Nanohybrid Shish-Kebabs: Periodically Functionalized Carbon Nanotubes**

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Due to their extraordinary mechanical, electrical, and optical properties, carbon nanotubes (CNTs) have attracted great attention in recent years.1-3 In order to transfer their outstanding properties from nano- to macroscale, one essential step involves assembling and processing of CNTs,4,5 which is hindered by their intrinsic poor solubility and processability.6-10 It has been recognized that, to disperse CNTs for processing purposes, their surface has to be modified; so emerges the field of CNT functionalization.11,12 Both chemical functionalization techniques and non-covalent wrapping methods have been employed.13-20 The first technique involves covalently linking a functional group directly to the CNT surface or to surface defect sites (such as CNT-bound carboxylic acids),13-16 whilst the second method involves using surfactants, oligomers, biomolecules, and polymers to ‘wrap’ CNTs to enhance their solubility. A number of surfactants as well as rigid conjugated molecules have been successfully used to modify CNT surface chemistry. It is anticipated that these molecules form strong π-stacking with the CNTs, resulting in surfactant:functional molecule-coated CNTs and hence the CNT surface properties can be altered. Small and co-workers proposed the use of water-soluble polymers, such as polyvinylpyrrolidone (PVP) and poly(styrene sulfonate) (PSS), to enhance the solubility of the CNT in water.17 CNT-induced polymer crystallization has also been investigated in isotactic polypropylene/CNT nanocomposites.21,22 In another parallel research field, carbon materials, in various forms, have been known to be able to induce polymer crystallization.23-29 Epi-taxial growth of polymers such as polyethylene (PE), nylon-6, etc., on a graphite surface has been observed using scanning tunneling microscopy (STM) and transmission electron microscopy (TEM) techniques.23-25 Carbon fibers (CFs), which are ~10 μm in diameter, have been used to induce polymer crystallization (transcrystallization).26-29 It has also been demonstrated that a number of polymers (such as polypropylene, PE, nylon-6,6, poly(phenylene sulfide), etc.) can epitaxially grow on CF surfaces.26-29 This motivated us to investigate carbon-nanotube-induced polymer crystallization and to use this technique for CNT functionalization. Compared with pre-

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viously reported PVP wrapping techniques to functionalize CNT, mixing a crystalline polymer with CNTs could lead to three scenarios: the polymer could 1) phase separate from the CNTs and the CNTs aggregate/precipitate from the solution; 2) wrap the CNT and enhance CNT solubility, as PVP does;[17] or 3) crystallize onto the CNT surface. It is envisaged that if CNT-induced crystallization does occur (case 3), polymers could form a crystalline layer on the CNT, which ‘wraps’ the latter and, therefore, modifies its surface.

In this communication, we report a novel method to periodically functionalize CNTs using controlled polymer crystallization. By controlling crystallization conditions, polymer single crystals were periodically decorated onto both single-walled and multiwalled CNTs (SWNT and MWNTs). The periodicity of the polymer single crystals can be controlled to be 20–70 nm. Since polymers can be easily removed by etching/dissolution, this method could open a new route for periodically introducing multiple functionality onto individual CNTs. Furthermore, polymer nanocomposites have also been achieved using a single-crystal-functionalized CNT as the precursor.

In order to achieve controlled functionalization of CNTs, a polymer solution crystallization technique was employed. CNTs were unbundled in a dilute polymer solution using an ultrasonicication method. Before agglomeration of the unbundled CNTs occurs, the CNT/polymer solution was brought to the crystallization temperature ($T_c$) at which point the polymer crystallizes on the CNT surface to result in CNT/polymer hybrid nanostructures. Both PE and nylon-6,6 have been used to decorate MWNTs and SWNTs. For nylon-6,6 crystallization, glycerin was used as solvent and p-xylene was used for PE crystallization. [30,31] Detailed experimental procedures are shown in Scheme 1 and can also be found in the Experimental section.

