Modification of Carbon Nanotubes: Water-Soluble Polymers Nanocrystal Wrapping to Periodic Patterning with Assistance of Supercritical CO_2

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Introduction

Since their discovery, carbon nanotubes (CNTs) have attracted great attention due to their extraordinary mechanical, electrical, and optical properties.[1–3] However, their poor solubility and processability have hindered chemical manipulations and their further use in applications.[4–6] So study on CNT functionalization is very necessary.[7–11] Because of this purpose, both chemical functionalization techniques and noncovalent wrapping methods have been reported. As functionalization of CNT is growing popular in nanotechnology, many new green techniques have been employed. Application of supercritical carbon dioxide (SC CO_2) in the processing and modification of CNT is one of the choices. SC CO_2 is nonflammable, nontoxic, and easy to obtain and is consequently promoted to be green, sustainable, and useful in many nanostructure synthesis, such as filling or functionalizing nanotubes with molecular anchors.[12,13] Andrei N. Khlobystov et al. recently reported a new and facile solvent-free method for coating insulating polymer onto the nanotubes using SC CO_2 as a good alternative to organic solvent.[14] On the other hand, the solubility of SC CO_2 is poor for many polymers but very high in many solvents; this leads to a reduction in the solvent strength of the organic solvent, i.e., SC CO_2 can act as an antisolvent to enhance the precipitation or absorption of polymers on the surface of the CNT.[15–18] In our previous study, we have developed a simple supercritical CO_2 antisolvent-induced polymer epitaxy method (SAIPE method), with which the nanohybrid shish-kebabs of PE decorated CNTs not only can be achieved but also their sizes and periodicity can be controlled.[17,18] This work not only provides a new route to periodically functionalize CNTs but also 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. These interesting experimental results motivated us to go on investigating the water-soluble polymers and study their modification on CNTs with assistance of SC CO_2 antisolvent techniques. Our end purpose is widening the field of CNT functionalization and exploring their potential applications in biological systems.

Smally and his colleagues proposed the use of water-soluble polymers, such as poly(vinylpyrrolidone) (PVP) and poly(styrenesulfonate) (PSS), to enhance the solubility of CNT in water.[19] Their valuable work opens the door to solution chemistry on pristine nanotubes and cast insight into biologically relevant systems. At the same time, it is reported in their study that poly(ethylene glycol) (PEG) and poly(vinyl alcohol) (PVA) were not so successfully wrapped on CNTs as other polymers such as poly(vinylpyrrolidone) (PVP), poly(styrenesulfonate) (PSS), poly(1-vinylpyrolidone-*co*-vinyl acetate), poly(1-vinylpyrolidone-*co*-acrylic acid), poly(1-vinylpyrolidone-*co*-(dimethylamino)ethyl methacrylate), poly(vinyl sulfate), etc. In this study, we report using SAIPE method to modify CNTs with those two kinds of water-soluble polymers, PEG and PVA. For PEG, two molecular weight polymers, $M_{w\,6000}$ and $M_{w\,10000}$, are studied.

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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 %. They were purified as follows: Proper quantities of crude SWCNTs 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 heated up to 120 °C and refluxed for 3 h. After the centrifugation and later washing with hot distilled water until pH was 7.0, the oxidized SWCNTs were dried in vacuum oven at 35 °C for 24 h. PEG_{6000} (M_w 6000) was purchased from Sinopharm Chemical Reagent Co., Ltd. (China), and PEG_{10000} (M_w 10 000) was supplied by the Kermal Chemical Reagent Co., Ltd. (China). PVA (M_w 77 000) was purchased from Xiangzhong Chemical Plant, Hunan (China).

Nanocrystals wrapped on CNTs were obtained by the SAIPE method.[17,18] Both for PEG and PVA crystallization, dimethyl sulfoxide (DMSO) was used as the solvent. 0.1 mg of SWNTs was dispersed in 1 g of DMSO and ultrasonicated for 1 h before being added to definite concentration of PEG/DMSO or PVA/DMSO solution. The mixture was then quickly transferred into the SC CO_2 apparatus to reach the determined conditions of temperature and pressure for PEG and PVA, respectively. The crystallization time was controlled to be 3 h for all samples. A field emission scanning electron microscope (JEOL JSM-6700F) was used to characterize the morphology of the polymer functionalized CNTs. Transmission electron microscopy (FEI Tecnai G^2 20) experiments were conducted with an accelerating voltage of 120 or 80 kV.

