Nanohybrid Shish-Kebabs: Supercritical CO_2-Induced PE Epitaxy on Carbon Nanotubes

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ABSTRACT: In this study, we develop a facile and efficient method for period-decorating carbon nanotubes (CNTs) using a supercritical (SC) CO_2 antisolvent-induced polymer epitaxy (SAIPE) method. It helps the epitaxy growth of PE on CNTs under a series of suitable experimental conditions, forming a nanohybrid shish-kebab (NHSK) structure. With the variation of a series of experimental conditions or peripheral effect, such as different solvent, PE concentration, CNTs concentration and SC CO_2 pressure, the NHSK structure, i.e., the size of the lamellae and the interval between them along the stem, can be varied. When *p*-xylene was used as the solvent for PE and single-walled CNT (SWCNT), the size of the lamellae can be adjusted from 80−120 to 125−250 nm with the change of the PE concentration. Using the same solvent *p*-xylene, with the change of SC CO_2 pressure, the size of the lamellae can be changed from 125−250 to 300−400 nm. When dichlorobenzene (DCB) was used as the solvent for PE and SWCNT, with the increase of the SWCNT concentration, from 0.002 to 0.006 and 0.01 wt %, the size of the lamellae can be reduced from 305−420 to 280−400 and 85−200 nm. In comparison to the experimental result with *p*-xylene used as the solvent, it is found that the decorated CNTs have more excellent dispersion when DCB was used as the solvent. Our experimental results indicate that the SAIPE method is effective for both SWCNTs and multiwalled CNTs (MWCNTs). Therefore, this work not only provides a new route to periodically functionalize CNTs with a controllable and adjustable method, but also it can be anticipated to open a gateway for making use of peculiar properties of SC CO_2 to help functionalize CNTs in an environmentally benign manner.

1. Introduction

Because of the extraordinary mechanical, electrical, and optical properties, carbon nanotubes (CNTs) have attracted tremendous attention in recent years.[1–5] However, during the process of transferring their outstanding properties to practical applications, there are some problems resulting from their intrinsic poor solubility and processability.[6–8] As a result, further functionalization and modification of the CNT surface is necessary. The chemical functionalization techniques and noncovalent wrapping methods are most commonly used.[9–12] However, for the first method, while the advantage is that the linkage between the functional groups and the surface of the CNTs is permanent and mechanically stable, the decreased electrical and mechanical properties are often observed after functionalization because the covalent bonds linked to the wall of the CNTs break the sp^2 conformation of the carbon atom and cause the disruption of the wall of the CNTs.[13,14] With respect to the second method, it means wrapping CNTs with surfactants, oligomers, biomolecules, and polymers to enhance the solubility and comparability of CNTs with organic solvents. Although after wrapping, the quintessential nanomaterials with the excellent properties of CNTs can be obtained without disruption of the structure of the CNTs,[15] the weaker interaction between the wrapping molecules and the CNTs will undoubtedly limit their applications in practice.

Considering the excellent mechanical properties of crystalline polymers as well as the possible specific chain registry of different polymers upon CNTs,[16–20] wrapping CNTs with crystalline polymers is an ideal functionalization method. This method can not only retain the structural integrity of CNTs but also overcome the disability of the noncovalent modification method. Li et al. has performed a lot of work and achieved some attractive results in this area.[21–24] They found the epitaxial growth of polyethylene and nylon-6,6 on the surface of CNTs, forming a unique nanohybrid shish-kebab (NHSK) structure. The solubility and processability of CNTs were greatly improved by the modification. They can be further used to fabricate polymer/CNT nanocomposites.

In recent years, various supercritical fluids (SCFs) processing methods have been widely used for the production of polymer-based materials, such as foams, microparticles, and fibers.[25] Among SCFs, supercritical (SC) CO_2 is the most popular one because it is nonflammable, nontoxic, cheap, and easy to obtain. In addition, the solubility of SC CO_2 or compressed CO_2 in many organic solvents is very high, which will lead to a decrease of the solvent strength of the organic solvents. Consequently, the solubility of the solute will decrease as well. This phenomenon is defined as the SC CO_2 antisolvent effect.[26,27] This effect has been used to fabricate nanomaterials, which are difficult to prepare by traditional techniques, such as $C_{60}/(CO_2)_{0.95}$,[28] Eu_2O_3-coated CNTs,[29] platinum/CNT nanocomposite,[30] metal nanowire-filled CNT nanocomposites,[31] and poly(2,4-hexadiyne-1,6-diol)/CNT nanocomposites.[26] Although a variety of nanomaterials have been prepared by the SC CO_2 antisolvent method, very few efforts have been dedicated to use the reduced solvent power to induce polymer crystallization in SC CO_2 and further to fabricate nanomaterials through this method.

