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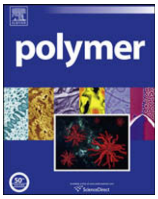

Formation of polymer/carbon nanotubes nano-hybrid shish–kebab via non-isothermal crystallization

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A B S T R A C T

Multi-walled carbon nanotubes (MWNTs) periodically decorated with polyethylene (PE) lamellar crystals had been prepared using the non-isothermal crystallization method. The morphology and structure of polyethylene attached to MWNTs were investigated by means of transmission electron microscopy (TEM). A nano-hybrid shish–kebab (NHSK) structure was observed wherein the average diameter of PE lamellar crystals varies from 30 to 150 nm with average periodicity of 35–80 nm. The TEM images of samples obtained at 125 °C showed that MWNTs were first wrapped by a homogeneous coating of PE with few subglobules, then PE chains epitaxially grew from the subglobule and formed lamellar crystals perpendicular to the carbon nanotube axis. It is suggested that the homogeneous coating plays a key role in the formation of NHSK structures. And the formation process was discussed based on the intermediate state images of samples obtained at 95 °C. While NHSK structures cannot be formed by using polypropylene (PP). This may attribute to the zigzagged conformation of PP chains on the surface of MWNTs, which hinders the formation of homogeneous coating of PP on it.

1. Introduction

The discovery of carbon nanotubes and carbon nanotube based materials has inspired scientists for a range of potential applications due to their extraordinary mechanical, electrical, and optical properties [1–3]. The polymer/carbon nanotube composites have attracted wide attention. However, fabrication of homogeneous nanocomposites with carbon nanotubes remains a great technical challenge. Due to the CNTs' intrinsic poor solubility, they often self-assembled in bundles, which limited their application. Surface functionalization is an effective and necessary approach to improve its compatibility with solvent or polymer matrix. Covalent functionalization of carbon nanotubes has been envisaged as a very important method for nanotubes processing and application [4–6]. Although a variety of chemical routes have been investigated to achieve nanotube solubility, the conjugation of the CNTs sidewall is disrupted, and electrical and mechanical properties of the covalent functionalized CNTs decrease dramatically compared to the pristine ones due to the breaking of the sp^2 conformation of the carbon atom. On the other hand, the non-covalent method involves wrapping of the nanotubes by surfactants, polymerizable monomer and polymers [7–12]. And the integrity of CNTs' sidewall structure is preserved, since the wrapping molecules is fixed onto CNTs by Van der Waals force or by forming π-stacking.

Numerous studies show that carbon materials, in various forms, are able to induce polymer crystallization. Tracz et al. [13] observed highly ordered contact layers of polyethylene crystallized from the melt on highly oriented pyrolytic graphite (HOPG) by atomic force microscopy. Czerw et al. [14] used the carbon nanotubes to pattern a high molecular weight polymer. The resulting regularity of poly-(propionylethylenimine-co-ethylenimine) (PPEI-EI) on CNTs suggested a "nanotube-driven" crystallization process. Based on the former studies, Li et al. [15–17] reported the controlled polymer solution crystallization method to achieve polymer decorated CNTs. PE and Nylon 66 were found to be able to periodically grow along the CNT axis and form nano-hybrid shish–kebab (NHSK) structures. The formation mechanism of the NHSK was attributed to "size-dependent soft epitaxy". Zhang et al. [18] also reported the formation of NHSK using supercritical CO_2 as antisolvent to induce polymer epitaxial growth on CNTs. These studies offered a new route to functionalize any kinds of pristine CNTs with different diameter or chirality. And the NHSK can be used as templets to prepare nanomaterials with special properties, because of the unique structures of the NHSK.

Meanwhile there is plenty of research work being done in the field of molecular dynamics simulations of the interaction between

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polymer chains and carbon nanotubes [19–25]. Yang et al. [19] studied the isothermal crystallization process of PE chain on SWNT (10, 10), which indicated that PE chain was first adsorbed onto the SWNT surface, and then orientated to an ordered lamellae. Wei [20] found that CNT induced high orientation of the PE chains along the nanotube axis, which was correlated with the high density in the first adsorption layer around CNT (10, 0). Liu et al. [21] also reported that PE tended to form an extended conformation to wrap carbon nanotubes, while PP adopted a zigzagged conformation on the nanotubes surface instead of helical conformation.

