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Selective D₂ adsorption enhanced by the quantum sieving effect on entangled single-wall carbon nanotubes

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Abstract

The quantum sieving effect of D_2 over H_2 is examined at 40 and 77 K by means of experiments and GCMC simulations, for two types of single-wall carbon nanotubes that are distinguishable by their unique entangled structures; (1) a well-bundled SWCNT and (2) loosely-assembled SWCNT produced by the super growth method (SG-SWCNT). Oxidized SWCNT samples of which the so-called internal sites are accessible for H_2 and D_2 , are also studied. Experimental H_2 and D_2 adsorption properties on the well-bundled SWCNTs are compared with the simulated ones, revealing that pore-blocking and restricted diffusion of the molecules suppress the high selectivity of D_2 over H_2 . The non-oxidized SG-SWCNT assembly shows the highest selectivity among the SWCNT samples, both at 40 and 77 K. The high selectivity of the SG-SWCNT assembly, which is pronounced even at 77 K, is ascribed to their unique assembly structure.

S Online supplementary data available from stacks.iop.org/JPhysCM/22/334207/mmedia

1. Introduction

Quantum sieving is a potential technique for the separation of isotopes [1-3]. It was first proposed by Beenakker *et al* [1] that molecules confined in a cylindrical pore, of which the size is comparable to that of the molecule, behave as a one-dimensional gas, resulting in energetically favorable

adsorption of heavier molecules than lighter ones due to the difference of zero-point energy. The quantum sieving is predominant, especially for hydrogen isotopes, because of a large ratio of those masses that enhances the difference of interaction potentials stemming from the quantum effect. Single-wall carbon nanotube (SWCNT), single-wall carbon nanohorn, activated carbon fibers, zeolites, and metal–organic

framework materials are the candidates for microporous materials for separation of H₂ and D₂, which have been investigated by virtue of simulations and experiments [2-17]. An intriguing case that arises from SWCNT is their unique entangled structure, the so-called bundle or rope. SWCNTs aggregate with each other mainly due to the van der Waals interaction, so that bundled SWCNTs usually form a triangular lattice [18]. An interstitial site is made up between three SWCNTs comprising a bundle. Synthesized SWCNTs usually have diameter around 1 nm, so that the effective pore width of the interstitial sites for the (10, 10) SWCNT, of which the diameter is \sim 1.4 nm, is slightly larger than the classical size parameter of H₂ ($\sigma_{\rm ff} = 0.2958$ nm) [19]. The quantum sieving should be pronounced in the interstitial sites, therefore theoretical studies have been devoted to elucidate the effect on the interstitial sites [2, 20]. For further understanding of the quantum sieving in the interstitial sites, controlling the effective pore width of the interstitial sites is required experimentally. However, there is a difficulty in experiments, because SWCNTs are tightly packed with each other in the solid-state form. Recently, Hata et al succeeded in producing SWCNTs with a high yield and purity by the so-called 'super growth' method (denoted as SG-SWCNT, hereafter) [21]. The preceding N₂ adsorption isotherm analysis revealed that SG-SWCNTs showed a super-high specific surface area $(1200 \text{ m}^2 \text{ g}^{-1})$ [22], which was fairly close to the geometrical surface area of a free-standing SWCNT (1315 m² g⁻¹) [23]. It is worth noting that the apparent density of SG-SWCNT is much smaller than other SWCNT samples [24], and thereby SG-SWCNTs do not form a dense bundle structure. On the other hand, SG-SWCNTs can be densely contracted by drying after dipping in some solvents [25, 26]. Thus, SG-SWCNT provides unique assembly structures in that most of the carbon atoms comprising a SWCNT can be regarded as surface atoms, giving us a new standpoint for the interstitial site, which is distinguishable from the trigonally packed structure of the bundle.

In this context, we experimentally investigate supercritical H_2 and D_2 adsorption properties at 40 and 77 K on two types of SWCNTs, which differ in their aggregation structures: (1) a well-bundled SWCNT sample with a narrow diameter distribution and (2) a SG-SWCNT. The pore and aggregation structure of both SWCNT samples were characterized with different techniques. The temperature dependence of H_2 and D_2 adsorption properties on both SWCNTs was determined experimentally and with quantum molecular simulation. The difference in H_2 and D_2 adsorption properties of both SWCNT samples is associated with the pore and aggregation structures.