The Nobel laureate of the 1991 Nobel Prize in physics, Dr. Pierre-Gilles de Gennes referred soft matter or complex fluid[32,33] in his lecture; Soft matters include polymer, liquid crystal, biomacromolecules, and colloid, etc. They are usually characterized by the strong response to a weak effect, and this response can induce the structure change.[33] With respect to polymers, the structure change implicates the chain building. PE should be susceptive to the peripheral effect because it is a type of soft matter. Meanwhile, PE can rebuild its chains to crystalline structures.[22–24] In the study of Li et al., PE epitaxy on CNTs was carried out by changing the temperature with the solution crystallization method. Although PE epitaxy on CNTs to form a NHSK structure can be achieved by a traditional solution

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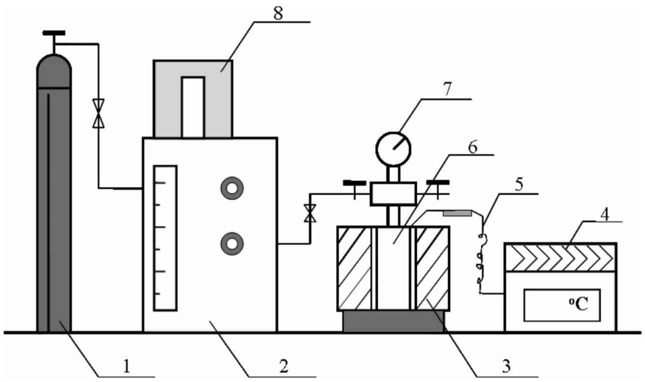
Scheme 1. SC CO_2 Apparatus Description Diagram[a]



[a] 1, gas cylinder; 2, syringe pump; 3, heating-jacket; 4, temperature controller; 5, thermoelectric couple; 6, high-pressure vessel; 7, pressure gauge; and 8, cooling jacket.

crystallization method, developing an environmentally friendly technique to construct this microstructure and carrying out the periodic functionalization of CNTs are still challenging works. In our previous study, we have successfully achieved the periodic patterning of PE on CNTs with the help of a SC CO_2 antisolvent effect.[34] In comparison to a traditional solution crystallization method, such as an antisolvent to induce polymer crystallization or epitaxy, SC CO_2 is more benign to the environment. In this study, on the basis of a previous study, we try to explore more experimental conditions or peripheral effects and use them to change the PE epitaxy condition. In addition, the ultimate purpose is to achieve the controllable decoration for CNTs by adjusting the diameter and periodic interval of the “kebab” on CNTs. At the same time, the mechanism of SC CO_2-assisted PE eptaxy on CNT is further investigated. We believe that this work can open a gateway for delicate functionalization of CNTs in a controlled means, and this alternative for functionalizing CNTs is more benign to the environment.

2. Experimental Section

The single-walled carbon nanotubes (SWCNTs) were supplied by Carbon Nano Materials R&D Center, Chengdu Desran Technology Co., Ltd. (China) with a purity of 80 wt %. The multiwalled CNTs (MWCNTs) were purchased from Aldrich. They were purified as follows: Proper quantities of crude CNTs were added into a three-necked flask containing sulfuric acid and nitric acid at the ratio of 3:1 by volume. The suspension was sonicated in an ultrasonic bath for 40 min and then refluxed at 120 °C for 3 h. After the oxidized CNTs were centrifuged and washed with hot distillated water until a pH of 7.0, they were dried in a vacuum oven at 35 °C for 24 h. Linear polyethylene (melt flow index, MFI = 12 g/10 min) was purchased from Aldrich. Both *p*-xylene and dichlorobenzene (DCB) were purchased from Sinopharm Chemical Reagent Co., Ltd. (China).