In current work, we explored the feasibility of synthesizing PE/MWNTs NHSK structures by non-isothermal crystallization method. Compared with previously reported crystalline polymer periodically wrapping to functionalize CNTs via an isothermal solution crystallization technique, non-isothermal crystallization method would be attractive since the manipulation process is easier and similar to the actual industrial process. The formation mechanism of this method was investigated based on the intermediate state obtained at different stages and the MD simulation results reported. PP was also employed in our studies due to the different repeat unit arrangement and conformation between PP and PE.

2. Experimental section

Pristine MWNTs (purity was about 95%, average diameter range 10–20 nm, length range 5–20 μm) were purchased from Alfa Aesar, and used without any additional treatment to preserve the integrity of CNTs' sidewall structure. PE (7020, melt flow rate (MFI) = 7.5 g/10 min) used in this study was supplied by Xinjiang Dushanzi International Petroleum & Chemical Ltd. PP (1300, MFI = 1.1 g/10 min) was purchased from Beijing Yanshan Petrochemical Co., Ltd. 1,2-Dichlorobenzene (DCB) and *p*-xylene were purchased from Shanghai Lingfeng Chemical Reagents Co. Ltd.

PE/MWNT NHSK was prepared by non-isothermal crystallization method. 2 mg PE was dissolved in 8 g DCB at 125 °C. 1 mg MWNTs was dispersed in 2 g DCB and ultrasonicated for 3 h and then added to PE/DCB solution and hold at 125 °C for 10 min. The mixture was cooled from 125 °C to room temperature spontaneously at a cooling rate of 1 °C/min when the temperature was higher than 80 °C. Sample was filtered and washed by hot *p*-xylene after crystallization to remove uncrystallized PE. In order to investigate the intermediate state of NHSK formation process, samples were collected at different temperature during the non-isothermally crystallization. For PP/MWNTs crystallization, the mixing of solution was kept at 170 °C for 10 min and then cooled to room temperature spontaneously.

The morphology of PE or PP functionalized MWNTs was characterized by transmission electron microscopy (TEM). Samples were collected on a TEM grid and conducted using a JEOL-2100 microscope with an accelerating voltage of 200 kV.

3. Results and discussion

3.1. Formation of PE/MWNTs NHSK using non-isothermal crystallization

Fig. 1a and b shows the TEM images of PE-decorated MWNTs after non-isothermal solution crystallization from 125 °C to room temperature. It is evident that MWNTs were periodically decorated with PE crystal lamellae (edge-on views) forming the NHSK structures, which was similar to the NHSK structures formed by isothermal crystallization method under 90 °C for 1 h, as shown in Fig. 1c and d. And the inset to Fig. 1b is the corresponding Fast Fourier transform (FFT) diffraction pattern of the NHSK structures. The clear polycrystalline rings with lattice fringe spacing about 0.41 nm corresponded to crystal faces of (110) of PE. Fig. 2 displays the high magnification TEM image of the NHSK structures after non-isothermal crystallization. A thin coating of PE, with uniform

