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Chemically-Responsive Sol−Gel Transition of Supramolecular Single-Walled Carbon Nanotubes (SWNTs) Hydrogel Made by Hybrids of SWNTs and Cyclodextrins

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Single-walled carbon nanotubes (SWNTs) have received a great deal of interests because of their unique structural, electrical, and mechanical properties.[1] However, their applications have been extremely limited because of their low solubility in solvents. Therefore, solubilization of SWNTs has been one of hot topics for the past few years. For solubilization of SWNTs in solvents, chemical modification of SWNTs[2] and physical adsorption of organic molecules on SWNT surfaces[3] are useful strategies. Soluble SWNTs in aqueous media are obtained using $\pi-\pi$ interaction between pyrene having ionic groups and SWNTs by Nakashima and co-workers.[4] Furthermore, successful donor−acceptor systems based on soluble SWNTs have been recently demonstrated by Prato and co-workers.[5] Herein, we report novel chemically responsive supramolecular SWNT hydrogel by using soluble SWNTs functionalized cyclodextrin (CD) moieties on SWNT surface. Since CD shows high solubility in water, water-soluble SWNTs carrying CDs are obtained by using $\pi-\pi$ interaction between pyrene modified β-CDs (Py-β-CDs, Supporting Information for experimental details) and SWNTs (Py-β-CD/SWNT hybrids, Scheme 1). CD forms host−guest complexes with various kinds of guest compounds,[6] thus vacant CD cavities of Py-β-CDs around SWNT are able to capture guest molecules on SWNT surface. In this study, by utilizing host−guest interaction between β-CDs of Py-β-CD/SWNT hybrids and polymers carrying guest moieties, supramolecular SWNT hydrogels are successfully prepared.

SWNTs produced by the method of high-pressure decomposition of carbon monoxide (HiPco Process) were obtained by Carbon Nanotechnologies, Inc. The HiPco SWNTs were purified according to the literature.[7] Py-β-CD/SWNT hybrids were prepared by sonication of Py-β-CD (20 mg, 0.014 mmol) in 5 mL of 0.1 M NaOH with 1 mg of SWNTs. During the sonication, the aqueous solution changed from colorless to black, indicating solubilization of SWNTs in aqueous solution. After the sonication, insoluble SWNTs were removed by centrifugation. The supernatant was dialyzed against 0.1 M NaOH for a week to remove excess free Py-β-CD from the solution. The black solution of Py-β-CD/SWNT hybrids was homogeneous and stable for more than a month (Figure 1a, insert i), while SWNTs were insoluble with native β-CD (Figure 1a, insert ii). This observation indicates that the pyrene moiety in Py-β-CD plays an important role for solubilization of SWNTs. Figure 1a shows UV−vis−NIR spectra for Py-β-CD/SWNT hybrids. In the range of 500−1300 nm, typical SWNT van Hove singularities were found, indicating homogeneous dispersion of SWNTs. In the region of 250−400 nm (Figure 1b), characteristic pyrene absorptions were observed. The pyrene absorption peaks of Py-β-CD/SWNT hybrids were slightly red-shifted (2 nm) compared with that of Py-β-CD, indicating $\pi-\pi$ stacking between SWNTs and pyrene moieties of Py-β-CD. The slight shifts were also observed in SWNT/pyrene systems.[5b,c] Furthermore, the $\pi-\pi$ interaction was confirmed by fluorescence spectra (Figure 1b). Under dilute conditions, Py-β-CD showed strong monomer fluorescence, while the fluorescence was largely quenched in Py-β-CD/SWNT hybrids. The same trends were observed in covalently and noncovalently linked SWNT/pyrene derivatives.[2d,5] In addition, the $\pi-\pi$ interaction was also estimated by variable-temperature ^{1}H NMR measurements (Supporting Information). The broad signals of pyrene protons of Py-β-CD/SWNT hybrids were hardly changed by heating, indicating that the pyrene moiety of Py-β-CD was strongly adsorbed on the SWNT surface. Weight percentages of Py-β-CD in Py-β-CD/SWNT hybrids were ca. 48 wt % by TGA measurements and composition was characterized by X-ray photoelectron spectroscopy (XPS) measurements (Supporting Information).