The experimental apparatus is illustrated in Scheme 1. A typical experimental process is as follows: PE was dissolved in a different solvent *p*-xylene or DCB at a suitable temperature. A total of 0.1 mg of purified CNTs was dispersed in *p*-xylene or DCB solution. The solution was ultrasonicated for 2–3 h at 45 °C, and the CNTs were homogeneously dispersed in the solution. In addition, the dispersion was then added into PE/*p*-xylene or PE/DCB solution. After equilibration, the mixture was quickly transferred into a 50 mL stainless-steel autoclave at the crystallization temperature depending upon the used solvent. CO_2 was then charged into the autoclave to achieve the desired pressure within a short time. After the SC fluid condition was kept for certain time, the system was slowly depressurized and the sample was collected and labeled. A field emission scanning electron microscope (JEOL JSM-6700F) was used to characterize the morphology of the PE functionalized CNTs. Transmission electron microscopy (FEI Tecnai G^2 20) experiments were conducted with an accelerating voltage of 120 kV.

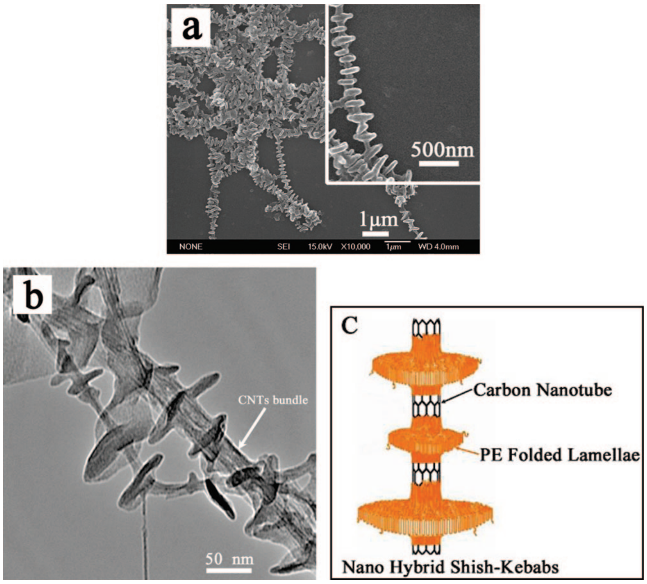


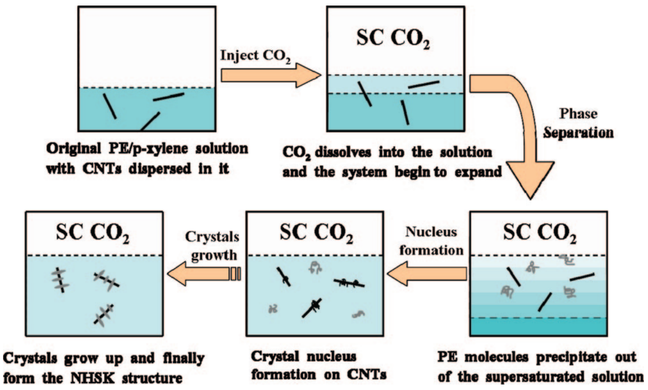
Figure 1. PE/SWCNT NHSK structure obtained by PE epitaxy in SC CO_2 at 110 °C and 9.0 MPa and PE and SWCNT concentrations of 0.02 and 0.002 wt %, respectively. (a) SEM image shows that SWCNTs are decorated by disk-shaped PE single crystals, and PE-functionalized SWCNTs are therefore obtained. (b) TEM image of the PE/SWCNT NHSK structure. (c) Schematic representation of the PE/SWCNT NHSK structure.

