

Creation of Hierarchical Carbon Nanotube Assemblies through Alternative Packing of Complementary Semi-Artificial β -1,3-Glucan/Carbon Nanotube Composites

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Abstract: Much attention has been focused on exploiting novel strategies for the creation of hierarchical polymer assemblies by the control of the assembling number or the relative location among neighboring polymers. We here propose a novel strategy toward the creation of “hierarchical” single-walled carbon nanotube (SWNT) architectures by utilizing SWNT composites with cationic or anionic complementary semi-artificial β -1,3-glucans as “building blocks”. These β -1,3-glucans are known to wrap SWNTs helically, to create

one-dimensional superstructural composites. If the cationic composite is neutralized by an anionic composite, a well ordered SWNT-based sheet structure was created. Transmission electron microscopy (TEM) observation revealed that this sheet structure is composed of highly-ordered fibrous assemblies of SWNTs. This suggests that the

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cationic and anionic composites are tightly packed through electrostatic interactions. Moreover, both of the final assembly structures are readily tunable by adjusting the cation/anion ratio. The self-assembling modulation of functional polymers is associated with the progress in ultimate nanotechnologies, thus enabling us to create numerous functional nanomaterials. We believe, therefore, that the present system will extend the frontier of SWNT research to assembly chemistry including “hierarchical” superstructures.

Introduction

Creation of highly-ordered assemblies by using functional polymers as building blocks, which would lead to novel chemical and physical properties depending on their assembling modes, is of great concern, owing to their potential ap-

plications as fundamental nanomaterials. One can easily imagine, however, that this approach is much more difficult than their creation by using functional low molecular-weight compounds. So far, alignment of functional polymers such as π -conjugated polymers has been achieved through chemical or physical techniques that utilize liquid crystal phases,^[1] patterned surfaces,^[2] and mechanical shearing of polymer films.^[3] These strategies have been successful in preparing ordered polymer assemblies on a mesoscopic level. On the other hand, tuning physicochemical properties of polymer assemblies in nanoscale, for which individual polymers must be manipulated during their self-assembling process, have not yet been achieved successfully because of the lack of an established strategy. So far, much attention has been focused on exploiting novel strategies for the creation of hierarchical polymer assemblies by the control of the assembling number or the relative location among neighboring polymers, and is expected to endow exceptional functionalities in the assembled structures. The most expeditious way to create such hierarchical polymer architectures in a bottom-up manner is to utilize the self-assembling capabilities of polymers, where functional polymers bearing molecular recognition groups act as building blocks in the organization processes. Unlike the self-assembling system of small mole-

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cules,^[4] only a few attempts have been reported for the creation of such hierarchical architectures from polymers.^[5] The difficulty in the polymeric system arises from how one can introduce self-assembling capabilities into a polymer backbone without losing its inherent functionality and from how to assemble the polymers through specific interpolymer interactions without the influence of the nonspecific bundling nature.

We recently demonstrated that natural polysaccharide β -1,3-glucans act as a one-dimensional host that can include the hydrophobic guest polymers, such as single-walled carbon nanotube (SWNT),^[6] poly(aniline),^[7] and poly(thiophene),^[8] into the tubular hollow constructed by the helical structure inherent to β -1,3-glucans,^[9] to result in the creation of water-soluble one-dimensional nanocomposites.^[10] The system has several lines of unique advantage: 1) when chemically modified β -1,3-glucans are used as one-dimensional hosts, the exterior surface of the resultant nanocomposites can be utilized as an interaction site for the construction of supramolecular architectures and, 2) the strong interpolymer interactions among guest polymers are perfectly suppressed by the wrapping effect of β -1,3-glucans, which insulates one piece of guest polymer to maintain its original functionality. Therefore, if a β -1,3-glucan, which incorporates molecular recognition groups on its exterior surface, wraps a guest polymer, the resultant composite would acquire the potential to self-assemble and, in turn, create a specific hierarchical architecture. Accordingly, we synthesized two new kinds of complementary semi-artificial curdlans (one kind of β -1,3-glucans), i.e., ammonium-modified curdlan (cur-N^+) and sulfonate-modified curdlan (cur-SO_3^-),^[11] expecting that the mixture of these two composites in an appropriate ratio results in the creation of a hierarchical architecture, owing to the electrostatic interaction. To estimate the feasibility of this idea, we chose single-walled carbon nanotube (SWNT) as a guest polymer,^[12] which is now regarded as one of the most attractive future materials in nanotechnology (Figure 1).^[13]

Results and Discussion

Preparation of complementary semi-artificial curdlan/SWNT composites: Firstly, we prepared SWNT composites utilizing cur-N^+ or cur-SO_3^- as one-dimensional hosts (see

