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Communication

Polycyclopentene Crystal-Decorated Carbon Nanotubes by Convenient Large-Scale In Situ Polymerization and Their Lotus Leaf-Like Superhydrophobic Films

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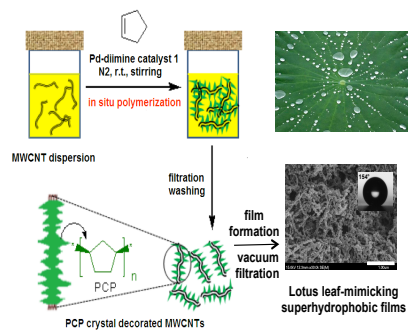
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Abstract: In situ Pd-catalyzed cyclopentene polymerization in the presence of MWCNTs is demonstrated to effectively render, in a large scale, polycyclopentene crystal-decorated MWCNTs. Controlling the catalyst loading and/or time in the polymerization offers a convenient tuning of the polymer content and the morphology of the decorated MWCNTs. Appealingly, films made of the decorated carbon nanotubes through simple vacuum filtration show the characteristic lotus leaf-like superhydrophobicity with high water contact angle (> 150°), low contact angle hysteresis (< 10°), and low water adhesion, while being electrically conductive. This is the first demonstration of the direct fabrication of lotus leaf-like superhydrophobic films with solution-grown polymer crystal-decorated carbon nanotube.



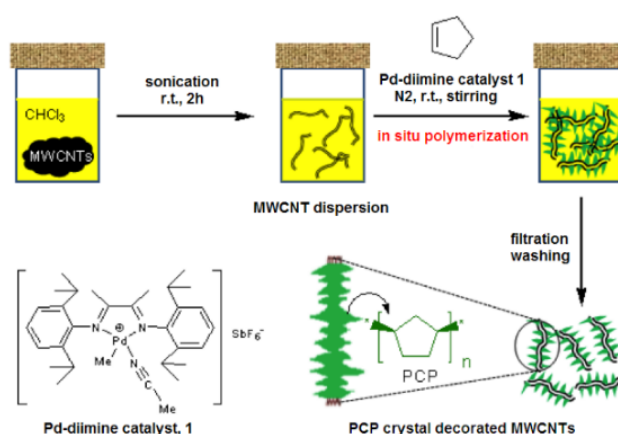
1. Introduction

Decoration of carbon nanotubes (CNTs) with polymer crystals is a unique noncovalent strategy for the functionalization of CNTs.^[1] In this regard, both single- and multi-walled CNTs (SWCNTs and MWCNTs) have been demonstrated to induce polymer crystallization from their solutions or melts, leading to the formation of nano-hybrid shish-kebab (NHSK) or the transcrystalline structures.^[1,2] In particular, the transcrystalline structure forms when the fibrous CNT filler can initiate a high density of active nuclei on its surface, which force the crystal growth only in the direction normal to the CNT axis. Thus far, the CNT-based transcrystalline structure has only been seen in few cases under appropriate conditions.^[3] On the contrary, the NHSK structure, first discovered by Li et al.,^[4] develops at reduced densities of active nuclei, with the CNTs (shish) decorated periodically with polymer crystal lamellae (kebabs). Through quiescent isothermal solution crystallization, CNT-based NHSK structures have been extensively synthesized by Li's and other groups with the use of various semicrystalline polymers,^[1] including polyethylene (PE),^[4,5] nylon,^[4,6] polypropylene,^[7] etc. A size-dependent soft epitaxy mechanism has been proposed by Li et al. for the formation of the NHSK structures.^[4] Alternatively, other methods, including supercritical CO₂-induced polymer crystallization,^[8] physical vapor deposition,^[9] and shear-induced crystallization from polymer melts or solutions,^[10] have also been developed by various groups for the preparation of CNT-based NHSK structures. The unique NHSK or transcrystalline structure imparts the decorated CNTs with some valuable properties. When used to construct polymer nanocomposites, both NHSK and transcrystalline structures have been demonstrated to render stronger polymer-CNT interactions and facilitate more effective load transfer to the CNTs.^[3c,6b,10a,c] Meanwhile, Li et al. have also shown that films made of PE crystal-decorated SWCNTs of the solution-grown NHSK structure by vacuum filtration exhibit rose petal-like sticky superhydrophobicity due to the hierarchical roughness created by the NHSK structures.^[11]