3. Results and Discussion

3.1. Using *p*-Xylene as the Solvent for PE and CNTs. In our previous study, MWCNTs were chosen as the modification subject when *p*-xylene was used as the solvent for PE and SC CO_2 was used as the antisolvent. The antisolvent effect of SC CO_2 helps PE separate out and epitaxy on CNTs. In this study, SWCNTs were used as the modification subject to study and to prove the SC CO_2 antisolvent-induced polymer epitaxy (SAIPE) method. The experimental result is shown in Figure 1. From Figure 1, it can be seen that, when SWCNT was used as the modification subject, PE can grow epitaxy on CNTs and the shish-kebab structure was formed. The detailed experimental condition is that the PE and SWCNT concentrations are 0.02 and 0.002 wt %, respectively, under the condition of CO_2 at 110 °C and 9.0 MPa. The characteristic structure of the functionalized CNTs is reflected in the field emission scanning electron microscope (FESEM) image (Figure 1a) and transmission electron microscopy (TEM) image (Figure 1b). The inset of Figure 1a shows an enlarged segment of the shish-kebab structure, which reflects the more detailed morphology of the CNTs. The peculiar morphology is very similar to the classical polymer shish-kebab structures formed in an elongation/shear flow field.[35–37] The schematic representation is illustrated in Figure 1c.

The SAIPE method can be illustrated in Scheme 2. SC CO_2 cannot dissolve PE but is miscible with *p*-xylene at suitable conditions. Therefore, SC CO_2 is used as the antisolvent for PE in the PE/*p*-xylene system. With the charge of CO_2 to the PE/*p*-xylene system, the volume of the liquid phase *p*-xylene is expanded because of the dissolution of CO_2 and its solvent power on PE is reduced, which can lead to the phase separation and PE molecules precipitate out of the supersaturated solution. At the same time, because of the reduced viscosity and surface tension of the *p*-xylene-rich phase on account of the dissolution

Scheme 2. SC CO_2 Antisolvent-Induced PE Epitaxy on CNTs To Form NHSKs



of CO_2, PE can be adsorbed on the surface of CNTs. Therefore, it reaches the step of nucleus formation. Then, it is the next procedure, i.e., crystal growth procedure. With the increasing amount of PE wrapping, PE begins to align along CNTs to decrease the polymer surface energy as the description of folded-chain lamella theory. In addition, a typical NHSK structure is formed. The central shish is CNTs; along the CNTs stems, disk-shaped PE single-crystal lamellae are periodically perpendicular to the stem axis.

3.2. Effect of the Polymer Concentration on the NHSK Structure in *p*-Xylene. Using the SAIPE method, PE can have epitaxy on SWCNTs. The next challenging task is to achieve the controlled functionalization for SWCNT by adjusting the size and period of PE crystallization. As a characteristic soft matter, PE should be susceptive to environmental change or peripheral effects. In the SAIPE procedure, the variation of the polymer concentration is a type of outside effect. We increased the PE concentration from 0.006 to 0.01, 0.02, and 0.04 wt %, respectively, and study the effect of the PE concentration. The experimental results are shown in parts a−d of Figure 2. It is found that, with an increase of the PE concentration in *p*-xylene, its decoration effect on CNTs is apparently different, although at any PE concentrations above, the shish-kebab structures are obtained. The corresponding diameters of lamellar are found to be 80−120, 140−220, 125−250, and 100−180 nm, separately. The information of the data is shown in Table 1, and it can be seen that, with an increase of the PE concentration in *p*-xylene, it exists an inclination that the diameter of the lamellar first increases and then decreases. On the basis of these results, it can be seen that, as a peripheral effect in the SAIPE method, a change of the PE concentration indeed can help adjust the modification of CNTs.

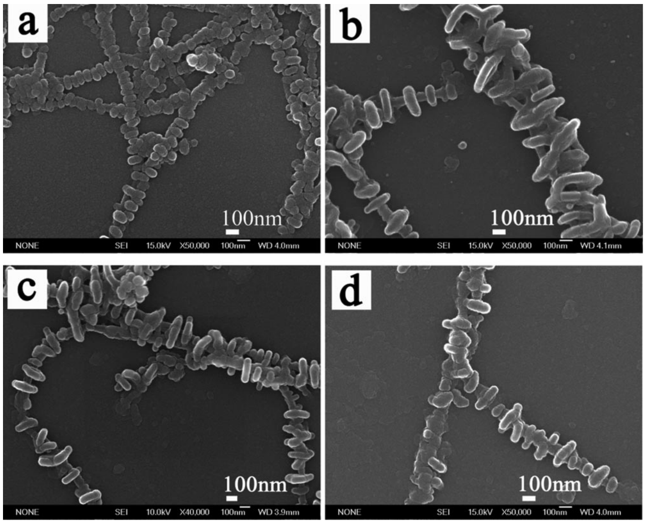


Figure 2. SEM images of the PE/SWCNT NHSK structure produced in the same SC CO_2 conditions (110 °C, 9.0 MPa) at a CNT concentration of 0.002 wt % with different PE concentrations: (a) 0.006 wt %, (b) 0.01 wt %, (c) 0.02 wt %, and (d) 0.04 wt %.

