

Lectin-mediated Supramolecular Junctions of Galactose-derivatized Single-walled Carbon Nanotubes

Kazunori Matsuura, Kentaro Hayashi, and Nobuo Kimizuka*

Department of Chemistry and Biochemistry, Graduate School of Engineering, Kyushu University,
Hakozaki 6-10-1, Higashi-ku, Fukuoka 812-8581

(Received November 5, 2002; CL-020936)

β -Galactoside-modified single-walled carbon nanotube (Gal-SWNT) is newly synthesized. Its solubility in water is increased by adsorption of lection molecules on the sidewalls and supramolecular junctions are formed in the presence of galactose-specific lectins.

Carbon nanotubes¹ have been attracting much interest as building blocks for molecular electronics, because of their high electronic conductivity, chemical inertness, mechanical toughness, and elasticity.² Integration of single-walled carbon nanotubes (SWNTs) into useful devices is a challenging issue, and it requires their controlled self-organization and fabrication of nanotube-junctions. The insolubility of nanotubes in any solvent has hindered developing viable strategies for the above issues. Solubilization of SWNTs in organic media has been devised by the covalent modification of end groups³ and side walls.⁴ Noncovalent functionalization of SWNTs was also devised by helically wrapping the side walls by conjugated polymers.⁵ On the other hand, the use of water soluble polymers⁶ render SWNTs soluble in aqueous media, and noncovalent anchoring of pyrene derivatives has been applied to assemble proteins on the side walls.⁷ Helical crystallization of streptavidin on the side wall of multiwalled nanotubes was also reported.⁸

In spite of these developments, the ability to organize SWNTs in desired configuration is still in its infancy.⁹ Especially it is only recently that the synthesis of covalent nanotube junctions has been reported.¹⁰ In this paper, we report on the noncovalent network formation of SWNTs based on the specific interaction between lectins and carbohydrates. SWNTs modified with β -galactoside at the terminal was newly synthesized and their interaction with β -galactose-specific peanuts lectin (PNA) was investigated.¹¹

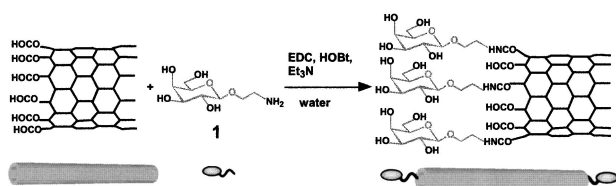


Figure 1. Preparation of β -galactoside-modified single-walled carbon nanotube (Gal-SWNT).

A carboxy-terminated, shortened SWNT was prepared by modifying the reported procedures.^{3a,12} It was further condensed with primary amine-terminated β -galactoside (Gal) derivative 1 by using 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride (EDC) and 1-hydroxybenzotriazole hydrate (HOBt) as condensing agents.^{13,14} FT-IR spectrum of the Gal-SWNT conjugate (cast on BaF₂ plate) showed the presence of amide, $\nu_{C=O}$ (at

1713.3 cm⁻¹) and δ_{N-H} (1604.5 cm⁻¹) peaks, indicating that the β -galactoside groups were successfully introduced at the SWNT carboxy-ends. The modification of the carboxyl groups was further supported by the decreased water solubility of the modified SWNTs, which is consistent with decrease in the number of carboxylate groups. The obtained Gal-SWNT conjugate is not molecularly dispersible in water, since the presence of aggregates with diameter of ca. 175 \pm 54 nm was confirmed by dynamic light scattering (DLS, Otsuka electronics, 7000DL). Scanning electron microscopy (SEM, Hitachi S-5000) of the aqueous dispersions also showed the presence of flocculated nanotubes (Figure 2a).