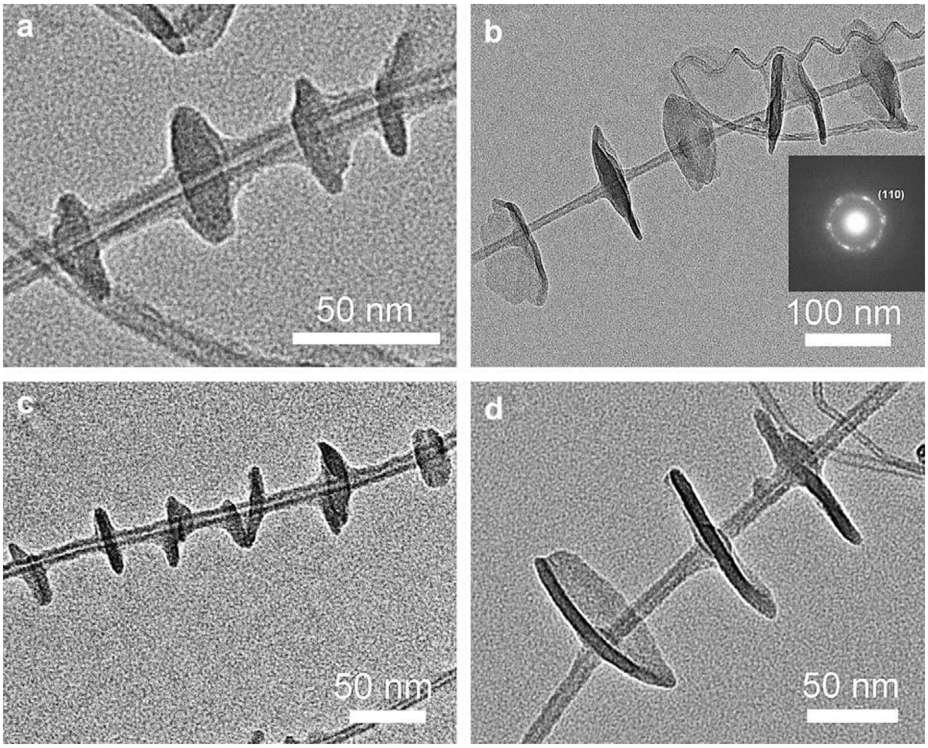


Fig. 1. TEM images of PE/MWNTs NHSK. (a) and (b) prepared by non-isothermal crystallization; (c) and (d) prepared by isothermal crystallization under 90 °C for 1 h; The inset to (b) is the FFT diffraction pattern of the NHSK structures.

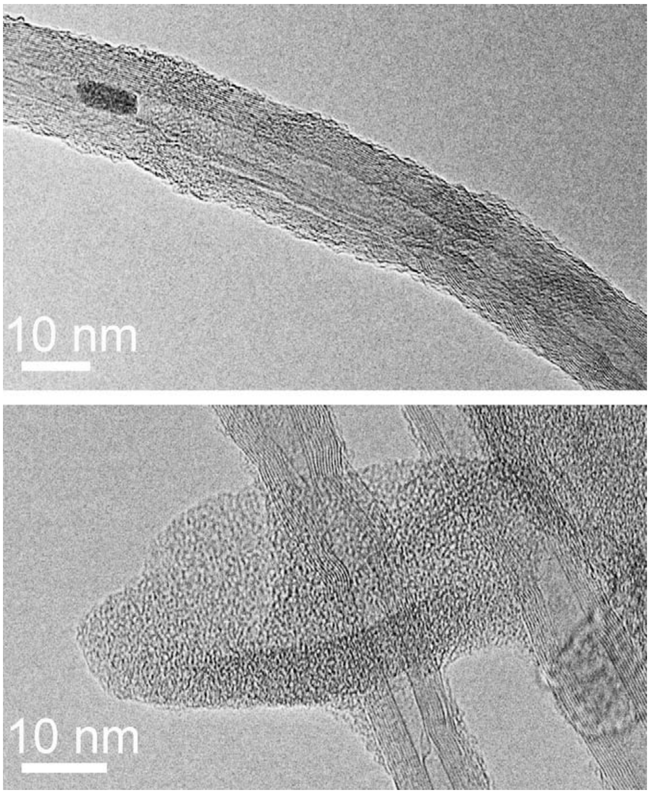


Fig. 2. The high magnification TEM image of NHSK prepared by non-isothermal crystallization method.

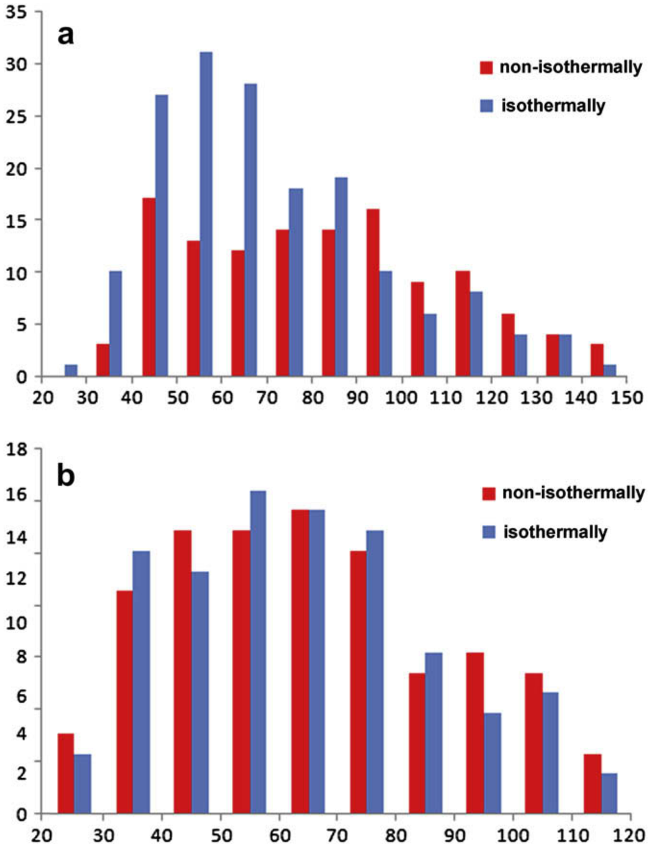


Fig. 3. The distributions of (a) lamellas diameter and (b) periodicity of both non-isothermal crystallization and isothermal crystallization method.