Figure 1a shows a scanning electron microscopy (SEM) image of the PE-functionalized MWNTs obtained from the procedure above ($T_c=103^\circ$C). A straight, isolated MWNT can be clearly seen. Notice the tube is decorated with disc-shaped objects that are uniform in size and periodically located along the CNT. These disc-shaped objects are edge-on views of the polymer single crystal lamellae and the peculiar morphology is similar to the classical polymer shish-kebab structures formed in an elongation/shear flow field.[32] The CNT/polymer system in this case was not under external flow during crystallization and it is the MWNT that induces nucleation of the polymer chains upon the MWNT surface. Figure 1b shows a TEM micrograph of a similar structure without Pt shadowing, and Figure 1c is the schematic representation of this nano

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**Scheme 1.** Formation process of PE/CNT nanohybrid shish-kebabs (NHSKs).

**Figure 1.** PE/MWNT NHSK structure produced by crystallization of PE on MWNTs at 103°C in p-xylene for 0.5 h: a) SEM image shows that MWNTs are decorated by disc-shaped PE single crystals and PE-functionalized MWNTs can therefore be achieved. b) TEM image of enlarged PE/MWNT NHSK structures. a) and b) show that periodicity of the kebabs is ~50–70 nm. c) Schematic representation of the PE/CNT NHSK structure. For clarity, a SWNT was used. The PE forms folded lamellar single crystals on the CNT surface with polymer chains perpendicular to the lamellae.
hybrid structure. The CNT forms the central stem and PE periodically grows on the CNT. Figure 1, therefore, resembles ‘nanohybrid shish-kebabs’ (NHSKs). From Figure 1b, the ‘shish’ (MWNT) possesses a diameter of 12.7 nm. Along the MWNT, the single crystal lamellae (kebabs) are perpendicular to the MWNT axis. Average intervals of the adjacent lamellae are ~50–70 nm and the diameter of the lamellar crystals is ~60–80 nm.

The formation of the NHSK structures is attributed to the controlled polymer crystallization on the CNT surface. The nucleation process begins after CNTs and PE are dispersed in p-xylene at a relatively high temperature (120 °C). The temperature of the mixture, consisting of un bundles, naked CNTs and ‘free’ polymers chains, is lowered to the Tc (103 °C) for crystallization. Agglomeration occurs within ~0.5 h for pure CNT in p-xylene because the un bundled CNTs are not stable. With PE in the system, however, three processes could occur: PE crystallization by homogeneous nucleation; PE crystallization on the CNT surface (secondary nucleation); and CNT agglomeration. Since CNTs provide an external surface for PE to nucleate on and, being at a relatively high Tc, this secondary nucleation is energetically more favorable compared with PE homogeneous nucleation. Furthermore, if the polymer crystallization kinetics is faster than that of the CNT agglomeration, the CNTs will be wrapped by PE single crystals and these crystals provide steric hindrance to prevent CNT agglomeration, as is the case observed here.

What is immediately noticeable from Figure 1 is that the polymer kebabs periodically decorate the CNTs and the NHSKs are, therefore, periodically functionalized CNTs. Periodical functionalization of CNTs is an extremely challenging task due to the small size of the CNTs. Very few reported CNT functionalization studies have been dedicated to determining how the functional groups arrange on the CNT surface. [3] Recently, Kruse and coworkers carefully investigated the structure of the CNTs functionalized by a Bingel reaction. [3] The authors were able to identify long range, regular patterns of the functional groups on the individual CNT surfaces using scanning tunneling microscopy techniques. A clear periodicity of ~4.6 nm was observed and the cause of the periodicity was attributed to a postulating induced reactivity. [3] The periodicity in our observation is much larger (70 vs. 4.6 nm). We suggest that the molecular origin of the periodicity observed in the NHSK might be related to the concentration gradient and the heat dissipation at the lamellar growth front. In polymer shish-kebab structures, it has been recognized that the kebabs are epitaxially grown on the shish surface and the polymer chains composing the shish and kebabs are parallel to each other. As shown in Figure 1c, in the case of a PE/CNT NHSK, the PE polymer chains are possibly also parallel to the CNT axis, leading to the orthogonal orientation of the PE lamellae with the tube axis. There are two possible growth mechanisms of the PE on the CNT surface: first, epitaxial growth of PE on the CNT, and second, due to their small diameter, the CNTs themselves can be considered as macromolecules and the polymer chains might prefer to align along the tube axis regardless of the lattice matching between the polymer chain and the graphitic sheet. A detailed molecular origin of the kebab periodicity and the relationship between the CNT conformation and polymer chain orientation are currently under investigation.

