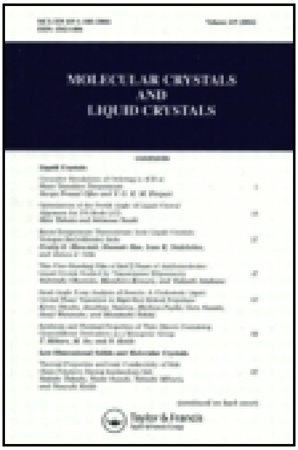

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Carbon nanotubes prepared from polymer microspheres by spinning and carbonizing

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CARBON NANOTUBES PREPARED FROM POLYMER MICROSPHERES BY SPINNING AND CARBONIZING

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Multi-wall carbon nanotubes (CNTs) with diameters between 10 nm and 20 nm were prepared by melt spinning, stabilizing and carbonizing of fine core/shell-1/shell-2 polymer microspheres. Microspheres were synthesized by three-steps soap free emulsion polymerization of methylmetacrylate (MMA) and acrylonitrile (AN) using potassium persulfate (KPS) as a polymerization radical initiator. The final composition of microspheres was PMMA core/PAN shell-1/PMMA shell-2 and diameter ca. 500 nm. The outer PMMA layer played the role of a matrix polymer. Microspheres were directly melt spun at ca. 300°C followed by stabilization of PAN at 220°C in oxygen and carbonization at 1000°C in nitrogen. TG-DTA study was used for clarifying the PAN thermal behavior during CNTs synthesis. SEM, TEM and HRTEM were used in characterizing the microspheres and CNTs morphology.

Keywords: carbon nanotubes; melt spinning; core/shell microspheres; soap-free emulsion polymerization

INTRODUCTION

Several synthetic methods of CNTs [1–4] have been developed since their discovery [5]. Previously, our group successfully synthesized carbon nanotubes from the phenolic resins as a carbon precursor by use of polymer blend method [6]. However, through the work the preparation of uniform microcapsules showed to be a difficult process and the yield of CNTs as well as their diameters did not satisfy our ideas completely. Here we report the recent results on CNTs prepared by spinning, stabilizing and carbonizing of fine core/shell-1/shell-2 (referred to as C/S-1/S-2 in text) polymer particles. The principle of previous and present method is basically the same, but the crucial steps of method have been improved. C/S-1/S-2 microspheres are made from two kinds of polymer, one is a carbon precursor polymer and the other one is polymer disappearing completely at heat treatment. Microcapsules are prepared by three steps soap-free emulsion polymerization of methylmetacrylate (MMA) and acrylonitrile (AN) using potassium persulfate KPS as a radical polymerization initiator. Final composition of microspheres is PMMA core/PAN shell-1/PMMA shell-2. The outer PMMA shell plays the role of a matrix polymer and the need of using the other matrix polymer is eliminated. As-synthesized microspheres are after freeze drying subjected to melt spinning using a conventional apparatus [7]. In this process, the microspheres are elongated extensively and general rule is the better the elongation; the thinner the carbon nanotubes can be prepared. Spinning is followed by stabilization of PAN in an oxidative atmosphere at 220°C and by carbonization in the inert atmosphere at 1000°C. During carbonization the core and shell-2 PMMA disappears completely and the CNTs derived form elongated PAN shells remain.

EXPERIMENTAL

In our experiment, fine polymethylmetacrylate (PMMA) core microspheres were synthesized by polymerizing of 35 ml methylmetacrylate (MMA) in 350 ml of water at 70–80°C for 8 h using 35 mg potassium persulfate (KPS) as a radical initiator. Subsequently 90 ml of the resulting PMMA emulsion (corresponding to 8 ml of MMA) was mixed with 2 ml of AN, followed by 8 h polymerization of AN at 70–80°C using 5 mg KPS to form PMMA core/PAN shell microspheres (referred to C/S in the text). To prepare C/S-1/S-2 microspheres, 24 ml of MMA and 35 mg of KPS was added into the 350 ml of C/S microspheres emulsion followed by 8 h polymerization of MMA at 70–80°C. The atmosphere kept during all three partial polymerization systems was the inert atmosphere of nitrogen and the sufficient distribution of monomers was achieved by an intensive stirring. After freeze-drying the C/S-1/S-2, microspheres were melt spun at 300°C and stabilized in oxygen at 220°C for 3 h.

