

CHARGE TRANSFER INTERACTION BETWEEN SUPER GROWTH SINGLE WALL CARBON NANOTUBES AND METHYLENE BLUE

Fitri Khoerunnisa¹, Toshihiko Fujimori³, Tsutomu Itoh³,
Tomonori Ohba¹, Hirofumi Kanoh¹,
Kenji Hata², and Katsumi Kaneko^{3,*}

¹Graduate School of Science, Department of Chemistry, Chiba University, 1-33 Yayoi, Inage, Chiba, 263-8522 (Japan)

²Nanotubes Research Center, National Institute of Advanced Industrial Science and Technology, 1-1-1 Higashi, Tsukuba, Ibaraki, 305-8565 (Japan)

³Institute of Carbon Science and Technology, Shinshu University 4-17-1 Wakasato, Nagano, 380-8553 (Japan)

Introduction

Chemical functionalization of carbon nanotubes is essential to take full advantage of these properties and to extend their utilization. Typically, the chemical modification of carbon nanotubes can be carried out through covalent bond directly to the nanotube surface or via non-covalent adsorption of functional molecules to the surface. The functionalization of SWCNT with dye molecules is a promising technique due to the extension of photosensitization function on many fields such as sensor, semiconductor, solar cell, electrochemistry, etc. Various dye compounds have been used to expand photosensitive function of SWCNT [1]. Methylene blue is one of electroactive dyes having heterocyclic aromatic structure that can be expected to strongly interact with the SWCNT to donate more attractive electronic properties. Here, we have elucidated the presence of charge transfer interaction between SWCNT and methylene blue (MB) dye.

Experimental

We used super growth SWCNT sample fabricated by chemical vapor deposition. Oxidation treatment of super growth SWCNT under mixed N₂/O₂ gases was carried out for opening the tube space, simply noted as SWCNT. Hereafter the MB functionalization on SWCNT was carried out through liquid phase adsorption at room temperature. Morphological structure and nanoporosity changes of SWCNT have been investigated by SEM and adsorption isotherm of nitrogen at 77 K. The functionalization of MB on SWCNT has been examined by FTIR spectroscopy. MB functionalized SWCNT was intensively characterized thoroughly using Raman spectroscopy, XPS, and optical absorption spectroscopy.

Results and Discussion

The MB adsorption on SWCNT in the liquid phase gives the adsorption isotherm of Langmuir type with saturated adsorbed amount of 150±10 mg.g⁻¹ of coverage 0.11, reducing the specific surface area of SWCNT by 35 % (Fig.1). This is due to the fractional hindering of their nanopores with MB

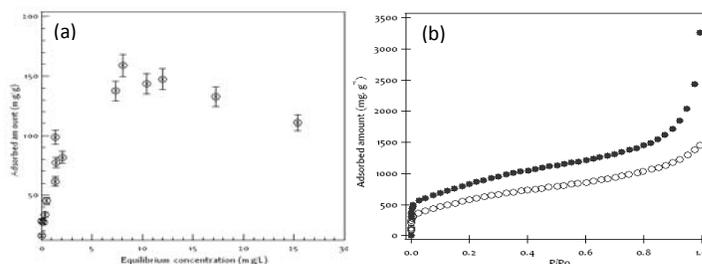


Fig. 1(a) Adsorption isotherm of MB solution on SWCNT; (b) Nitrogen adsorption isotherms at 77 K on SWCNT (●) and MB-adsorbed SWCNT (○)

molecules. SEM images (Fig.2) demonstrate the fracture surface, where the breakage of forest bundle structures of SWCNT can be clearly observed. In addition, MB adsorption also improves the dispersion state of SWCNT resulted in the formation of more void entangle network of SWCNT. The functionalization mechanism of SWCNT with MB involving some functional groups can be elucidated from FTIR spectra, shown in Figure 3.

