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Synthesis and characterization of larger diameter carbon nanotubes from catalytic pyrolysis of polypropylene

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Abstract

Carbon nanotubes with larger diameter of about 160 nm have been synthesized through catalytic decomposition of polypropylene and maleated polypropylene using Ni as catalysts in autoclave at 700 °C. Field emission scanning electron microscopy (FESEM), Transmission electron microscopy (TEM) and high-resolution transmission electron microscope (HRTEM) images reveal the morphologies and structures of carbon nanotubes. The possible growth process of carbon nanotubes was also discussed. The results indicate that reaction temperature, maleated polypropylene and Ni catalysts play key roles in the synthesis of large diameters carbon nanotubes. Also, using waste polypropylene as starting material for preparing carbon nanotubes is feasible.

Keywords: Carbon nanotubes; Pyrolysis; Catalysts; Raman spectroscopy

1. Introduction

The outstanding mechanical, electrical, and chemical properties of carbon nanotubes (CNTs) have motivated extensive research for their synthesis, functionalization, and potential application [1]. Particularly, in the field of synthesis, various methods have been developed for the preparation of CNTs such as arc discharge [2], pyrolysis [3], laser vaporization [4] and thermal chemical vapor deposition [5]. Catalytic decomposition of hydrocarbons is a promising means to produce CNTs on a large scale[6,7]. Synthesis of CNTs through thermal decomposition of polymer/catalysts has also been reported. Maksimova et al. [8,9] reported that CNTs with a diameter of about 20 nm had been prepared by decomposition of polyethylene and polyvinyl alcohol using iron catalysts under a nitrogen flow. Previous reports also indicate that the diameters of synthesized CNTs are mostly less than 100 nm, and CNTs with larger diameters are rarely reported.

In this study, we report a simple method for synthesizing CNTs with average diameter of about 160 nm through catalytic decomposition of polypropylene (PP) and maleated polypropylene (MA-PP) using Ni as catalysts in an autoclave at 700 °C. The yield of carbon nanotubes was about 80% through FESEM and TEM observation of the as-prepared product.

2. Experimental

All reagents are commercially available and used without further purification. In a typical experiment, PP (2.00 g), MA-PP (0.50 g) and metal Ni powders (0.50 g) were added into an autoclave of 20 ml capacity. The autoclave was tightly sealed and heated in an electric stove. The stove temperature was raised to 700 °C at a heating ramp rate of 10 °C/min, and maintained for 12 h, then allowed to cool to room temperature naturally. It was found that the final product in the autoclave included many dark precipitates and some residual gases. The dark product was collected and washed with dilute HCl aqueous solution, absolute ethanol, and distilled water. The final product was dried in a vacuum at 60 °C for 6 h.

The X-ray diffraction (XRD) pattern was performed on a Rigaku (Japan) D/max-γA X-ray diffractometer with Cu-Kα radiation ($\lambda = 1.54178$ Å). FESEM (JEOL JSM-6700F) and scanning electron microscopy (SEM, KYKY-1010D) were

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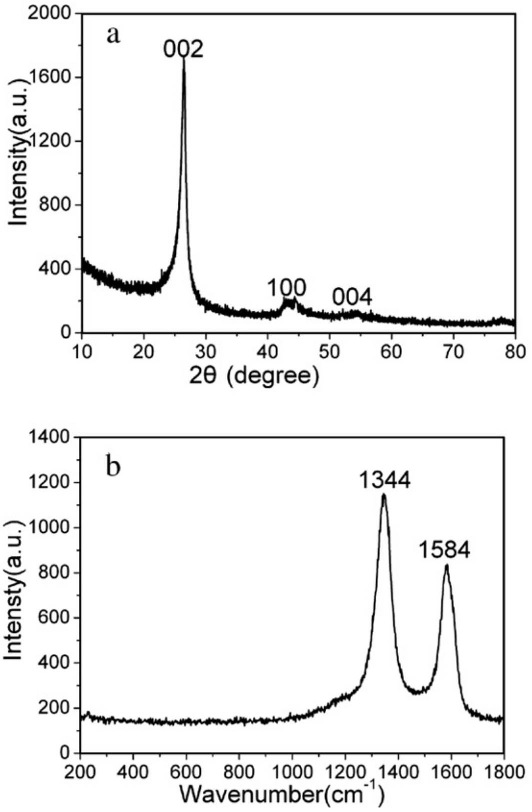

Fig. 1. (a) X-ray diffraction pattern of the final product at 700 °C for 12 h; (b) Raman spectrum of the final product at 700 °C for 12 h.

employed to observe the morphologies of products. TEM images, selected area electron diffraction (SAED) patterns and HRTEM images were taken on a Hitachi H-800 transmission electron microscopy and a JEOL-2010 transmission electron microscopy. The Raman spectrum was investigated at ambient temperature on a Spex 1403 Raman spectrometer (Ar ion laser, 514.5 nm).