All above-mentioned methods for the synthesis of polymer crystal-decorated CNTs (predominantly, NHSK structures) often require special and strict conditions while at small production scale (e.g., high temperature and very dilute polymer solutions at ca. 0.1 mg/mL) for the periodic epitaxial growth of polymer crystals from the CNTs and the employed semicrystalline polymers must be synthesized beforehand. More convenient one-step large-scale methods, combining polymerization and crystallization in situ in a single step while undertaken at facile conditions, are highly desired. Several groups reported previously the synthesis of PE-CNT nanocomposites by in situ metallocene-catalyzed ethylene polymerization in the presence of CNTs.^[12] Therein; PE-coated CNTs with sausage-like structures were often produced. The formation of NHSK structures was only observed in few cases,^[12a,i] but with limited control over the structure and the content of the decorating polymer crystals. Meanwhile, no application was demonstrated with the PE-CNT NHSKs produced therein. In this paper, we report a one-step large-scale in situ synthesis of polycyclopentene (PCP) crystal-decorated MWCNTs by convenient, direct Pd-catalyzed polymerization of cyclopentene in the presence of MWCNTs while under facile conditions. PCP is a highly crystalline polymer synthesized by catalytic addition polymerization and is typically featured with high melting point (up to 395 °C depending tacticity).^[13] Its use should render beneficially the crystal structures with higher temperature stability compared to PE crystals. However, PCP has not been previously employed to decorate CNTs. Herein, MWCNTs decorated with PCP crystals of high melting point (220 °C) at tunable content are easily obtained with the in situ polymerization method. More distinctly, films fabricated with the PCP crystal-decorated MWCNTs are demonstrated to show valuable lotus leaf-like superhydrophobicity.

2. Results and Discussion

The in situ polymerization of cyclopentene is undertaken in the presence of MWCNTs with the use of a Pd–diimine catalyst, $[(\text{ArN}=\text{C}(\text{Me})-(\text{Me})\text{C}=\text{NAr})\text{Pd}(\text{Me})(\text{NCMe})]^+\text{SbF}_6^-$ ($\text{Ar}=2,6\text{-}(\text{iPr})_2\text{C}_6\text{H}_3$) (**1**), simply at room temperature (ca. 23 °C) under N_2 with mild magnetic stirring. Scheme 1 depicts schematically this in situ polymerization method. As a unique class of late transition metal catalysts,^[14] Pd–diimine catalysts similar to **1** have been previously demonstrated to produce cis-1,3-enchained high-molecular-weight PCP with high melting point of ca. 240 °C at similar conditions.^[15] In this polymerization system, the feed concentrations of MWCNTs and cyclopentene are fixed at 2.5 and 115 mg/mL, respectively, in a fixed volume (20 mL) of chloroform as solvent. This feed concentration of MWCNTs is much higher compared to those typically used in the small-scale isothermal solution crystallization method,^[4-6] thus facilitating the more effective larger-scale synthesis herein. The loading amount of catalyst **1** and the polymerization time are the parameters that are tuned in the system to change the structure of resulting PCP crystal-decorated MWCNTs, including the content of PCP crystals and the morphology. An increase of either one, while at otherwise identical conditions, should lead to the enhanced PCP yield in the polymerization.



Scheme 1. Pd-catalyzed cyclopentene polymerization in the presence of MWCNTs for in situ synthesis of PCP crystal-decorated MWCNTs.