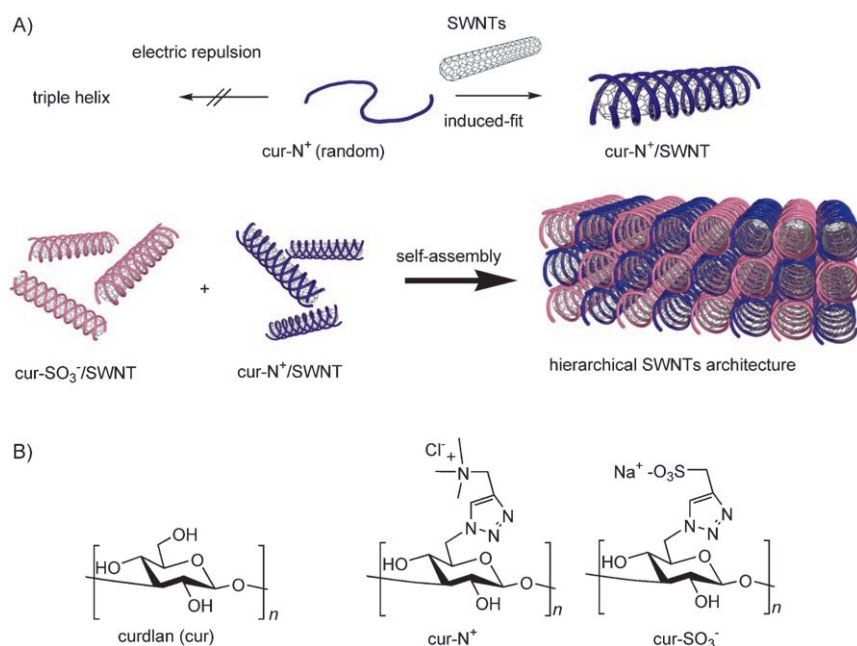


Figure 1. A) Proposed concept for creating the hierarchical SWNT architecture from the one-dimensional building blocks through the electrostatic interaction. All processes including wrapping of SWNTs by curdlan and self-assembling of the resultant composites proceed in a supramolecular manner. B) Repeating unit of natural curdlan and two kinds of semi-artificial curdlan with cationic and anionic moieties, respectively.

the Experimental Section). Figure 2 shows the Vis-NIR spectra of the aqueous solutions of the composites prepared. The Vis-NIR spectra displays characteristic absorption bands that we can reasonably assign to the SWNTs and verifies that SWNTs are solubilized into water by wrapping them with cur-N^+ or cur-SO_3^- . Judging from the peak sharpness of the spectra, the SWNTs are included into the helical structures constructed by cur-N^+ or cur-SO_3^- in a 1:1 ratio. It is well-known that a SWNT can be entrapped into the cylindrical micellar structure created by SDS (sodium dodecyl

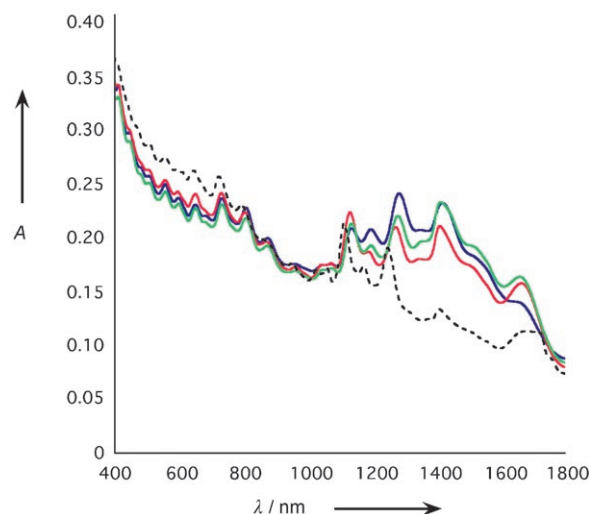


Figure 2. Vis-NIR spectra of cur-N^+ /SWNT composite (blue line), cur-SO_3^- /SWNT composite (red line), SDS/SWNT (dotted black line), and the sheet-like structure (green line): D₂O, 1.0 cm cell, room temperature.

sulfate).^[14] Here, one may expect that the spectral feature of the obtained composite can be directly compared with that of the SDS/SWNT mixture. One can see from Figure 2 that the spectral features as well as the peak sharpness of both composites, i.e., cur-N⁺/SWNT composite and cur-SO₃⁻/SWNT composite, are similar to that of the SDS/SWNT mixture. This indicates that individual SWNTs are actually wrapped by cur-N⁺ or cur-SO₃⁻. Atomic force microscopy (AFM) observations of the composites support this view more quantitatively; indeed fibrous composites (1.5–1.7 nm height) can be observed after casting them on mica surface (Figure 3A,B, and S1 in the Supporting Information). Taking the diameter of the SWNT used into consideration, the 1.6 nm height (average) implies that both composites consist, mostly, of one piece of SWNT.^[6] Furthermore, it can be seen from the magnified image (Figure 3C) that the periodical helical structure is constructed on the composite surface. This finding indicates that SWNTs are included in the hydrophobic cavity constructed by cur-N⁺ or cur-SO₃⁻.

These AFM images are basically very similar to those previously observed for natural β -1,3-glucan/SWNT composites.^[6] Furthermore, in the present system, the amount of curdlan wrapping on SWNTs can be estimated by using a phenol/sulfuric-acid reaction system that indicates the curdlan/SWNT ratio can be estimated to be 0.33 (w/w) for cur-N⁺/SWNT and 0.46 (w/w) for cur-SO₃⁻/SWNT. From these results, it is worthy to mention here that cur-N⁺ and cur-SO₃⁻ have the similar wrapping capability for SWNTs, resulting in the similar helical pattern on SWNTs. The findings suggest that cur-N⁺/SWNT composite and cur-SO₃⁻/SWNT composite may be used as “complementary” one-dimensional building blocks to create higher-order hierarchical self-assembled architectures of SWNTs.

