Nanotube Synthesis

Synthesis of Multiwalled Carbon Nanotubes by Catalytic Combustion of Polypropylene**

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Nanostructured carbon materials[1,2] have attracted much interest owing to their variety in structure, predicted unique properties, and potential applications.[3–6] Carbon nanotubes (CNTs) are the most important one-dimensional nanostructured material. With progress in applications of CNTs, synthetic methods for the production of large quantities of CNTs at reasonable prices, such that the process is economically feasible, are imperative. Catalytic decomposition of hydrocarbons is a promising means to produce carbon nanotubes on a large scale.[7,8] Recently the catalytic flame synthesis of CNTs was reported.[9–11] This method has several advantages, for example, it is inherently easier to scale up relative to other production methods that employ electricity.[12–17] Whatever the method of synthesizing CNTs, most of the carbon sources are usually gaseous organic molecules.[18–20] Alternatively, and of interest here, is the much less examined possibility to use polymers as carbon sources in the flame synthesis of CNTs.

Synthesis of CNTs starting from polymers as carbon sources offers the additional advantages of energy-saving and environmental protection. Sustaining development and an increasing demand for petroleum call for the large amount of virtually nondegradable polyolefins to be recycled, in place of the current practice of incineration and landfilling. From an energetic point of view, reutilization of used polyolefins for CNTs seems to be a better choice than direct consumption of C_2H_4, C_3H_6, and other compounds from a petroleum source. This is also of benefit to the recycling of used polyolefins as the properties of recycled materials are usually inferior to those of the parent materials. The key question in the conversion of nondegradable polyolefins into CNTs is then whether the polyolefins can be transformed into small organic molecules to be the source of carbon in the synthesis of CNTs. Some efforts have been made in the conversion of polymers

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into CH_4, C_2H_2, C_3H_6, and so on,[21–25] proving the possibility of synthesizing CNTs with polymers as the carbon source. Syntheses of CNTs or other nanostructured materials in situ through thermal decomposition of polymer/catalyst or polymer/metal mixtures from polyethylene, poly(vinyl alcohol), and polytetrafluoroethene under inert atmosphere have also been reported.[26–29]

Herein, we demonstrate a novel catalytic combustion method of synthesizing multiwalled carbon nanotubes (MWNTs) in situ in high yield from polypropylene (PP) as the carbon source in the presence of an organic-modified clay (OMC) and a supported nickel catalyst (Ni-cat; see Experimental Section). Maleated polypropylene (PP-MA) was used as a compatibilizer to improve the dispersion of OMC and Ni-cat in the PP matrix. In preliminary experiments in the absence of OMC, although the yield of MWNTs from burning composites of PP/PP-MA/Ni-cat increased with an increasing content of Ni-cat, the yield is not yet high enough in terms of a catalyzed reaction. This mainly results from quick volatilization of pyrolytic products of PP in an open reaction system. Recent research has shown that clay in polymer/clay nanocomposites imposed gas-barrier properties and flame retardancy of polymers by creating a maze or “tortuous path” for the progress of the gas molecules through the matrix resin.[30–34] The presence of clay in the combustion synthesis should aid in increasing the yield of MWNTs. Indeed, upon burning PP/PP-MA/OMC/Ni-cat composites, the yield of MWNTs increases with an increasing content of the OMC (Table 1).

X-ray powder diffraction (XRD) patterns of the PP/PP-MA/OMC/Ni-cat composites (Figure 1) show the XRD peaks from the OMC at angles lower than 10° and infer the intercalated structure of the PP/PP-MA/OMC/Ni-cat composite. After burning, the diffraction peaks of PP and OMC in the charred residue disappeared completely, whereas those of Ni-cat remained. Meanwhile two new diffraction peaks appeared, one of which is ascribed to the clay without surfactants and the other to carbon materials with graphitic structure. The charred residue was purified with nitric acid and hydrofluoric acid to remove amorphous carbon, the clay, and most of the Ni-cat, except for a part of the Ni-cat that was enwrapped by the MWNTs. Then only a strong diffraction peak at 25.7° appeared which coincides approximately with that of the (002) diffraction of graphite.

Table 1: Effect of OMC content on the yield of the MWNTs by combustion of PP composites.