Results and Discussion

Modification of Single-Walled Carbon Nanotubes with PVA. Figure 1 shows the transition electron microscopy (TEM) micrograph of PVA 70 000 decorated single-walled CNTs (SWCNTs) at different experimental conditions. The experimental conditions for the modification of SWCNTs is that reaction system of PVA concentration (0.006 wt %) and SWCNT concentration (0.004 and 0.006 wt %) in DMSO were treated in SC CO_2 condition of 110 °C/13 MPa for 3 h. The experimental results apparently indicate that the sidewalls of SWCNTs are decorated with some dots. The average diameters of the dots are in the range of 2−5 nm, and we call these dots as nanocrystals, shown in the scheme of Figure 1C. And the experimental results in the Supporting Information can show single crystals growth from the dots of nanocrystals. There are two pictures of PEG decorated nanotubes in the Supporting Information, and from them, it can be observed the cube crystals' growth along the CNTs, which are in single crystal form. Because of the tiny size of the crystals as well as the hydrophilic property of the water-soluble PVA wrapped on CNTs, this method could open a new route to introduce potential use of the polymer nanocrystals and biocompatible properties onto the individual CNTs and exlpore new applications such as biosensors. Furthermore, some ordered patterning of nanohybrid structures on the basis of nanocrystals have also been discovered in our series of experiments. It may provide fundamental insight

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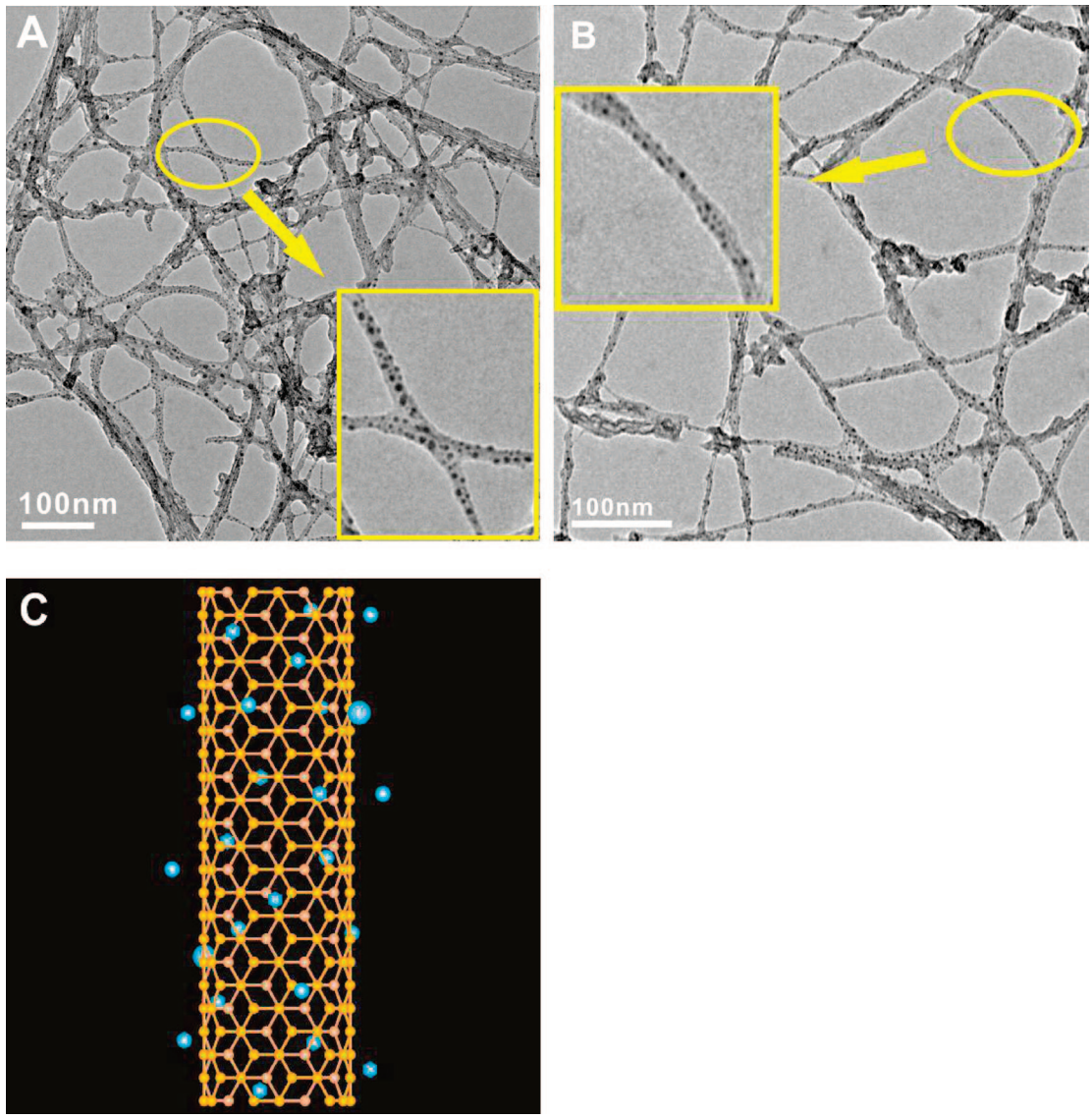