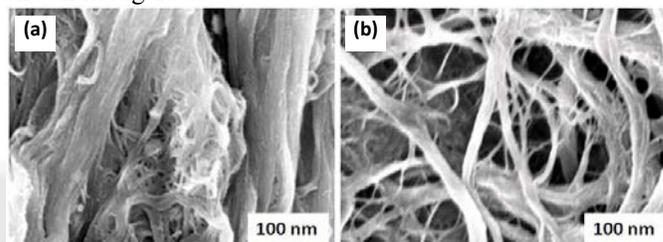


Fig. 2 SEM images of SWCNT (a) and MB-adsorbed SWCNT (b)

Originally, the FTIR spectrum of SWCNT (Fig.3a) shows the strong and broader peak at 3420 cm⁻¹, corresponding to O-H stretching. The peak at 2921 cm⁻¹ represents C-H stretching vibration from CH₂ group, while the peak at 1637 cm⁻¹ is possibly assigned to C=O stretch bands of carbonyl group or C=C stretching of benzene ring. The bands at 1385 and 1083 cm⁻¹ are attributed to C=C symmetric stretching and C-H wagging modes, respectively. MB functionalization on SWCNT demonstrates amine functional groups vibration modes, resulted in the new peak at 1232, 1454 and 1539 cm⁻¹ corresponding to C-N, -N(CH₃)₂ and N-H in plane stretching vibration, respectively [2].

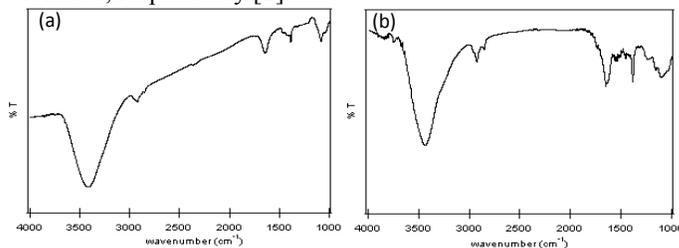


Fig. 3 FTIR spectra of SWCNT (a) and MB-adsorbed SWCNT (b)

In addition, another peak appears at 1100 cm⁻¹ assigned to C-O-C stretching. The notable frequency shift of OH stretching is observed from 3420 to 3443 cm⁻¹. The weak peaks around 3700~3800 cm⁻¹ stem from C-N symmetric stretching. Accordingly, these IR results confirm the formation

of linkage between amine groups of the MB with either oxygen functional group or benzene ring of the SWCNT in the covalent functionalization.

Figure 4 presents the Raman spectra of the radial breathing modes (RBM) and G band, which are important for elucidating the electronic properties of SWCNT under the MB treatment [4]. Originally, SWCNT shows the strong peak and weak sub-peak at 1592 cm^{-1} (G⁺ band) and 1576 cm^{-1} (G⁻ band). On the other hand, multiple peaks of RBM indicate the distribution of the tubes diameter. Initially, the RBM peaks at 165 and 186 cm^{-1} corresponding to tube diameters of 1.50 and 1.33 nm , come from the semiconducting nanotubes according to the Kataura-plot [3]. In addition the weak peaks at higher frequency around $220\sim 232\text{ cm}^{-1}$ and 271 cm^{-1} are assigned to metallic nanotubes of the diameter less than 1.2 nm . The MB adsorption on SWCNT induces the shift of G-band to the lower frequencies i.e. from 1592 to 1590 cm^{-1} and from 1577 to 1571 cm^{-1} , resulting in the narrower G-band peak. The MB molecules also influence the RBM peaks of SWCNT, in which the peak shifts from 165 to 171 cm^{-1} and from 186 to 180 cm^{-1} indicate the modification of the semiconducting nanotubes. Moreover, the peak shifting at 225 cm^{-1} and around $271\sim 268\text{ cm}^{-1}$ suggests intensification of metallic character. These results show MB molecules effectively changes the electronic properties of SWCNT due to charge transfer interaction between MB and SWCNT.

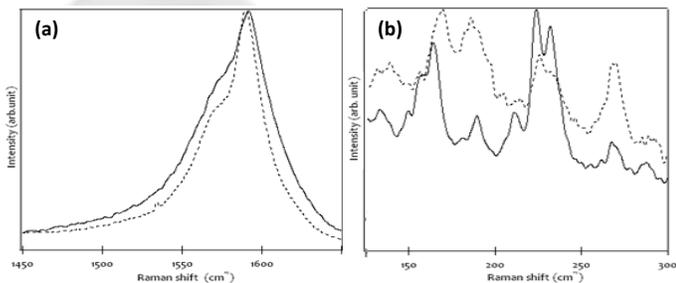


Fig. 4(a) The G band and (b) radial breathing modes (RBM) of SWCNT (—) and MB-adsorbed SWCNT (...)

