Periodic Patterning on Carbon Nanotubes: Supercritical CO_2-Induced Polyethylene Epitaxy

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Introduction. In recent years, supercritical fluids (SCFs) due to their special properties such as low viscosity, high diffusivity, and near zero surface tension, have been widely used in the field of materials science.[1] Among SCFs, supercritical CO_2 (SC CO_2) is the most popular because it is nonflammable, nontoxic, inexpensive, and naturally abundant and has consequently been promoted as a sustainable solvent.[2,3] The solubility of SC CO_2 or compressed CO_2 in many organic solvents is very high, which will lead to a reduction of the solvent strength in solutions. With the reduction of the solvent power, the solubility of the solute will decrease and this phenomenon is defined as SC CO_2 antisolvent effect.[4] The antisolvent effect of SC CO_2 has been used to fabricate nanomaterials which are difficult to prepare by traditional techniques, such as filling CNTs[5,6] and modification of the surface of CNTs.[4,7−9] Further benefit of SC CO_2 is its pressure-dependent density. This unique property can allow selective fractioning of polymers by molecular weight via changing the operating pressure.[10,11]

Since their discovery, CNTs have attracted tremendous attention due to their extraordinary mechanical, electrical, and optical properties.[12−14] However, during the process of transferring their outstanding properties to practical applications, there are always some problems resulting from their intrinsic poor solubility and processability.[15−17] In order to overcome these limitations and broaden their applications in practice, functionalizing CNTs or modifying CNTs' surface is necessary. For this purpose, both chemical functionalization techniques and noncovalent wrapping methods have been reported.[18] For the chemical modification, the decreased electrical and mechanical properties are often observed because the covalent bonds linked to the CNTs' wall break the sp^2 conformation of carbon atom, which therefore disrupts the conjugation of the CNT wall.[19,20] For the noncovalent wrapping, although the excellent properties of CNTs can be obtained without disruption of their structure integrity,[18] the weaker interaction between the wrapping molecules and the CNTs undoubtedly will limit their applications in practice.

Distinguished from other supermolecules which are just wrapping CNTs and disrupt the van der Waals interaction that causes CNTs aggregation, periodically wrapping CNTs with crystalline polymers should be an ideal functionalization method due to the excellent mechanical properties of crystalline polymers as well as the possible specific chain registry of different polymers upon CNTs.[21,22] This method not only can retain the structure integrity of CNTs, but also can overcome the disadvantages of noncovalent modification method. In this field of crystalline polymer modifying CNTs, some valuable results have been achieved by the research group of Christopher Y. Li.[23−25] In the study of Li et al., PE epitaxy on CNTs was realized through changing temperature by solution crystallization method. Although PE epitaxy on CNTs forming NHSK structure could be achieved by a traditional solution crystallization method, developing an environment-friendly technique to construct this microstructure and realizing the periodic functionalization of CNTs are still challenging works.

Our interest is to explore a facile method using SC CO_2 as antisolvent to induce polymer epitaxial growth on CNTs (SAIPE method) for the purpose to modify CNTs. In virtue of the peculiar properties of low viscosity, high diffusivity, near zero surface tension and pressure-dependent density of supercritical fluid, selective fractioning of crystalline polymer by molecular weight on account of different experimental pressure and their adsorption on CNTs can be realized. Making use of these rating polymers of different molecular weight, CNTs can be decorated with more delicate structure. What's more, varying SC CO_2 conditions, the controlled crystal size on CNTs can be expected. In this study, the feasibility and the mechanism of this method are investigated. We anticipate that this work can open a gateway for functionalization of CNTs with a controlled means and more subtle modification of CNTs can be obtained as well.

Results and Discussion. In this study, the SAIPE method can be illustrated in Scheme 1. SC CO_2 cannot dissolve PE, but it is miscible with *p*-xylene under suitable conditions. So SC CO_2 is used as antisolvent for PE in the PE/*p*-xylene system. With the charge of CO_2 to PE/*p*-xylene system, the volume of the liquid-phase *p*-xylene is expanded due to the dissolution of CO_2, and its solvent power on PE is reduced, which can lead to phase separation and PE molecules precipitating out of the supersaturated solution. At the same time, due to reduced viscosity and surface tension of *p*-xylene rich phase on account of the dissolution of CO_2, PE can be adsorbed on the surface of CNTs, and then wrap them. With the increasing amount of PE wrapping, PE begins to align along CNTs in order to decrease the surface energy as the description of folded-chain lamella theory. And the perpendicular lamellae are formed and can exert their decorating effect on the CNTs.

