively attribute this phenomenon to the presence of Mo elements in the catalyst.

In summary, the Mo and Mg elements have been successfully applied to promote and preserve the activity of Ni catalysts for synthesis of the MWNTs from PP by a simple one-step combustion method. The as-synthesized product gave clean MWNTs with straight and double helical structures in good yield as demonstrated by SEM, TEM, and TGA. In this unique catalytic system, the synergistic effects of Mo and Mg on the Ni catalysts may address some critical problems that currently plague carbon nanotube synthesis. This process is not limited to PP systems, and further studies along this line are in progress. Because of the simplicity and high yield of this route, it may potentially be applied on the scale of industrial production.

References and Notes

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