Interestingly, when β -galactoside-specific lectin from *Peanut arachis hypogaera* (PNA, M_w = 120 kDa, Wako pure chemicals) was added to the turbid aqueous dispersions of the Gal-SWNT conjugates (0.2 mg/mL) and incubated for 36 h (temperature, 25°C), the turbid dispersion was changed to a clear aqueous solution. A drop (10 μ L) of the clear aqueous mixture was placed on mica and it was freeze-dried to give SEM specimens. At the PNA concentration of 12 μ M, the Gal-SWNT conjugates are no more flocculated and are highly dispersed with some cross-links (Figure 2b). On the other hand, further increase in PNA concentration (60 μ M) leads to developed network structures that consist of linear nanowires (length, over several μ m) and junctions (Figure 2c).¹⁵ Such junctions were not observed for the nonspecific mixtures of PNA (concentration, 60 μ M) and carboxy-terminated SWNTs or β -glucoside-modified SWNT (Glc-SWNT, data not shown).

These observations have two important features. First, the width of the wires observed in Figures 2b and 2c is ca. 20–30 nm, and this is larger than the sum of nanotube diameter (ca. 1.2–1.5 nm) and the thickness of deposited platinum (4–6 nm). The increased water-solubility of the Gal-SWNT/PNA mixture must be ascribed to the nonspecific adsorption of PNA to the hydrophobic sidewall of SWNTs, similarly to the case of streptavidins.⁸ The wrapping by PNA (size, ca. 6–8 nm) promotes the dissolution of SWNT aggregates, leading to the dispersion of SWNTs-bundles as schematically shown in Figure 3. Such nonspecific adsorption of lectins to SWNTs was also suggested for the unmodified carboxy-terminated SWNTs and β -glucoside-modified SWNTs (Glc-SWNT), since their water solubility was also increased by the addition of PNA. Likewise, when concanavalin A (Con A) was added to the Gal-SWNT, flocculates were not observed (Figure 2d). It is noteworthy that the network structures were not formed for these nonspecific mixtures.

Second, the observed μ m-sized nanostructures (Figure 2c) are much longer than that of the carboxy-terminated SWNT (average length, 330.6 \pm 60.9 nm as determined by SEM). These elongated structures are only observed for the Gal-SWNT/PNA mixture. Therefore it is possible that the specific interaction between PNA molecules adsorbed on SWNTs-bundles and Gal at the edges of