The experimental apparatus shown in Figure S1 and the detailed experimental procedure can be found in the Supporting Information. Figure 1 shows the scanning electron microscopy (SEM) micrograph of PE decorated multiwalled CNTs (MWCNTs) under different SC CO_2 conditions. They apparently indicate that the typical NHSK structure was formed. The central shish is MWCNTs, along the MWCNTs stem, disk-shaped PE single-crystal lamellae are periodically perpendicular to the stem axis. The peculiar morphology is very similar to the classical polymer shish kebab structures formed in an elongation/shear flow field.[26−28] Their sketch maps are illustrated in Scheme 2. Furthermore it can be found that under different SC CO_2 conditions, different epitaxial crystal sizes and periods can be obtained, and the calculated data are shown in Table 1. With the SC CO_2 temperature decreasing from 120 to 100 °C, at the same experimental pressure, the average lamellar crystals diameters, thicknesses, and periodicities increase from 167 to 183 nm, from 68 to 96 nm, and from 80 to 100 nm, respectively. According to the literature,[29] at the same pressure of 9 MPa, the solvent density of CO_2 at 120 °C is 147.42 kg/m^3, while at 100 °C, it is 165.49 kg/m^3. So it can be concluded that adjusting epitaxial crystal size can be realized by changing SC CO_2 solvent density via changing experimental temperature.

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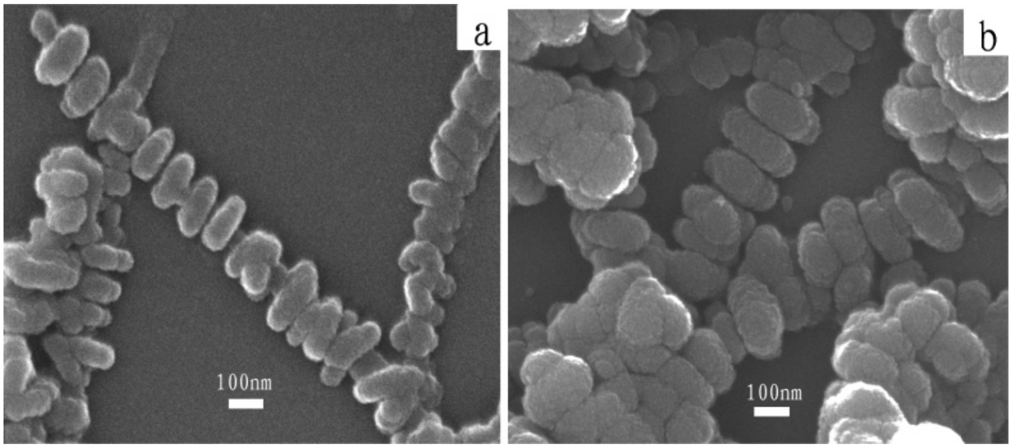
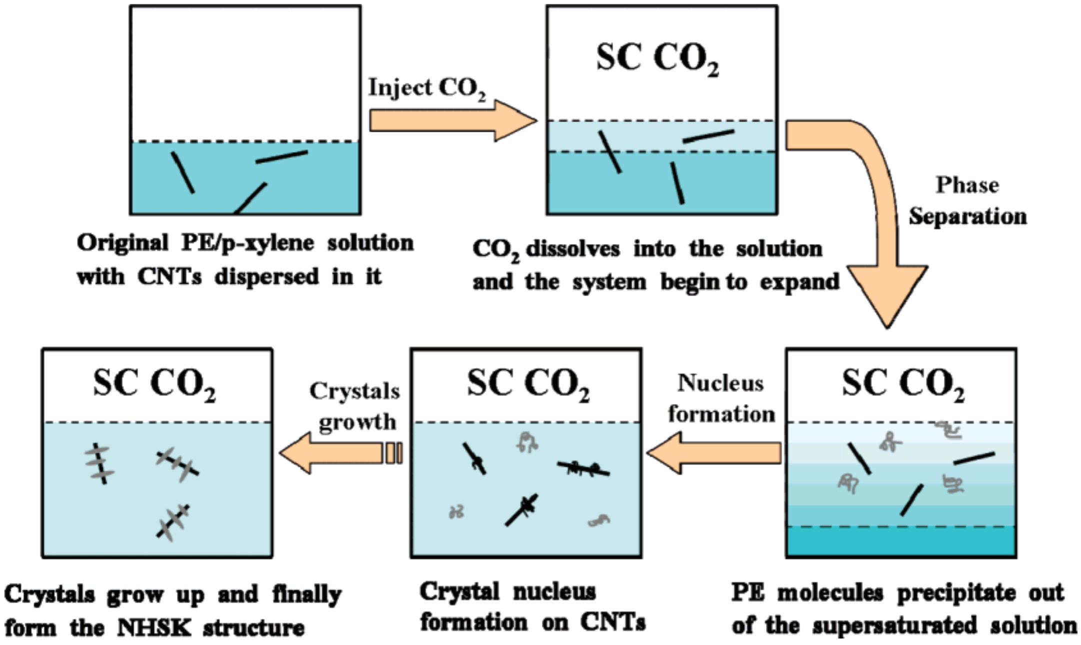