Nylon-6,6 was also used to decorate the CNT surfaces to tune the surface chemistry of the resulting NHSKs. Figure 2a shows an SEM image of nylon-6,6/CNT NHSKs. The un bundled NHSKs are clearly seen and each CNT has been periodi-odically decorated with nylon-6,6 lamellar crystals along the entire tube. Figure 2b shows a TEM image of the nylon-6,6/ CNT NHSK and the inset of the figure shows an enlarged segment of the tube. The CNT diameter is ~12 nm and the periodicity of the kebabs is ~20–30 nm as opposed to ~50–70 nm in the PE/CNT NHSKs, suggesting that the periodicity also depends on the nature of the decorating polymers.

In order to demonstrate that the controlled polymer crystallization method also works for different types of CNTs, high-pressure CO (HiPeCo) SWNTs were also used for PE crystallization. Figure 3 shows the TEM image of the PE/SWNT NHSKs. NHSK structures are again evident and of particular interest is that in some of the NHSK structures, a bundle of SWNTs are wrapped, instead of a single tube. This may arise due to two possible causes; first, the SWNTs were not completely exfoliated, and second, the SWNTs may agglomerate before nucleation occurs. Fractions of SWNTs with PE crys-
tallized around the bundle captured the ‘state of the CNT agglomeration’ in p-xylene solution. This image, therefore, can be considered as the direct visualization of the ‘degree of exfoliation/agglomeration’ of SWNTs in the p-xylene solution at the time of polymer crystallization.

Compared with naked CNTs, these NHSKs are easier to disperse in a polymer matrix since their surfaces are functionalized. The size of the kebabs can also be easily controlled by tuning the crystallization conditions. Figure 4a shows a nylon-6,6/MWNT shish-kebab crystallized at 172 °C for 0.5 h. Due to greater supercooling and faster crystallization kinetics, much larger diameter kebabs (~150 nm) have grown on the MWNT surface. The inset of the figure shows the enlarged tip of Figure 4a. A single MWNT can be clearly seen protruding out of the NHSK and the body of the CNT is buried inside the NHSK. Adding more nylon-6,6 to a nylon-6,6/CNT NHSK suspension and further crystallization at 185 °C leads to the formation of nylon-6,6 spherulites, as shown in Figure 4b. Nylon-6,6/CNT NHSKs are dispersed and located in these hybrid spherulites, which can be considered as CNT/polymer nanocomposites with controlled CNT dispersion. It should be noted that, due to the large size of the spherulites, a number of NHSKs are probably trapped within one spherulite and the number should depend on the crystallization conditions. Detailed work is ongoing to obtain further experimental evidence. Figure 4c shows the formation process of nylon-6,6 spherulites containing NHSK.

In summary, for the first time, polymer single crystals have been successfully grown onCNT surfaces. It is evident that CNTs can induce polymer secondary nucleation and the resulting NHSK structures possess a unique, controllable periodicity of the kebab polymer single crystals. This, in effect, opens a gateway to functionalizing CNTs in an ordered and controlled manner, a challenging task yet to be explored. Both SWNTs as well as MWNTs have been successfully decorated with PE and nylon-6,6, implying that this might be a generic method for CNT functionalization. The NHSK structures can also be used to fabricate polymer/CNT nanocomposites with controllable CNT dispersion. Furthermore, by coupling crystalline polymers with functional groups, ordered multifunctionality could be realized on individual CNTs.

