

Enhanced Hydrogen Adsorptivity of Fullerene-pillared Single Wall Carbon Nanotube

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Introduction

Nanoporous carbon has been expected to be a promising storage material for supercritical methane and hydrogen in order to construct a clean energy society. In particular, single wall carbon nanotube (SWCNT) is a hopeful applicant. SWCNT is essentially an interfacial material, being remarkably different from other solid materials, because all component carbon atoms are exposed to both surfaces of different nanoscale curvatures. SWCNT has a huge geometrical surface area of $2630 \text{ m}^2 \text{ g}^{-1}$, being the same as graphene. The effective surface area of SWCNT for molecules varies with its tube diameter and the target molecular size. In case of SWCNT, not only the large surface area, but also two kinds of surfaces of the positive and negative curvatures can be applicable to establish unique material science and technology. Also SWCNT tends to form the bundle structure of the hexagonal symmetry. The SWCNT bundle has two kinds of adsorption sites of the interstitial sites and groove ones in addition to the internal and external tube surfaces. In particular, the interstitial sites surrounded by three SWCNTs are important for adsorption of supercritical gases, because the interstitial site has the deepest interaction potential well for an adsorbed molecule. However, the interstitial pore width is just comparable to the size of a small molecule. Then, the capacity of the interstitial spaces is very limited, although they are quite promising adsorption sites even for supercritical gases. It is important to increase the capacity of the interstitial sites in the nanotube bundles. The highly ordered double wall carbon nanotube (DWCNT) having a relatively large intertube gap prepared by Endo et al shows an excellent adsorptivity for supercritical hydrogen. [1] Therefore, we need to expand the interstitial spaces with keeping the hexagonal symmetry of the SWCNT bundle in order to promote adsorption of

supercritical hydrogen. On the other hand, we need to hold a moderate intertube distance in order to guarantee the intensive interaction potential well for the target molecule. The size of a C_{60} molecule is 1 nm and the electronic state of the C_{60} is similar to that of SWCNT. Then, if we can insert C_{60} molecules in the SWCNT bundle to some extent, the produced C_{60} intercalated SWCNT should offer appropriate adsorption sites for supercritical hydrogen.

In this presentation, we report a sonication-aided production method of the C_{60} intercalated SWCNT, which shows an enhanced hydrogen adsorptivity [2].

Experimental

We prepared SWCNTs by the laser ablation of a graphite rod in the presence of Ni and Co, which give an X-ray diffraction (XRD) peak due to the ordered hexagonal bundle structure were prepared. We used closed SWCNT samples to show clearly the effect by the C_{60} -pillaring. The nanoporosity was measured by N_2 adsorption isotherm at 77 K after pretreatment of the SWCNT sample in vacuo. The tube diameter was measured from the radial breathing mode (RBM) band of Raman spectrum, providing the diameter of 1.37 nm. C_{60} -pillared SWCNT was prepared by the sonication of SWCNT in C_{60} -toluene solution of different C_{60} concentration. The C_{60} -pillaring-treated SWCNT is designated as SWCNT- $\text{C}_{60}(x)$, where x is the C_{60} -doped amount on 1 g of SWCNT in $\text{g g}_{\text{SWCNT}}^{-1}$. The doped C_{60} amount was determined by TG. The ordered structure change of the SWCNT bundle was measured by X-ray diffraction with MoK_α . The bundle structure was observed high resolution transmission electron microscope. The surface state analysis of the SWCNT- $\text{C}_{60}(x)$ was carried out by Raman spectroscopy and X-ray photoelectron spectroscopy.

Results and Discussion

Figure 1 shows the C_{60} -doped amounts against the C_{60} concentration of toluene solution ($\text{g L}_{\text{Toluene}}^{-1}$). The C_{60} uptake vs. C_{60} concentration curve has a step near $0.7 \text{ g g}_{\text{SWCNT}}^{-1}$ of the uptake and $0.5 \text{ g L}_{\text{Toluene}}^{-1}$ of the C_{60} concentration; the step indicates the formation of a stable structure between C_{60} and SWCNT. The uptake at the step almost corresponds to the perfect filling of the interstitial spaces by C_{60} molecules, which is estimated from the interstitial spaces in the model structure of an SWCNT bundle and the uptake of C_{60} for a trigonal arrangement. The corresponding amount is indicated by the dotted line in Fig. 1.

