Nanowindow-Induced Molecular Sieving Effect in a Single-Wall Carbon Nanohorn

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Subnanoscale windows (nanowindows) were donated to the walls of single-wall carbon nanohorns (SWNHs) by oxidation in oxygen at different temperatures of 573−693 K. We determined the accessibility of internal nanospaces of the SWNHs through nanowindows to He, Ar, N_2, CH_4, SF_6, and C_{60}. An explicit molecular sieving effect of SWNHs due to the nanowindow was shown.

Introduction

A single-wall carbon nanohorn (SWNH)[1−3] is a family of single-wall carbon nanotubes (SWNT).[4] SWNH has a closed horn-shaped tip with a cone angle of about 20° and the mean diameter and length are 2−4 nm and about 40−50 nm, respectively. SWNHs are associated to form a radial aggregate with a spherical form having a diameter of 80−100 nm. The horn-shaped tips of the SWNHs stick out at the surface of the spherical aggregate and the bottoms of the SWNHs coalesce at the center of the spherical aggregate. SWNHs are more suitable for adsorption studies than usual SWNTs, because they are obtained without metal catalysts with a high production rate of 10 g/h, and SWNH samples of high purity are available for adsorption measurement. Oxidation provides nanoscale windows on the SWNH particle, and thereby gaseous molecules are accessible to the internal nanospace through the nanowindows.[5] The internal porosity of the SWNH particle and the interstitial porosity of SWNH aggregates can be separately determined by N_2 adsorption at 77 K.[6−8] The internal adsorbed density of supercritical H_2 or CH_4 is comparable to the density of bulk liquid H_2 or CH_4.[9−11] The preceding studies showed that the presence of nanowindows and partial orientation of SWNH particles are indispensable to realize the high density of supercritical gases adsorbed in the internal nanospace. Consequently, elucidation and control of the nanowindow size are intensively requested. In this Letter, the molecular sieve effect of SWNHs having nanowindows is described.

Experimental Section

SWNH particles were prepared by laser ablation of graphite in an Ar atmosphere at room temperature.[1] SWNH particles were oxidized at 573, 623, and 693 K in O_2 for 10 min to control the size and number of nanowindows. The molecular sieving effect was probed by the adsorption capacity of SWNHs for molecules with various diameters: He, Ar, N_2, CH_4, SF_6, and C_{60}, which have diameters of 0.26, 0.335, 0.363, 0.32, 0.525, and 0.92 nm, respectively.[12−14] These molecules were selected to clarify the molecular sieving effect, because they are almost spherical and they interact with SWNHs through only the London dispersion force without any specific interaction. Adsorption isotherms in internal nanospaces of SWNHs were measured at 303 K for He, Ar, N_2, CH_4, and SF_6 after preevacuation of SWNH particles at 423 K in 1 mPa.[15] The preceding studies on adsorption of supercritical CH_4 and H_2 showed that internal nanospaces through nanowindows are available for supercritical gases.[10,11] Hence, supercritical gas adsorption was used for examination of molecular sieving effect. The possible adsorption capacity for C_{60} was estimated from TEM images.

Results and Discussion

Figure 1 shows adsorption isotherms of Ar, N_2, CH_4, and SF_6 on SWNH assemblies oxidized at 573, 623, and 693 K. The order of the adsorption amount depends on the probe molecule and the oxidation temperature. For example, SWNH oxidized at 623 K has the greatest Ar adsorption, whereas the amount of SF_6 adsorption on SWNH oxidized at 623 K is much smaller than that on SWNH oxidized at 693 K. The difference in the adsorptivity reflects the size difference of the nanowindows. The initial adsorption capacity available for each probe molecule was estimated from the fraction of the Henry law constant under the assumption of the linear relation,[5,16,17] although this assumption can be applied to the low fractional filling. This initial adsorption capacity should be fit for evaluation of molecular sieving effect. As for C_{60}, the possible adsorption capacity was used instead of the initial adsorption capacity.

The initial adsorption capacity as functions of the probe molecule and the oxidation temperature is shown in Figure 2.