3. Result and discussion

Fig. 1a shows the XRD pattern of the sample after it was treated by 6.0 mol/L HCl aqueous solution. It contains three characteristic peaks at about 26.0°, 43.5° and 54.5°, indexed with 002, 100 and 004 diffraction planes of hexagonal graphite (JCPDS card files, no. 41-1487), respectively. No other noticeable peaks induced by impurities can be observed in the XRD pattern. The representative Raman spectrum (Fig. 1b) of the sample shows the typical features of CNTs. In detail, there exist two strong peaks at 1584 cm^{-1} and 1344 cm^{-1}, corresponding to the typical Raman peaks of graphitized carbon nanotubes. The peak at 1584 cm^{-1} is attributed to the Raman-active E_{2g} in-plane vibration mode and is related to the vibration of sp^2-bonded carbon atoms in a two-dimensional hexagonal lattice. The peak at 1344 cm^{-1} is associated with vibrations of carbon atoms with dangling bonds in plane terminations of disordered graphite. The intensity of D-band peak is stronger than that of G-band peak, which originates from the in-plane defects of the product preventing the layer from extending.

The morphology of the product was investigated by FESEM and TEM. Fig. 2a shows a typical FESEM image of the product. It is found that large quantities of one-dimensional nanostructures were obtained. Inset in Fig. 2a is a magnified FESEM image of such one-dimensional nanostructures, showing hollow tube structure. It implies that the product was CNTs. The tubular structures were further characterized by TEM. The TEM images indicate that the product is assuredly nanotubes. From Fig. 2b, the average outer diameters of the CNTs are about 160 nm with wall thickness of about 45 nm, but occasionally few CNTs with thinner diameters are observed. The yield of CNTs was about 80% by FESEM and TEM observation. Fig. 2c displays a single nanotube with outer and inner diameters of 162 nm and 46 nm,

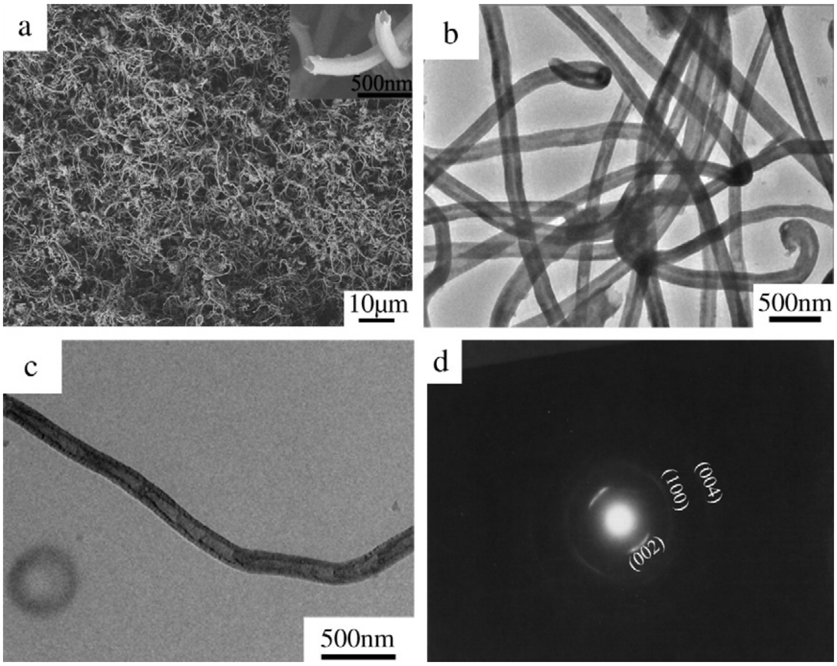

Fig. 2. (a) FESEM images of CNTs and CNTs with open tips (inset); (b) TEM image of several CNTs; (c) TEM image of a single CNT; (d) SAED pattern of the CNT.

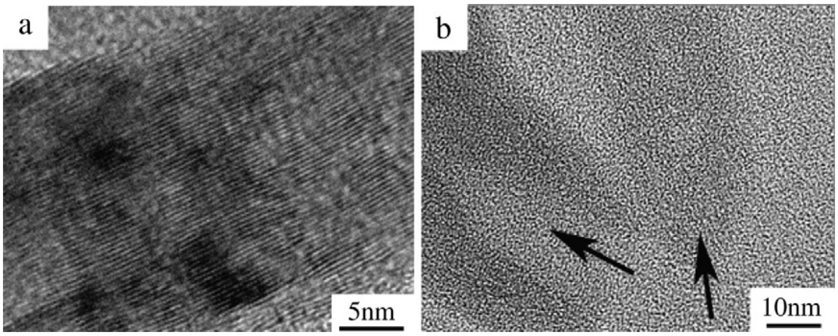

Fig. 3. (a) HRTEM image of the wall of CNT; (b) HRTEM image of the tips of CNTs.

respectively. SAED pattern (in Fig. 2d) was taken on the CNT. The SAED pattern exhibits a pair of small but strong arcs for 002, together with a ring for 100 and a weak ring for 004 diffractions. The appearance of 002 diffractions as a pair of arcs indicates some orientation of the 002 planes in the carbon tubes. Detailed structure information of the CNTs was observed through HRTEM. HRTEM image displayed in Fig. 3a shows that the wall consists of many layers of carbon sheets, and the lattice fringes can be clearly identified. The average value of (002) plane spacing is 0.34 nm, which is consistent with the information obtained from the XRD result. The HRTEM image from Fig. 3a also reveals that the stacking faults exist in the wall structure of CNTs. Fig. 3b displays the HRTEM image of tips of CNTs. It shows that one tip of the as-synthesized CNTs may be open, and the other one is close.