Self-assembly of the complementary composites: In the present system, the final structures as well as self-assembling behaviors are predominantly governed by the initial cur-N⁺/cur-SO₃⁻ ratio in the mixture. To create well-developed two- or three-dimensional hierarchical architectures from these one-dimensional composites, the cationic charges on the cur-N⁺/SWNT composite must be neutralized by the anionic charges on cur-SO₃⁻/SWNT composite. Based on this working hypothesis, we prepared first the two respective cur-N⁺/SWNT and cur-SO₃⁻/SWNT composite solutions to contain the same concentration of SWNT and by using the same volume. To monitor the neutralization process, the zeta-potential values were measured. The zeta-potential value of an aqueous solution containing cur-N⁺/SWNT composite was estimated to be +48.9 mV, whereas an aqueous solution containing cur-SO₃⁻/SWNT composite showed -49.5 mV. Both solutions were very stable without precipitate formation for several weeks at room temperature. Once these two solutions were mixed in the same volume under the very diluted condition (for the experimental procedures, see the Supporting Information), the zeta-potential value of the resultant mixture showed -0.53 mV without accompanying precipitate formation, thus indicating that the potential charges on these composites are almost neutralized to give a self-assembling composite through the electrostatic interaction.

To confirm the type of self-assembling architectures created during this neutralization process, we cast the resultant aqueous mixture on a substrate and observed the morphologies by various microscopes (AFM images are shown in Figure 3D). As shown in Figure 3D, we observed a well-developed sheet structure with micrometer-scale length, which is entirely different from the very fine fibrous structures observed for individual cur-N⁺/SWNT and cur-SO₃⁻/SWNT composites (Figure 3A,B). The scan profile of the sheet structure also revealed that several thin layers were piled up to form the sheet-like structure, the surface of which is almost flat in the micrometer range (Figure 3E). We could also confirm the creation of the similar sheet structure by scanning electron microscopy (SEM) (see the Supporting Information, Figure S2). The presence of SWNTs in the created sheet structure was evidenced by Raman spectroscopic

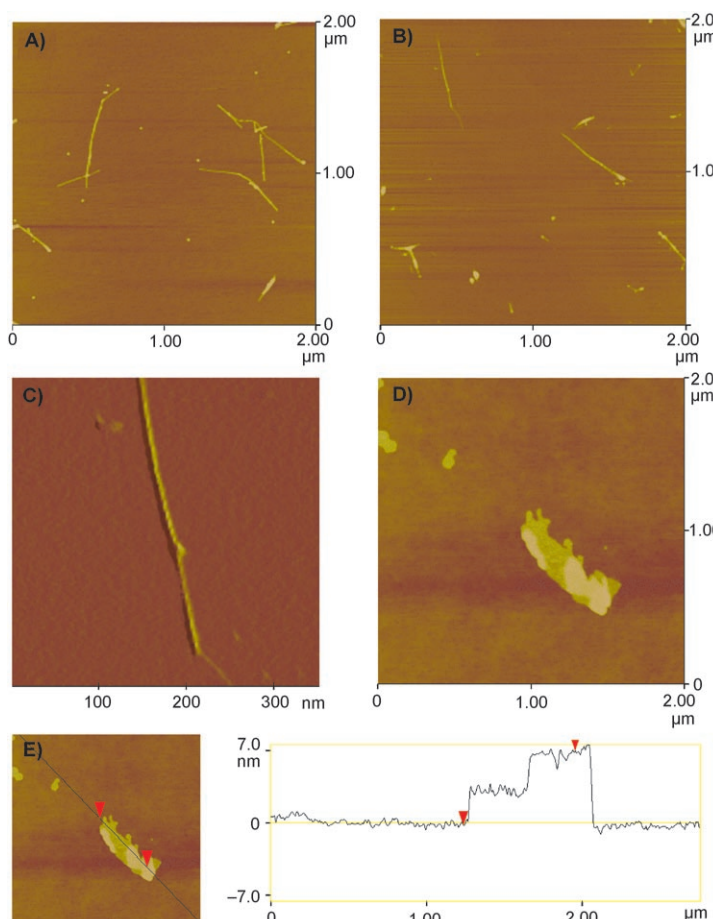


Figure 3. AFM images of A) cur-N⁺/SWNT composite and B) cur-SO₃⁻/SWNT composite, respectively. C) Magnified AFM image of (B). D) AFM image of the sheet-like structure after mixing cur-N⁺/SWNT composite and cur-SO₃⁻/SWNT composite. E) Height profile of the sheet-like structure: the AFM tip was scanned along the black line. In this AFM image, the thickness of each thin layer is estimated to be ≈ 3.5 nm.

measurements; that is, the sheet structure provides characteristic SWNT peaks at 262 cm^{-1} and 1592 cm^{-1} (see the Supporting Information, Figure S3), which are assignable to the radial breathing mode (RBM) and G-band of SWNT, respectively.