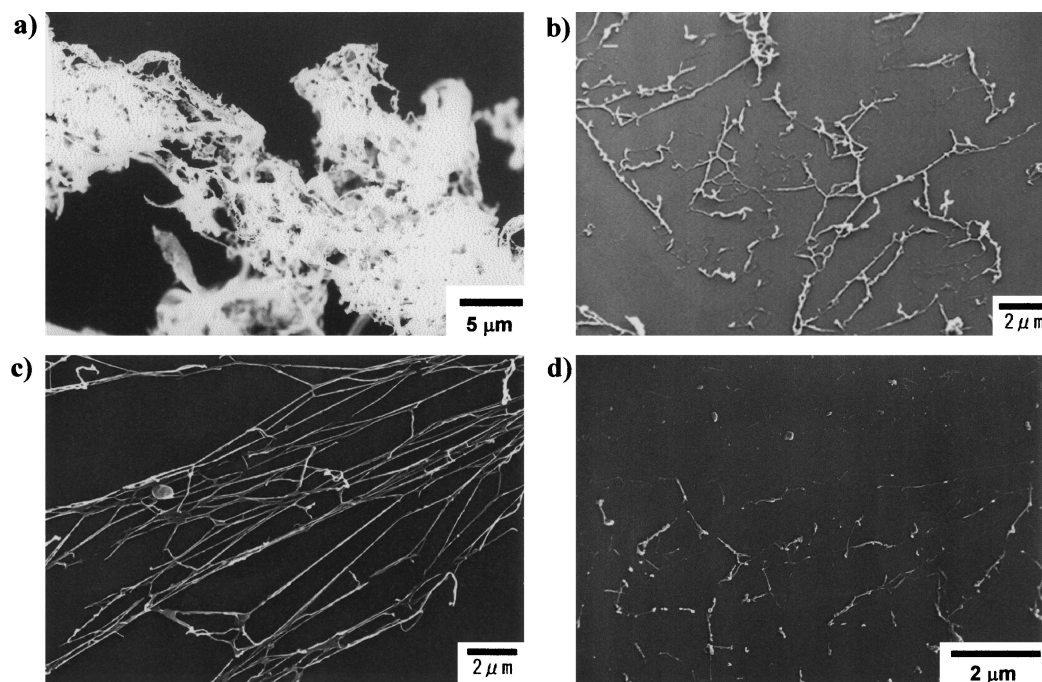


Figure 2. Scanning electron micrographs of Gal-SWNT in the presence or absence of lectins. (a) [PNA] = 0 μM , (b) [PNA] = 12 μM , (c) [PNA] = 60 μM , (d) [ConA] = 10 μM . The dropped solutions ([CNT] = 0.2 mg/mL) on mica were freeze-dried and coated with platinum (thickness, ca. 4–6 nm) prior to the observation.

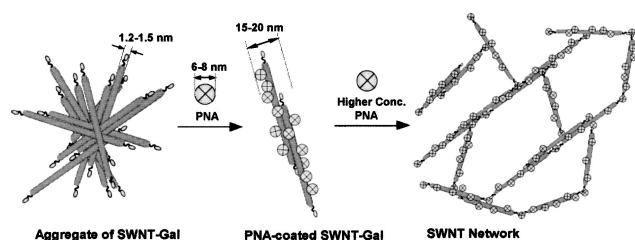


Figure 3. Schematic illustration of (i) wrapping of carbon nanotubes with lectins and (ii) formation of nanotube junctions mediated by Gal-PNA interaction. Binding of PNA on the sidewalls of SWNTs enhances the solubility of nanotubes.

another SWNTs-bundles forms linear junctions, in addition to the branched junctions.¹⁶

In conclusion, sugar-modified SWNTs are nonspecifically wrapped by lectins and are dispersed in water as highly soluble nanotubes. The specific interaction between terminal β -galactose and PNA molecules produces supramolecular junctions of the PNA-packaged nanotubes. The present noncovalent connection of SWNTs would be useful in the synthesis of nanotube architectures.

This work was supported by a grant-in-aid for COE Research “Design and Control of Advanced Molecular Assembly Systems” (no. 08CE2005) from the Ministry of Education, Culture, Sports, Science, and Technology of the Japanese Government.