Table 1. Size of the Lamellae in the PE/SWCNT NHSK Structure Produced in the Same SC CO_2 Conditions (110 °C, 9.0 MPa) at a CNT Concentration of 0.002 wt % with Different PE Concentrations: (a) 0.006 wt %, (b) 0.01 wt %, (c) 0.02 wt %, and (d) 0.04 wt %

sample	lateral size of the lamellar crystals (nm)	thickness of the lamellar crystals (nm)	periodicity of the lamellar crystals (nm)[a]
a	80–120	35–60	45–75
b	140–220	55–90	105–190
c	125–250	60–95	95–220
d	100–180	60–75	95–125

[a] Periodicity is defined as the distance between the adjacent lamellar centers.

We attribute this phenomenon to the following reasons: At the same SC CO_2 pressure, with an increasing PE concentration in the system, more free PE chains separate out because of the SC CO_2 antisolvent effect. These precipitated PE chains can crystallize in two forms: (1) the homogeneous nucleation of PE itself and (2) the heterogeneous nucleation of PE on CNTs. On the one hand, when the PE concentration lies in a certain range because of the fact that CNTs provide an external surface for PE to nucleate on and the crystallization temperature (T_c) is relative high (110 °C), from the viewpoint of the crystallization theory, PE chains are more inclined to heterogeneous nucleation on CNTs. On the other hand, from the viewpoint of thermodynamics, because of the dissolution of CO_2 in *p*-xylene, the viscosity and surface tension of the *p*-xylene-rich phase decrease and this is helpful for the adsorption of PE on CNTs. Both of the two reasons could induce the diameters of the lamellar increase with the PE concentration. However, with a further increasing PE concentration, there is the possibility that excessive free PE chains separate out under the effect of the SC CO_2 antisolvent, which results in the amount of PE chains being much more than the amount of CNTs and the homogeneous nucleation becoming dominant. In addition, there is a probability that the number of nucleations increases, which leads to the formation of more lamellae. Therefore, much more PE chains are consumed, and it impedes the increase of the “kebabs”. The information about these data is shown in Table 1. From the table, we can see that, besides the variation of the diameter of lamella with the shift of the PE concentration, the average periodicity or interval between the adjacent kebabs can also be tuned by changing the PE concentration. At a low PE concentration of 0.006 wt %, the kebab along the shish is more compact and the intervals are in the range of 45 to 75 nm, which is much less than that of a higher PE concentration. Therefore, we can conclude that adjusting the polymer concentration in the SAIPE method is an effective approach to control the period and size of polymer crystallization.

3.3. Effect of SC CO_2 Pressure on the NHSK Structure in *p*-Xylene. For SCF, experimental pressure has an important effect on the solvent power. In addition, this can become the second outside effect if the PE concentration variation is regarded as the first peripheral effect. Therefore, we tune the experimental pressure of SC CO_2 from 9 to 11 and 13 MPa and study the effect of SC CO_2-induced PE epitaxy on CNTs. The obtained results are shown in parts a−c of Figure 3. For these three cases, the average diameter of the PE kebab is about 125−250, 300−400, and 100−300 nm, respectively, for 9.0, 11.0, and 13.0 MPa, as indicated in Table 2. We find that the