**Experimental**

Purified HiPeCo SWNTs were purchased from Carbon Nanotechnologies Inc. Multiwalled carbon nanotubes (MWNTs) were purchased from Aldrich and washed with 2.4 M nitric acid for 0.5 h. The resulting MWNTs were then centrifuged, collected, and dried in a vacuum oven. Nylon-6,6 ($M_n = 10000 \text{ g mol}^{-1}$) was supplied by the Dupont Company. Linear polyethylene (melt flow index, MFI = 12 g (10 min)$^{-1}$) and glycerin were purchased from Aldrich and used as received.

Nanoemboid shish-kebabs were obtained by solution crystallization using CNTs as seeds. For PE crystallization (see Scheme 1), p-xylene was used as the solvent. 0.1 mg of MWNTs was dispersed in 1 g of p-xylene and ultrasonicated for 1–2 h before being added to a 4 g (w/w) 0.01 % PE/p-xylene solution. The mixture was then quenched to a preset $T_c$. The crystallization time was controlled to be 0.5 h. The crystallization temperature was 103 and 104 °C for the MWNTs and SWNTs, respectively. The crystallization time was ~0.1–3 h. The samples were isothermally filtered to remove uncrystallized materials before microscopic observation. For nylon-6,6 solution crystallization, glycerin was used as the solvent and the concentration was ~0.01 % (w/w). Nylon-6,6 was dissolved in glycerin at 240 °C. The MWNTs (0.1 mg) were then dispersed in 1 g glycerin and ultrasonicated for 1–2 h at 40 °C and then added to a 9 g (w/w) 0.01 % nylon-6,6/glycerin solution. The mixture was then quenched to the preset $T_c$. The crystallization time was controlled to be 0.5–3 h. The sample was also isothermally filtered after crystallization to remove the uncrystallized materials. Glycerin was exchanged with isopropyl alcohol for

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Figure 3. TEM micrograph of PE/SWNT NHSKs produced by crystallization of PE on SWNTs at 104 °C in p-xylene for 0.5 h. Note that in some of the NHSKs, a bundle of SWNTs (dotted arrows), instead of one single tube (solid arrows), form the shish. These bundles can also serve as the seeds for PE crystallization. This image can thus be considered as the direct visualization of the ‘degree of exfoliation/agglomeration’ of SWNTs in the p-xylene solution at the time of polymer crystallization.

Figure 4. a) TEM micrograph of an NHSK obtained by crystallizing nylon-6,6/MWNT/glycerin solution at 172 °C for 0.5 h. b) SEM micrograph of nylon-6,6 spherulites formed by using NHSK (Fig. 2a) as seeds to further crystallize pure nylon-6,6 at 185 °C. c) Formation process of CNT-containing nylon-6,6 spherulites.
TEM sample preparation. TEM experiments were conducted using a JEOL-2000FX microscope with an accelerating voltage of 120 kV. SEM experiments were carried out using a FEI/Phillips XL30 field emission environmental SEM with an acceleration voltage of 15 kV.

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[32] It was observed during the 1960s, and recently demonstrated using Langevin simulation, that if a polymer solution (i.e., 5 % polyethylene/xylene) is under an extension/shear flow, polymer chains might undergo a coil-stretch transition and the stretched polymer chains could aggregate and form extended fibrillar crystals. The remaining coil polymer chains could then crystalize on the fibrillar crystals in a periodic fashion, forming the so-called shish-kebab morphology. The stretched polymer is the shish and the disc-shaped folded lamellae are kebabs. See (a) A. Keller, H. W. Kolmar, in: Materials Science and Technology—A Comprehensive Treatment, Vol. 18, (Ed., H. E. H. Meijer), VCH, Weinheim, Germany 1997; (b) A. J. Pennings, J. Polym. Sci., Part C: Polym. Symp. 1977, 59, 55; (c) I. Dukovski, M. Muthukumar, J. Chem. Phys. 2003, 118, 6648.