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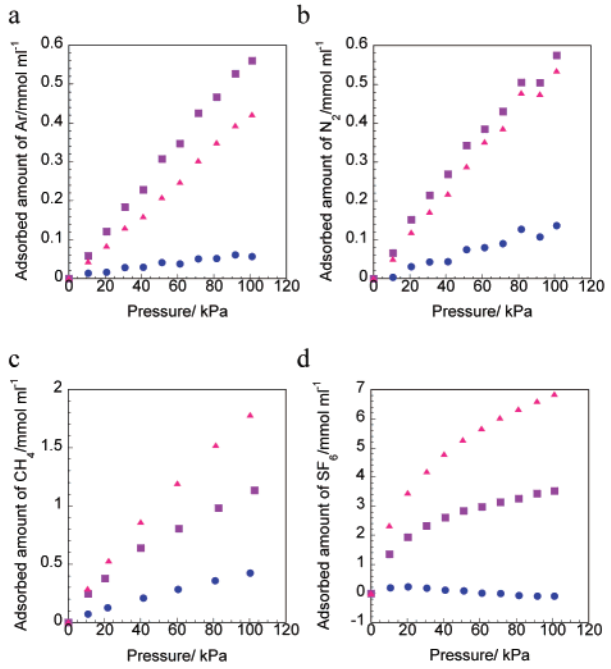


Figure 1. Adsorption isotherms in internal nanospaces of SWNH for different probe molecule: (a) Ar, (b), N_2, (c) CH_4, and (d) SF_6. (●), (■), and (▲) denote SWNH treated at 573, 623, and 693 K, respectively.

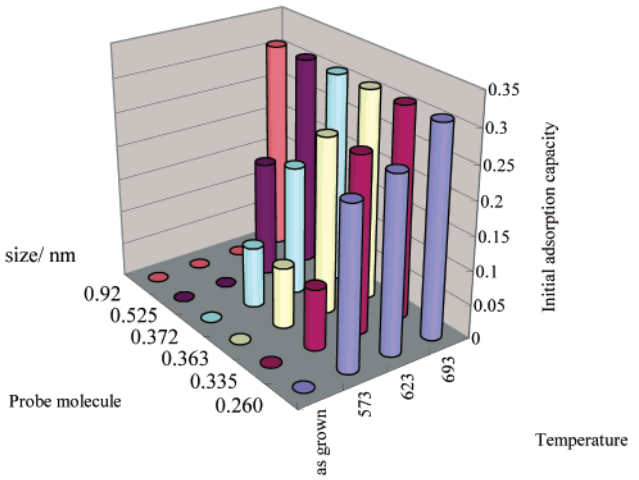
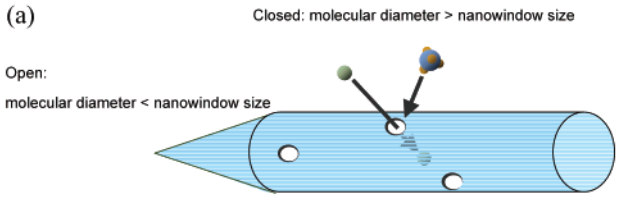


Figure 2. Molecular sieving effect of SWNH oxidized at different temperatures.

Here, the steep jump in the initial adsorption capacity shows the critical change in the nanowindow size. SWNH oxidized at 693 K can accept all probe molecules, indicating that the minimum size of the nanowindow is 1 nm. SWNH oxidized at 623 K can adsorb all probe molecules except for C_{60}, and thereby the nanowindows size should be in the range 0.53−0.92 nm. In a similar way, the nanowindow size of SWNH oxidized at 573 K is in the range 0.37−0.53 nm. Thus, nanowindows show an excellent molecular sieving property, as shown in Figure 3. Hence, a more precise oxidation control can donate an excellent molecular-sieving nature to SWNH assemblies.



(b)

temperature	closed pore	initial adsorption capacity					
		He	Ar	N_2	CH_4	SF_6	C_{60}
		0.2602	0.335	0.3632	0.3721	0.525	0.92
		(nm)					
K	ml g^{-1}	ml g^{-1}	ml g^{-1}	ml g^{-1}	ml g^{-1}	ml g^{-1}	ml g^{-1}
as grown	0.36	0	0	0	0	0	0
573	0.12	0.24	0.09	0.09	0.09	0	0
623	0.10	0.26	0.26	0.26	0.19	0.17	0
693	0.05	0.31	0.31	0.31	0.31	0.31	0.31

Figure 3. Molecular sieving model (a) and dependence of the internal capacity on molecular size and shape (b).

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