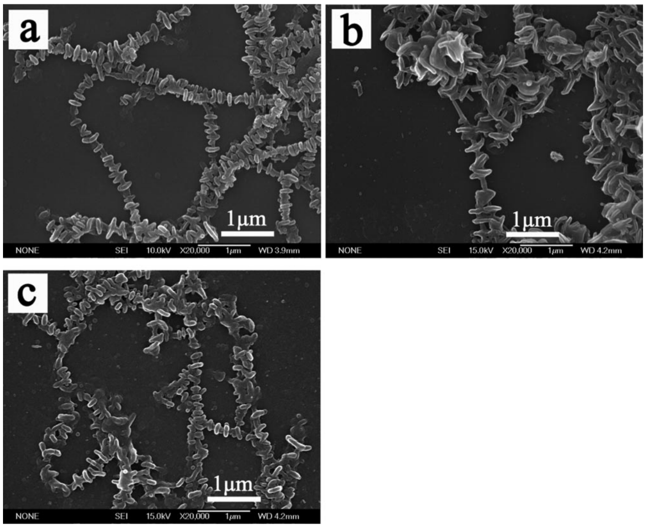


Figure 3. SEM images of the PE/SWCNT NHSK structure produced in the same PE concentration (0.02 wt %) and CNT concentration (0.002 wt %) but at different SC CO_2 pressures: (a) 9.0 MPa, (b) 11 MPa, and (c) 13 MPa.

Table 2. Size of Lamellae in the PE/SWCNT NHSK Structure Produced in the Same PE Concentration (0.02 wt %) and CNT Concentration (0.002 wt %) but at Different SC CO_2 Pressures: (a) 9.0 MPa, (b) 11 MPa, and (c) 13 MPa

sample	lateral size of the lamellar crystals (nm)	thickness of the lamellar crystals (nm)	periodicity of the lamellar crystals (nm)[a]
a	125–250	60–95	95–220
b	300–400	70–105	200–270
c	100–300	80–115	85–150

[a] Periodicity is defined as the distance between the adjacent lamellar centers.

variation trend for the size of the “kebab” is similar to that of the changing PE concentration. We attribute this phenomenon to the following reasons: With an increasing pressure of SC CO_2, the amount and speed of CO_2 dissolved in *p*-xylene increase and the solvent power of *p*-xylene decreases; therefore, more PE can be deposited and the diameter of the “kebab” first increases. Whereas, if the CO_2 pressure is excessively high, both the amount and speed of the PE precipitation are greatly increased and can induce the increase of the nucleation number, which can lead to the formation of more lamellae. Therefore, there exists an optimum SC CO_2 pressure at which the “kebab” size is in the maximum, which is 11 MPa.

3.4. Using DCB as the Solvent for PE and CNTs. In this study, in addition to investigating *p*-xylene used as the solvent in the SAIPE method for the modification of CNTs, the other solvent DCB is also studied.

3.5. Effect of the CNTs Concentration on the NHSK Structure in DCB. According to the study of other researchers,[38] it is known that DCB is one of the best solvents for SWCNTs. Sometimes we need to enhance the efficiency of CNTs functionalization by increasing their amount; therefore, here when using DCB as the solvent for PE in the SAIPE method, we try to change CNTs concentration for the purpose of achieving the controllable CNTs functionalization. In other words, in the SAIPE procedure, the variation of the CNTs concentration can be regarded as a type of outside effect. In our study, it is regarded as the third outside effect, listed after (i) the effect of the polymer concentration and (ii) the effect of the SC CO_2 pressure. We enhanced CNTs concentration from 0.002 to 0.006 and 0.01 wt %, respectively, and the experimental results were shown in Figure 4. These experimental results indicate that when using DCB as the solvent for CNTs, CNTs indeed have more excellent dispersion than that in *p*-xylene. It is easy to obtain the single-decorated CNTs, and the corresponding diameters of lamellar for them are 305−420, 280−400, and 85−200 nm, respectively, as indicated in Table 3. It shows the inclination that the diameters of the epitaxy lamellar decrease with the increase of the CNTs concentration in DCB. It is easy to imagine that, for PE heterogeneous nucleation and crystallization on CNTs, the greater the amount of well-dispersion CNTs, the less PE amount on the same CNT. Therefore, it is not helpful for the increase of the epitaxy lamella size.