Figure 1. TEM images of PVA dots decorated SWCNTs produced in the same SC CO_2 conditions (110 °C/13 MPa for 3 h) and PVA concentration in DMSO (0.006 wt %), but with different CNTs concentrations: (A) 0.004 wt % CNTs; (B) 0.006 wt % CNTs. (C) Schematic representation of PVA/SWCNT dotted structure.

into better understanding the nucleation and crystallization process of polymers on CNTs.

The formation of the nanohybrid structure with nanocrystals wrapping on SWCNTs is attributed to a relevant easy heteronucleation and the limited crystal growth of the polymer heteronucleus on the surface of SWCNTs. The mechanism is suggested as follows. With the injection of CO_2, the original PVA/DMSO solution with unbundled SWCNTs became supersaturated, and then PVA molecules precipitated. There is a competition between homogeneous nucleation of PVA crystallization and nucleation of PVA on the surface of SWCNTs (secondary nucleation). It is no doubt that the latter is dominant since CNTs provide an external surface for PVA to nucleate on and energetically make it more favorable compared with the homogeneous nucleation. So in a short time, there spawned heteronucleus of PVA on the SWCNTs everywhere. We suggested three possibilities about how to make these unsteady nucleuses stabilize. First, if the nucleuses were formed from a part of a single macromolecular chain, the rest part of the chain entwined in the lattice for the crystal growth, and it can form single-chain single crystal stabilized on the surface of CNTs. Second, if the nucleuses were formed from several macromolecular chains and the crystal growth by these chains entwining each other. Third, it was also possible to form a primary particle from several nucleuses, and then it might grow as a spathic nanocrystal. These possibilities could well explain the tiny size of the PEG crystals wrapped on the SWCNTs as well as these nanocrystals in different sizes. From another point of view, the PVA nanocrystals on the SWCNT could be regarded as a steady intermediate state, which could further form ordered patterning of nanohybrid structure when suitable experimental conditions are achieved.

As indicated in our previous study, in the SAIPE procedure, the variation of CNTs concentration can be regarded as a type of outside effect.[18] It is looked as the third outside effect, listed after (i) effect of polymer concentration and (ii) effect of SC CO_2 pressure. We decrease CNTs concentration from 0.004 and 0.006 wt % to 0.002 wt %, and the experimental results are shown in Figure 2. The TEM micrograph in Figure 2 shows the totally different micromorphology of PVA modified SWCNT in lower concentration of SWCNT of 0.002 wt % compared to that of 0.004 and 0.006 wt %. In order to further confirm our experimental phenomenon, scanning electron microscopy (SEM) was employed to characterize the decorated SWCNTs. The