thickness of 1–3 nm, could be seen surrounding the whole nanotubes, and it is thicker at the location adjacent to crystal lamellae. Fig. 3 gives the distributions of lamellar crystal diameter and periodicity of NHSKs obtained by both non-isothermal crystallization and isothermal crystallization method, based on the TEM images of 100–200 lamellae. The diameters of lamellar crystals were in the range of 30–150 nm. The lamellae sizes of sample prepared by isothermal crystallization concentrated in 40–90 nm, while those prepared by non-isothermal crystallization showed a wider distribution. This phenomenon can be attributed to the effect of different undercooling during non-isothermal crystallization process, where new lamellae were continuously initiated from the CNT surface during cooling. Nevertheless, the periodicities of both methods were almost in the same range of 35–80 nm, indicating that the crystallization temperature has rare influence on it.

Interestingly, the diameters of most crystal lamellae (with thickness about 7–15 nm) are proportional to the periodicity. The reason for this is probably that lamellae with large periodicity are capable of absorbing more chains to epitaxially grow on it and, consequently, they could grow much bigger. For the lamellae prepared by non-isothermally crystallized, $D/l = 1.4–1.7$ (D is diameter of a crystal lamella, l is the average distance between the adjacent lamellae), while for the lamellae prepared by isothermally crystallized, $D/l = 1.1–1.4$. And the different values of D/l obtained from these two methods may result from different undercooling.

The TEM images of Figs. 1 and 2 show that the thickness of crystal lamellae was quite different (~7–25 nm) in one sample. The thickness of crystal lamellae is affected by the crystallization time as reported [26]. PE crystal lamellae can thicken spontaneously due to active sliding motions of PE chains during crystallization, following a logarithmic law $d_c = C_1 \log t + C_2$ (d_c is the thickness of crystal lamellae, t is the crystallized time, C_1 and C_2 are constants). The MWNTs are decorated with PE lamellae of different sizes and thickness after the same crystallization process. It is expected that crystal nucleation on MWNTs and crystal growth occur simultaneously. For the crystal lamellae formed at early stage, the final size and thickness are larger. To confirm this, we investigated the formation process of NHSK and captured the intermediate state of PE lamellae at 95 °C.

3.2. Formation process of PE/MWNTs NHSK using non-isothermal crystallization

It is important to study what happened at the beginning of this process, and the following experiment was performed. A sample was held at 125 °C for 10 min and then quenched into liquid nitrogen. From the TEM image (Fig. 4a), it can be seen that no NHSK structure formed. The inset to Fig. 4a is the FFT diffraction pattern of the sample. There was no polycrystalline rings observed, indicating that PE chains deposited randomly on the MWNTs surface in amorphous phase. It is understandable that PE cannot form crystals at this high temperature. While the high magnification TEM image (Fig. 4b) shows that a thin homogeneous PE coating with a few subglobules (which may served as nuclei for the growth of crystal lamellae) have already formed. It suggests that the formation of NHSK is initiated as PE chains align along MWNTs axis, forming the homogeneous coating. To further confirm this, we prepared NHSK structures using very lower PE concentration (0.002 wt%, about 10% of the former), and the TEM images are shown in Fig. 4c and d. It can be found that most of MWNTs were wrapped with a thin PE coating and only a few parts of MWNTs were decorated by small PE crystal lamellae with a diameter of about 30 nm. It also indicated that the homogeneous PE coating on MWNTs surface was formed firstly