TEM is a powerful tool to study how SWNTs are arranged in the obtained sheet structure. Figure 4 shows several TEM images obtained from different regions on a specimen supporting grid. In the lower-magnified TEM image (Figure 4A), we could recognize a sheet structure extending to several micrometer length, the size of which is almost consistent with that observed in AFM and SEM images. In addition, it can be seen from Figure 4B that the sheet structure is composed of highly-ordered fibrous assemblies. Since the TEM images were obtained without staining, the observed contrast should arise from the presence of SWNTs. The electron diffraction pattern (inset in Figure 4B) reveals that the fibrous assembly has some crystalline nature, suggesting that cationic and anionic composites are tightly packed through the electrostatic interaction. The regular alignment of the composite in the thin layer was supported by a polarization microscope imaging method (see the Supporting Information, Figure S4). This view is also supported by the magnified TEM image. In Figure 4C, cur-N⁺/SWNT composite and cur-SO₃⁻/SWNT composite can be recognized as a dark layer with very regular intervals. The periodicity of the dark layer is estimated to be $\approx 2\text{ nm}$, which is almost consistent with the diameter of the individual composite obtained by the AFM height profile. The finding implies that cur-N⁺/SWNT composite and cur-SO₃⁻/SWNT composite interact with their exterior surfaces to form the

thin layer. Furthermore, in other sheet structures (Figure 4E), two kinds of dark layers appear regularly; one dark layer shows at $\approx 10\text{ nm}$ intervals and another dark layer shows at $\approx 2\text{ nm}$ intervals. As seen in Figure 4F, the periodicity of the narrow dark layer can be quantitatively estimated to be 1.6 nm by utilizing the Fourier-filtered image, the value of which is consistent with that estimated from Figure 4C. We consider that the wide dark layers with $\approx 10\text{ nm}$ intervals (Figure 4E) are ascribed to a moiré pattern created by the overlap of a few sheets. Accordingly, the results support the view that, in the present system, a thin layer consisting of highly-ordered fibrous assemblies with 1.6 nm intervals is a fundamental structure, which is able to regularly stack on one another, leading to the formation of the sheet structures. Notably, the Vis-NIR spectral features of this sheet-like architecture are almost the same as those of cur-N⁺/SWNT composite and cur-SO₃⁻/SWNT composite as shown in Figure 2. This fact supports the view that cur-N⁺ and cur-SO₃⁻ act as a sheath for SWNTs, so that the direct interaction among SWNTs can be suppressed even in the sheet-like structure, making the practical application as electronic and photoactive devices possible. The EDX (energy-dispersive X-ray spectroscopy) analysis provides direct evidence that the sheet-like structure is made up of cur-N⁺/SWNT composite and cur-SO₃⁻/SWNT composite. In Figure 4D, two characteristic peaks are detected at 0.39 eV and 2.30 eV , which are assignable to nitrogen and sulfur arising from cur-N⁺ and cur-SO₃⁻, respectively. It is still unclear, at present, why the 2-D sheet structure, but not the 3-D packed structure, is formed from cur-N⁺/SWNT and cur-SO₃⁻/SWNT composites. However, dynamic light scattering

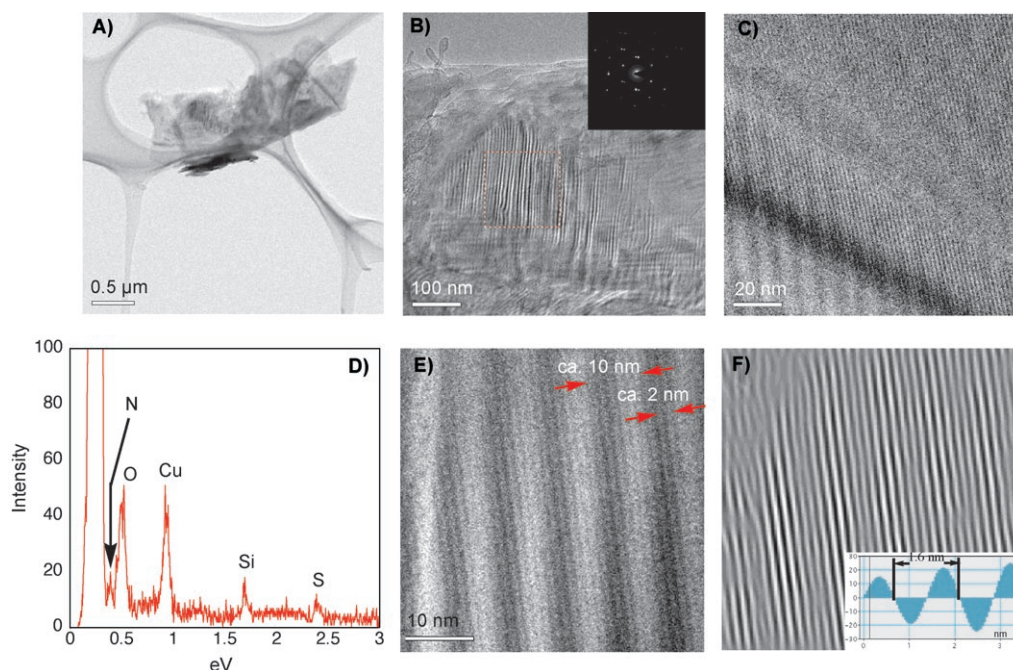


Figure 4. TEM image of A) sheet-like structure (low magnification), B) and C) magnified images of the thin layer (inset: electron diffraction pattern obtained from the sheet). D) Elemental analysis of the sheet-like structure based on EDX. The spectrum was corrected from the red-square in (B). E) Magnified TEM image of the sheet-like structure containing several thin layers. F) Fourier translation image of (D) and extracted periodical patterns.