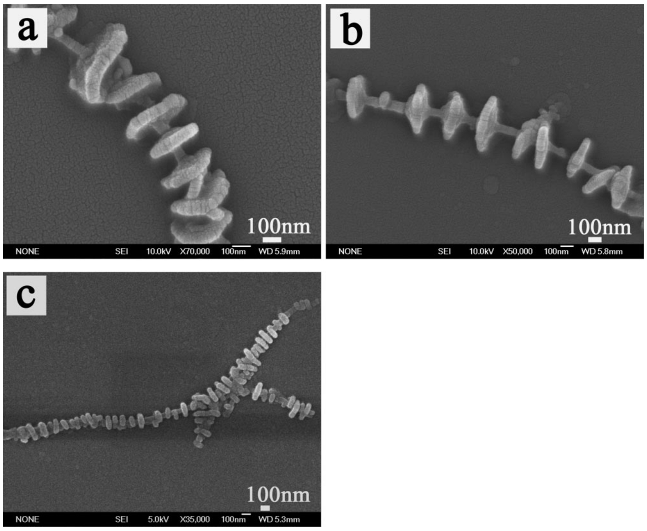


Figure 4. SEM images of the PE/SWCNTs NHSK structure produced in the same SC CO_2 conditions (100 °C and 16 MPa) and PE concentration in DCB (0.006 wt %) but with different CNTs concentrations: (a) 0.002 wt % CNTs, (b) 0.006 wt % CNTs, and (c) 0.01 wt % CNTs.

Table 3. Size of the Lamellae in the PE/SWCNT NHSK Structure Produced in the Same SC CO_2 Conditions (100 °C and 16.0 MPa) but with Different CNTs Concentrations in DCB: (a) 0.002 wt % CNTs, (b) 0.006 wt % CNTs, and (c) 0.01 wt % CNTs

sample	lateral size of the lamellar crystals (nm)	periodicity of the lamellar crystals (nm)[a]
a	305–420	175–210
b	280–400	140–190
c	85–200	60–110

[a] Periodicity is defined as the distance between the adjacent lamellar centers.

3.6. From SWCNT to MWCNT in the NHSK Structure in DCB. Besides the study of SWCNT as the modification subject in DCB, MWCNTs used as the “stem” for PE epitaxy were also studied. Our experimental result indicates again the excellent dispersion of DCB on the CNTs, and it can also be observed clearly that the decorated MWCNTs are totally dispersed in the solvents and there is no trend to congregation. The experimental result is shown in Figure 5. Similar to our previous study about MWCNT in *p*-xylene, here, we still can observe that, during the polymer epitaxy process with the SAIPE method, crystal nucleation on CNTs and crystal growth can occur simultaneously. We obtained a group of TEM pictures about the process of PE epitaxy, which are shown in Figure 6. Figure 6a captured the intermediate state of the PE modification process. At this state, the deposited PE molecular chains did not form crystals. The crystal was finally formed as shown in parts b and c of Figure 6. Figure 6d is the wider range, where the CNTs are decorated. At any period when crystalline is growing, new nucleus may form anywhere. This is due to the

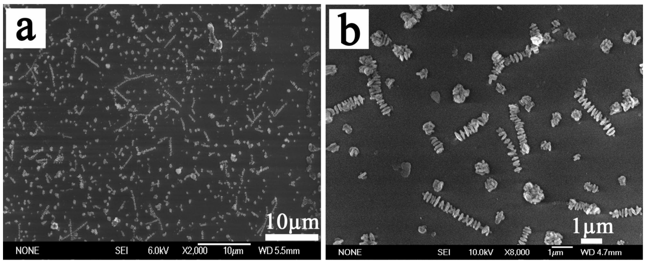


Figure 5. SEM images of the PE/MWCNTs NHSK structure produced in SC CO_2 conditions (100 °C and 16 MPa) for 3 h. The PE concentration in DCB is 0.01 wt %, and CNTs concentration is 0.014 wt %.

