

# Characterization of Aromatic Molecule-Tiled Single Wall Carbon Nanotube

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## Abstract

We adsorbed tetracene and phenanthrene on SWCNT produced by laser abrasion in toluene. Tetracene adsorption was more than six times greater than that of phenanthrene. X-ray photoelectron spectroscopic examination clearly showed that tetracene and phenanthrene molecules efficiently coated the SWCNT external surfaces. The remarkable difference between the adsorption amounts of tetracene and phenanthrene was caused by the nanoscale curvature effect of the tube surface resulting in a difference in the molecule-surface contact. The adsorption of tetracene and phenanthrene caused a significant high frequency shift in the radial breathing mode (RBM) of the Raman band of the SWCNT, indicating an intensive  $\pi$ - $\pi$  interaction between these polycyclic aromatic hydrocarbons and the external SWCNT surface.

## Introduction

Single wall carbon nanotube (SWCNT) has gathered a great attention from fundamental sciences and technologies, because SWCNT has a great application potential due to the unique physical and chemical natures. A single graphene layer has huge surface area of 2630 m<sup>2</sup>/g and all carbon atoms are faced to both surfaces. As SWCNT consists of the single graphene layer, SWCNT has also large surface area. However, the both surfaces of SWCNT have different natures depending on the nanoscale curvature. The internal tube space of negative curvature can more strongly interact with accessible molecules than the external tube surface of the positive curvature; the internal tube space can work as a quite strong adsorption site for accessible molecules. However, SWCNTs often form the bundle structure which gives the surface structure different from that of isolated SWCNT: the SWCNT bundle has three surface sites for molecules such as the internal tube pores, the interstitial pores, and the groove sites on the surface of the bundle. In this case, the interstitial pores have the deepest interaction potential well for molecules and thereby these pores are expected for adsorption sites for supercritical hydrogen or methane. However, the adsorption capacity of the interstitial pores is not so great. Accordingly, we need to improve the interaction strength for molecules by controlling the electronic states of SWCNT.

Doping of organic and inorganic dopants in single wall carbon nanotube (SWCNT) is a hot topic in order to obtain the desirable electronic properties. One of family substances for organic dopants is polynuclear aromatic hydrocarbon (=AH)s. The solid state PAHs are conductive due to the delocalization of shared electrons in double bonds of their fused benzene rings ( $\pi$ -electrons). Therefore many theoretical calculations on effects of doping on electronic structures of SWCNT have been published. We have proposed liquid phase adsorption technique of polynuclear aromatic hydrocarbon (PAHs) to control the electronic properties of SWCNT to have better adsorption characteristics for supercritical gases (Suzana et al, 2006, in press).

## Experimental

The SWCNT samples were produced using the laser ablation method with Ni and Co as catalysts at 1423K. The SWCNTs were treated with 15% hydrogen peroxide and heated at 373K for 35 minutes. Thermogravimetry revealed that only 4% of the catalyst metal remained and there was virtually no amorphous phase. The Raman spectra were measured using a 532 nm Frequency-Doubled Nd:YAG Laser (1.8 mW). Adsorption isotherms of tetracene and phenanthrene from toluene solution at 293 K were measured on SWCNTs dispersed by ultrasonication. The concentration difference of PAH in the solution measured by UV-Vis spectrophotometry before and after adsorption was used to determine the adsorption isotherms. The XPS experimental conditions were the same for all samples and were as follows: acceleration tension 10 kV, emission current 10 mA (Mg Ka X-ray source), room temperature, and vacuum 10<sup>-7</sup> Pa.

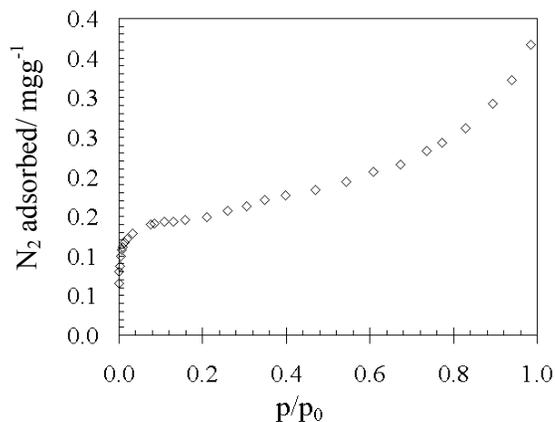


Figure 1. N<sub>2</sub> adsorption isotherm of SWCNT at 77 K.

