Water Soluble Single-walled Carbon Nanotubes Using Inclusion Complex of Cyclodextrin with an Adamantane Derivative

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Single-walled carbon nanotubes (SWNTs) were soluble in aqueous media by using host–guest complex between sodium adamantanecarboxylate (AdCNa) and β-cyclodextrin (β-CD), while SWNTs were insoluble with AdCNa or β-CD.

Single-walled carbon nanotubes (SWNTs) have been an area of intense research since their discovery in 1991 because of their unique structural, electrical, and mechanical properties and potential applications.[1] However, their applications have been extremely limited due to their low solubility. Therefore, solubilization of SWNTs has been one of hot topics over the past decade. For solubilization of SWNTs in solvents, chemical modification of SWNTs[2] and physical adsorption of organic molecules on SWNT surfaces[3] are useful strategies. Among them, as a solubilizer of SWNTs, α-, β-, and γ-cyclodextrins (α-, β-, and γ-CDs) have been also studied.[4] However, it is difficult to solubilize SWNTs with these CDs under mild conditions according to the previous paper because cavity size of these CDs is too small to form *pseudo*-rotaxane complex with SWNTs.[4c] SWNTs were solubilized by forming *pseudo*-rotaxane complex with large-ring CD such as η-CD composed of 12 glucopyranose units. There is only one example of soluble SWNTs with α-, β-, and γ-CDs under severe treatment. SWNTs were soluble in aqueous media with α-, β-, and γ-CDs by using high-speed vibration milling technique.[4d]

Herein, we first report water-soluble SWNTs under mild conditions by using host–guest inclusion complex between CD and guest compound. Surprisingly, SWNTs were soluble in aqueous media with host–guest complex, while SWNTs were insoluble with only CD or guest compound. α-CD and β-CD were used as hosts, sodium adamantanecarboxylate (AdCNa) and adamantylamine hydrochloride ($AdNH_3Cl$) were used as guests, respectively (Figure 1a). It is well known that β-CD forms strong host–guest complex with AdCNa.[5]

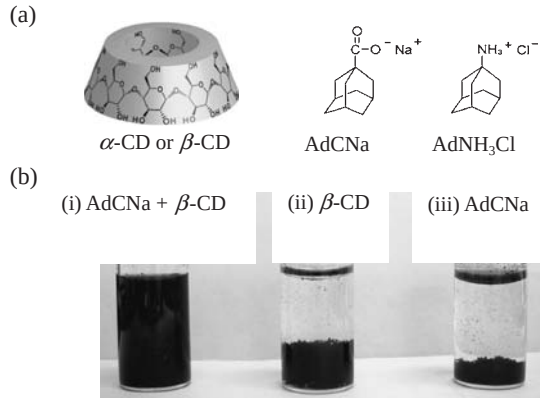

Figure 1. (a) α-CD and β-CD (hosts), AdCNa and $AdNH_3Cl$ (guests) for solubilization of SWNTs. (b) Photographs of aqueous solutions (5 mL) containing SWNTs (1 mg) after sonication with (i) β-CD (3.52 mM) and AdCNa (3.52 mM), (ii) β-CD (3.52 mM), and (iii) AdCNa (3.52 mM).

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 as described previously.[6] To a suspension of SWNTs (1.0 mg) in aqueous solution (5.0 mL), β-CD (20 mg) and AdCNa (2.14 mg, 1 equiv. to β-CD) were added. The resulting solution was sonicated for 3 h at room temperature. 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 homogeneous black solution and stable for more than a month (Figure 1b(i)). Solubility of SWNTs was 0.83 mg mL^{-1}. On the other hand, SWNTs were insoluble with β-CD (Figure 1b(ii)) or AdCNa (Figure 1b(iii)). These observations indicate that SWNTs are soluble using the mixture of β-CD and AdCNa. Figure 2a shows UV–vis spectra of the supernatants containing SWNTs solubilized by the mixture of β-CD and AdCNa. In the region of 500–900 nm, typical SWNT van Hove singularities were observed, indicating homogeneous dispersion of SWNTs. Solubilities of SWNTs were measured by the absorbance at 500 nm (Figure 2b). In the presence of β-CD, the solubility of SWNTs was increased by adding AdCNa. On the other hand, in the absence of CD, SWNTs were insoluble upon addition of AdCNa. In the presence of α-CD, SWNTs were also insoluble in aqueous solution with AdCNa. This is because AdCNa forms complexes with β-CD more favorably than with α-CD.[5] When cationic $AdNH_3Cl$ was used as a guest compound instead of AdCNa, SWNTs were hardly soluble even with β-CD due to the low binding constant of host–guest complex between