Figure 5 shows deconvolution result through the Gaussian-Lorentzian mixed function after background subtraction with the Shirley method. Mainly, C 1s peak divided into several components. Initially, the C 1s peak of SWCNT shows the strongest peak at 284.2 eV assigned to carbon double bonding (C=C) and the sub-peak at 285.3 eV corresponded to the carbon single bonding (C-C). The presence of other sub-peaks in the relatively high binding energy region are assigned to the related carbon oxide groups such as C-O, C=O, and COO at 286.2 , 288.1 , and 209.1 eV [4], respectively. The broader peak at 290.8 eV which is overlapping with COO peak is assigned to $\pi\text{-}\pi^*$ plasmon. The C=C/C-C (sp^2/sp^3) ratio and C/O atomic ratio of SWCNT are smaller than those of MB-adsorbed SWCNT (Table 1), indicating that MB molecules are interacted with and adsorbed on the oxygen functional group

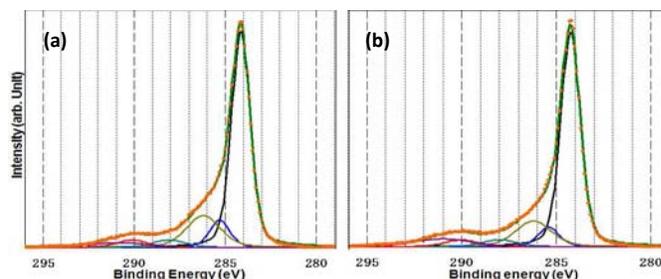


Fig 5. Deconvoluted C 1s peak of X-ray photoelectron spectra for SWCNT (a) and MB-adsorbed SWCNT (b)

of SWCNT. As, the sp^2 and sp^3 carbons represent the presence of graphitic structure and functional groups structures, respectively, the increase of C=C/C-C ratio suggests the interaction of MB with surface functional groups. The $\pi\text{-}\pi^*$ peak possibly increases after MB adsorption, suggesting that MB adsorption influences the π -electron network of SWCNT. Hence MB molecules should be adsorbed on the conjugated π -electrons and surface functional groups of SWCNT.

Table 1. Peak Intensity Ratio of C=C/C-C and C/O Atomic Ratio Determined from XPS

Sample	Ratio	
	C=C/C-C	C/O atomic
SWCNT	8.0	15.5
MB-adsorbed SWCNT	11.0	31.8

Conclusions

The MB adsorption from solution can varies electronic structure of SWCNT through charge transfer interaction. The future study on the adsorption state of MB and electronic structure should provide a concise controlling method of the electronic structure of SWCNT.

Acknowledgments. We thank to G-COE of Chiba University for graduate fellowship. This work was partially supported by Japanese Governmental Grant in Aid for Scientific Research A.

References

- [1] Kuzmany H, Kukovec A, Simon F, Holzweber M, Kramberger Ch, Pichler T. Functionalization of carbon nanotubes. *Synth. Met.* 2004; 141: 677-686.
- [2] Bahr JL, Yang J, Kosynkin DV, Bronikowski MJ, Smalley RE, Tour JM. Functionalization of carbon nanotubes by electrochemical reduction of aryl diazonium salt: A bucky paper electrode. *JACS* 2001; 123: 6536-6542.
- [3] Kataura H, Kumazawa Y, Maniwa Y, Umezumi I, Suzuki S, Ohtsuka Y, Achiba Y. Optical properties of single-wall carbon nanotubes. *Synth. Met.* 1999; 103: 2555-2558.
- [4] Utsumi S, Honda H, Hattori Y, Kanoh H, Takahashi K, Sakai H, Abe M, Yudasaka M, Iijima S, Kaneko K. Direct evidence on C-C single-wall carbon nanohorn aggregates. *Phys. Chem. Lett C.* 2007; 111: 5572-5575.