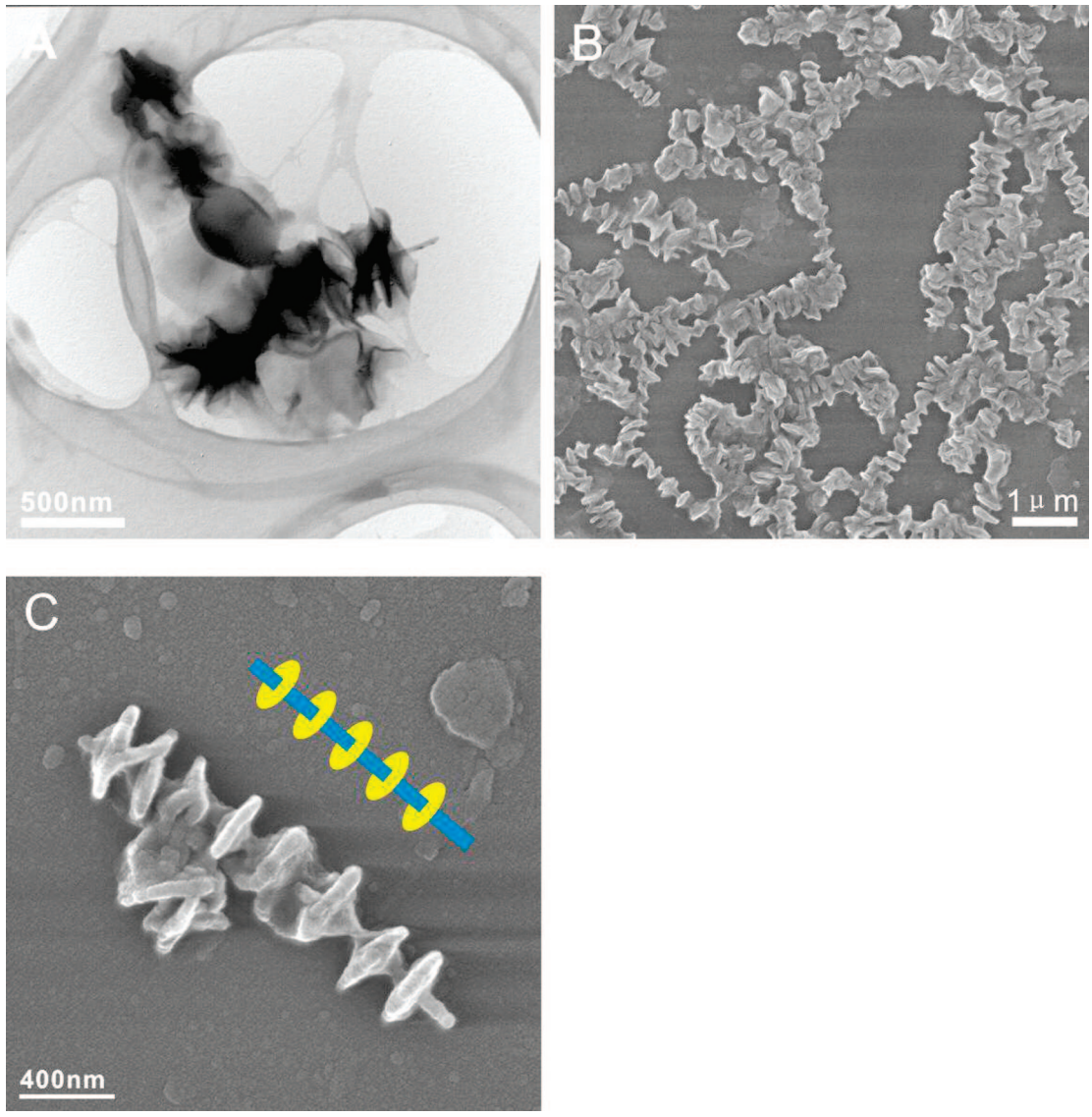
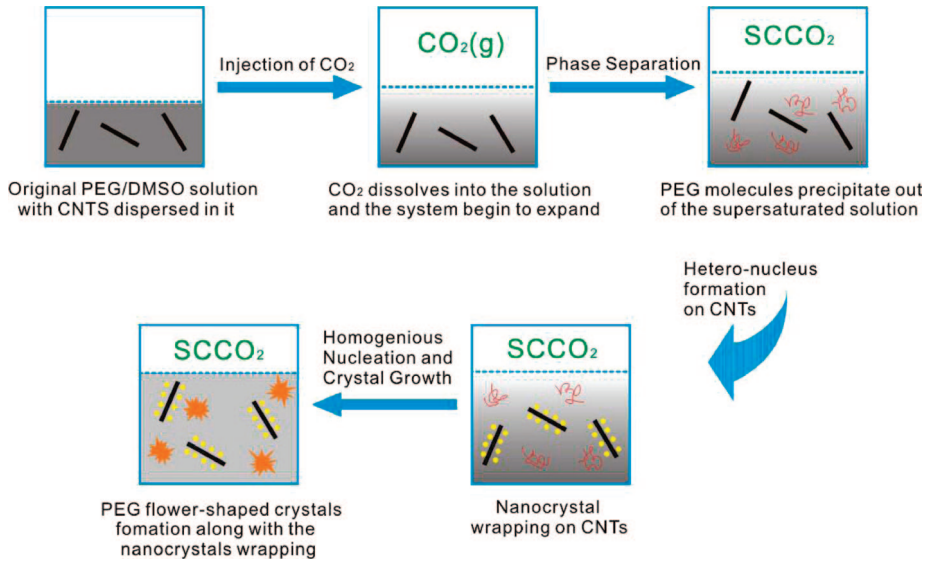