From the atomic force microscopic (AFM) image of Py-β-CD/SWNT hybrids on mica substrate, nanotubes were observed and the average size of the tubes was about 2.4−2.5 nm (Supporting Information). Considering that the average diameter of the HiPco SWNT is 1.1−1.2 nm,[8] and that the size of β-CD is 0.6−0.8 nm,[6] the height measurement suggests that the nanotubes observed are SWNTs sandwiched with CDs. From a scanning tunneling micro-

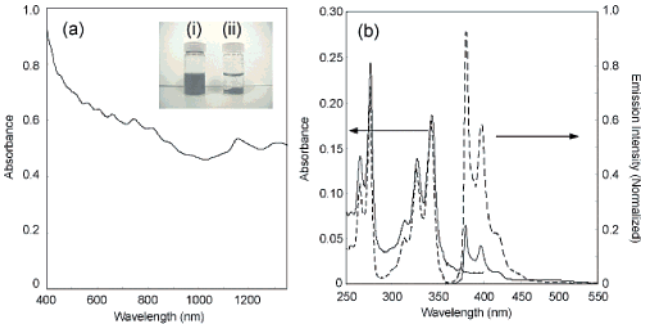
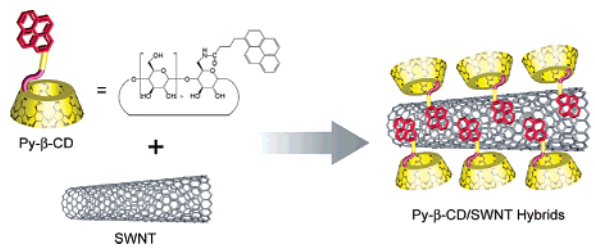


Figure 1. (a) UV−vis−NIR spectrum of Py-β-CD/SWNT hybrids (0.47 mM of Py-β-CD) (insert: photos of aqueous solutions of SWNT with (i) Py-β-CD and (ii) β-CD.) (b) UV−vis and emission spectra of Py-β-CD (4.76 μM, dash line) and Py-β-CD/SWNT hybrids (4.76 μM of Py-β-CD, solid line) with matching absorption at the 338 nm excitation wavelength. The solution of Figure 1b was diluted to 1.0% of that in Figure 1a.

Scheme 1. Modification of CDs on SWNT Surface by Using Py-β-CDs



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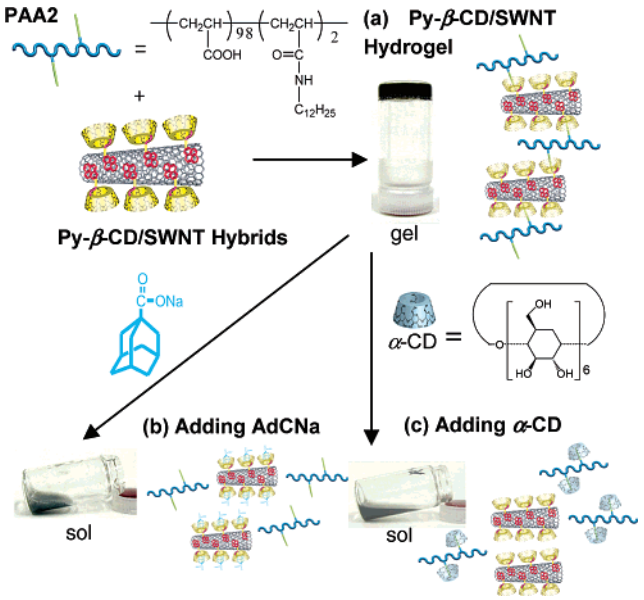
Scheme 2. (a) Py-β-CD/SWNT Hydrogel with PAA2. Gel to Sol Transitions upon Addition of (b) Competitive Guest AdCNa and (c) Competitive Host α-CD.



scopic (STM) image, aggregation of the nanotubes was observed on HOPG substrate and small molecules were found around the aggregation of nanotubes, which also indicate that SWNTs were wrapped with CDs (Supporting Information).

