NANO
LETTERS

2001
Vol. 1, No. 4
197−199

Porosity Evaluation of Intrinsic Intraparticle Nanopores of Single Wall Carbon Nanohorn

K. Murata and K. Kaneko*

*Chemistry, Material Science, Graduate School of Natural Science and Technology,
Chiba University 1-33 Yayoi, Inage, Chiba 263-8522, Japan*

W. A. Steele

*Department of Physics and Chemistry, Pennsylvania State University,
University Park, Pennsylvania 16802*

F. Kokai and K. Takahashi

*Laser Research Center, Institute of Research and Innovation, 1201 Takada,
Kashiwa, Chiba 277-0861, Japan*

D. Kasuya,[†] M. Yudasaka,[‡] and S. Iijima[†,‡,§]

*Japan Science and Technology Corporation, NEC Corporation, 34 Miyukigaoka,
Tsukuba 305-8501, Japan, Department of Physics, Meijo University,
1501 Shiogamaguchi, Tenpaku, Nagoya 468-8502, Japan, and Japan Science and
Technology Corporation*

Received January 29, 2001 *(Revised Manuscript Received March 2, 2001)*

ABSTRACT

The adsorption isotherm of N_2 in internal nanopores of the single wall carbon nanohorn (SWNH) particles was compared with that of the external surfaces of the SWNH assembly. The presence of two strong adsorption sites of the internal nanopores and external nanopores of the assembly were evidenced by the analysis of the adsorption isotherm. The calculated interaction potential of the external nanopore was much deeper than that of the internal nanopore.

The single wall carbon nanohorn (SWNH)[1,2] is a new material that is similar to single wall carbon nanotube (SWNT)[3]. The SWNHs form assemblies that have a "*Dahlia*-flower"-like structure, as shown in the TEM image in Figure 1. The SWNH has a horn shape, which distinguishes it from SWNT. The differences between SWNH and SWNT, except for its shape, are the high yield (> 95% from transmission micrographs) and milder preparation conditions of SWNH. The SWNH is prepared at room temperature by CO_2 laser ablation without a catalyst.[1] Hence, pure samples of SWNHs are available more easily than are pure samples of SWNT. In this letter, we report the porosities from the internal spaces of the SWNH particle and the interstitial structure of SWNH assembly by high-resolution N_2 adsorption measurement.

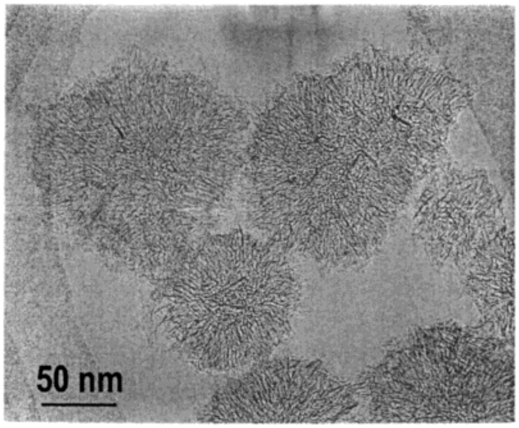

Figure 1. TEM image of SWNH assembly.

---

* Corresponding author. E-mail: kaneko@pchem2.s.chiba-u.ac.jp. Fax: +81-43-290-2788.

[†] Meijo University.

[‡] Japan Science and Technology Corporation.

[§] NEC.