Figure 1. SEM images of PE/MWCNT NHSK structure formed in the same PE concentration (0.006 wt %) and MWCNT concentration (0.002 wt %), but at different SC CO_2 conditions: (a) 120 °C /9 MPa; (b) 100 °C /9 MPa, for 3 h.

Scheme 1. Sketch of the Antisolvent Process and the Epitaxial Growth of PE on CNTs



Scheme 2. Sketch of Classical PE Shish Kebab Structures Formed in an Elongation/Shear Flow Field (Left) and Sketch of NHSK Structure Formed with the Antisolvent Process and the Epitaxial Growth of PE on CNTs (Right)

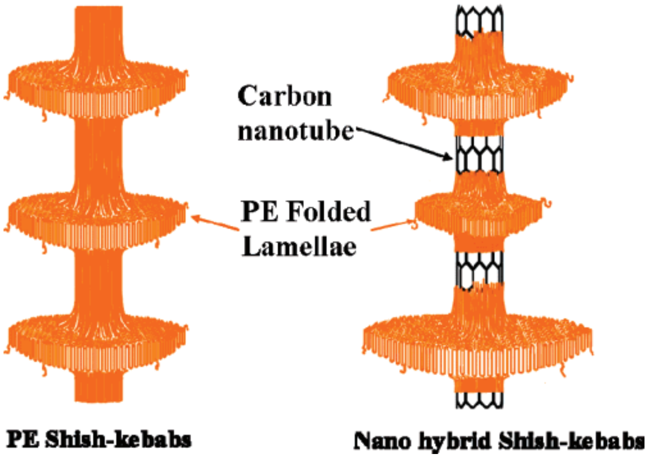


Table 1. Size of Shish Kebab Obtained from SEM Images

sample	av. lateral size of the folded-chain lamellar crystals/nm	av. thickness of the folded-chain lamellar crystals/nm	av. periodicity of the folded-chain lamellar crystals/nm[a]
a	167	68	80
b	183	96	100

[a] Periodicity is defined and calculated as the distance between the adjacent lamellar center.

On the basis of classical crystallization theory, for the solution crystallization, there is the following equation:

$$\Delta G = \Delta\mu = \mu_s - \mu_c \approx RT\sigma$$

Here μ_s is the beginning chemical potential of the solute, μ_c is the ending chemical potential of crystal, σ is the supersaturation degree of solution. With PE in the system, there are two possibilities: PE crystallization by homogeneous nucleation and PE crystallization on the CNT surface (secondary nucleation). Two mechanisms can support the latter possibility. From the point view of crystallization theory, since CNT provide an external surface for PE to nucleate on and at the relative high crystallization temperature of 100 or 120 °C, the secondary nucleation is energetically more favorable compared with PE homogeneous nucleation. From the point view of thermodynamics, because of the dissolution of CO_2 in *p*-xylene, the viscosity