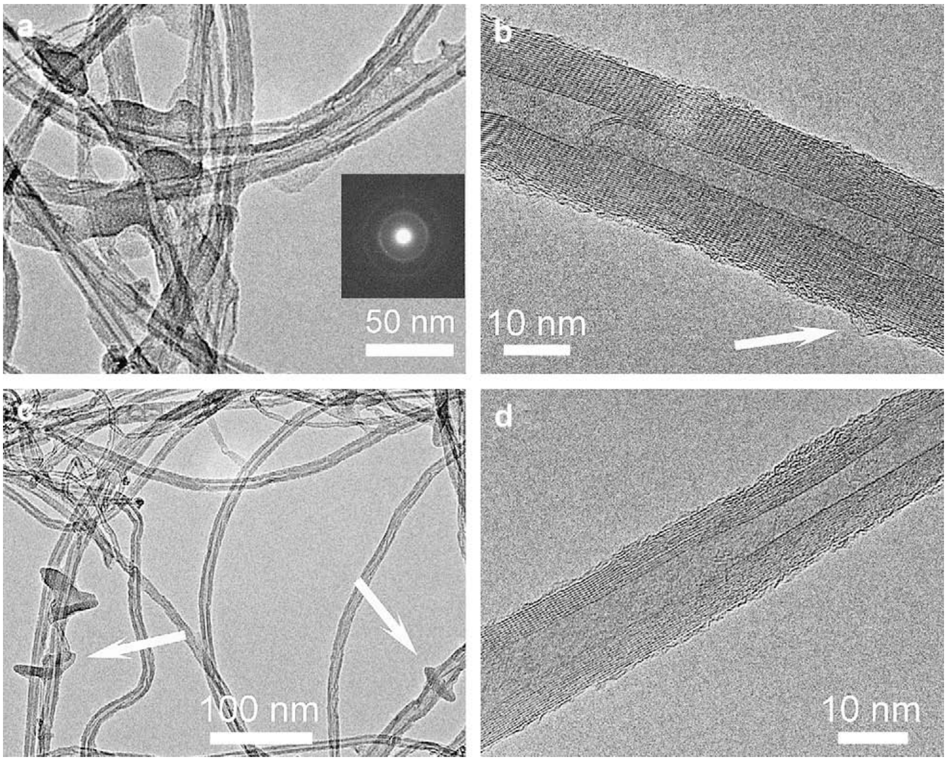
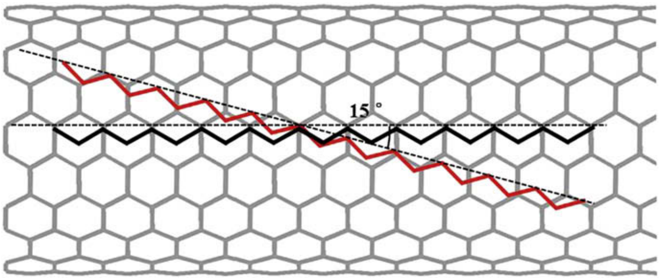


Fig. 4. (a) TEM image and (b) high magnification TEM image of PE/MWNTs sample obtain after holding in 125 °C for 10 min; (c) and (d) shows NHSK prepared with lower PE concentration (0.002 wt%); The inset to (a) is the FFT diffraction pattern of the sample.

during the crystallization process before the growth of crystal lamellae. The formation of the homogeneous coating at the first stage of crystallization process coincided with the proposal discussed by Yang et al. [19]. They investigated the relaxation process of a single PE chain on a SWNT surface based on the MD simulation. It proceeded in following steps: first, some segments of PE chains were anchored onto the SWNTs surface; subsequently, the segments displaced along the surface, and dragged their neighboring segments onto the surface; finally, the PE chain formed a uniform coating until almost all the segments contacted SWNTs. And the simulations also indicated that subglobules would appear during the later stage of this process.

We speculated that the homogeneous PE coating played a key role in the formation of NHSK structures. According to the "size-dependent soft epitaxy" mechanism, in which PE crystal lamellae (kebab) directly epitaxially grow from the sidewall of MWNTs, the growth of NHSK depended on the diameter of MWNTs. As the MWNTs diameter was quite small, approaching the radius of gyration of PE (about 10–20 nm for the PE used in this experiment), PE chains preferred to align along the MWNTs axis, because of geometric confinement, regardless of the lattice matching between the PE chains and the graphitic sheet of MWNTs surface. However, in this work, it was clear that PE crystal lamellae epitaxially grew from the homogeneous coating, which consists of several layers of PE chains, instead of sidewall of MWNTs. Due to the strong interaction between PE chains and MWNTs, the orientation of the first layer chains of the homogeneous coating, which directly contacted to the MWNTs sidewall, should be mainly determined by the lattice of the graphitic sheet. Taking the CNT (10, 0) for example, the angle between the orientation of the first layer PE chains and the tube axis tended to 8°and 12.5°, based on MD simulations. While for the CNT (10, 10), the angle tended to 15°, as shown in Scheme 1 (the red chain); and for the CNT (40, 40), the angle was 0°, 20°, 31°, 41°and 60°[20]. Clearly, most of the first layer chains of the homogeneous coating did not align along the nanotube axis. We assumed that lattice distortion or chains slide occurred in the homogeneous PE coating, because of geometric confinement caused by curvy surface of MWNTs. Consequently, PE chains of the surface layer of the homogeneous coating tended to align along tube axis (the black chain in Scheme 1), and PE crystal lamellae could epitaxially grow from the coating and perpendicular to the MWNTs axis. So disregarding the CNTs chirality, the strict lattice matching between PE chains and the graphitic sheet, and the geometric confinement can be satisfied simultaneity, due to the existence homogeneous PE coating.