We have first investigated the effect of the loading amount of **1** on the resulting PCP-decorated MWCNTs. Polymerization runs were carried out at different catalyst loading (15,

25, 35, and 45 mg, respectively) for the same time (72 h). Figure 1 shows the transmission electron microscopy (TEM) images of the resulting decorated MWCNTs (termed as d-MWCNT1, d-MWCNT2, d-MWCNT3, and d-MWCNT4, respectively). Figure S1 in Supporting Information shows their scanning electron microscopy (SEM) images, along with that of bare MWCNTs. A control run was also undertaken in the absence of MWCNTs at the catalyst loading of 35 mg, rendering neat PCP. Figure S2 shows the SEM and TEM images of the neat PCP. Thermogravimetric analysis (TGA, see Figure S3) shows that the four decorated MWCNT samples have a PCP content of 10, 68, 79, and 89 wt%, respectively, as per the weight loss at 600 °C since bare MWCNTs have negligible weight loss at 600 °C while neat PCP produced in the control run has the complete weight loss by 600 °C.

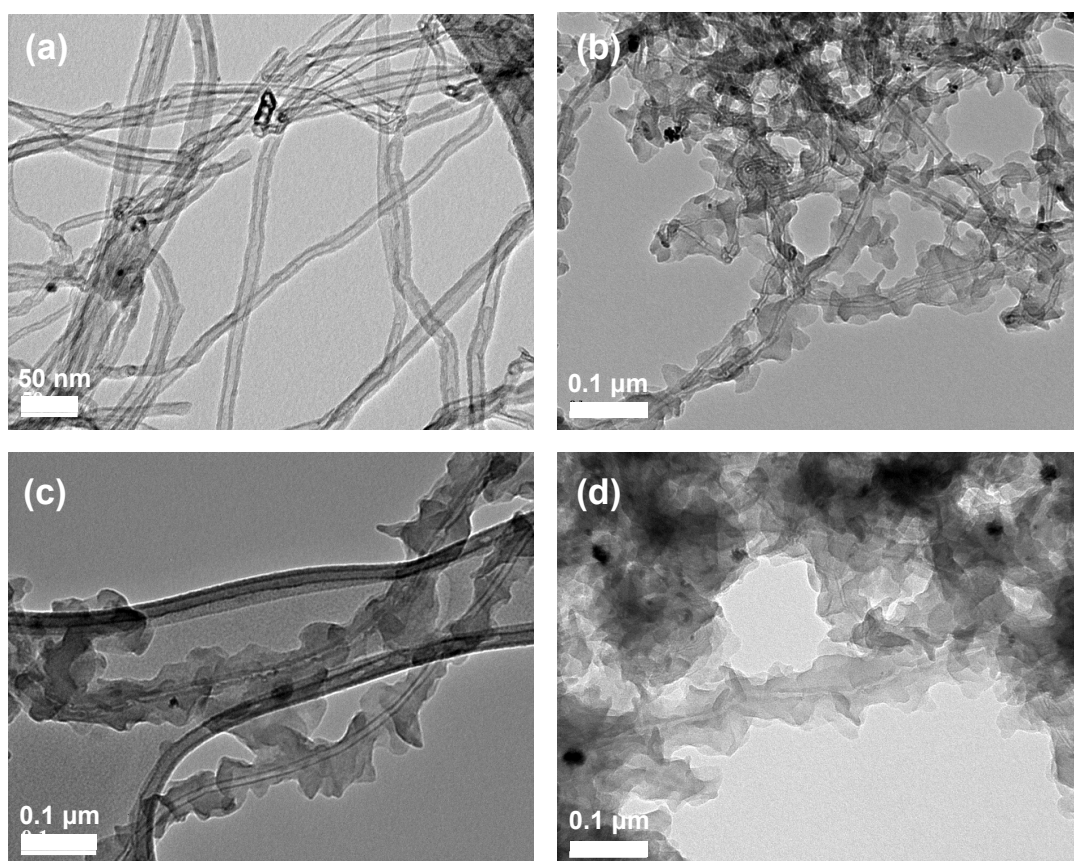


Figure 1. TEM images of d-MWCNT1 (a), d-MWCNT2 (b), d-MWCNT3 (c), and d-MWCNT4 (d) produced at the catalyst 1 loading of 15, 25, 35, 45 mg, respectively.