10.1021/nl015509m CCC: $20.00
Published on Web 03/21/2001

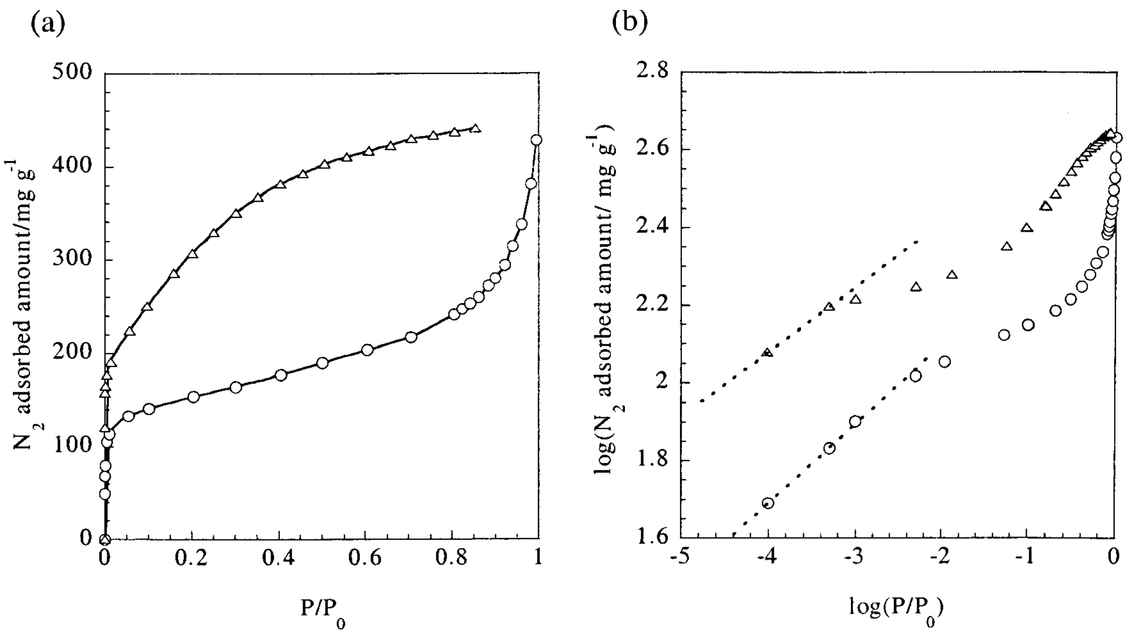

Figure 2. Nitrogen adsorption isotherm at 77 K on SWNH assembly: external surface (○); intrinsic micropore (△). The broken line shows the initial slope of the isotherm.

The detailed preparation method of samples is published in a previous article.[1] We studied SWNH (NH) and SWNH (NH-ox) treated at 693 K in a pure oxygen atmosphere. The high-resolution N_2 adsorption isotherm was measured at 77 K. The particle density[4−6] ρ_p was determined by the high-pressure helium buoyancy measurement at 303 K. Here ρ_p is defined by $\rho_p = 1/(V_s + V_c)$, where V_s is the volume of solid part and V_c is the volume of closed pores and pores in which the N_2 molecule cannot enter.[5,6]

The obtained ρ_p values of NH and NH-ox are 1.25 and 2.05 g/mL, respectively. In the case of NH, the ρ_p is much smaller than the solid density ρ_s of graphite (2.27 g/mL), but close to the calculated value from the approximate geometry of the closed hollow structure. Hence, the internal micropore of the NH does not communicate with the outside. The closed pore volume of NH, which is calculated from $V_c = 1/\rho_p - 1/\rho_s$, is 0.36 mL/g. On the other hand, the value ρ_p of NH-ox is close to the solid density of graphite. The closed pore volume of NH-ox is only 0.047 mL/g. Therefore, 85% of closed pores of NH are opened by the oxidation treatment.

Pores having pore width $w < 2$ nm and those of 2 nm $< w < 50$ nm are called micropores and mesopores, respectively, according to the IUPAC classification.[7] However the pore width of the internal pores of these NH particles is close to the critical size of 2 nm. Therefore, the term "nanopores" is used in this letter because nanopores, including micropores and small mesopores, have been often used.

N_2 molecules are adsorbed in internal nanopores and external surfaces of NH-ox particles, whereas they are adsorbed only on the external surfaces of NH particles. Here the external surface includes the external pores. Consequently, the subtraction of the adsorption isotherm of NH from that of NH-ox provides the adsorption isotherm of N_2 only in the internal nanopore of the single SWNH particles. Thus, adsorption isotherms of N_2 on the external surface and in the internal nanopores of SWNH can be determined separately, as shown in Figure 2.

Table 1: Porosity of Intrinsic Micropores and Interstitial Surface for SWNH Assembly

	specific surface area			
	micropores ($m^2\ g^{-1}$)	mesopores and external surface ($m^2\ g^{-1}$)	micropore volume (mL g^{-1})	avg w (nm)
intrinsic pores	318		0.36	2.3
interstitial pores	200	108	0.11	1.1

The adsorption isotherm on the external surface is of type II of the IUPAC classification,[7] whereas the adsorption isotherm of the internal pores is basically of type I, having characteristics of adsorption on microporous solid. From the TEM observation, the adsorption isotherm for the internal pores of the main tube structure is similar to that of slit-shaped carbon micropore systems of $1.2 < w < 1.4$ nm.[8] Although the appearance of the isotherm on the external surfaces is close to type II, as mentioned above, it has a quite sharp rising in the initial stage and a gradual increase from the medium pressure. The high-resolution α_s plot[9,10] of the separated adsorption isotherms on the internal nanopores and the external surfaces provides the surface area, pore volume, and average pore width. The pore width of the internal nanopore of SWNH is 2.3 nm, being close to the critical size for the classification of micropores and mesopores, as mentioned above. On the other hand, there are small nanopores of the pore width $w = 1.1$ nm in the assembly structure of SWNH particles in addition to the mesopores and external surface. Here, the small nanopores should originate from the ordered arrangement of SWNH particles, as explained below.To examine the initial stage of adsorption, the logarithm of P/P_0 is used in Figure 2b. Henry's law constant was determined by the virial plot.[11,12] Henry's law constant of the external surfaces is 1.54×10^{14}

mg/g kPa and that of internal nanopores is 2.1 × 10^6 mg/g kPa. The remarkable difference of Henry's constant should come from the interaction potential depth difference.