Stabilized sample was finally carbonized in nitrogen at 1000°C for 30 min. Temperature of stabilization rose at 5°C/min to 150°C and then by 1°C/min to 220°C and the heating rate during carbonization was kept on 5°C/min. Obtained black powder was observed by scanning electron microscopy (SEM, JEOL JSM 5300, operated at 20 KeV) and transmission electron microscopy (HRTEM, JEOL JEM-4000FX, acceleration voltage 400 KeV). To see the accurate diameter of PAN shell of C/S, the cross-section specimen was prepared by dispersion of microspheres in epoxy polymer and cut using freezing microtome. Sample after staining in OsO_4 vapour was observed by transmission electron microscopy.

In order to understand the thermal behavior and weight changes of PAN during whole CNTs preparation process, TG-DTA study of PAN has been performed (Rigaku, Thermo Plus TG 8120). PAN sample was subjected to the spinning, stabilizing and carbonizing model heat treatments, step by step. The heat treatments were the same as the one used in the real CNTs synthesis. The only one difference is the temperature of carbonization model treatment (900°C). TG-DTA profiles of PMMA and PAN without any model treatments were recorded too.

RESULTS AND DISCUSSION

Figure 1 shows the SEM photographs of PMMA (a), C/S (b) and C/S-1/S-2 (c) uniform microspheres. Diameters of PMMA, C/S and C/S-1/S-2 are 330–340 nm, 350–360 nm and 490–500 nm, respectively.

Figure 1d shows the cross-section photograph of C/S. The diameter of PMMA core and PAN shell is 295 nm and 20–30 nm, respectively. The spinnability of C/S-1/S-2 was high, particularly due to the high spinnability of PMMA and good homogeneity of sample. Figure 2a showing the SEM photograph of melt spun fibers approves this fact.

Fibers are uniform in diameters, ca. 15 μm and the surface is smooth. The SEM image of sample after stabilization and carbonization can be seen on Figure 2b. Sample contains fibrous structures aligned in one direction.

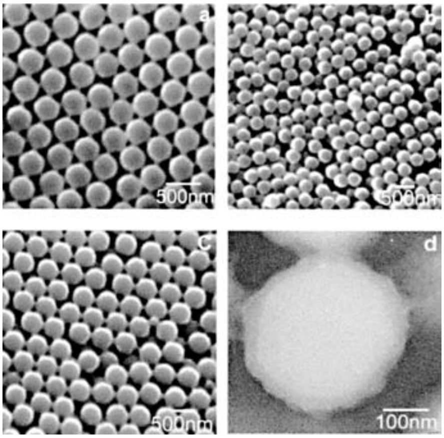

FIGURE 1 SEM photographs of (a) PMMA, (b) C/S, (c) C/S-1/S-2 and (d) cross-section TEM photograph of C/S. Thickness of PAN coating is 20–30 nm.

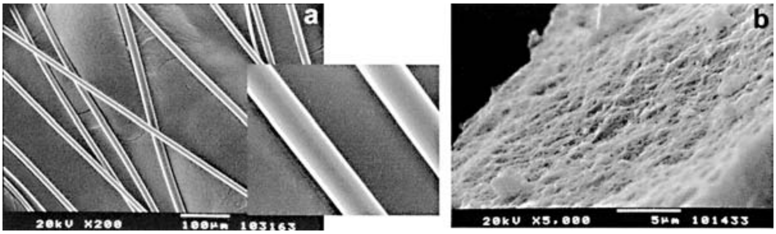

FIGURE 2 SEM photographs of (a) melt spun fibers with the detail of side surface, (b) sample after stabilization and carbonization.

Low magnification TEM photograph of the same sample is shown on Figure 3a. The MWCNTs are characterized by being straight and having the closed tips and further HRTEM study revealed their detailed structure. As Figure 3b and 3c show, the walls of nanotubes are made from graphene sheets. The diameter of tube on Figure 3a is 12 nm and the diameter of hollow is 2.1 nm. CNT on Figure 3b is thicker; diameters of tube and hollow are 19.5 nm and 2.8 nm, respectively. TG-DTA profiles of PMMA, as-synthesized PAN and profiles of PAN subjected to spinning, stabilizing and carbonizing modulation are shown on Figure 4. As expected, PMMA disappears completely at ca. 400°C and the decomposition is accompanied by a broad endothermic peak at 365°C (Fig. 4a). On the other hand, as synthesized and no-stabilized PAN gives 35 wt% of carbon yield after heating at 1000°C (Fig. 4b). The strong exotherm appearing at 280°C belongs to

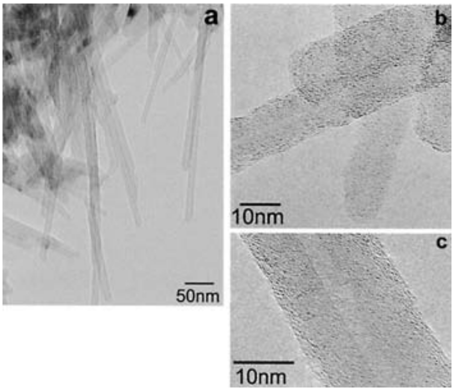

FIGURE 3 (a) Low-magnification TEM photograph of CNTs, (b), (c) HRTEM images of these CNTs. The diameter of central tube and hollow on (b) is 12 nm and 2.1 nm, respectively. Diameter of CNT on (c) is 19.5 nm and the diameter of hollow is 2.8 nm.