Due to its low PCP content, d-MWCNT1, produced at the lowest catalyst loading among the four, does not show significant difference in terms of nanotube morphology compared to the bare MWCNTs from the TEM and SEM images, with no clear observation of the PCP decoration on the nanotubes within the resolution limit. PCP likely forms a thin layer around the MWCNTs in this sample, which is not clearly visible under TEM or SEM. On the contrary, all the nanotubes in the d-MWCNT2, d-MWCNT3, and d-MWCNT4 are clearly decorated with PCP (see Figure 1(b)–(d)). Their morphology resembles the typical NHSK structures prepared by isothermal solution crystallization of PE or nylon on CNTs, with the MWCNTs serving as the shish and the decorated PCP of various irregular shapes as kebabs. Meanwhile, large agglomerates formed purely of PCP are not seen. With the increase of PCP content from d-MWCNT2 to d-MWCNT4, the quantity of PCP kebabs appears to gradually increase. While there are locations on the nanotubes not decorated by the PCP kebabs in d-MWCNT2, all the nanotubes in d-MWCNT4 appear to be fully decorated and the kebabs are bigger, approaching to resemble the transcrystalline structures.^[3] The morphology of these decorated MWCNTs is distinctively different from that of neat PCP. The neat PCP appears as loose aggregates of finer particles with a coral-like surface morphology of abundant patterned roughness (see Figure S2).

In PE-CNT NHSK structures produced by isothermal solution crystallization, the PE crystals often form orthogonal disc-shaped lamellae decorating periodically the CNTs.^[4,5] In comparison, the shape of the PCP kebabs herein is relatively irregular, with no disc-shaped lamellae observed. Meanwhile, the lateral thickness of the PCP kebabs is at about 100 nm, with no well-defined periodicity. The irregular NHSK structures seen here are reasoned to result from the much faster crystallization kinetics in this in situ polymerization system in comparison with the slow isothermal solution crystallization. The driving force for polymer crystallization is the free-energy change involved in the phase transformation and is

proportional to the supercooling, ΔT defined as $\Delta T = T_m - T_c$, with T_m and T_c denoting the melting and crystallization temperatures, respectively.^[4] Herein, T_m of the PCP crystals (shown below) is much higher than that of PE crystals while T_c (room temperature herein) is much lower than that (ca. 100 °C) typically employed for the isothermal solution crystallization of PE. The much greater ΔT herein accounts for the relatively irregular PCP crystal morphology on MWCNTs. Additionally, the surface defects on MWCNTs may also contribute to the irregular NBSK structures. Such NBSK structures with irregular polymer crystal morphology have been commonly observed in crystallization systems involving higher supercooling, such as nylon-CNT NBSKs prepared by isothermal solution crystallization^[4,6] and physical vapor deposition,^[9] PE-CNT NBSKs prepared by CO₂-induced solution crystallization,^[8] and PE-CNT NBSKs prepared by in situ polymerization.^[12a,i]

We have further investigated the evolution of the NBSK structures during the course of an in situ polymerization run carried out at the catalyst loading of 35 mg. Figure S4 shows the TEM images of the resulting PCP-decorated MWCNTs (termed as d-MWCNT5 to d-MWCNT8, respectively) sampled after the different polymerization time of 1.5, 5, 8, and 15 h, respectively, from the run. According to their TGA weight loss at 600 °C (see Figure S5), the four samples have a PCP content of 31, 56, 67, and 73 wt%, respectively. The increasing PCP content upon the extension of polymerization time confirms the continuous conversion of cyclopentene into PCP over the course of polymerization as expected. As shown in Figure S4(a), no shish-kebab structures are observed in d-MWCNT5. From the inset in Figure S4(a) at a higher magnification, the MWCNTs appear to be coated with a non-uniform layer of PCP having a thickness up to ca. 6 nm. This indicates that, at the early stage of polymerization, the produced PCP is adsorbed onto the nanotubes as a surrounding layer. From Figure S4(b), small polymer kebabs (see circled areas) decorated on the nanotubes can be found in d-MWCNT6 produced at 5 h. The further extension of the polymerization to 8 and 15 h leads to