2. Experimental methods

An as-grown SWCNT sample produced by laser ablation method [27, 28] was purified by the following method; refluxing under 15% aqueous H_2O_2 solution at 373 K for 5 h, then subsequently adding 1 M aqueous HCl solution, stirring the mixture for ~20 h. After filtration of the solution, the SWCNT sample was dried under ambient conditions. The resultant purified-SWCNT sample was used as the specimen

(denoted as LA-SWCNT hereafter). An as-grown SWCNT sample produced by the Super Growth method (SG-SWCNT) was used without any purification [21]. Cap-opened SWCNT samples were prepared by partial oxidation at 783 K under O_2 gas flow for LA-SWCNT [29], and 693 K under N_2/O_2 (8:2) gas flow for SG-SWCNT [30]. Hereafter, those oxidized samples are denoted as oxLA-SWCNT and oxSG-SWCNT, respectively.

LA-SWCNT and SG-SWCNT were annealed at 1773, 1873, 1973, 2073, and 2273 K under 1 Pa for 2 h. In order to reduce impurity gases in a furnace, vacuum pumping (<1 Pa) and succeeding introduction of Ar gas (99.99%) were carried out twice before heating to the target temperatures. The annealed samples are denoted as the sample/annealing temperature (for example, LA-SWCNT/1773).

Morphological information of LA-SWCNT and SG-SWCNT was obtained by a transmission electron microscope (JEOL Ltd JEM-4000FX2) operated at 400 kV. Previous to the TEM observations, the specimens were ultrasonically dispersed in ethanol, depositing the droplets onto a copper grid covered with carbon membranes.

Powder x-ray diffraction (XRD) patterns of LA- and SG-SWCNT were collected by using synchrotron radiation x-ray ($\lambda = 0.100$ nm) at the BL02B2 beam line of Spring-8 in Japan. The samples were sealed in a glass tube after pretreatment at 423 K under 0.1 mPa for 2 h.

 N_2 adsorption isotherms at 77 K for LA-SWCNT, oxLA-SWCNT, SG-SWCNT, and oxSG-SWCNT were measured by volumetric adsorption equipment (Autosorb-1, Quantachrome). H_2 and D_2 adsorption isotherms at 77 K for LA-SWCNT, oxLA-SWCNT, SG-SWCNT, and oxSG-SWCNT were also measured by the volumetric adsorption equipment. H_2 and D_2 adsorption isotherms at 40 K for LA-SWCNT, oxLA-SWCNT, SG-SWCNT, and oxSG-SWCNTs were measured by a laboratory-designed volumetric adsorption equipment. All adsorption isotherms were measured after pretreatment of the samples at 423 K under 0.1 mPa for 2 h.

Raman measurements for LA-SWCNT, SG-SWCNT, and those of annealed samples, were carried out with a singlemonochromator micro-Raman spectrometer using a backscattering configuration (JASCO NRS-3100) under ambient conditions. Raman spectra were acquired with 532 nm (Nd:YAG laser) and 632.8 nm (He–Ne laser) excitations. The laser power density was $\sim 10^8$ Wm⁻² at the sampling points.

3. Theory and simulation method

3.1. Fluid-fluid interaction potentials

The Lennard-Jones (LJ) potential was used to model fluid–fluid interaction potentials:

$$V_{\rm LJ}(r) = 4\varepsilon_{\rm ff} \left[\left(\frac{\sigma_{\rm ff}}{r} \right)^{12} - \left(\frac{\sigma_{\rm ff}}{r} \right)^6 \right],\tag{1}$$

where r is the distance between two particles. The H₂ and D₂ molecules were treated as structureless spherical particles. The LJ interaction parameters used in this study were $\sigma_{\rm ff} = 0.2958$ nm and $\varepsilon_{\rm ff}/k_{\rm B} = 36.7$ K for H₂ [19]. The exact same parameters of the H₂ molecule were used for the D₂ molecule. The Feynman–Hibbs (FH) effective potential [31] was used to introduce the quantum effect into the statistical properties obtained from the classical GCMC simulations for hydrogen isotopes adsorption. In the FH treatment, a quantum fluid molecule with mass *m* is represented by a Gaussian wavepacket of width $\hbar/(12mk_{\rm B}T)^{1/2}$, and thereby the effective potential can be obtained by a convolution integral of the classical LJ potential with the Gaussian distribution of the molecular position over the whole space (Gaussian FH effective potential). The following quadratic FH effective potential is derived by expanding the Gaussian FH effective potential to the second order [32, 33]:

$$V_{\rm FH}(r) = V_{\rm LJ}(r) + \frac{\hbar^2}{24\mu k_{\rm B}T} \left[V_{\rm LJ}''(r) + \frac{2}{r} V_{\rm LJ}'(r) \right], \quad (2)$$

where \hbar , $k_{\rm B}$, and T are the Dirac constant, the Boltzmann constant, and temperature, respectively, and $\mu = m/2$ is reduced mass of a pair of interacting fluid molecules.

The FH effective potential is applicable to systems under usual densities and $\lambda_{\rm B}^* \leqslant 0.5 \ (\lambda_{\rm B}^* = \hbar/(mk_{\rm B}T\sigma^2)^{1/2}),$ where *m* and σ are the mass and size of the fluid molecule, respectively [32, 33]. The λ_B^* value of H₂ at 77 K is 0.47, so that the FH method should be identical to the rigorous path integral method at 77 K. Though the FH method cannot reproduce an exact quantum behavior of hydrogen isotopes at 40 K ($\lambda_{\rm B}^*$ = 0.65 for H₂), we examined the applicability of the FH method at 40 K by comparing adsorption isotherms of H₂ on a slit-shaped graphite model (the physical width defined as the internuclear distance between graphite walls was set as 0.74 nm) using the FH method and the rigorous path integral method [31] (see supporting information available at stacks.iop.org/JPhysCM/22/334207/mmedia). The adsorption isotherm simulated by the FH method shows good agreement with that of the rigorous path integral method. The FH method is applicable, even at 40 K, as far as adsorption isotherms of the quantum fluids are concerned.

3.2. Solid-fluid interaction potentials

For hydrogen–SWCNT interaction potentials, we assumed that a SWCNT can be modeled as an infinitely long cylindrical tube with a smooth wall. Solid–fluid interaction potentials based on the classical LJ potential for the internal and external sites of SWCNT can be calculated by integrating the pairwise LJ potential (equation (1)) over the infinitely long tube. For the internal site of a SWCNT, the interaction potential is given by [34]

$$V_{\rm LJ}^{\rm endo}(r, R) = \pi^2 \rho_{\rm s} \varepsilon_{\rm sf} \sigma_{\rm sf}^2 \left[\frac{63}{32} \frac{F(-4.5, -4.5, 1.0; \beta^2)}{[R^*(1-\beta^2)]^{10}} - 3 \frac{F(-1.5, -1.5, 1.0; \beta^2)}{[R^*(1-\beta^2)]^4} \right].$$
(3)

For the external site of a SWCNT, the interaction potential is given by:

$$V_{\rm LJ}^{\rm exo}(r,R) = \pi^2 \rho_{\rm s} \varepsilon_{\rm sf} \sigma_{\rm sf}^2 \left[\frac{63}{32} \frac{\delta^{11} F(-4.5, -4.5, 1.0; \delta^2)}{[R^*(1-\delta^2)]^{10}} - 3 \frac{\delta^5 F(-1.5, -1.5, 1.0; \delta^2)}{[R^*(1-\delta^2)]^4} \right], \tag{4}$$



Figure 1. A schematic of the bundled SWCNT model. σ_{ss} and d_t indicate the van der Waals gap and tube diameter, respectively. $\sigma_{ss} = 0.34$ nm and $d_t = 1.356$ and 1.491 nm for the (10, 10) and (11, 11) SWCNTs, respectively, were used for the GCMC simulation.