Figure 2. PVA/SWCNT NHSK structure obtained in SC CO_2 at 110 °C/13 MPa for 3 h, and PVA concentration and SWCNT concentration are 0.006 and 0.002 wt %, respectively. (A) TEM image shows PVA-functionalized SWCNTs; (B, C) SEM images of PVA/SWCNT NHSK structure that are decorated by disk-shaped PVA single crystals, and PVA-functionalized SWCNTs are therefore obtained.

Scheme 1. Sketch of the SAIPE Procedure about PEG_{6000} Flower-Shaped Crystals Formation



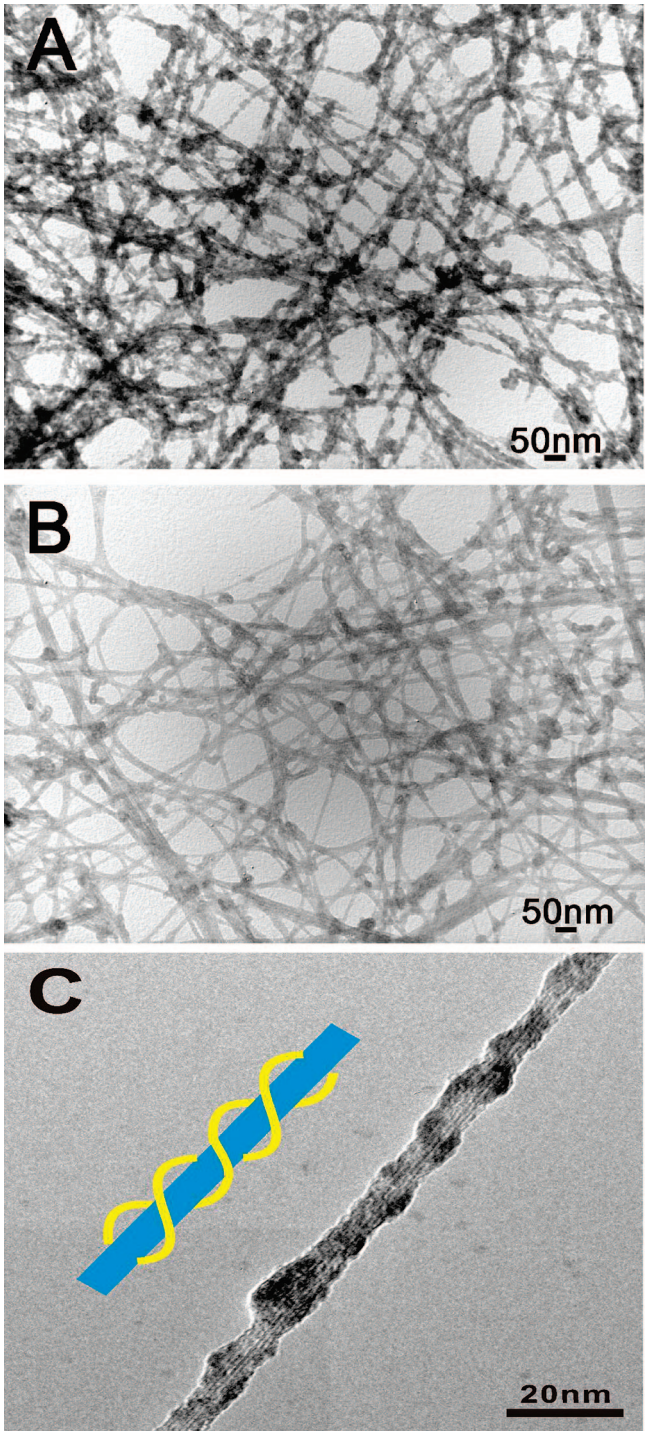


Figure 3. TEM images of PEG_{10000} wrapping decorated SWCNTs produced in the same SC CO_2 conditions (55 °C/12 MPa for 3 h) and PEG_{10000} concentration in DMSO (0.01 wt %), with different CNTs concentrations: (A) 0.004 wt % CNTs; (B) 0.008 wt % CNTs. (C) TEM image of enlarged PEG_{10000}/SWCNT wrapping structure in the same experimental conditions as (A).