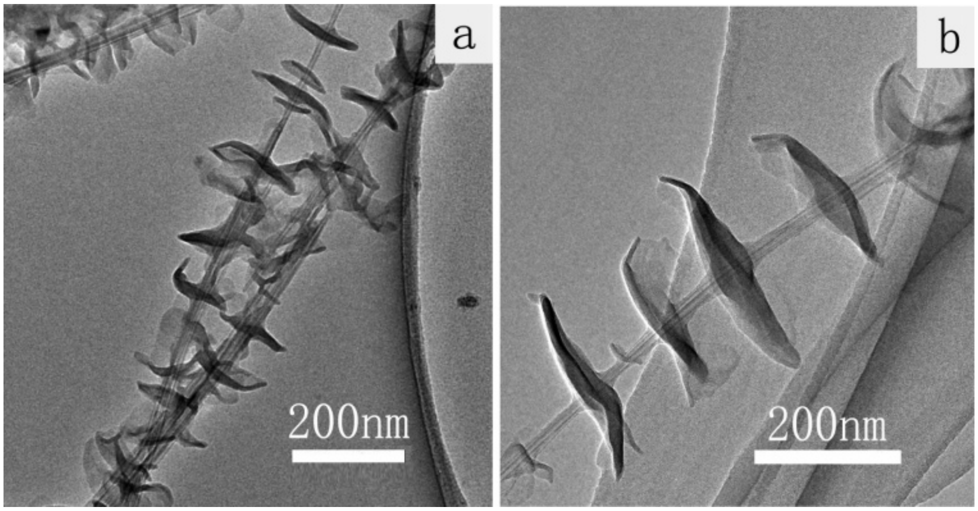


Figure 2. TEM images of PE/MWCNT NHSK structure formed in the same PE concentration (0.006 wt %) and MWCNT concentration (0.002 wt %), but at different SC CO_2 conditions: (a) 120 °C /9 MPa; (b) 100 °C /9 MPa, for 3 h.

Figure 3. Abstracts of different crystal lamellas from the edge-on view about the NHSK structure.

and surface tension of *p*-xylene-rich phase decrease, and this is helpful for the adsorption of PE on CNTs. During the crystallization process, the value of σ has a determined effect on the crystal nucleation and growth on the CNTs. At the same experimental pressure of 9 MPa, because CO_2 solvent density at 100 °C is higher than that of 120 °C, the volume of the liquid phase at 100 °C is more expanded due to the dissolution of more CO_2, and the density and the solvent power of *p*-xylene rich phase decrease more. So the supersaturation degree of the system at 100 °C is higher, and accordingly more PE molecules can be separated out and precipitated on CNTs to cater for the crystallization growth and formation of bigger epitaxial lamella size.

In order to further confirm the interior structure of NHSK, transmission electron microscopy (TEM) studies of the two samples were carried on. The TEM micrographs are shown in Figure 2. It can be more clearly observed the NHSK structure, in which the center stems of CNTs are decorated with various shapes of lamellar crystals. The crystal lamellae can be abstracted to the different shapes illustrated in Figure 3, including disk shape, dish shape, crescent shape, and anisomerous shape. Generally, the closer to the center, the thicker of the crystal lamellae is. As regard to the relation of the lamella crystal shapes with their functionalization on CNTs, it is hard to give a concrete statement now. However, it is necessary to find out how the various shape formed. In Figure 4a, the crystal lamella in crescent shape is observed. From the magnified image of Figure 4b, we can find the defect of the CNTs and their crossbedded structure. So it could be supposed that these factors cause the epitaxial lamella not perpendicular to the stem of CNTs, but produce aberrance. In addition, it can be suggested that the various shape of epitaxial lamella are also due to their forming process, which can be shown in Figure 5, and it will be stated in the following part.

In addition to the various shape of crystal lamella decorated on CNTs, from Figure 2, it can be found that their sizes also vary in a wide range. This finding inspired us to investigate the origin of these crystal lamellas in different sizes. We obtained a group of TEM pictures shown in Figure 5. Figure 5a captured the intermediate state of PE modification process. From it, we find macromolecular chains enwinding each other and forming a thin layer of PE molecules, which were deposited on CNTs surface. At this state, the deposited PE molecular chains did not form crystals. In Figure 5b, it seemed that the PE layer was growing and becoming thicker. Only when it reached a certain degree, with the increasing amount of PE wrapping around CNTs, did PE began to align along the carbon nanotube axis in order to decrease the surface energy as the description of folded-chain lamella theory. The crystal was finally formed as shown in Figure 5, parts c and d. Parts e and f of Figure 5 are the wider range where the CNTs are decorated. In Figure 5d, we can apparently observe the distinct size of crystal lamellas. The smaller one is about 47 nm, and the bigger one is even more than 200 nm. It means that the CNTs can be modified with different size of PE lamella, and at the same time, PE molecular chains even can precipitate on CNTs. This phenomenon indicates that during the polymer epitaxy process with SAIPE method, crystal nucleation on CNTs and crystal growth can occur simultaneously. At any period when crystalline is growing, a new nucleus may form anywhere. This also maybe contributes to the second reason for the various shape of epitaxial lamella, besides the crossbedded structure of CNTs as stated above.