References and Notes

- 1 S. Iijima, *Nature*, **354**, 56 (1991).
- 2 P. M. Ajayan, *Chem. Rev.*, **99**, 1787 (1999).
- 3 a) J. Liu, A. G. Rinzier, H. Dai, J. H. Hafner, R. K. Bradley, P. J. Boul, A. Lu, T. Iverson, K. Shelimov, C. B. Huffman, F. Rodriguez-Macias, Y.-S. Shon, T. R. Lee, D. T. Colbert, and R. E. Smalley, *Science*, **280**, 1253 (1998). b) J. E. Riggs, Z. Guo, D. L. Carroll, and Y.-P. Sun, *J. Am. Chem. Soc.*, **122**, 5879 (2000). c) B. Li, Z. Shi, Y. Lian, and Z. Gu, *Chem. Lett.*, **2001**, 598.
- 4 a) P. J. Boul, J. Liu, E. T. Mickelson, C. B. Huffman, L. M. Ericson, I. W. Chiang, K. A. Smith, D. T. Colbert, R. H. Hauge, J. L. Margrave, and R. E. Smalley, *Chem. Phys. Lett.*, **310**, 367 (1999). b) V. Georgakilas, K. Kordatos, M. Prato, D. M. Guldi, M. Holzinger, and A. Hirsch, *J. Am. Chem. Soc.*, **124**, 760 (2002).
- 5 a) A. Star, J. F. Stoddart, D. Steuerman, M. Diehl, A. Boukai, E. W. Wong, X. Yang, S.-W. Chung, H. Choi, and J. R. Heath, *Angew. Chem., Int. Ed.*, **40**, 1721 (2001). b) J. Chen, H. Liu, W. A. Weimer, M. D. Halls, D. H. Waldeck, and G. C. Walker, *J. Am. Chem. Soc.*, **124**, 9034 (2002).
- 6 a) M. J. O’Connell, P. Boul, L. M. Ericson, C. Huffman, Y. Wang, E. Haroz, C. Kuper, J. Tour, K. D. Ausman, and R. E. Smalley, *Chem. Phys. Lett.*, **342**, 265 (2001). b) A. Star, D. W. Steuerman, J. R. Heath, and J. F. Stoddart, *Angew. Chem., Int. Ed.*, **41**, 2508 (2002).
- 7 R. J. Chen, Y. Zhang, D. Wang, and H. Dai, *J. Am. Chem. Soc.*, **123**, 3838 (2001).
- 8 F. Balavonine, P. Schultz, C. Richard, V. Mallouh, T. W. Ebbesen, and C. Mioskowski, *Angew. Chem., Int. Ed.*, **38**, 1912 (1999).
- 9 a) H. Shimoda, S. J. Oh, H. Z. Geng, R. J. Walker, X. B. Zhang, L. E. McNeil, and O. Zhou, *Adv. Mater.*, **14**, 899 (2002). b) J. Chen and W. A. Weimer, *J. Am. Chem. Soc.*, **124**, 758 (2002). c) M. R. Diehl, S. N. Yaliraki, R. A. Beckman, M. Barahona, and J. R. Heath, *Angew. Chem., Int. Ed.*, **41**, 353 (2002).
- 10 P. W. Chiu, G. S. Duesberg, U. Dettlaff-Weglikowska, and S. Roth, *Appl. Phys. Lett.*, **80**, 3811 (2002).
- 11 Modification of nanotubes with glucosamine has been recently reported, but their interaction with lectins was not investigated: F. Pompeo and D. E. Resasco, *Nano Lett.*, **2**, 369 (2002).
- 12 SWNT (SE-grade, purity > 85%, $\phi = 1.2\text{--}1.5\text{ nm}$, Aldrich, 10.02 mg) in $\text{H}_2\text{SO}_4/\text{HNO}_3$ (15 mL) was ultrasonicated with a probe-type sonicator (30–50 W) for 60 min under ice-cooling. After diluting the mixture with deionized water (100 mL), the crude cut nanotube was filtered through PTFE membrane filter (Advantec, pore size = 0.1 μm). It was then washed with deionized water until the pH of the filtrate became neutral. The mixture was purified with gel permeation chromatography (Sephadex G-25, eluted with water). Average length of the cut SWNT as determined by SEM was $330.6 \pm 60.9\text{ nm}$.
- 13 **1** was synthesized according to the literature: A. Y. Chernyak, G. V. M. Sharma, L. O. Krishana, A. B. Levinsky, and N. K. Kochetkov, *Carbohydr. Res.*, **223**, 303 (1992).
- 14 The cut SWNT (0.98 mg) was dispersed in an aqueous solution (0.5 mL) of **1** (3.85 mg, 17 μmol), EDC (3.43 mg, 18 μmol), HOBt (2.31 mg, 17 μmol), and triethylamine (5.23 mg, 51 μmol). After rigorously stirring the mixture for 72 h at room temperature, it was dialyzed (cut off $M_w = 8000$) against deionized water to remove the low-molecular weight species.
- 15 Formation of the network structure depends on the sample preparation. When the aqueous solution of the Gal-SWNT/PNA was dropped on mica and was allowed to evaporate under reduced pressure at ambient temperature, such network structures were not obtained. It is therefore possible that the developed network structures are produced during the freeze-drying process.
- 16 The apparent average diameters of the aggregate in aqueous solution were determined by DLS. The diameter in the absence of PNA ($175 \pm 54\text{ nm}$) was increased to $321 \pm 54\text{ nm}$ after the addition of PNA (60 μM , incubated for 12 h).