To investigate the growth process of periodical PE crystal lamellae, samples were obtained when temperature decreased to 95 °C, and then isothermally filtered to remove the uncrystallized PE. A series of TEM images of the intermediate state of crystal lamellar growth process are shown in Fig. 5. Fig. 5a shows a wide range TEM image of the sample. It is obvious that there are only few parts of MWNTs decorated by PE crystal lamellae. As shown in Fig. 5b and c, the sizes of the crystal lamellae are generally smaller than those of the final ones shown in Fig. 1a and b, indicating that



Scheme 1. The orients of PE chains compared to CNT (10, 10): the first layer of chains (the red) and the surface layer of chains (the black). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

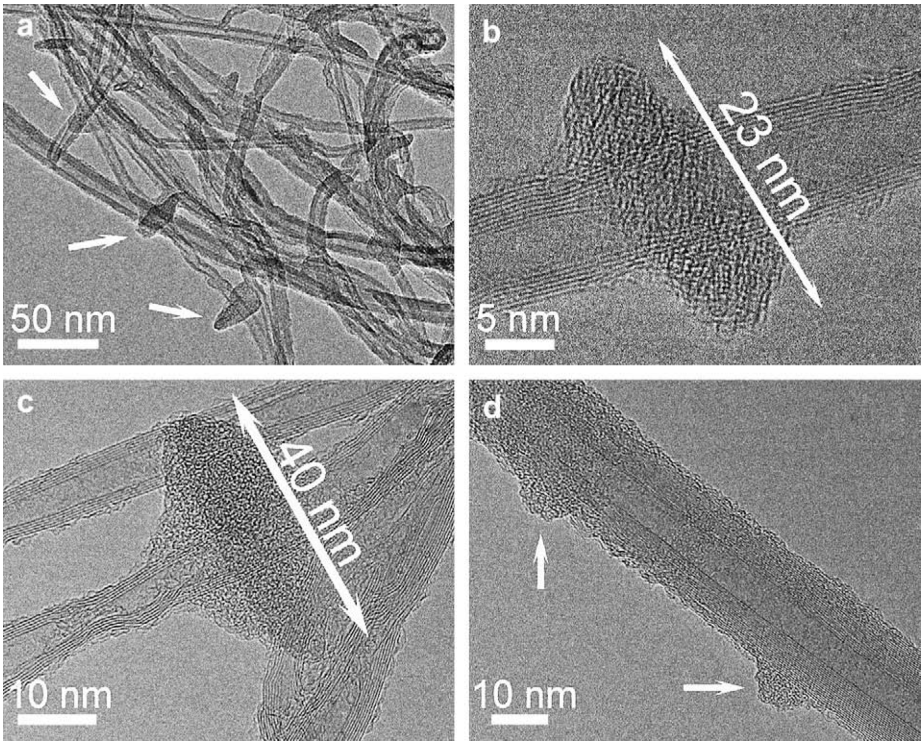
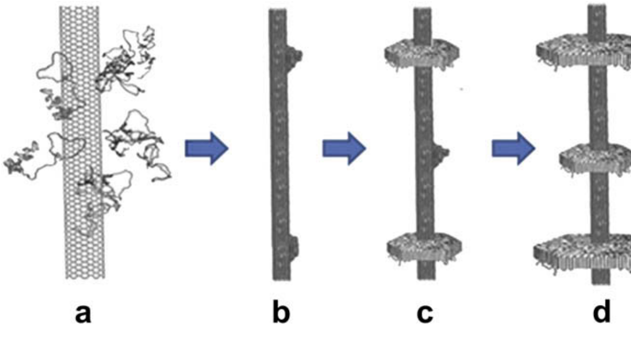