By utilizing host−guest interactions between polymers having guest groups and β-CDs of Py-β-CD/SWNT hybrids, nanocomposites of polymer and SWNTs were prepared. Poly(acrylic acid) (M_w = 250 000) carrying 2 mol % of dodecyl groups (Scheme 2, PAA2) was used as a guest polymer. Dodecyl groups in PAA2 form host−guest complexes with α-CD and β-CD.[9] By mixing Py-β-CD/SWNT hybrids (0.28 mM of Py-β-CD) and PAA2 (7 g/L) in 5 mL of 0.1 M NaOH (Scheme 2a), a homogeneous SWNT hydrogel formed. In contrast, the solutions of PAA2 (7 g/L), mixture of 6-Py-β-CD (0.28 mM) and PAA2 (7 g/L), SWNTs (1 mg) and PAA2 (7 g/L) in 5 mL of 0.1 M NaOH were sol state, indicating that Py-β-CD/SWNT hybrids were necessary to form hydrogel with PAA2. These data indicate that host−guest complexes between β-CD moieties immobilized on the SWNT surface and dodecyl groups in PAA2 act as cross-links to form network structures which showed gel-like behavior.[10] Furthermore, SWNT hydrogels composed of Py-β-CD/SWNT hybrids and PAA2 changed to sol by adding competitive guests or host compounds. When sodium adamantane carboxylate (AdCNa, 100 equiv to dodecyl moieties of PAA2) was added to the hydrogel as a competitive guest, gel to sol transition was observed (Scheme 2b). This result indicates dissociation of the host−guest complexes between β-CDs of Py-β-CD/SWNT hybrids and dodecyl groups of PAA2 because AdCNa strongly interacts with β-CD compared with dodecyl group. Upon addition of α-CD (100 equiv to dodecyl groups of PAA2) as a competitive host, the gel also changed to sol (Scheme 2c). It is because dodecyl moieties form complexes with α-CD more favorably than with β-CD.[8] From these observations, the formation of SWNT hydrogel by mixing Py-β-CD/SWNT hybrids and PAA2 results from the complex between β-CD of Py-β-CD/SWNT hybrids and dodecyl groups of PAA2.

In conclusion, we synthesized hybrids of SWNTs and CDs by immobilization of Py-β-CDs on SWNT surface. Py-β-CD/SWNT hybrids were soluble in aqueous media. Furthermore, supramolecular SWNT hydrogels were synthesized by host−guest interactions between β-CDs of Py-β-CD/SWNT hybrids and dodecyl groups of PAA2. The supramolecular SWNT hydrogel exhibited gel to sol transition by adding competitive guest and host. To the best of our knowledge, this is the first example of gel to sol changeable SWNT hydrogel via supramolecular formation, while supramolecular networks from cyclodextrin polymers and guest polymers have been reported.[11] Future work will focus on modification of SWNT with functional groups such as chromophores, medicines, electron donors, and acceptors toward solar energy conversion, fluorescence labels in biomedicine, and photo-oxidation of guest by means of host−guest interaction using Py-β-CD/SWNT hybrids because CD forms host−guest complexes with various kinds of functional compounds.

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Supporting Information Available: Experimental section, variable-temperature ^{1}H NMR spectra, TG analysis, XPS measurements, AFM and STM images of Py-β-CD/SWNT hybrids, ^{1}H NMR spectra of Py-β-CD/SWNT hybrids with PAA2. This material is available free of charge via the Internet at http://pubs.acs.org.

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(10) Formation of the host−guest complex between dodecyl group of PAA2 and β-CD of Py-β-CD/SWNT hybrids was checked by ^{1}H NMR measurements (Supporting Information).

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