N_2 adsorption isotherms at 77 K showed the porosity change clearly. The initial uptake steeply increased with the increase of the C_{60} amount up to $0.646 \text{ g g}_{\text{SWCNT}}^{-1}$. This indicates addition of predominant amounts of micropores in the SWCNT bundles. The micropore volume increases from 0.80 ml g^{-1} to 0.16 ml g^{-1} at the concentration of $0.646 \text{ g g}_{\text{SWCNT}}^{-1}$, and then decreases rapidly with the increase of the concentration. Hence this concentration should give the most optimum C_{60} -pillared

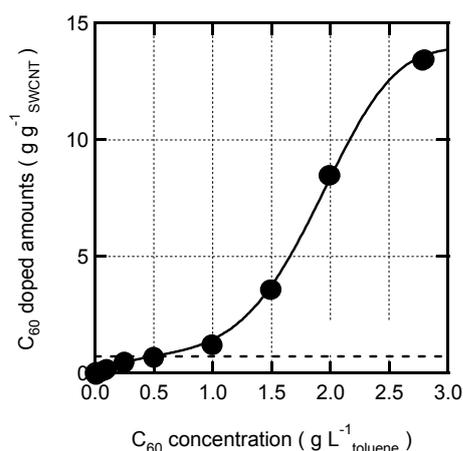


Fig. 1 Relation between C₆₀-doped amount on SWCNT and C₆₀-toluene solution concentration. C₆₀-doped amounts on 1 g of SWCNT (g g⁻¹ SWCNT) are plotted against C₆₀-dissolved toluene solutions.

structure for the acceptance of C₆₀ molecules in the interstitial sites of the SWCNT bundles. The treating with higher C₆₀ concentration should block the interstitial spaces and coat the external surfaces of the SWCNT bundles. The Raman spectra of C₆₀-treated SWCNT, SWCNT, and C₆₀-SWCNT had the individual peaks which were mutually different from each other. We observed the C₆₀ peak at 1467 cm⁻¹ above the C₆₀ concentration of 3.58; the very weak C₆₀ peak was also observed in the SWCNT-C₆₀(1.68). Thus, surface sensitive Raman measurement evidences absence of C₆₀ molecules on the external surfaces of SWCNT bundles. XPS examination also supports that C₆₀ molecules are almost absent on the external surfaces of the SWCNT bundles. The C1s XPS of SWCNT, SWCNT-C₆₀(0.646), and C₆₀. SWCNT, SWCNT-C₆₀(0.646), and C₆₀ had the peak at 284.0 eV, 284.2 eV, and 285.3 eV, respectively. We applied the curve fitting analysis to the peak of SWCNT-C₆₀(0.646), giving that the surface content of C₆₀ was only 10%. Consequently, the majority of C₆₀ molecules in SWCNT-C₆₀(0.646) should be in the internal positions of the SWCNT bundles. High resolution transmission electron microscopy (TEM) observation clearly shows the presence of C₆₀ molecules in the interstitial sites, as shown in Fig. 2. Figure 2 shows the cross-section image of SWCNT-C₆₀(0.646) and which has the expanded hexagonal arrays. The tetragonal arrays were also observed in other cross-section images. The intertube distance of the expanded bundle is evaluated to be 2.2 nm, giving the interlayer distance of 1.9 nm for hexagonal symmetry and 1.8 nm for tetragonal symmetry, respectively under the assumption of the uniform bundle structure of each symmetry. The geometrical values of the interlayer distances for both symmetrical structures are 2.03 and 1.92 nm, respectively, being close to the observed ones from TEM. Therefore, SWCNT-C₆₀(0.646) has a mixed structure of hexagonal and tetragonal symmetries. The X-ray diffraction patterns of SWCNT-C₆₀(0.646), SWCNT bundle,

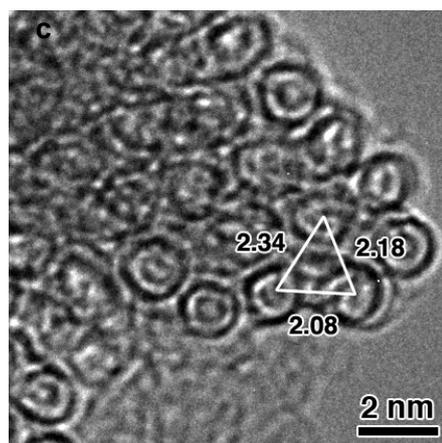


Fig. 2 TEM image of SWCNT-C₆₀(0.646).

and C₆₀ crystals were determined. C₆₀ crystals had no diffraction peak in this range, whereas the original SWCNT bundle had a considerably sharp peak 2.81° corresponding to the interlayer distance ($d=1.44$ nm (experimental)) of the hexagonal lattice of SWCNT arrays. The peak assures the presence of the superlattice structure of the SWCNT bundles.

This original superlattice peak became weak with the C₆₀-pillaring treatment. On the contrary, a broad peak appeared around $2\theta=2.0^\circ$, corresponding to the interlayer distance of ≈ 2.0 nm. This 2.0 nm is just the average value of 2.03 nm and 1.92 nm derived from the TEM-derived two structure models. Thus, XRD intensively supports the formation of C₆₀-pillared SWCNT bundles. However, the pillared structure is not necessarily regular.

The supercritical H₂ adsorption isotherms of SWCNT varied through intercalation of C₆₀ molecules. The H₂ adsorption isotherms at 77 K had an adsorption hysteresis, indicating the presence of entrance blocking due to very narrow pores. The C₆₀ pillaring enhances H₂ adsorptivity remarkably.

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