Fig. 5. TEM images of samples obtained at 95 °C.

the crystal lamellae would keep growing with the temperature decreased. Fig. 5d also shows a couple of subglobules with the distance about 45 nm between them. This indicates that subglobules can form at any time during the crystallized process. Consequently, crystal growth is accompanied with the formation of new nuclei. The reason for this phenomenon is attributed to the fact that dynamics of the transition of a polymer chain from random conformation to extended chain or folded chain conformation strongly depended on molecules size and the initial conformation of the chains [27–29]. As a result, chains with larger size could crystallize at earlier stage with low undercooling. And the smaller chains crystallized later as undercooling increasing. Furthermore, at the same undercooling, chains with the same size would crystallize at different time, since the initial conformation of chains in the solution was different.

The formation process of NHSK is shown in Scheme 2. First, PE chains near the MWNTs were adsorbed onto the nanotube surface as soon as they were mixed in the solution (Scheme 2-a), in order to reduce the high surface free energy of MWNTs. Secondly, with the increasing of wrapping chains, they began to slide along tubes and changed into extended chain conformation, which had lower entropy than that of fold chain [27], forming a homogeneous coating around MWNTs with few subglobules (Scheme 2-b). We assumed that PE chains were in extended chain conformation based on the MD simulation results of other groups. For example, Wei proposed that the PE chains with 100-units are in well extended and ordered structures on the surface of SWNTs at low temperature [20]. While Yang's MD simulations indicated that PE chains' (with 1000-units, which is more similar to the PE used in our work) stems align parallel to the SWNTs axis [19]. Thirdly, with temperature decreased, PE chains epitaxially grew from subglobules of the homogeneous coating and formed the crystal lamellae. And at the same time, new subglobules also formed simultaneously (Scheme 2-c). Finally, crystal lamellae kept growing and formed NHSK structures (Scheme 2-d).



Scheme 2. Formation process of PE/MWNTs NHSK structures.

3.3. PP wrapping MWNTs by non-isothermal crystallization

To investigate the generality of this non-isothermal crystallized method, PP was also employed to prepare NHSK using this method. However, PP/MWNTs NHSK structures could not be achieved by both non-isothermal crystallized and isothermal crystallized method. From the high magnification TEM image as shown in Fig. 6, it can be observed that although some PP chains wrapped around MWNTs to reduce the high surface free energy of CNTs, they did not form a homogeneous coating as PE chains did. The alignment of polymer chains on the MWNTs surface depends on strict lattice matching between chains and graphitic lattice, which are determined by both molecular structures and MWNTs chiralities. As mentioned before, according to the MD simulation, PE chains are in extended chain conformation, while PP has a zigzagged conformation on the CNTs surface, instead of helical conformation as in crystal [21]. The difference of conformation between PE and PP on the surface is caused by the side group of CH_3 on PP chains. So strictly, it is the molecular structure, which determines the chains alignment on the MWNTs surface, prevents PP to form NHSK

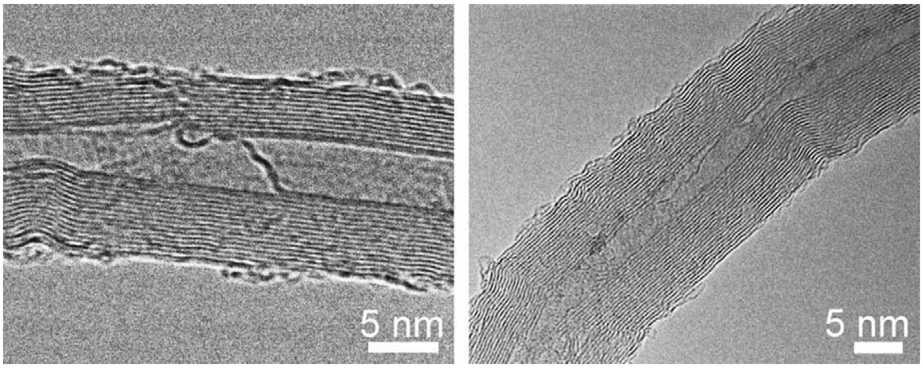


Fig. 6. High magnification TEM image of PP wrapping MWNTs.

structures. It is interested that PE, Nylon 6,6, PVA, PBT, all of which are in zigzagged conformation in crystal, had already been used to prepare NHSK successfully. However, PP and PEG with helical conformation in crystal could not be able to form NHSK till now. And this would be another proof that the homogeneous coating played a key role in the formation of NHSK structures.