(DLS) measurements revealed that the self-assembling aggregates, the size of which is not as large as the sheet-like structures observed by TEM, are formed at least in the initial aqueous solution. This self-assembling aggregate would be further organized into the sheet-like structure during slow evaporation of water on a substrate surface. When the two kinds of solutions were mixed at high concentration (above 0.79 mg mL^{-1}), black precipitate was formed. These results suggest the view that slow-organization process of the composites would be indispensable for the creation of the sheet-like structure. It is worthy to emphasize through the present work that the hierarchical SWNT architecture can be finally created by just mixing two kinds of aqueous solution containing cur-N⁺/SWNT composite and cur-SO₃⁻/SWNT composite in the appropriate ratio.

Attempt toward the creation of SWNT architectures with controlled size and assembling number: It is generally accepted in the molecular assembling systems that the mixture of the oppositely-charged small molecules tends to result in nonspecific irregular assemblies through electrostatic interactions, but when either cationic or anionic polymer exists excessively, specific regular structures with the well-controlled size and assembling number can be created.^[4] This concept may be applicable to the present polymer assembling system; the size of the hierarchical architecture as well as the assembly composite number would be controllable by just changing the [cur-N⁺/SWNT]/[cur-SO₃⁻/SWNT] feed ratio. To test this intriguing idea, we mixed an aqueous cur-N⁺/SWNT composite solution with an excess amount of an aqueous cur-SO₃⁻/SWNT composite solution, adjusting the [cur-N⁺/SWNT]/[cur-SO₃⁻/SWNT] ratio to 1:5. Upon mixing these solutions, it was confirmed that there was no precipitate formation. The DLS analysis of the mixture revealed that cur-N⁺/SWNT composite and cur-SO₃⁻/SWNT composite form a self-assembly structure, the size of which is larger than those of individual composites. Furthermore, the zeta-potential value of the resultant aqueous solution indicates that the obtained assembly structure has the highly anionic surface (-33.2 mV), suggesting that cur-N⁺/SWNT composite is surrounded by cur-SO₃⁻/SWNT composite to give a bundle structure. In such a case, one may imagine that electrostatic repulsion among the created bundle assemblies would suppress undesired further aggregate formation. The TEM images indeed support this view (Figure 5C,D) and the many fibrous SWNTs bundles (10–20 nm diameters) can be recognized, which are larger than those of individual composites shown in Figure 5A,B. Taking the narrow distribution in diameter and the anionic surface into consideration, one- or two-pieces of cur-N⁺/SWNT composite would be surrounded by several cur-SO₃⁻/SWNT composites. To further extend these findings, we prepared the mixtures under various [cur-N⁺/SWNT]/[cur-SO₃⁻/SWNT] ratios. In the [cur-N⁺/SWNT]/[cur-SO₃⁻/SWNT] ratios from 1:5 to 1:10, the mixture gave the fibrous bundle structure similar to those in Figure 5C,D. On the other hand, when the [cur-N⁺/SWNT]/[cur-SO₃⁻/SWNT] ratio was increased from 1:5