the gradual enlargement of the kebabs and meanwhile the growth of more kebabs (see Figures S4(c) and (d)). This trend of morphology evolution resembles that of NHSK structures, but differs from that of transcrystalline structures. Similar evolution of NHSK structures was previously observed in CO₂-induced PE epitaxy^[8a] and PE non-isothermal solution crystallization in the presence of MWCNTs.^[16] In the case of transcrystalline structures, the morphology evolution is very different: the transcrystalline layer of isotactic polypropylene on CNT fibers was observed to grow uniformly along the entire fiber axial length even in the very beginning of crystallization and the extension of time just led to the gradual thickening of the layer.^[3a]

In this unique in situ polymerization system, polymer production and crystallization occur simultaneously. The polymer chains, once produced, are reasoned to undergo fast crystallization given the large supercooling, i.e., polymerization as the rate-controlling step for the crystal formation. From the trend shown in Figure S4, the PCP chains produced in the beginning of the polymerization precipitate and adsorb on the MWCNTs forming a surrounding layer, which serves as heterogeneous nucleation sites for subsequent epitaxial growth of the lamellae.^[17] From the increasing number of PCP kebabs over time seen in the TEM images, we also reason that crystal nucleation on MWCNTs continues to occur during the course of polymerization. Along with epitaxial growth of the crystal lamellae, new nuclei may simultaneously form elsewhere. This also contributes to the relatively irregular PCP kebabs observed herein.

Figure S6 shows the x-ray diffraction (XRD) pattern of d-MWCNT7 as a representative sample, along with those of bare MWCNTs and neat PCP for comparison. The neat crystalline PCP shows a broad XRD peak from 13 to 26° with peak maximum at 19.9°, which is typical of cis-enchained PCP produced with Pd- and Ni-diimine catalysts.^[15] The bare

MWCNTs show a characteristic broad peak from 24 to 32°, with peak maximum at 28.8°.^[18] The diffraction pattern of d-MWCNT7 is superimposed by the peaks of neat PCP and bare MWCNTs. Figure S7(a) shows differential scanning calorimetry (DSC) first heating curves of the nascent d-MWCNTs, along with that of neat PCP. Due to the low PCP content, the curves for both d-MWCNT1 and d-MWCNT5 are nearly featureless. Neat PCP has a broad melting endotherm up to ca. 256 °C with peak maximum at 224 °C. The d-MWCNT samples instead show narrowed melting endotherms (up to about 235 °C) with slightly lowered peak maximum temperatures (196–216 °C). The slightly lowered peak maximum temperatures are indicative of the slightly thinner lamella in the d-MWCNTs than the neat PCP. Figure S7(b) illustrates the subsequent DSC cooling curves of the samples. The neat PCP shows a broad crystallization exotherm covering nearly the entire temperature window (from 270 to ca. 50 °C) with peak maximum at 192 °C. Such broad melting and crystallization peaks are indicative of broad tacticity distribution within the neat PCP chains. Like their corresponding melting endotherms, the crystallization exotherms of the d-MWCNT samples are also much narrower with the peak maximum at about 191–203 °C. With the increase of the PCP content, the peak maximum temperature of the d-MWCNT samples in both heating and cooling curves shows only small marginal changes. This may result from the great breadth of the peaks, which leads to insensitive changes in the peak maximum temperature at different PCP content. Amorphous phase should be present in the neat PCP and the polymer decorating the MWCNTs. However, due to the absence of melting enthalpy data for perfect polycyclopentene crystals, polymer crystallinity in the neat PCP and d-MWCNT samples, however, cannot be calculated from the DSC results.