A series of relevant experiments were carried out through altering experimental parameters to investigate the effect of reaction conditions on the formation of CNTs. It is obvious that the reaction temperature, Ni catalysts, and MA-PP played critical roles in the formation of CNTs. The reaction initiated at 400 °C, and the main product was amorphous carbon. CNTs have been produced at 500 °C, and the yield of CNTs was enhanced with the increase of temperature. The product possessed about 80% CNTs at 700 °C. Carbon solid spheres were the only product (in Fig. 4a and b), when Ni were absent from the reaction system. It indicated that Ni may be as catalysts in the decomposition of PP. MA-PP might contribute to two actions in the growth process of CNTs. MA-PP was used as a compatibilizer to improve the dispersion of Ni in PP, and then carbon atoms with Ni catalysts form a homogenous system. Except for the action, MA-PP may also reduce the velocity of carbon atoms distribution. If the velocity of carbon atoms distribution on catalysts surface is slow, the graphite layers will form CNTs. On the contrary, the graphite layers produce solid carbon spheres (in Fig. 4c and d), when the velocity of carbon atoms distribution is fast.

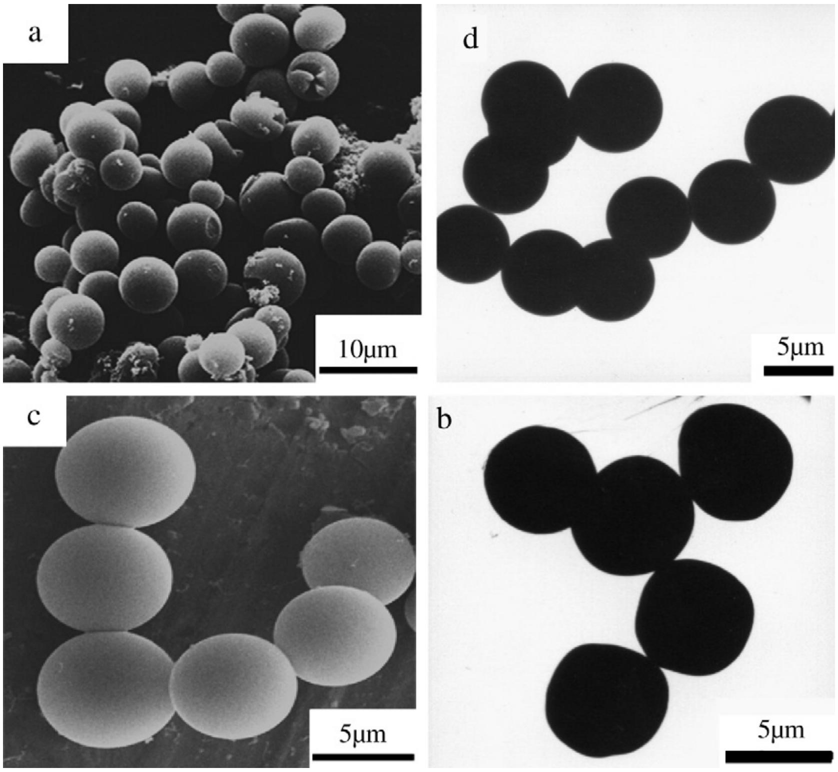

Fig. 4. (a) and (b) SEM and TEM images of carbon solid spheres when Ni catalysts were absent, respectively; (c) and (d) SEM and TEM images of carbon solid spheres when MA-PP were absent, respectively.

The large variety of the products at different experimental parameters implies that it is complex in the reaction system. Although the detailed mechanism is not fully understood at the present, it is likely that PP and MA-PP began to fuse at relevant temperature, and PP and Ni were mixed uniformly under the assistance of MA-PP. With the increment of temperature, PP and MA-PP began to decompose to form carbon atoms around Ni particles, and Ni acted dehydrogenation catalysts in the experiment. Ni particles were segregated to form carbon-surrounded Ni particles. A high surface packing density of Ni particles facilitates the growing nanotubes to grow along direction. According to the experimental progress, the growth of CNTs may follow the bottom growth mechanism [10–12]. Of course, due to the complexity of experimental process, the exact formation process of CNTs still needs further research.

In summary, CNTs with average diameter of about 160 nm were synthesized from catalytic decomposition of PP and MA-PP with Ni as catalysts. The toxic or corrosive reagents have been completely avoided. Based on the experimental results, a possible growth process for the CNTs is proposed. Reaction temperature, Ni catalysts, and MA-PP played key roles in synthesis of larger diameter CNTs. Because of the cleanness, simplicity and high yield of this route, it may potentially be applied on industrial production.

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