Enhanced Hydrogen Adsorptivity of Fullerene-pillared Single Wall Carbon Nanotube

Miki Arai,1 Shigenori Usutani,1 Mamiko Kanamaru,1 Koki Urita,1 Yoshikito Fujimori,2 Noriko Yoshizawa,3 Daisuke Noguchi,1 Katsuhiro Nishiyama,2 Yoshiyuki Hattori,1 Fujio Okino,4 Tomonori Ohba,1 Hideki Tanaka,2 Hirofumi Kanoh,1 and Katsumi Kaneko6

1Graduate School of Science, Chiba University, 1-33 Yayoi, Inage, Chiba 263-8522, Japan
2Department of Mechanics and Systems, Tokyo University of Science, Suwa, 5000-1 Toyohira, Chino 391-0292, Japan
3Division of Energy Technology, Center for Advanced Carbon Materials, National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba 305-8565, Japan
4Faculty of Textile Science and Technology, Shinshu University, 3-15-1 Tokida, Ueda 386-8567, Japan
5Department of Chemical Engineering, Kyoto University, Nishikyo-ku, Kyoto 615-8510, Japan
6Exotic Nanocarbon Project, Shinshu University, Wakasato, Nagano 380-8553, Japan

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 has a huge component carbon atoms are exposed to both surfaces of different nanoscale curvatures. SWCNT is essentially an interfacial material, being remarkably different from other solid materials, because all kinds of adsorption sites of the interstitial sites and groove of the hexagonal symmetry. The SWCNT bundle has two kinds of surfaces of the positive and negative curvatures can vary with its tube diameter and the target molecular size. In this presentation, we report a sonication-aided production method of the C₆₀ 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 C₆₀-pillaring. The nanoporosity was measured by N₂ adsorption 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. C₆₀-pilled SWCNT was prepared by the sonication of SWCNT in C₆₀-toluene solution of different C₆₀ concentration. The C₆₀-pilled-treated SWCNT is designated as SWCNT-C₆₀(x), where x is the C₆₀-doped amount on 1 g of SWCNT in g⁰₆₀ g⁻¹. The doped C₆₀ amount was determined by TG. The ordered structure change of the SWCNT bundle was measured by X-ray diffraction with MoKα. The bundle structure was observed high resolution transmission electron microscope. The surface state analysis of the SWCNT-C₆₀(x) was carried out by Raman spectroscopy and X-ray photoelectron spectroscopy.

Results and Discussion

Figure 1 shows the C₆₀-doped amounts against the C₆₀ concentration of toluene solution (g L⁻¹ toluene). The C₆₀ uptake vs. C₆₀ concentration curve has a step near 0.7 g g⁻¹ of the uptake and 0.5 g L⁻¹ toluene of the C₆₀ concentration; the step indicates the formation of a stable structure between C₆₀ and SWCNT. The uptake at the step almost corresponds to the perfect filling of the interstitial spaces by C₆₀ molecules, which is estimated from the interstitial spaces in the model structure of an SWCNT bundle and the uptake of C₆₀ for a trigonal arrangement. The corresponding amount is indicated by the dotted line in Fig.1.

N₂ adsorption isotherms at 77 K showed the porosity change clearly. The initial uptake steeply increased with the increase of the C₆₀ amount up to 0.646 g g⁻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 g g⁻¹, and then decreases rapidly with the increase of the concentration. Hence this concentration should give the most optimum C₆₀-pilled
structure for the acceptance of C_{60} molecules in the interstitial sites of the SWCNT bundles. The treating with higher C_{60} concentration should block the interstitial spaces and coat the external surfaces of the SWCNT bundles. The Raman spectra of C_{60}-treated SWCNT, SWCNT, and C_{60}. SWCNT and C_{60} had the individual peaks which were mutually different from each other. We observed the C_{60} peak at 1467 cm^{-1} above the C_{60} concentration of 3.58; the very weak C_{60} peak was also observed in the SWCNT-C_{60}(1.68). Thus, surface sensitive Raman measurement evidences absence of C_{60} molecules on the external surfaces of SWCNT bundles. XPS examination also supports that C_{60} molecules are almost absent on the external surfaces of the SWCNT bundles. The C1s XPS of SWCNT, SWCNT-C_{60}(0.646), and C_{60}. SWCNT, SWCNT-C_{60}(0.646), and C_{60} 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-C_{60}(0.646), giving that the surface content of C_{60} was only 10%. Consequently, the majority of C_{60} molecules in SWCNT-C_{60}(0.646) should be in the internal positions of the SWCNT bundles. High resolution transmission electron microscopy (TEM) observation clearly shows the presence of C_{60} molecules in the interstitial sites, as shown in Fig. 2. Figure 2 shows the cross-section image of SWCNT-C_{60}(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-C_{60}(0.646) has a mixed structure of hexagonal and tetragonal symmetries. The X-ray diffraction patterns of SWCNT-C_{60}(0.646), SWCNT bundle, and C_{60} crystals were determined. C_{60} 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 C_{60}-pillaring treatment. On the contrary, a broad peak appeared around 2θ=2.0°, 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 C_{60}-pillared SWCNT bundles. However, the pillared structure is not necessarily regular.

The supercritical H_{2} adsorption isotherms of SWCNT varied through intercalation of C_{60} molecules. The H_{2} adsorption isotherms at 77 K had an adsorption hysteresis, indicating the presence of entrance blocking due to very narrow pores. The C_{60} pillaring enhances H_{2} adsorpitivity remarkably.

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