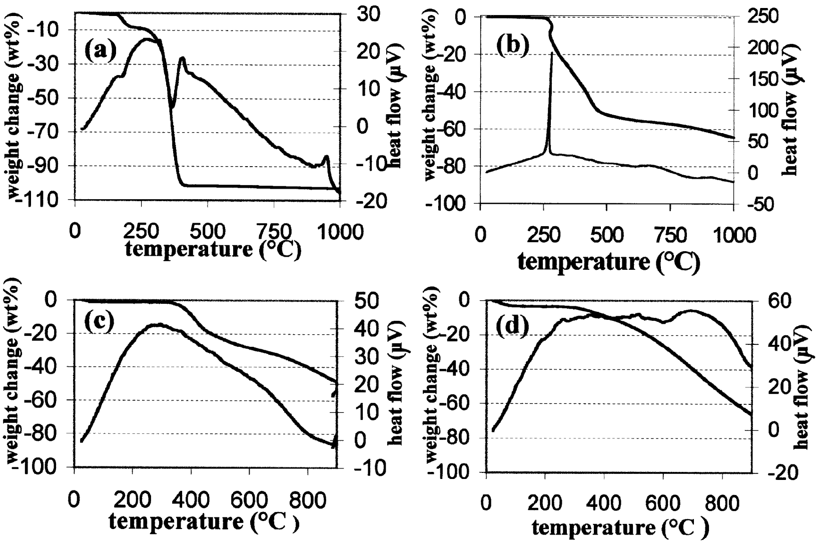

FIGURE 4 TG-DTA profiles of (a) PMMA, (b) as-synthesized PAN, (c) PAN heated to 900°C after spinning and stabilization modulation, (d) PAN heated to 900°C after spinning modulation, but no stabilization modulation.

the intramolecular polymerization of nitrile groups [8]. Figure 4c shows the TG-DTA data of PAN after heating at 900°C previously subjected to spinning modulation followed by stabilization modulation. The exotherm is not showing up and carbon yield increased to 45 wt%. The importance of PAN stabilization in an oxidative atmosphere for the increasing of carbon yield and the thermal properties become clear from Figure 4d, which represents the TG-DTA profile of PAN heated up to 900°C previously subjected to spinning modulation but no stabilization modulation. The total carbon yield of thus treated PAN is 36 wt%, which is almost same value as the carbon yield resulted from as-synthesized PAN sample subjected directly to the heat treatment (Fig. 4b). The absence of exotherm on DTA curve means that the intramolecular polymerization of nitrile group occurs at the spinning process. Presented TG-DTA data clarified, to a certain extent, the thermal behavior of PAN during the CNTs preparation. However, the detailed mechanisms of stabilization of the precursors for PAN-based carbon fibers, which we drew on, is complicated and not clear until now even though an intensive research in order to clarify this phenomenon has been done. The explanation of relatively high degree of graphene sheets developing in CNTs in spite of low carbonization temperature can be found in the severe stretching of the C/S-1/S-2 microspheres during the spinning process what resulted in a preferred orientation of PAN molecules along the fiber axis, the memory of which remained in the CNT after carbonization. Such a technique is used practically to prepare PAN-based high performance carbon fibers[9]. Moreover, the elongation and stretching of PAN as a microsphere's shell-1 is supported by spinning and elongation effect of core-PMMA and shell-2 and PMMA represent the polymer with high elongation performance.

We believe presented method to be an appropriate candidate for low-cost mass production method of CNTs. In addition, the very recent results suggest that the fine structural and morphological control of CNTs is achievable by changing the PAN shell thickness and the heat treatment temperature. These results will be published soon.

CONCLUSIONS

We presented a synthetic method for CNTs based on the spinning, stabilizing and carbonizing of PMMA core/PAN shell-1/PMMA shell-2 microspheres. CNTs derived from elongated PAN shells were left after PMMA disappeared during the heat treatment. The interested result we have obtained is that the nanotubes walls consist of more or less developed graphene sheets in spite of low heat treatment temperature. TG-DTA study approved the efficiency and importance of the PAN stabilization for the resultant carbon yield. A consecutive research is being conducted in order to clarify the uncertain facts as well as in order to prepare CNTs differing in their morphology.

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