Following their convenient successful synthesis, we have further discovered the application of the above PCP-decorated MWCNTs for the fabrication of lotus leaf-like superhydrophobic films. CNT films are known for their exceptional mechanical and electrical properties.^[19]

Superhydrophobic CNT films endowed with additional superhydrophobic surface properties by controlling their surface roughness and functionality are valuable for various applications.^[20] Simple, convenient techniques for rendering superhydrophobic CNTs films are highly desired. With the use of PE-SWCNT NHSKs prepared by isothermal solution crystallization, Li et al. first demonstrated the fabrication of rose petal-like sticky superhydrophobic CNT films.^[11] Therein, the films were featured with high static water contact angle (up to 152°) but large contact angle hysteresis (115°) and high water surface adhesion. Nevertheless, lotus leaf-like superhydrophobic CNT films with characteristic high water contact angle (> 150°), low contact angle hysteresis (< 10°), and low water adhesion have not been previously reported yet with the simple, direct use of solution-grown polymer crystal-decorated CNTs. Though Li et al. subsequently reported that surface coating of the solution-grown PE-SWCNT NHSKs with polytetrafluoroethylene by chemical vapor deposition rendered films with lotus-leaf like superhydrophobicity and electrical field-induced, reversible lotus-to-rose transition,^[21] the requirement of additional surface coating makes their procedure inconvenient.

Herein, films with the thickness in the range of 50–100 μm have been conveniently prepared with three representative PCP crystal-decorated MWCNTs (d-MWCNT1 to d-MWCNT3) and the bare MWCNTs, respectively, through the simple vacuum filtration method. Figure 2 illustrates the SEM images of the top surface of the films, along with their wetting behavior determined with the sessile drop technique. The nanotubes in bare MWCNTs and d-MWCNT1 show relatively smooth surface. In the case with d-MWCNT1, this should result from the low content of PCP coating. On the contrary, the nanotubes in d-MWCNT2 and d-MWCNT3 are clearly covered by an irregular, rough layer of PCP coating. The film prepared with bare MWCNTs has a contact angle of 93°, which is close to the typical value of 82° reported for films of SWCNT films and graphite.^[11] Meanwhile, a film of the neat PCP shows

a hydrophobic surface with an intrinsic contact angle of 122°. On the contrary, the films fabricated with the decorated MWCNTs show significantly enhanced contact angles (155, 152, 154°, respectively) with no clear dependence on the PCP content. In particular, it is surprising to see that the film of d-MWCNT1 is also featured with high contact angle (155°) despite its low PCP content. In agreement with the above TEM evidence seen in Figure S4, this further confirms that the low content of PCP is coated effectively on the nanotubes.