4. Conclusions

In conclusion, we have demonstrated that non-isothermal crystallized method is a feasible and facile way to prepare PE/MWNTs NHSK structures. And based on the intermediate state of formation process, it is obvious that before the epitaxial growth of crystal lamellae, the whole MWNTs were coated with a thin homogeneous PE coating with subglobules, which played a key role in the formation of NHSK structures. We also found that the subglobules formed at different time, and served as nuclei for the growth of crystal lamellae. PP/MWNTs NHSK structures could not be prepared, which may be due to the zigzagged conformation of PP on the surface of MWNTs, hindering the formation of homogeneous PP coating on the MWNT surface.

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References

[1] Baughman RH, Zzkhidov AA, Heer de WA. Science 2002;297(5582):787–92.
[2] Whitby M, Quirke N. Nat Nanotechnol 2007;2(2):87–94.
[3] Dresselhaus MS, Dresselhaus G, Jorio A. Annu Rev Mater Res 2004;34(1):247–78.
[4] Hill DE, Lin Y, Rao AM, Allard LF, Sun YP. Macromolecules 2002;35(25):9466–71.
[5] Viswanathan G, Chakrapan N, Yang H, Wei BQ, Chung H, Cho K, et al. J Am Chem Soc 2003;125(31):9258–9.
[6] Blake R, Gun'ko YK, Coleman J, Cadek M, Fonseca A, Nagy JB, et al. J Am Chem Soc 2004;126(33):10226–7.
[7] Gong XY, Liu J, Baskaran S, Voise RD, Young JS. Chem Mater 2000;12(4):1049–52.
[8] Fukushima T, Kosaka A, Ishimura Y, Yamamoto T, Takigawa T, Ishii N, et al. Science 2003;300(5628):2072–4.
[9] Star A, Kevin Grant YL, Ridvan L, Stoddart JF, Steuerman DW, Diehl MR, et al. Macromolecules 2003;36(3):553–60.
[10] Star A, Stoddart JF, Steuerman D, Diehl M, Boukai A, Wong EW, et al. Angew Chem Int Ed 2001;40(9):1721–5.
[11] Moore VC, Strano MS, Haroz EH, Hauge RH, Smalley RE, Schmidt J, et al. Nano Lett 2003;3(10):1379–82.
[12] Zheng M, Jagota A, Semke ED, Diner BA, Mclean RS, Lustig SR, et al. Nat Mater 2003;2(5):338–42.
[13] Tracz A, Kucinska I, Jeszka JK. Macromolecules 2003;36(26):10130–2.
[14] Czerw R, Guo ZX, Ajayan PM, Sun YP, Carroll DL. Nano Lett 2001;1(8):423–7.
[15] Christopher Y Li, Li LY, Ni CY, Kodjie SL, Tenneti KK. Adv Mater 2005;17(9):1198–202.
[16] Li LY, Li YC, Ni CY. J Am Chem Soc 2006;128(5):1692–9.
[17] Li LY, Yang Y, Yang GL, Chen XM, Hsiao BS, Chu BC, et al. Nano Lett 2006;6(5):1007–12.
[18] Zhang F, Zhang H, Zhang ZW, Chen ZM, Xu Q. Macromolecules 2008;41(12):4519–23.
[19] Yang H, Chen Y, Liu Y, Cai WS. J Chem Phys 2007:094902.
[20] Wei CY. Nano Lett 2006;6(8):1627–31.
[21] Liu W, Yang CL, Zhu YT, Wang MS. J Phys Chem C 2008;112(6):1803–11.
[22] Yang MJ, Koutsos V, Zaiser M. J Phys Chem B 2005;109(20):10009–14.
[23] Zheng QB, Xue QZ, Yan KY, Hao LZ, Li Q, Gao XL. J Phys Chem C 2007;111(12):4628–35.
[24] Cheng Y, Liu GR, Li ZR, Lu C. Physica A 2006;367:293–304.
[25] Wei CY. Phys Rev B 2007;76:134104.
[26] Strobl G. Prog Polym Sci 2006;31(4):398–442.
[27] Perkins TT, Smith DE, Chu S. Science 1997;276(5321):2016–21.
[28] Smith E, Babcock HP, Chu S. Science 1998;281(5381):1335–40.
[29] Smith DE, Babcock HP, Chu S. Science 1999;283(5408):1724–7.