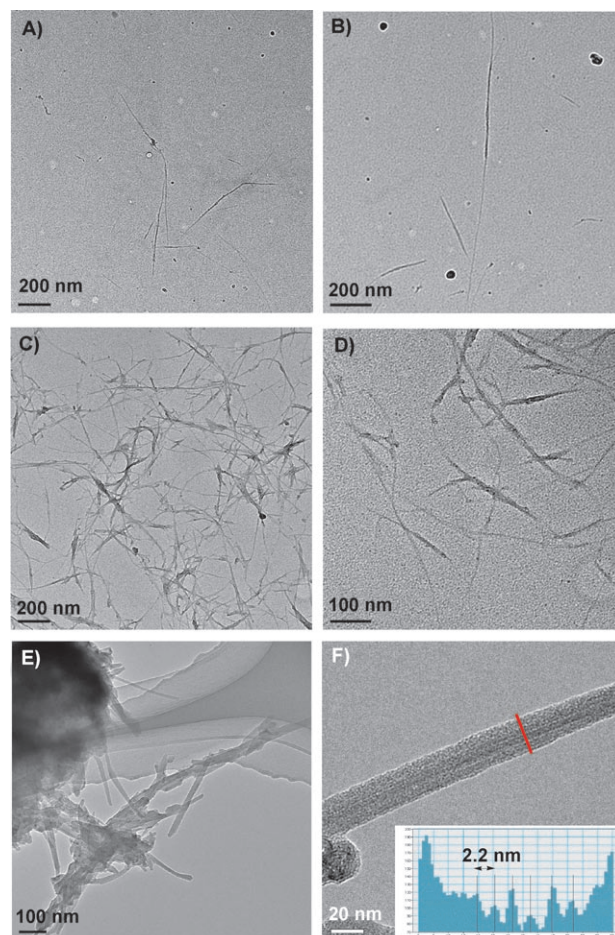


Figure 5. TEM images of A) cur-N⁺/SWNT composite and B) cur-SO₃⁻/SWNT composite. C) Fibrous bundle structure containing the limited number of SWNTs ([cur-N⁺/SWNT]/[cur-SO₃⁻/SWNT] = 1/5). D) Magnified TEM image of (C). E) Larger bundle structure ([cur-N⁺/SWNT]/[cur-SO₃⁻/SWNT] = 1/3). F) Magnified TEM image of (E) (inset: extracted periodical patterns obtained along the red line).

to 1:3, the diameter of the bundle structure became larger, accompanied by the increase in the zeta-potential from -33.2 mV to -17.8 mV (Figure 5E,F). In Figure 5F, one can see that the bundle structure is also composed of highly-ordered fibrous assemblies as seen in Figure 4C. The periodicity of the layer is estimated to be $\approx 2 \text{ nm}$, which is almost consistent with that observed for the sheet-like structure. These results substantiate our hypothesis that the self-assembling hierarchical architecture is predictable and controllable by tuning the ratio of cur-N⁺/SWNT composite and cur-SO₃⁻/SWNT composite.

Conclusion

In summary, we have demonstrated that the creation of hierarchical SWNT architectures can be easily achieved through the electrostatic interactions between cur-N⁺/SWNT composites and cur-SO₃⁻/SWNT composites. The resultant hierarchical architectures as well as the self-assembling process-

es are strongly affected by the initial $[\text{cur-N}^+/\text{SWNT}]/[\text{cur-SO}_3^-/\text{SWNT}]$ ratio; that is, upon mixing the same concentration of composites, the well-developed sheet structure is formed, whereas an excess amount of one composite over the other results in the bundle structure with the uniform diameter. The fibrous bundle structures have some charge on their exterior surface, so they are utilizable as building blocks for further organization. As curdlan can entrap a variety of guest polymers in an induced-fit manner,^[10] the present concept is more broadly applicable to the design of hierarchical architectures from other functional polymers if they are appropriately included in β -1,3-glucan polysaccharides. We believe, therefore, that considering the serious difficulties in the creation of hierarchical architectures from synthetic polymers, the present system can open new paths to accelerate development of the polymer assembly systems and can extend the frontier of polymer-based functional nanomaterials.

Experimental Section

General: Vis-NIR spectroscopic studies were performed by using a SHIMADZU UV-3100 spectrophotometer. Raman spectra of c-SWNTs/polysaccharide composites were obtained by using a JASCO NRS-2000 laser Raman spectrometer (Ar laser, 514 nm). DLS data and zeta-potential values were obtained by using Sysmex Zetasizer Nano. Transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) images were acquired by using a JEOL TEM-2010 (accelerate voltage 120 kV) and a TECNAI-20, FEI (accelerate voltage 200 kV), respectively. The c-SWNTs/s-SPG solution was placed on a copper TEM grid with a holey carbon support film. The TEM grid was dried under reduced pressure for 6 h before TEM observation. Energy dispersive X-ray spectroscopy (EDX) spectra and EDX line scan profiles were obtained using a TECNAI-20, FEI. Atomic force microscopy (AFM) images were acquired in air using a NanoScope IIIa (tapping mode). The sample was cast on mica and dried for 6 h under reduced pressure before AFM observation.

Materials: Curdlan used here was purchased from Tokyo Kasei Kogyo. SDS was purchased from Wako Pure Chemical Industries. Single-walled carbon nanotubes (SWNTs) produced by means of the HiPco (high-pressure decomposition of carbon monoxide) process and were obtained from Carbon Nanotechnologies (lot no: po304). Chemical modification on native curdlan was carried out basically according to the preceding paper reported by us.^[11] Here, 6-azido-6-deoxycurdlan was synthesized as a common intermediate for cur-N^+ and cur-SO_3^- . The synthetic route is shown in Scheme S1 (see the Supporting Information).

Synthesis of cur-N^+ : Propargyl bromide (9.1 mmol) was dissolved in 50 mL of dry THF and cooled in an ice bath. To the resultant THF solution, trimethylamine (32 mmol) was added and the mixture was stirred for 24 h. After removing solvent, the residue was washed with THF several times followed by drying to give 1-trimethylammonium-2,3-propyne chloride as yellow powder (yield 91 %).

