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Solubilization and debundling of purified single-walled carbon nanotubes using solubilizing agents in an aqueous solution by high-speed vibration milling technique†

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Purified single-walled carbon nanotubes (SWNTs) and cyclodextrins (CDs) mixed by a mechanochemical 'high-speed vibration milling technique' (HSVM) are soluble in an aqueous solution because of the formation of SWNT·CDs complexes and the debundling of SWNTs.

The easy availability of single-wall carbon nanotubes (SWNTs) has increasingly invited exploration of their outstanding novel physical and chemical properties.[1,2] However, in spite of their vast potential, applications have been extremely limited because of the difficulty in (i) dissolving in all types of solvents and (ii) removing contaminants. Several lines of investigation have been devoted so far toward compensating for the drawback of (i), for example, through covalent functionalization by hydrophobic or hydrophilic substituents,[3] mixing with water-soluble polymers[4] and chemical or mechanical cutting.[5,6] On the other hand, a standard procedure mitigating both drawbacks (i) and (ii) is ultrasonication in strong acid to cut the SWNTs into short pieces, followed by light etching to introduce oxygen-containing groups, such as phenolic hydroxides and carboxylic acids.[5] Atomic force microscopy (AFM) and transmission electron microscopy (TEM) images confirmed that the SWNTs are separated completely from impurities such as metal particles and amorphous carbons.[7] However, when an aqueous solution of the purified SWNTs is allowed to stand for several days, a precipitate forms from mutual adhesion of SWNTs by van der Waals interactions. Especially when the purified SWNTs were treated by vacuum drying, the SWNTs form a film-like solid at the bottom of the glassware; the solid cannot be redissolved in an aqueous solution again.

Recently, Komatsu *et al*. reported that the solubility of a C_{60}·γ-CD complex in an aqueous solution (1.4×10^{-3} M) by a mechanochemical 'high-speed vibration milling technique' (HSVM) is higher than those by refluxing an aqueous solution of a γ-CD and C_{60} (8×10^{-5} M) and by the classical ball-milling method (1.5×10^{-4} M).[8] While the mechanism remains unclear, it can be presumed that the C_{60} was partially disaggregated upon sufficient mixing with γ-CD. Herein, we report higher solubilization and debundling of SWNTs from the formation of SWNT·solubilizing agent complexes by HSVM. We purchased the SWNTs used in this study from Carbon Nanotechnologies, Inc., Texas, USA (Fig. 1a). The SWNTs were cut into appropriate lengths, as described previously.[9] The purified SWNTs can be dispersed relatively well in an aqueous solution, but some tend to aggregate into bundles, even in these dispersions. We employed freeze-drying and obtained a flocculent solid of SWNTs to obtain and redissolve the purified dry solids (Fig. 1b).

Mixtures of the flocculent SWNTs (20 mg) and CDs or saccharides (5.0 μmol) were placed in an agate capsule together with two agate mixing balls. They were vigorously mixed by shaking at a rate of 3500 rpm for 10 min using a high-speed vibration mill. The solid mixtures were dissolved in 1.0 mL of an aqueous solution to give a black emulsion. After centrifugation (6200 rpm, 10 min, 20 °C), all nondispersed SWNTs were removed from the solutions (Fig. 1c–1e). Supplementary Fig. 1 shows the UV-vis spectra of these solutions. Solubilities of SWNTs were determined by measuring the absorbance of their solutions at 500 nm and by using a specific extinction coefficient for SWNTs of $\varepsilon_{500} = 2.35 \times 10^4$ cm^2 g^{-1}.[10] Table 1 summarizes these results.

D-Glucose and maltoheptaose, which are monosaccharide and heptasaccharide, respectively, and are nonmacrocyclic compounds, scarcely extracted SWNTs (solubilities: 0.01 and 0.04 mg mL^{-1}). On the other hand, β-CD, which has the same sugar units as maltoheptaose, showed moderately high solubility of SWNTs (0.73 mg mL^{-1}). Solubility of the SWNT–*β*-CD system is 18 times higher than that of the SWNT–maltoheptaose system, indicating that a macrocyclic structure of solubilizing agents is an important factor in the interaction with SWNTs. The SWNT·*β*-CD complex gave a stable aqueous solution for more than a month.

As solubilizing agents, α-, β- and γ-CD were chosen to estimate the effect of ring size of the CDs on the solubility of SWNTs. The

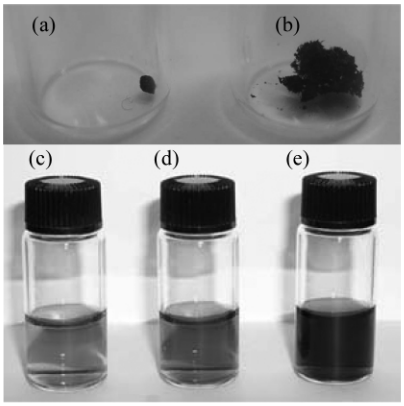

Fig. 1 Photographs of vials showing SWNT solids: (a) of commercial origin; (b) after freeze-drying [Each sample has identical weight (0.4 mg).]; and SWNTs in an aqueous solution after HSVM (c) in the absence of solubilizing agents; (d) in the presence of maltoheptaose and (e) in the presence of γ-CD. All saturated solutions were diluted to 1/20.

