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N_2 Adsorption in an Internal Nanopore Space of Single-Walled Carbon Nanohorn: GCMC Simulation and Experiment

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ABSTRACT

N_2 adsorption in the internal nanospace and on the external suface of the single SWNH particle is studied by grand canonical Monte Carlo simulation and is compared with the experimental result. The detailed comparison of the simulated adsorption isotherm with the experimental isotherm in the internal nanospaces provides 2.9 nm of the average pore width of the internal nanospaces.

The single-walled carbon nanohorn (SWNH) is a new material whose structure is similar to single walled carbon nanotube (SWNT). The SWNH particle has the shape of a horn or an ampoule, which is not a simple tube form. Basically, the wall consists of a single graphene sheet, and the internal space is not available for gas adsorption, because the internal space of the SWNH particle is closed. As the SWNH is prepared at room temperature by CO_2 laser ablation in the absence of metal catalyst, pure SWNH samples of greater amount are obtained more easily than SWNT.[1−3] SWNH particles form “Dahlia flower”-like assembly structures that have external micropores and mesopores. Also, a simple oxidation produces windows on the wall of the SWNH particle. It is possible to measure molecular adsorption in the internal nanospace using partially oxidized SWNH particles.[4] These authors succeeded to distinguish N_2 adsorption in the internal nanospaces and the external pores, which are often called interstitial pores, in the studies on SWNT. There is a great interest in the molecular process in the internal space of SWNT from fundamental and practical aspects. Nevertheless, it is still difficult to measure molecular adsorption in the internal space of SWNT.

Simulation and Experimental Section. The preceding HR-TEM examination[1] elucidated the shape of a single SWNH particle. One end of the single SWNH particle has a corn structure whose top has the average angle of $\pi/9$ on the TEM image, whereas another end is capped. However, the curvature of the cap is not definite in the previous HR-TEM study.[2] Accordingly, we approximated the geometrical structure by the combined form of the corn and tube. The contribution by the cap part is neglected.

The intermolecular interaction between different N_2 molecules was approximated by the one-center Lennard-Jones

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(LJ) potential. The used LJ parameters are $\epsilon_{ff}/k_B = 104.2$ K and $\sigma_{ff} = 0.3632$ nm. The interaction potential of an N_2 molecule with the tube wall was calculated using Steele's smooth-walled potential including a hypergeometric function, which was published in the preceding article.[3] This potential function can describe the interaction of a molecule inside and outside the tube. As to the corn part, we approximated the corn by the spinning fishing rod of a series of tubes of different diameters. The width and diameter of the tube were varied by 0.1 nm. Here, the used LJ parameters of a carbon atom are $\epsilon_{ss}/k_B = 30.14$ K and $\sigma_{ff} = 0.3416$ nm. Also the LJ cross parameters of ϵ_{sf} and σ_{sf} were obtained by use of the Lorentz−Berthelot rule. The grand canonical Monte Carlo (GCMC) simulation was done in the established procedure. The random movement, creation, and removal of a molecule make new configurations. They are accepted when they obey Metropolis's sampling scheme in proportion to $\exp(-\Delta E/kT)$ where ΔE is the change of total energy in the system.

To compare the simulated adsorption isotherm with the experimental one, the tube diameter D at the atom position must be associated with the effective pore width w, which can be determined experimentally by adsorption. We used the following relation.

$$w = \frac{D - 0.3}{\text{nm}} \tag{1}$$

In this study, the adsorption isotherm was calculated over the relative pressure range of 10^{-6} to 1 from $D = 2.0$ to 3.6 nm by every 0.1 nm.

The SWNH was synthesized by CO_2 laser ablation of graphite under Ar atmosphere of 101 kPa. The SWNHs were partially oxidized at 693 K, giving widows of molecular size on the wall. Almost all internal nanospaces of the SWNH particles become available for N_2 adsorption according to the preceding article.[4] The N_2 adsorption isotherms of SWNH and SWNH oxidized at 693 K were measured at 77 K by use of a volumetric apparatus (Quantachrome).

Results and Discussion. Experimental separation of adsorption in internal nonospaces and on external surfaces was done by subtraction of the N_2 adsorption isotherm of the SWNHs without the pore-wall windows from the isotherm of the partial oxidized SWNHs. As the oxidation treatment does not change seriously the assembly structure, adsorption isotherms both of N_2 in the internal nanospaces and on the exterior surfaces can be approximately distinguished, as shown in Figure 1. The N_2 adsorption on the external surfaces includes the adsorption both in the interstitial micropores having a greater interaction potential than the internal space and in the mesopores. Here, we will focus on adsorption only in the internal nanopore space. The GCMC simulation was carried out for the internal space of a single SWNH particle.