6-Azido-6-deoxycurdlan (100 mg) was dissolved in 100 mL of DMSO. To the resultant solution, 1-trimethylammonium-2,3-propyne chloride (250 mg), copper(II) bromide (10.0 mg), ascorbic acid (50 mg), and propylamine (5.2 mL) were added and the mixture was stirred for 60 h at room temperature. The reaction product was subjected to dialysis against distilled water (MWCO 8000) followed by lyophilization and washing with MeOH to give the ammonium modified curdlan (cur-N^+) in 96 % yield. Cur-N^+ : $M_w = 32000$, $M_w/M_n = 1.6$. ^1H NMR (600 MHz, D_2O , 60 °C) $\delta = 8.43$ (br, 1H, triazole-H), 4.91 (ibr, 1H, H^1), 4.71 (ibr, 2H, CH_2N), 3.85 (ibr, 2H, H^3 and H^6), 3.66 (ibr, 2H, H^5 and H^6), 3.40 (ibr, 2H, H^2 and H^4), 3.18 ppm (br, 9H, NCH_3); ^{13}C NMR (125 MHz, D_2O ,

25 °C) $\delta = 138.06$, 132.91, 105.2, 86.09, 75.96, 73.78, 71.23, 62.47, 55.35, 51.78 ppm.

Synthesis of cur-SO_3^- : to a mixed solvent containing MeOH (7 mL) and water (7 mL), propargyl bromide (2.0 mL) and Na_2SO_3 (2.9 g) were added. After stirring for 7 h at 65 °C, MeOH (120 mL) was added to the reaction mixture. An excess amount of Na_2SO_3 was removed by filtration followed by concentration to give a yellow solution. The resultant MeOH solution was washed with acetone to give 1-sulfo-2,3-propyne sodium salt as yellow precipitate (96 %). The click reaction with 6-azido-6-deoxycurdlan was carried out according to the same procedure as described above.

Cur-SO_3^- : $M_w = 34300$, $M_w/M_n = 1.4$. ^1H NMR (600 MHz, 10 mm NaOD/ D_2O , 60 °C) $\delta = 8.14$ (br, 1H, triazole-H), 4.88 (ibr, 1H, H^1), 4.69 (ibr, 2H, CH_2S), 4.31 (ibr, 1H, H^3), 3.85 (ibr, 2H, H^6), 3.62 (ibr, 1H, H^9), 3.43 (ibr, 1H, H^2), 3.30 ppm (ibr, 1H, H^4); ^{13}C NMR (125 MHz, 10 mm NaOD/ D_2O , 25 °C) $\delta = 129.74$, 104.75, 85.58, 75.98, 72.47, 71.54, 53.58, 50.43 ppm.

Preparation of $\text{cur-N}^+/\text{SWNT}$ and $\text{cur-SO}_3^-/\text{SWNT}$ composites: SWNTs (1.3 mg) were mixed with the aqueous solution containing cur-N^+ or cur-SO_3^- (1.0 mL, 5.0 mg mL^{-1}) and dispersed by sonication for 50 min using a probe type sonicator with the sample immersed in a water bath. To remove an excess amount of curdlan, the obtained homogeneous black solution was subjected to gel-column chromatography (Sephadex, G-100, eluted with water).

Confirmation of the composite purity: From the molecular weight of used curdlan, the fiber length of cur-N^+ and cur-SO_3^- can be estimated to be less than 0.2 μm , whereas that of SWNT is estimated to be more than 0.2 μm . Taking this fact into consideration, the purity of the obtained composite solution was confirmed according to the following procedure: The composite solution was subjected to filtration by using a PTFE membrane filter (pore size: 0.2 μm), expecting that the uncomplexed cur-N^+ or cur-SO_3^- would separate into the filtrate. Since cur-N^+ and cur-SO_3^- have a characteristic absorption band at around 230 nm that can be ascribed to the triazole unit, the existence of uncomplexed cur-N^+ or cur-SO_3^- in the filtrate can be easily detected by UV-vis spectra. Consequently, the UV-vis spectra thus obtained revealed that the composite solution did not contain any uncomplexed cur-N^+ and cur-SO_3^- , suggesting that the gel-column chromatography effectively works as a purification tool in the present system.

Phenol/sulfuric-acid reaction: Firstly, calibration curve was created by using mannose as a standard saccharide. An aqueous solution containing 5 % (w/v) phenol was then added to 200 μL of the mannose solutions. Immediately after addition of 1.0 mL of sulfuric acid to the mixture, the resultant solution assumed an intense yellow color. To complete the coloration reaction, the obtained solution was kept for 40 min at room temperature. The absorption maxima at 490 nm were plotted as function of several mannose concentrations. The composite solutions containing unknown amount of curdlans were treated with phenol followed by sulfuric acid according to the same procedure. From the calibration chart, the amount of curdlan wrapping on SWNT was estimated.

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- [1] a) H. Goto, K. Akagi, H. Shirakawa, *Synth. Met.* **1997**, *84*, 373;
b) T. M. Long, T. M. Swager, *J. Am. Chem. Soc.* **2002**, *124*, 3826;
c) K. P. Fritz, G. D. Scholes, *J. Phys. Chem. B* **2004**, *108*, 10141.
- [2] H. Xin, T. Woolley, *J. Am. Chem. Soc.* **2003**, *125*, 8710.