So compared to traditional solution crystallization method, CNTs can be decorated more subtly with the SAIPE method. This is due to the unique solvent properties of supercritical fluid such as low viscosity, high diffusivity, near zero surface tension, and pressure-dependent density. The formation mechanism is suggested as following. With the charge of CO_2 in PE/*p*-xylene system, the volume of the liquid phase is expanded gradually due to the dissolution of CO_2 in it. Before it reaches the high-pressure phase equilibrium for CO_2/PE/*p*-xylene system, with CO_2 and *p*-xylene permeating each other, the degree of reduced solvent power for *p*-xylene rich phase becomes higher. In addition, considering the molecular weight distribution of polymer, it can be imagined that during the initial period, high-molecular weight polymer first separates out and then does so successively for the lower molecular weight polymer. In other words, for the SAIPE method, with the antisolvent effect of SC CO_2, different molecular weight PEs in grade can separate

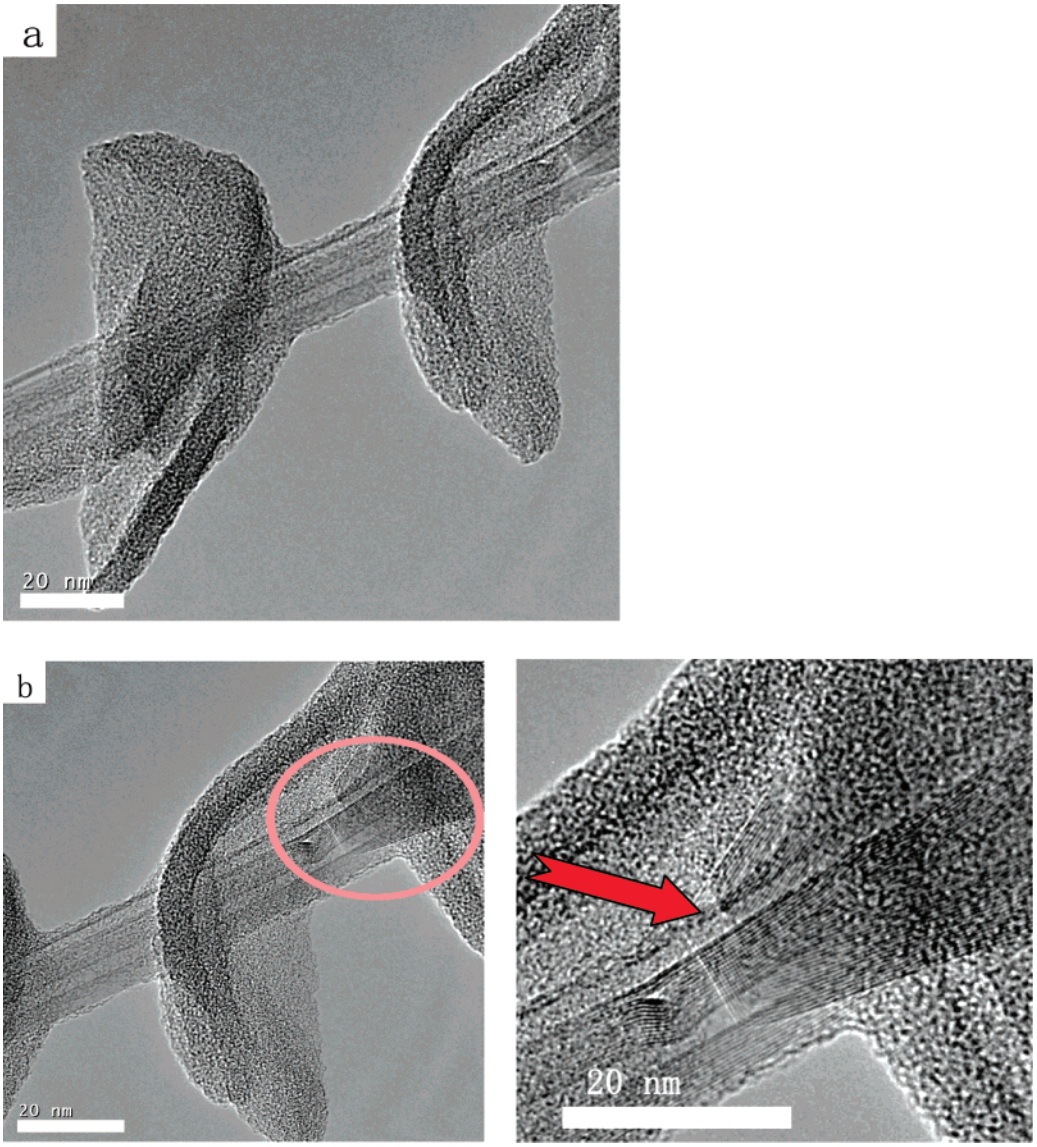


Figure 4. TEM images of PE/MWCNT NHSK structure formed in PE concentration (0.006 wt %) and MWCNT concentration (0.002 wt %), and SC CO_2 condition of 120 °C /9 MPa for 3 h.

out successively from the CO_2/PE/*p*-xylene system and produce epitaxy on CNTs. In the end, CNTs can be decorated with different size of crystal lamellae.

As stated above, secondary nucleation is superior to homogeneous nucleation for polymer epitaxy on CNTs from both the crystallization theory and thermodynamic theory. So the secondary nucleation is the main driving force for polymer coagulating on CNTs. No matter for traditional solution crystallization method or the SAIPE method, if polymers have the inclination of crystallization, they can berth on CNTs. For oligomers and PE molecular chains, which are hard to crystallize, they are difficult to precipitate on CNTs in