The simulated N_2 adsorption isotherms in the internal nanopore space for values of D from 2.5 to 3.3 nm are shown in Figure 2. These simulated adsorption isotherms have two gradual steps around $P/P_0 = 10^{-5}$ and 10^{-1}. The smaller the D value, the sharper the step. These simulated adsorption isotherms were compared with the experimental isotherm. Here, we used the observed nanopore volume per unit weight of SWNH for calculation of the adsorption amount. The observed adsorption isotherm in the internal nanopore space has a gradual increase above $P/P_0 = 0.4$, suggesting an imperfect subtraction of adsorption in the mesopores stemming from the interparticle assembly structure. Then we assumed that the saturated amount of adsorption in the internal space is equal to the adsorption amount at $P/P_0 = 0.4$. Thus, the experimental adsorption isotherm is compared with the simulated one in Figure 2. The simulated adsorption

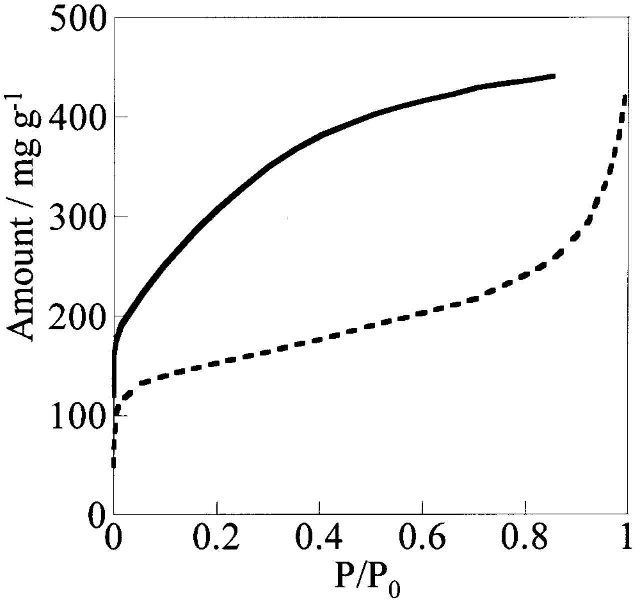

Figure 1. Adsorption isotherms of N_2 in the internal nanospace and external surface at 77 K. The solid and dashed curves denoted the internal and external isotherms, respectively.

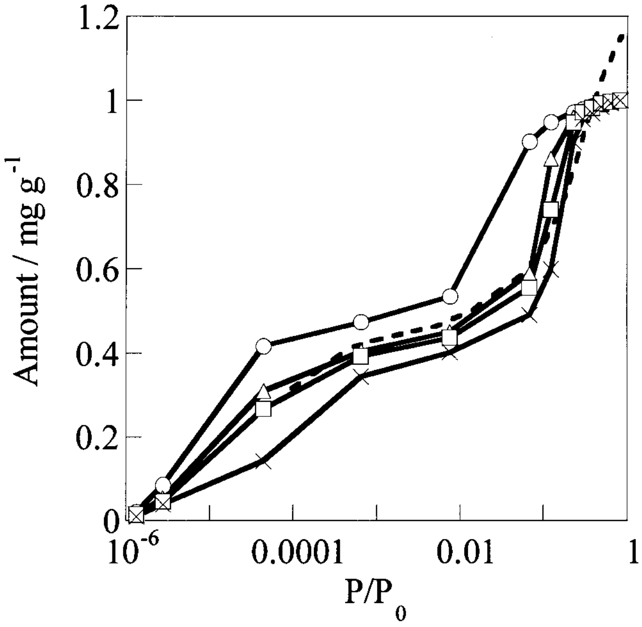

Figure 2. Simulated adsorption isotherms of N_2 in the internal nanospace at 77 K. The solid and dashed curves denoted the simulated and experimental isotherms, respectively. ○, $w = 2.5$ nm; △, $w = 2.9$ nm; □, $w = 3.0$ nm; and ×, $w = 3.3$ nm.