Samples	PP [wt%]	PP-MA [wt%]	OMC [wt%]	Ni-cat [wt%]	Yield of MWNTs [wt%]
PCM-0	85	10	0	5	5.24
PCM-1	82.5	10	2.5	5	7.48
PCM-2	80	10	5	5	13.75
PCM-3	77.5	10	7.5	5	32.65
PCM-4	75	10	10	5	41.16

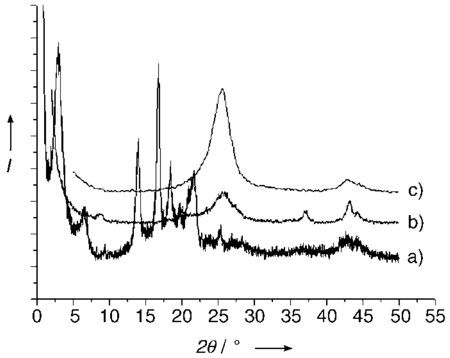

Figure 1. Powder X-ray diffraction patterns of a) PP/PP-MA/OMC/Ni-cat composite, b) its charred residue, and c) purified MWNTs (sample PCM-4).

The morphology of the purified charred residue was examined by scanning electron microscopy (SEM). A large quantity of tubelike nanostructures with diameters ranging from about 20 to 40 nm were obtained (Figure 2a). To further characterize the microstructure of the synthesized nanostructure, studies were made by transmission electron microscopy (TEM). Figure 2b clearly shows that the purified charred residue comprises MWNTs with hollow centers. The MWNTs produced have a diameter of about 33 nm. The wall structure of the carbon nanotube is seen from the higher magnification image of a typical MWNT in Figure 2c. The walls are composed of graphite sheets aligned along the axis of the tube, the outer and inner diameters of which are about 33 and 12 nm.

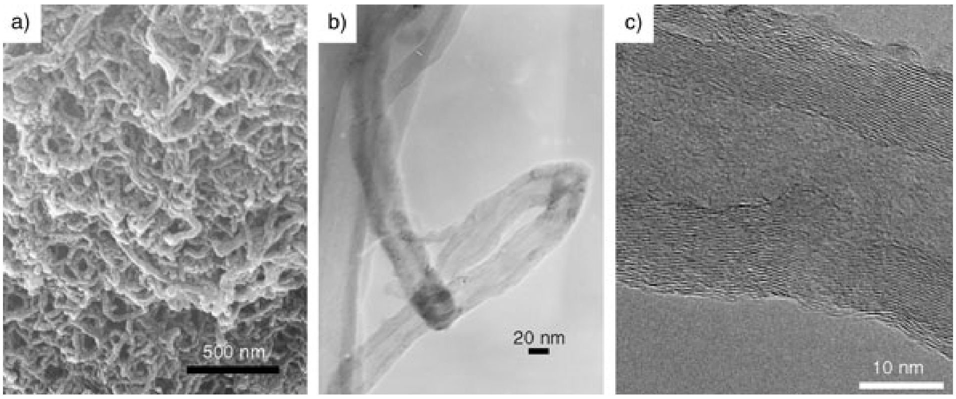

Figure 2. a) SEM image and b) TEM image of synthesized MWNTs; c) higher magnification TEM image of a typical MWNT.

Raman spectroscopy was used to further characterize graphitization of the MWNTs (Figure 3a). The peak at 1598 cm^{-1} (G-band) corresponds to an E_{2g} mode of hexagonal graphite and is related to the vibration of sp^2-hybridized carbon atoms in a graphite layer. The D-band at about 1359 cm^{-1} is associated with the vibration of carbon atoms with dangling bonds in the plane terminations of disordered graphite or glassy carbons.[35]