## Results and Discussion

The initial RBM of as-purified SWCNTs showed two peaks at 185 and 165  $\text{cm}^{-1}$ , which, using the Kataura plot corresponded to diameters of 1.35 and 1.50 nm, respectively. D-band intensity was almost non-detectable confirming that the quantity of the amorphous phase in the sample was negligible. Figure 1 shows the nitrogen adsorption isotherm of SWCNT at 77 K. The adsorption isotherm belongs to IUPAC type II. However, it has a vertical uptake near the  $P/P_0 = 0$ , indicating the presence of narrow micropores. The nitrogen adsorption isotherm gave 382  $\text{m}^2/\text{g}$  of specific surface area, which is a characteristic value of SWCNT bundles with mostly closed caps and very few nano-window openings. These characterization results are shown in the supporting material.

Adsorption isotherms of phenanthrene and tetracene on SWCNT at 303 K are shown in Figure 2. Both of isotherms are very different from each other. As the saturated solubility values of both PAHs in toluene were not found in the literature, we tried to determine them. The obtained values were scattered and therefore the abscissa is not expressed in terms of the relative concentration. The amount of phenanthrene adsorbed (50  $\text{mg}/\text{g}$ ) is very small compared with the adsorbed amount of tetracene (this difference should be observed even using the relative concentration expression). This remarkable difference may be associated with the molecular size and geometry difference between the molecules. Tetracene is a long 4-ring molecule with a large  $\pi$ -electron system, which makes it more suitable for adsorption by  $\pi$ - $\pi$  interactions along the nanotube axis than phenanthrene.

Figure 3 shows the contact model of phenanthrene, and tetracene with the curved SWCNT surfaces of 1.35 and 1.5 nm in diameter under the assumption that the molecular axis aligns with the tube axis and PAH molecules can adsorb only on the external surfaces. As the phenanthrene molecule does not have a simple rectangular structure, it cannot make a good contact with the curved SWCNT surface. On the other hand, tetracene can make a good contact with the SWCNT surface. The level of contact between the molecule and tube surface gives an indication of the strength of the  $\pi$ - $\pi$  interaction. Therefore, the adsorption amount difference is probably due to the  $\pi$ - $\pi$  contact difference between the molecules.

We confirmed the adsorption coatings using x-ray photoelectron spectroscopy. The C1s spectral change with surface coverage was examined. The spectra of the bare SWCNTs show a typical graphite peak at 284 eV, while the peaks of pure phenanthrene and tetracene are situated on the higher binding energy side. The progressive appearance of the peaks on the higher binding energy side as well as the disappearance of the graphite peak as increasing the surface coverage. This is clear evidence of surface coating of the external SWCNT surface with PAH molecules. A strong interaction between the SWCNT surface and these PAH molecules was also confirmed using Raman spectroscopy.

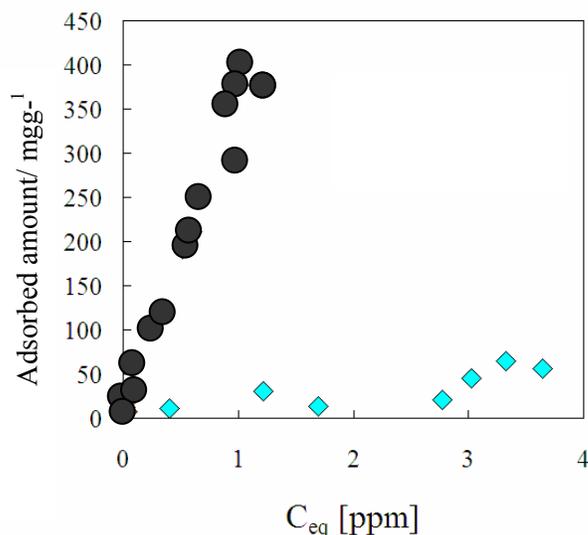


Figure 2. Liquid phase adsorption of tetracene and phenanthrene on SWCNT at 293 K.

● : tetracene and ◆ : phenanthrene

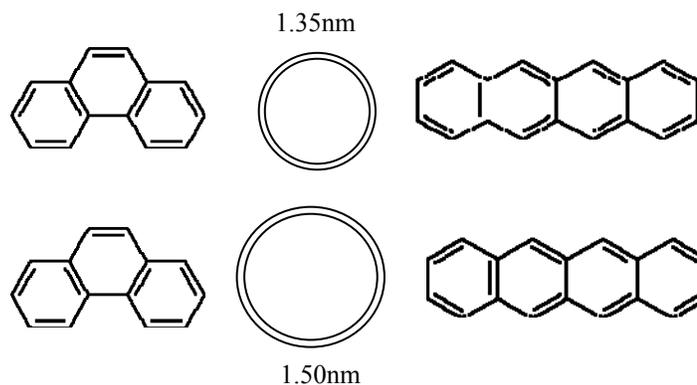


Figure 3. Geometrical contact of phenanthrene and tetracene on SWCNTs of different diameters of 1.35 and 1.50 nm.

## References

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