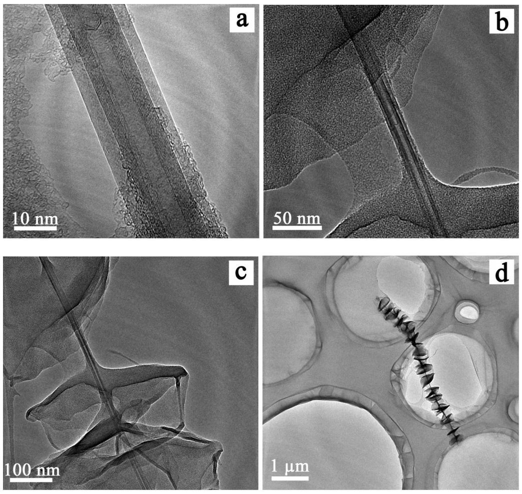


Figure 6. Group of TEM images of the PE/MWCNT NHSK structure formed in DCB, where the PE concentration is 0.006 wt % and the MWCNT concentration is 0.002 wt %, at the SC CO_2 condition of 100 °C and 16 MPa for 3 h. (a) Thin-layer PE molecules patterning on MWCNT. (b and c) More and more PE molecules align along the arrow orientation and begin to form crystal lamella. (d) Wider ranges where the CNTs are decorated.

unique solvent properties of SCF, such as low viscosity, high diffusivity, near zero surface tension, and pressure-dependent density. With the charge of CO_2 in the PE/DCB system, the volume of the liquid phase is expanded gradually because of the dissolution of CO_2 in it. Before it reaches the CO_2/PE/DCB high-pressure phase equilibrium, with CO_2 and DCB permeating each other, the degree of reduced solvent power for the DCB-rich phase become higher. In addition, considering the molecular-weight distribution of the polymer, at the initial period, high-molecular-weight polymers first separate out and then do successively for the lower molecular-weight polymers. Therefore, for the SAIPE method, different molecular-weight PE in grade can separate out successively from the CO_2/PE/DCB system and produce epitaxy on CNTs.

From a further study, it can be observed that it is the same for MWCNTs, with the different MWCNTs concentration in DCB, under the antisolvent effect of SC CO_2, their epitaxial lamella size can be varied. The experimental result is shown in Figure 7. Similar to the experimental result of SWCNTs used as the decoration subject, the diameters of the "kebab" decrease with the increase of the MWCNTs concentration. In addition, it can also be observed that compared to the higher concentration of MWCNTs, at a lower concentration of MWCNTs, for the formed nanohybrid shish-kebab structure, the "kebab" on the "shish" looks more ordered.

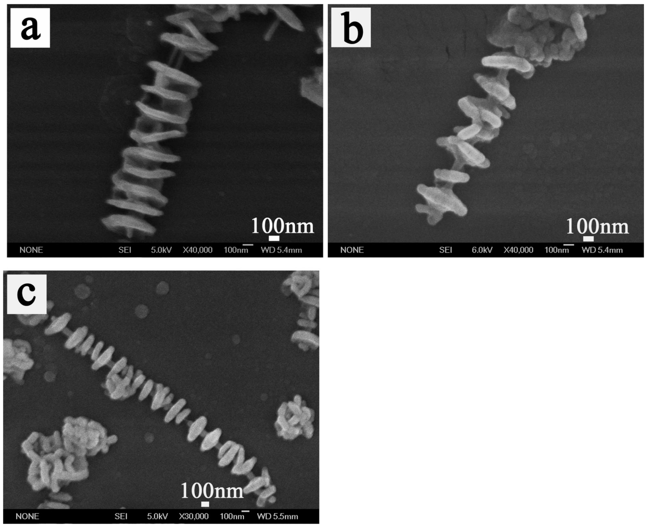


Figure 7. SEM images of the PE/MWCNTs NHSK structure produced in the same SC CO_2 conditions (100 °C and 16 MPa) and PE concentration (0.01 wt %) but with different CNTs concentrations: (a) 0.006 wt % CNTs, (b) 0.01 wt % CNTs, and (c) 0.014 wt % CNTs.

4. Conclusions

We have developed a simple SAIPE method, with which the nanohybrid shish-kebabs of PE decorated CNTs can not only be achieved but their sizes and periodicity can also be controlled. When four outside effects, (1) polymer solution concentration, (2) SC CO_2 pressure, (3) CNTs concentration, and (4) different solvent, are varied, the period and size of the expitaxy crystal can be easily adjusted. This supplies a new platform to periodic functionalizing CNTs in a controlled manner by an environmentally benign method. Furthermore, considering the special properties of SC CO_2 and its comparability with fluorinated or silicone polymer, coupling these kinds of polymers with functional groups or coupling general polymers with a fluorinated functional group, a kind of material composed of ordered multifunctionality on individual CNT could be achieved with this method.

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