the traditional solution crystallization method. However, in the SAIPE method, because of the antisolvent effect of SC CO_2, due to the reduced viscosity and surface tension of the *p*-xylene rich phase on account of the dissolution of CO_2, oligomers and PE molecular chains can be adsorbed on the surface of CNTs. Without the driving force of polymer crystallization on CNTs, the SC CO_2-assisted polymer and inorganic molecule wrapping CNTs have been observed by other researchers.[7,30−32]

So using SC CO_2 as antisolvent to induce PE epitaxy on CNTs for the purpose to functionalize CNTs, compared with solution crystallization method, it can decorate CNTs more delicately on account of two reasons. One is that during mixing of antisolvent CO_2 with *p*-xylene, rating PE can be separated out successively. The other one is that due to the low viscosity, high diffusion, and near zero surface tension of SC CO_2, oligomers and even PE chains can be absorbed on CNTs as shown in Figure 5a. Both of these two reasons contribute to various size and shape of the epitaxial lamellas.

Conclusions. In summary, PE epitaxy periodic patterning on CNTs to form NHSK structure with the assistance of antisolvent SC CO_2 was realized. For the first time, selective fractioning of polymers of different molecular weight during mixing of antisolvent CO_2 with *p*-xylene, and following their precipitation and decoration on CNTs were observed. This, in effect, supplies a new platform to delicately functionalize CNTs in a controlled manner. In addition, for this method, since changing temperature of antisolvent SC CO_2 can induce the variation of supersaturation degree of the PE/*p*-xylene system, which determines the formation of crystal nucleus and its growth, PE lamella crystal size and period can be controlled. Furthermore, considering the special properties of SC CO_2 and its comparability with fluorinated polymer, coupling the crystalline polymers with