- [3] N. Akima, Y. Iwasa, S. Brown, A. M. Barbour, J. Cao, J. L. Musfeldt, H. Matsui, N. Toyota, M. Shiraishi, H. Shimoda, O. Zhou, *Adv. Mater.* **2006**, *18*, 1166.
- [4] J.-M. Lehn, *Supramolecular Chemistry*, VCH, New York, **1995**.
- [5] a) Y. Kubo, Y. Kitada, R. Wakabayashi, T. Kishida, M. Ayabe, K. Kaneko, M. Takeuchi, S. Shinkai, *Angew. Chem.* **2006**, *118*, 1578; *Angew. Chem. Int. Ed.* **2006**, *45*, 1548; b) M. Ikeda, Y. Furusho, K. Okoshi, S. Tanahara, K. Maeda, S. Nishino, T. Mori, E. Yashima, *Angew. Chem.* **2006**, *118*, 6641; *Angew. Chem. Int. Ed.* **2006**, *45*, 6491; c) K. K. Ewert, H. M. Evans, A. Zidovska, N. F. Boussein, A. Ahmad, C. R. Safinya, *J. Am. Chem. Soc.* **2006**, *128*, 3998.
- [6] a) M. Numata, M. Asai, K. Kaneko, T. Hasegawa, N. Fujita, Y. Kitada, K. Sakurai, S. Shinkai, *Chem. Lett.* **2004**, *33*, 232; b) M. Numata, M. Asai, K. Kaneko, A.-H. Bae, T. Hasegawa, K. Sakurai, S. Shinkai, *J. Am. Chem. Soc.* **2005**, *127*, 5875.
- [7] M. Numata, T. Hasegawa, T. Fujisawa, K. Sakurai, S. Shinkai, *Org. Lett.* **2004**, *6*, 4447.
- [8] C. Li, M. Numata, A.-H. Bae, K. Sakurai, S. Shinkai, *J. Am. Chem. Soc.* **2005**, *127*, 4548.
- [9] T. Yanaki, T. Norisuye, H. Fujita, *Macromolecules* **1980**, *13*, 1462.
- [10] Amylose can also act as a helical host and form inclusion complexes with various functional guests, see: a) L. S. Choi, O.-K. Kim, *Macromolecules* **1998**, *31*, 9406; b) O.-K. Kim, J. Je, J. W. Baldwin, S. Kooi, P. E. Pehrsson, L. J. Buckley, *J. Am. Chem. Soc.* **2003**, *125*, 4426; c) J. Kadokawa, Y. Kaneko, H. Tagaya, K. Chiba, *Chem. Commun.* **2001**, 459; d) T. Kida, T. Minabe, S. Okabe, M. Akashi, *Chem. Commun.* **2007**, 1559; e) T. Sanji, N. Kato, M. Kato, M. Tanaka, *Angew. Chem.* **2005**, *117*, 7467; *Angew. Chem. Int. Ed.* **2005**, *44*, 7301; f) T. Sanji, N. Kato, M. Tanaka, *Org. Lett.* **2006**, *8*, 235. For self-assembled cyclodextrin nanotubes, see: g) A. Harada, J. Li, M. Kamachi, *Nature* **1993**, *364*, 516; h) M. Ceccato, P. L. Nostro, C. Rossi, C. Bonechi, A. Donati, P. Baglioni, *J. Phys. Chem. B* **1997**, *101*, 5094; i) K. Yoshida, T. Shimomura, K. Ito, R. Hayakawa, *Langmuir* **1999**, *15*, 910; j) T. Shimomura, T. Akai, T. Abe, K. Ito, *J. Chem. Phys.* **2002**, *116*, 1753; k) H. Okumura, Y. Kawaguchi, A. Harada, *Macromol. Rapid Commun.* **2002**, *23*, 781; l) Our recent review, see: K. Sakurai, K. Uezu, M. Numata, T. Hasegawa, C. Li, K. Kaneko, S. Shinkai, *Chem. Commun.* **2005**, 4383.
- [11] T. Hasegawa, M. Umeda, M. Numata, C. Li, A.-H. Bae, T. Fujisawa, S. Haraguchi, K. Sakurai, S. Shinkai, *Carbohydr. Res.* **2006**, *341*, 35.
- [12] a) S. Iijima, *Nature* **1991**, *354*, 56; b) S. Iijima, T. Ichihashi, *Nature* **1993**, *363*, 603.
- [13] For self-assembly of carbon nanotubes, see: a) H. Shimoda, S. J. Oh, H. Z. Geng, R. J. Walker, X. B. Zhang, L. E. McNeil, O. Zhou, *Adv. Mater.* **2002**, *14*, 899; b) R. Duggal, F. Hussain, M. Pasquali, *Adv. Mater.* **2006**, *18*, 29; c) H. Ko, V. V. Tsukruk, *Nano Lett.* **2006**, *6*, 1443; d) S. Badaire, C. Zakri, M. Maugey, A. Derre, J. N. Barisci, G. Wallance, P. Poulin, *Adv. Mater.* **2005**, *17*, 1673; e) A. Ishibashi, Y. Yamaguchi, H. Murakami, N. Nakashima, *Chem. Phys. Lett.* **2006**, *419*, 574.
- [14] M. J. O'Connell, S. M. Bachilo, C. B. Huffman, V. C. Moore, M. S. Strano, E. H. Haroz, K. L. Rialon, P. J. Boul, W. H. Noon, C. Kittrell, J. Ma, R. H. Hauge, R. B. Weisman, R. E. Smalley, *Science*, **2002**, *297*, 593.

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