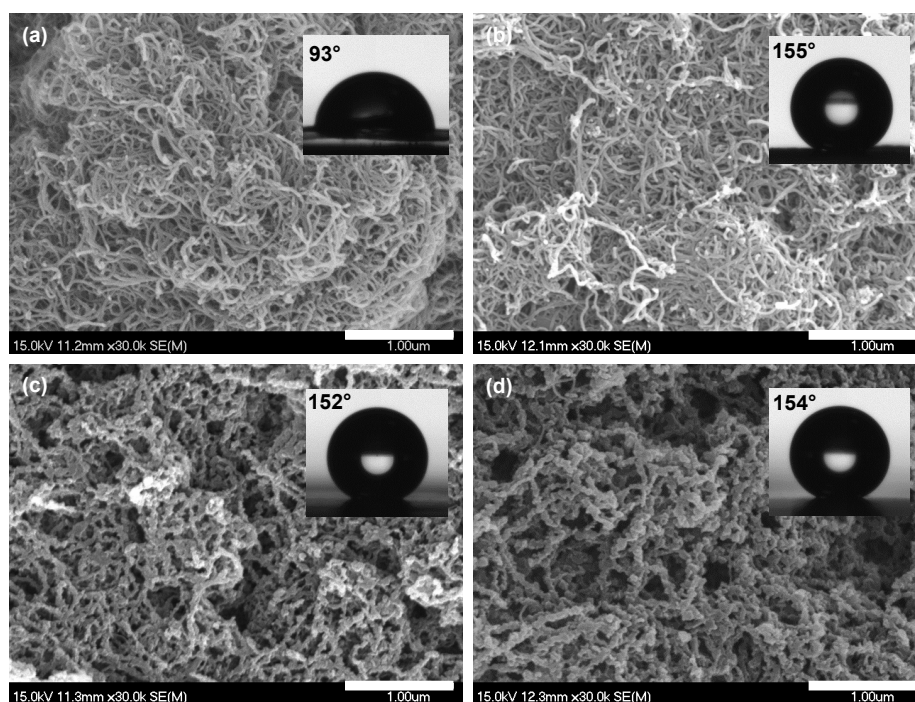


Figure 2. SEM images of films prepared with bare MWCNTs (a), d-MWCNT1 (b), d-MWCNT2 (c), d-MWCNT3 (d). Inset images are 2 μ L water droplets on the surface of the films with contact angle values.

The dynamic (advancing and receding) contact angles of the films were also determined. The advancing contact angles of the films of the three d-MWCNTs are 152, 146, 148°, respectively; the receding contact angles are 141, 136, 140°, respectively, indicative of very small hysteresis (8–11°). The sliding angles at which water droplets roll off the films are 8, 9, and 10°, respectively. Videos S1 and S2 show that falling water droplets bounce and easily roll off the films made of d-MWCNT2 and d-MWCNT3. These results confirm the lotus leaf-

like, superhydrophobic, low-water-adhesion surface (the Cassie-Baxter state) of the films fabricated with the PCP-decorated MWCNTs.^[22] This unique superhydrophobic surface should result from the change in surface functionality and the hierarchical nanoscale surface roughness created upon the decoration of the MWCNTs with PCP crystals through the in situ polymerization. These films are distinctively different from the rose petal-like superhydrophobic high-water-adhesion films made with PE-CNT NHSK structures by Li et al.^[11] Though the precise mechanism is to be investigated in further study, the difference between the two types of films is reasoned to stem from the different decorating polymer and nanoscale surface roughness.

Because of their MWCNT skeletons, the superhydrophobic films of the PCP-decorated MWCNTs are also electrically conductive. While the film of bare MWCNTs has a conductivity of 378 s/m, the films of the three d-MWCNTs show reduced conductivity values of 222, 0.28, and 0.13 s/m, respectively, due to the increasing content of the non-conducting PCP. Tuning the content of the decorating PCP by changing the loading amount of catalyst **1** or polymerization time in the in situ polymerization can thus effectively adjust the electrical conductivity of the superhydrophobic films fabricated with this range of decorated MWCNTs.

3. Conclusions

A simple, convenient in situ polymerization method under facile conditions is demonstrated for the large-scale synthesis of PCP crystal-decorated MWCNTs with tunable PCP content and morphology. It is further discovered that the decorated MWCNTs can render electrically conductive films featured with valuable lotus leaf-like superhydrophobicity simply via vacuum filtration. We anticipate the potential applications of these films in areas such as sensors, electrochemical devices, and coating.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Keywords: carbon nanotube; crystallization, polycyclopentene; polymer crystal; superhydrophobic films

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Table of Content Entry

TOC Text

A facile **in situ Pd-catalyzed cyclopentene polymerization method** is demonstrated to efficiently render polycyclopentene crystal-decorated carbon nanotubes having tunable nano-hybrid shish-kebab structures in a large scale. Appealingly, films made directly with the decorated carbon nanotubes show desired lotus leaf-like superhydrophobicity while being simultaneously electrically conductive.

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Polycyclopentene Crystal-Decorated Carbon Nanotubes by Convenient Large-Scale In Situ Polymerization and Their Lotus Leaf-Like Superhydrophobic Films

TOC Graphics