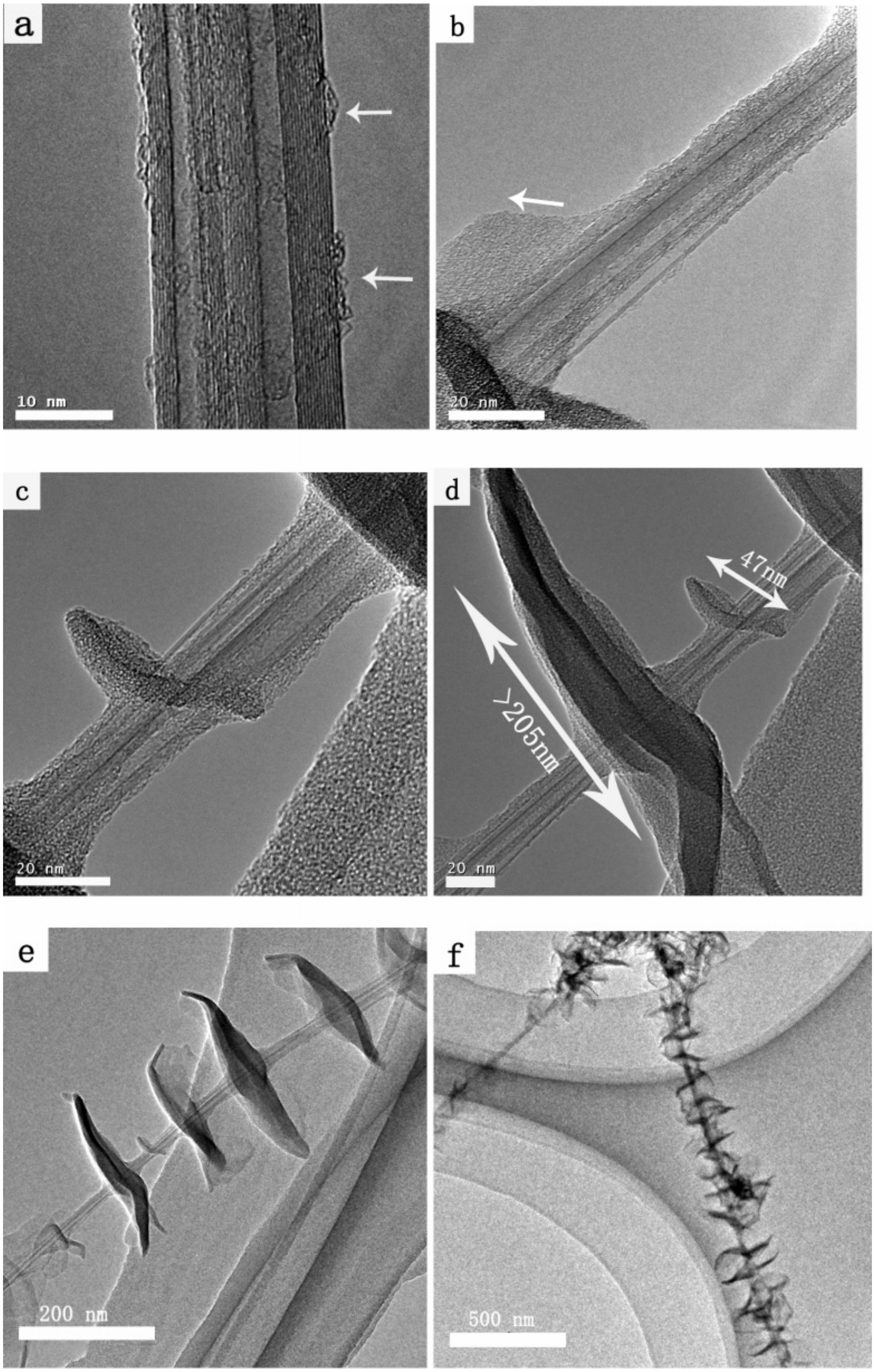


Figure 5. Group of TEM images of PE/MWCNT NHSK structure formed in PE concentration (0.006 wt %) and MWCNT concentration (0.002 wt %), and at SC CO_2 condition of 100 °C /9 MPa for 3 h. (a) A thin layer PE molecules patterning on MWCNT. (b) More and more PE molecules align along the arrow orientation. (c) Formation of crystal lamella. (d) Two lamella crystals with different lateral sizes as the arrows indicate. (e and f) Wider ranges where the CNTs are decorated.

functional groups or coupling general polymer with fluorinated functional group, ordered multifunctionality could also be realized on individual CNT.

In addition, polyethylene single crystal can be obtained efficiently with the SAIPE method and this may have a high potential for a further study of polymer crystallization as well as for materials science.

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Supporting Information Available: Text giving the Experimental Section and a figure showing the experimental apparatus.

This material is available free of charge via the Internet at http://pubs.acs.org.

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