The X-ray diffraction leads to a broad peak due to a partial parallel orientation of SWNH particles, indicating an interparticle distance of 0.4 nm for the tube part.[2] We calculated the interaction potential of the N_2 molecule with the graphene tubes both inside and outside of the central tube which is surrounded by other tubes of the triangular arrangement with the aid of the potential function. Here values of 2 nm as the diameter of the tube part of SWNH and 0.4 nm as the distance between the nearest neighbor tube-walls were used for the potential calculation. The detailed procedures of the potential calculation will appear in another journal.[13] The potential minimum of the internal nanopore inside the tube is -1280 K, whereas that of the external nanopore of the triangular arrangement of three SWNH particles is -2190 K. This potential difference coincides with the great difference of Henry's law constant. However, the preliminary GCMC simulation predicts the difficulty in adsorption of N_2 molecules in the external nanopores of the ordered triangular arrangement of SWNH particles. As the predominant adsorption occurs on the external pores, the real mutual arrangement of SWNH particles should be more disordered, providing the observed average width of 1.1 nm. We calculated the interaction potential for the loosely bound arrangement giving 1.0 nm of the effective width for the external pores; the potential depth is -1690 K, which is still much deeper than that of the internal nanopores. Even the potential depth of the internal nanopores is deeper than that of the flat graphite (-1150 K). The potential calculation supports observed adsorption behaviors of the SWNH assembly.

Thus, the high-resolution N_2 adsorption analysis can clearly elucidate the presence of internal nanopores, external micropores of the triangular arrangement of three particles, and interparticle mesopores in the assembly structure for partially oxidized SWNH particles.

Acknowledgment. This work was funded by Grant-in-Aid for Scientific Research B from the Japanese Government. D.K. and S.I. acknowledge the support of the U.S. Office of Naval Research (ONR-N000140010762).

References

(1) Iijima, S.; Yudasaka, M.; Yamada, R.; Bandow, S.; Suenaga, K.; Kokai, F.; Takahashi, K. *Chem. Phys. Lett.* **1999**, *309*, 165.
(2) Bandow, S.; Kokai, F.; Takahashi, K. Yudasaka, M.; Qin, L. C.; Iijima, S. *Chem. Phys. Lett.* **2000**, *321*, 514.
(3) Iijima, S.; Ichihashi, T. *Nature* **1993**, *363*, 603.
(4) Kaneko, K.; Shimizu, K.; Suzuki, T. *J. Chem. Phys*. **1992**, *97*, 8705.
(5) Ruike, M.; Kasu, T.; Setoyama, N.; Suzuki, T.; Kaneko, K. *J. Phys. Chem*. **1994**, *98*, 9594.
(6) Murata, K.; Kaneko, K. Kokai, F.; Takahashi, K.; Yudasaka, M.; Iijima, S. *Chem. Phys. Lett.* **2000**, *331*, 14.
(7) IUPAC Commission on Colloid and Surface Chemistry Including Catalysis; *Pure Appl. Chem*. **1985**, *57*, 603.
(8) Setoyama, N.; Suzuki, T.; Kaneko, K. *Carbon* **1998**, *36*, 1459.
(9) Rouquerol, F.; Rouquerol, J.; Sing, K. S. W. *Adsorption by Powders and Porous Solids*; Academic Press: San Diego, 1999.
(10) Kaneko, K.; Ishii, C. *Colloid Surf*. **1992**, *67*, 203.
(11) Ross, S.; Olivier, J. P. *On Physical Adsorption*; Wiley Interscience: New York, 1964.
(12) Zhang, S.-Y.; Talu, O.; Hayhurst, D. T. *J. Phys. Chem.* **1991**, *95*, 1722.
(13) Murata, K.; Kaneko, K.; Steele, W. A.; Kokai, F.; Takahashi, K.; Kasuya, D.; Hirahara, K.; Yudasaka, M.; Iijima, S.; submitted to *J. Phys. Chem.*

NL015509M