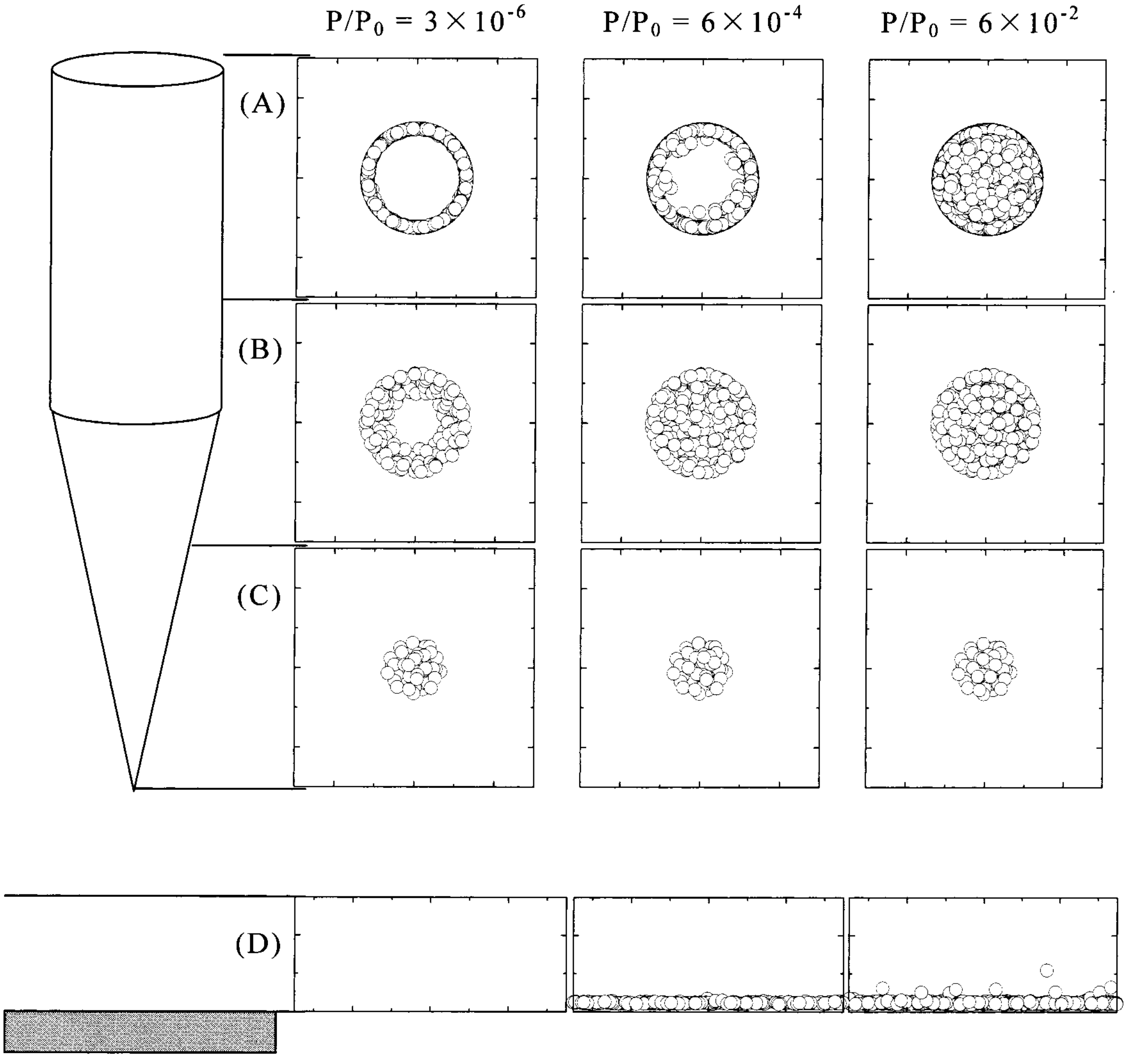

Figure 3. Images from axial direction at different relative pressure P/P_0. The images at the tube, neck, and tip are shown in the order (A) tube; (B) neck; (C) tip, and (D) flat graphite surface.

isotherm of $D = 3.2$ nm ($w = 2.9$ nm) coincides with the experimental one over the wide P/P_0 region from 10^{-4} to 10^{-1}. Then the average pore width w of the internal space of SWNH should be 2.9 nm, although HR-TEM observation suggested a smaller w value (2.0 nm). The tube part of the SWNH particle does not have uniform diameter, and furthermore SWNH particles form an assembly structure of so-called "Dahlia flower" shape. Primary SWNH particles overlap each other in the HR-TEM picture, giving rise to the underestimation. Also, this model does not take into account the real length of the tube part, which may provide the disagreement above $P/P_0 = 0.4$.

How are molecules adsorbed in the internal space? Figure 3 shows images from the axial direction corresponding to different adsorption amount. The images correspond to three regions: the tip, neck, and tube spaces. Also, the images on the flat graphite surface are shown for comparison. The adsorption processes at the three regions are considerably different from each other. Adsorption begins from the tip space and moves to the neck space according to the order of the interaction potential. At the tube space, molecules are adsorbed on the internal wall by a kind of multilayer adsorption. The predominant adsorption begins from much lower relative pressure than adsorption on the flat graphite surface because of the strong interaction potential. The images express explicitly the characteristic adsorption process in the internal nanospace.

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