Table 1 Absorbance and solubility of SWNTs in an aqueous solution by HSVM with solubilizing agents

Solubilizing agent[a]	Absorbance (500 nm)[b]	SWNTs solubility (mg mL^{-1})
—	0.04	0.02
D-glucose	0.02	0.01
Maltoheptaose	0.09	0.04
α-CD	1.03	0.44
β-CD	1.72	0.73
γ-CD	2.69	1.15
DM-β-CD	1.17	0.50
TM-β-CD	0.39	0.17

[a] [solubilizing agent] = 5 μM. [b] 1 mm cell; saturated solution; 25 °C.

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† Electronic supplementary information (ESI) available: UV-vis spectra. See http://www.rsc.org/suppdata/cc/b4/b402042a/

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increase of solubility in parallel with the ring size of the CDs could be attributed not to increasing solubilities of CDs in an aqueous solution (14.5, 1.85 and 23.2 mg mL^{-1}, respectively),[11] but to the increasing number of hydroxy groups of CDs (solubilities of SWNTs: 0.44, 0.73 and 1.15 mg mL^{-1}, respectively). Because the internal annular diameters of α-, β- and γ-CD are 4.7–5.3, 6.0–6.5 and 7.5–8.3 Å,[11] respectively, CDs cannot include SWNTs in the cavity, unlike other solubilizing agents such as DNA[12] or amylose.[4] Furthermore, CDs were not predicted to form a hydrophobic interaction with the SWNTs as a result of the CDs' hydrophilic surface. The SWNTs used in this study are functionalized by oxygen-containing groups at both the side and surface, some of which are phenolic hydroxides and carboxylic acids.[7] Therefore, CDs were expected to form multipoint hydrogen-bonding with carboxylic acids of SWNTs, even in the aqueous solution.

The solubility of SWNTs by unmodified β-CD was compared with those of methylated CDs to confirm the hydrogen-bonding effect. In comparison with β-CD, the solubilities of SWNTs by heptakis-(2,6-di-*O*-methyl)-β-cyclodextrin (DM-β-CD) and heptakis-(2,3,6-tri-*O*-methyl)-β-cyclodextrin (TM-β-CD) were decreased with the reduction of hydroxy groups of CDs (0.50 and 0.17 mg mL^{-1}, respectively). The formation of a hydrogen-bond between the CD and the SWNT was strongly supported by these results and by the higher solubilities of DM-β-CD and TM-β-CD than β-CD in an aqueous solution.

We measured the ^{1}H NMR spectra of SWNT·CD complexes in D$_2$O to further elucidate the interaction between the SWNTs and the CDs. In the absence of the SWNTs, the 1-positional OH protons of β-CD appeared as a doublet peak at 4.96 ppm in D$_2$O. The peak was markedly broadened and shifted to lower magnetic fields (5.01 ppm) by the addition of the SWNTs. Through the further addition of β-CD, signals for free β-CD and those for the complex did not appear separately (only 5.01 ppm), strongly indicating that the complexation–decomplexation exchange rate is faster than the ^{1}H NMR time-scale at room temperature and that the SWNT·β-CD complex does not form covalent bonds by HSVM.

The morphology of the SWNTs was observed by TEM (Fig. 2a–2c). The SWNTs, after cutting in strong acid, appear in bundles with diameters in the range of 10–50 nm (Fig. 2a). Bundles with a below 10 nm diameter were not observed. On the other hand, the SWNT·α-CD complex with a mean diameter of around 5 nm or more can be observed in the TEM micrographs (Fig. 2b), indicating that a SWNT with around 1 nm diameter was partially debundled. Furthermore, a part of the SWNT·γ-CD complex with a mean diameter of 1–2 nm can be observed in the TEM micrographs (Fig. 2c), indicating that a part of the SWNTs was well-dispersed in an aqueous solution and was debundled. These different morphologies of the SWNT·α-CD and the SWNT·γ-CD complexes engender the different solubilities of SWNTs. On the other hand, shortened SWNTs in the SWNT·γ-CD complex was observed. Whether the observation of short pieces results from 'soft cutting'[6] or from debundling remains unclear.

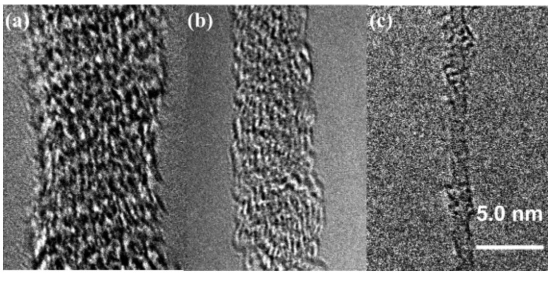

Fig. 2 TEM images of SWNT: (a) after purification, (b) after HSVM with α-CD, (c) after HSVM with γ-CD.

In conclusion, the present study has demonstrated that purified SWNTs after freeze-drying were dissolved in aqueous solution with solubilizing agents having OH groups utilizing HSVM. In particular, the SWNT·γ-CD complex can be dissolved in an aqueous solution in a concentration of 1.15 mg mL^{-1} because a part of SWNTs was debundled. It was suggested that the HSVM is extremely useful for simple preparations of the solubilization of SWNTs in an aqueous solution and that the debundling of SWNTs is very important for material preparation. These studies, which are currently under investigation in this laboratory, can be further extended to other solubilizing agents such as polymers or calixarenes by a HSVM.

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