experimental results are shown in Figure 2B,C. They apparently indicate that the typical nanohybrid shish-kebab (NHSK) structure is formed. The central shish is SWCNTs; along the SWCNTs stems, disk-shaped PVA single-crystal lamellae are periodically perpendicular to the stem axis. The peculiar morphology is very similar to the classical PE shish-kebab structures formed in an elongation/shear flow field,[19–21] and our previous study about PE-modified CNTs with the SAIPE method. As far as we know, it is the first time that the shish-kebab structure of PVA is obtained.

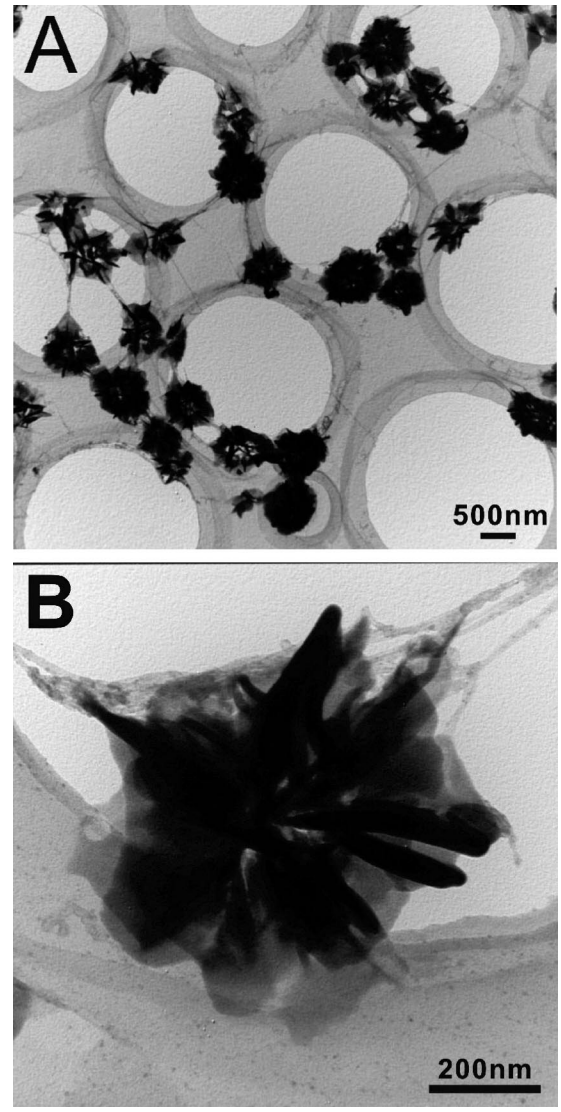


Figure 4. TEM images of PEG_{6000}-decorated SWCNTs produced in SC CO_2 conditions (48 °C/10.5 MPa for 3 h) and PEG_{6000} concentration in DMSO (0.006 wt %), with CNTs concentration of 0.002 wt %.