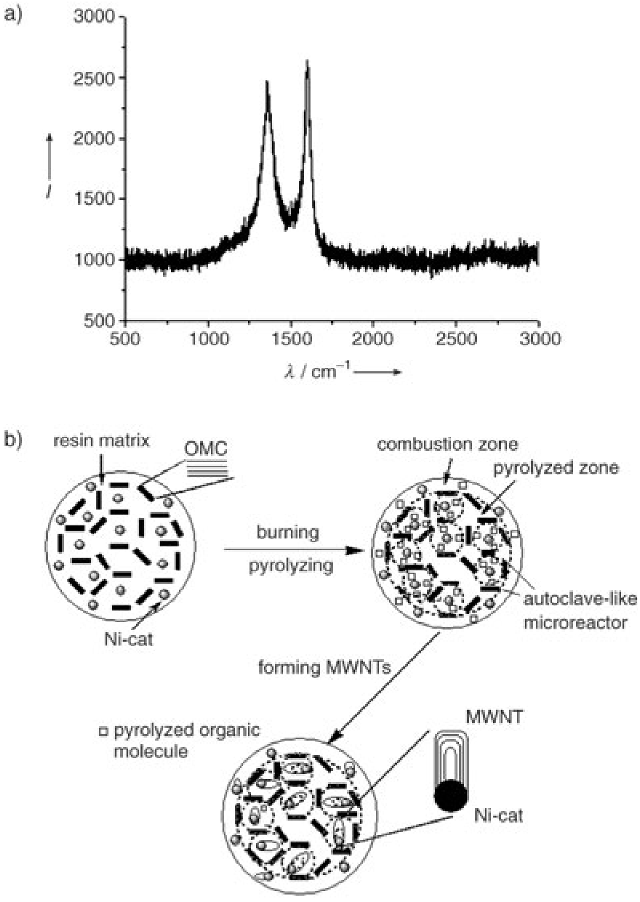

Figure 3. a) Raman spectra of the synthesized MWNTs; b) Schematic diagram of the catalytic combustion method to synthesize MWNTs from polymers as the carbon source.

The unique combination of clay and Ni-cat in the PP matrix leads to high yields of the MWNTs (Figure 3b). Under these conditions, the combustion procedure was accompanied by pyrolytic degradation of PP. In the burning zone, the presence of oxygen leads to combustion of PP with evolution of small molecules such as CO, CO_2, C_2H_4, and C_3H_6.[36] These molecules volatilize quickly and burn out, with only a few converted into MWNTs owing to a lack of contact time. However, a protective charred ceramic surface layer is formed as a result of the ablative reassembly of the clay layers on the composite surface and the charring polymer.[34] In the pyrolytic zone in the absence of oxygen, PP chains undergo endothermic chain scission to release pyrolyzed products that mainly consist of propylene, pentane, 2,4-dimethyl-1-heptene, 2,3-dimethyl-2-heptene, and other fragments, most of which are gases at 600 °C, according to GC–MS analysis. Owing to the resistance of gaseous permeability of the protective charred ceramic surface layer and the inner clay layers, which act like a sealed autoclave microreactor, the pyrolytic products are sealed within a PP matrix (to allow them more time to have interactions with the catalyst particles), dehydrogenated, and aromatized to form MWNTs. With increasing clay content, the barrier properties of clay become more prominent. Note that some aspects of the mechanism of formation of MWNTs during the above synthesis await further investigation.

In summary, we have demonstrated a simple method for the synthesis of MWNTs in situ by combustion of polypropylene in air in the presence of clay and a Ni catalyst. The unique combination of clay and the Ni catalyst in a PP matrix, which resembles a sealed autoclave-like microreactor, leads to high yields of the MWNTs. This process permits an easy synthesis of MWNTs on a large scale. Furthermore, it provides a new possible avenue in the disposal of used polypropylene and its nanocomposites as carbon sources by converting them into high-value MWNTs. This process is not limited to the PP polymer system and can be applied to other polymer systems. Further investigations to improve the quality of MWNTs synthesized by this method are currently in progress in our laboratory.

Experimental Section

Polypropylene (PP; melt flow index: 0.8 g min^{-1}, Panjin Chemical Co.), was mixed with an organic-modified clay (OMC; Closite 15A, Southern Clay), Ni catalyst (Ni-cat; supported on silica–alumina, Ni content ≈ 66 %, Alfa Aesar), and maleated polypropylene (PP-MA; acid value: 26 mg KOH g^{-1}) in a Brabender mixer at 100 rpm at 190 °C for 10 min. Then a piece of the above nanocomposite was placed in a crucible and heated with the flame of a gas lamp at 600 °C. The charred residue was cooled to room temperature and subsequently purified using hydrofluoric acid and nitric acid to eliminate clay, amorphous carbon, and Ni-cat. The yield of MWNTs was calculated as a ratio of the amounts of purified charred residue to polymer in the composite.

The purity and phase structure of the products were obtained by XRD using a Rigaku D/MAX-IIB powder X-ray diffractometer. SEM (XL30EsEM FEG field emission microscope, 20 kV) and TEM (JEM-2010, 200 kV) were used to characterize the morphology and microstructure, respectively, of the products obtained. Raman spectroscopy (T6400, λ_{ex}: 514.5 nm) was used to characterize graphitization of the carbon materials.

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