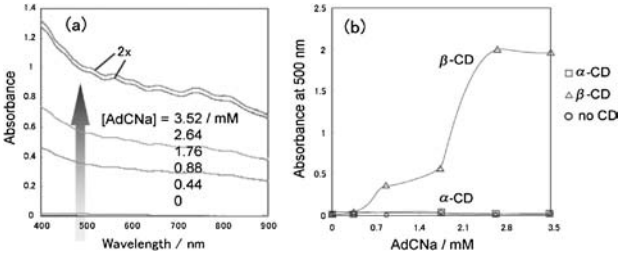

Figure 2. (a) UV–vis spectra of aqueous supernatants containing SWNTs and β-CD (3.52 mM) by adding AdCNa (0–3.52 mM). (b) Changes in absorbance intensities from soluble SWNTs at 500 nm in the presence of α-CD (3.52 mM, square), β-CD (3.52 mM, triangle) or in the absence of CD (circle) by adding AdCNa (0–3.52 mM).

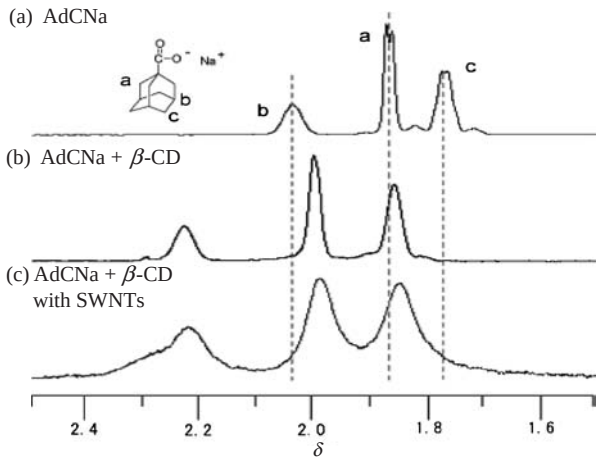

Figure 3. 270 MHz ^{1}H NMR spectra of (a) AdCNa (3.52 mM), (b) AdCNa (3.52 mM) with β-CD (3.52 mM) and (c) a supernatant containing SWNTs solubilized by the mixture of AdCNa (3.52 mM) with β-CD (3.52 mM) in D_2O at 30 °C.

cationic $AdNH_3Cl$ and β-CD.[7] From these observations, it is found that the host–guest complex between β-CD and AdCNa acts as a solubilizer of SWNTs.

Formation of the host–guest inclusion complex between β-CD and AdCNa in the presence of SWNTs was checked by ^{1}H NMR measurements (Figure 3). Upon addition of β-CD, the resonance bands due to methylene and methine protons of AdCNa exhibited down-field shifts (Figures 3a and 3b). The resonance bands were also observed at the same chemical shifts in the presence of SWNTs (Figure 3c), indicating formation of the host–guest complex between AdCNa and β-CD even in the presence of SWNTs. The broadening of these peaks in Figure 3c resulted from the existence of large diamagnetic ring currents in carbon nanotubes as previously reported.[8]

From tapping mode atomic force microscopic (TM-AFM) and transmission electron microscopic (TEM) images, nanotubes solubilized by the host–guest complexes between β-CD and AdCNa were observed.[10]

When pH of the supernatant containing SWNTs solubilized by AdCNa–β-CD complexes was changed from neutral (pH 7) to acidic condition (pH 3), aggregation of SWNTs occurred.[10] The observation indicate that electrostatic repulsive forces between carboxylate anions of AdCNa on SWNT prevent SWNTs from aggregation. Generally, carboxylic acid groups are deprotonated at neutral, while they are protonated and uncharged in acidic condition (under pH 4).[9] Upon addition of KCl salt (100 equiv. to AdCNa) to the supernatant, black solids also formed.[10] The observation results from salting out and also supports that the electrostatic repulsive forces prohibit aggregation of SWNTs.

From these observations, we propose the structure of soluble SWNTs with the host–guest complexes. The hydrophilic part is anionic carboxylate group of AdCNa, which is capable of inhibiting aggregation of SWNTs and disperse SWNTs in aqueous media. The hydrophobic part around adamantane moiety, which formed complex with β-CD, might cover on SWNT surface. Carbon nanotubes were insoluble with AdCNa, since the adamantane group may hardly cover on carbon nanotube's surface due to its bulkiness. Chemical structure of solubilizer greatly effects on solubility of SWNTs as previous paper reported.[3a] However, the adamantane group in the cavity of β-CD stably covers on carbon nanotube because β-CD formed the complex with AdCNa should assist physical binding between SWNTs and AdCNa. Detailed nanostructure study between SWNTs and host–guest complexes is now under way using various inclusion complexes.

In conclusion, host–guest complex between β-CD and AdCNa was found to solubilize SWNTs, while SWNTs were insoluble with only β-CD or AdCNa. Formation of the complex between β-CD and AdCNa is necessary to solubilize SWNTs. To the best of our knowledge, it is the first example of solubilization of SWNTs with host–guest inclusion complexes. It is little known that two different kinds of compounds cooperatively act as a solubilizer of SWNTs.

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