Modification of Single-Walled Carbon Nanotubes with PEG. Figure 3 shows the TEM micrographs of PEG_{10000}-decorated SWCNTs at different experimental conditions. It can be seen clearly that SWCNTs were indeed wrapped by PEG_{10000} with the SAIPE method. Comparing parts A and B of Figure 3, we can observe clearly that with the increase of SWCNT concentration on the condition of the same PEG concentration, the PEG wrapping degree on SWCNT decreases; i.e., at suitable SAIPE experimental conditions, there is a proper ratio for the polymer concentration and SWCNT concentration. At the ideal experimental condition and suitable proportion, the wrapping effect of PEG on CNTs can be perfect. Further from the enlarged TEM image of Figure 3C, we can find out surprisingly that PEG_{10000} wrapping on the SWCNTs be in the helical structure. Helical wrapping of CNTs with biomacromolecules has been reported.[22,23] In Smalley's study, some possible helical wrapping arrangement of PVP on SWCNT is suggested.[19] At the same time, it is referred in Smalley's study that PEG is not successfully wrapped on SWCNTs. Our study indicates that with the SAIPE method water-soluble polymers such as PEG

wrapping on CNTs can be successfully obtained, which are difficult to achieve with traditional solvents.

PEG $_{6000}$ is also studied to modify SWCNTs. The experimental condition is that CNTs concentration and PEG_{6000} concentration in DMSO are 0.002 and 0.0075 wt %, respectively, and the reaction system is treated in SC CO_2 conditions of 48 °C and 10.5 MPa for 3 h. Figure 4 shows the TEM micrographs of PEG_{6000}-decorated SWCNTs. We can observe PEG_{6000} flower-shaped crystals formed along the SWCNTs. It could be suggested that this is similar to the formation of helical wrapping of PEG_{10000}, and it is due to the further crystal growth; ordered nanohybrid patterning is formed based on the intermediate state of nanocrystals. The detailed formation procedure is illustrated in Scheme 1, which includes the homogeneous nucleus and crystal growth to form flowerlike structure in the later period.

From the study of PVA- and PEG-modified SWCNTs, we found that there are some connections between the nanocrystal wrapping and the various kinds of microscopic ordered patterning structures on SWCNTs. Slight change of the experiment condition has brought in various morphologies of the nanohybrid structure. This reminds us of the "soft matter" theory. Variation of experimental conditions during the SC CO_2 antisolvent process could be looked upon as a changing external field. Along with the green properties of SC CO_2, it might help to form ordered structures ranging from the nanoscale to microcosmic scale. And hence it may yield very desirable opportunities to manipulate the reaction system and produce smart polymer or colloidal material via change of parameters in the SAIPE procedure. This is currently under further investigation.

Conclusions

Wrapping SWCNTs with two kinds of water-soluble polymers, PVA and PEG, in SC CO_2 antisolvent process was carried out. For the first time, we achieved the periodic patterning of PVA in NHSK structure and periodic patterning PEG in helical or flowerlike structure, based on nanocrystals wrapping on the SWCNTs with the assistance of the SC CO_2. The modified SWCNTs could be well dispersed in aqueous solutions and exert their potential use in biologically relevant systems. Considering the SC CO_2 antisolvent process could provide a green route as well as a changing external field in the "soft matter" theory to produce special morphology of nanohybrid structure, it will be promising and of great potential to help soft matters such as polymer and biomacromolecules into new smart materials with facile and precise manipulation.

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Supporting Information Available: Experimental section. This material is available free of charge via the Internet at http://pubs.acs.org.

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