where $F(\alpha, \beta, \gamma; \chi)$ is the hypergeometric function; *R* is the radius of a SWCNT; ρ_s is the density of solid atoms in the tube wall; $\beta = R/r$, $\delta = r/R$, and $R^* = R/\sigma_{sf}$. The quantum hydrogen–SWCNT interaction potential, obtained by integrating the pairwise FH effective potentials, is given by

$$V_{\rm FH}^{\rm endo}(r,R) = V_{\rm LJ}^{\rm endo}(r,R) + \pi^2 \rho_{\rm s} \varepsilon_{\rm sf} \left(\frac{\hbar^2}{mk_{\rm B}T}\right) \\ \times \left[\frac{2541}{256} \frac{F(-5.5, -5.5, 1.0; \beta^2)}{[R^*(1-\beta^2)]^{12}} - \frac{25}{8} \frac{F(-2.5, -2.5, 1.0; \beta^2)}{[R^*(1-\beta^2)]^6}\right]$$
(5)

and

$$V_{\rm FH}^{\rm exo}(r,R) = V_{\rm LJ}^{\rm exo}(r,R) + \pi^2 \rho_{\rm s} \varepsilon_{\rm sf} \left(\frac{\hbar^2}{mk_{\rm B}T}\right) \\ \times \left[\frac{2541}{256} \frac{\delta^{13} F(-5.5, -5.5, 1.0; \delta^2)}{[R^*(1-\delta^2)]^{12}} - \frac{25}{8} \frac{\delta^7 F(-2.5, -2.5, 1.0; \delta^2)}{[R^*(1-\delta^2)]^6}\right], \tag{6}$$

for the internal and external sites of a SWCNT, respectively.

Solid–fluid interaction parameters σ_{sf} and ε_{sf} were obtained with the Lorentz–Berthelot combining rules:

$$\sigma_{\rm sf} = \frac{\sigma_{\rm ff} + \sigma_{\rm ss}}{2}, \qquad \varepsilon_{\rm sf} = \sqrt{\varepsilon_{\rm ff}\varepsilon_{\rm ss}}.$$
 (7)

The LJ interaction parameters used for carbon atom in this study were $\sigma_{ss} = 0.34$ nm and $\varepsilon_{ss}/k_B = 28.0$ K. We used $\mu = m$ for the quantum interaction between hydrogen and carbon atoms because we assumed that the carbon atoms in the SWCNT wall are linked together rigidly.

3.3. Simulation details

The grand canonical Monte Carlo (GCMC) method [35] was used to simulate H_2 and D_2 adsorption on three adsorption sites



Figure 2. TEM images of (a) LA-SWCNT and (b) SG-SWCNT. The insets show the diameter distribution histogram of the SWCNT samples obtained by TEM analysis. The solid lines indicate fitting curves of the histograms by a Gaussian function.



Figure 3. Synchrotron XRD patterns of LA-SWCNT and SG-SWCNT. Two-dimensional indices hk, which are characteristic of a triangular lattice SWCNT bundle, are explicitly observed for LA-SWCNT. The Bragg peak denoted by the asterisk is assigned to the 002 reflection of graphite. Q is the amplitude of a scattering wavevector given by $(4\pi \sin \theta)/\lambda$, where λ and 2θ are the x-ray wavelength and the scattering angle, respectively.

(the interstitial, internal, and groove sites) of a homogeneous SWCNT bundle model (figure 1). The GCMC simulations for the hydrogen isotopes adsorption were based on the FH effective potential. The probabilities of a single displacement, creation, and deletion were all set equal to 1/3. The system was equilibrated for 2.5×10^7 Monte Carlo steps, after which data were collected for another 2.5×10^7 steps. The fluid–fluid and solid–fluid interactions were truncated at distances of $5.0\sigma_{\rm ff}$ and $5.0\sigma_{\rm sf}$, respectively. For adsorption on the interstitial and internal sites, periodic boundary conditions were applied only along the tube axis (the *z*-direction). For adsorption on



Figure 4. N₂ adsorption isotherms on LA-SWCNT, oxLA-SWCNT, SG-SWCNT, and oxSG-SWCNT at 77 K.

the groove site [36], two tubes were modeled, and the apex of the tube at the periodically replicated boundary. Since the distance between the axis of two neighboring nanotubes is $(d_t + \sigma_{ss})$, where d_t is the diameter of a SWCNT and σ_{ss} is the van der Waals gap ($\sigma_{ss} = 0.34$ nm), one of the cell boundaries (x-direction) was fixed at this length. The height of the simulation box (y-direction) was set at 4 nm where a reflecting surface was used. Periodic boundary conditions were used in the x-direction and z-direction. The tube length was set to $10\sigma_{\rm ff}$. The GCMC simulations yield an absolute amount adsorbed (N_{abs}) , and thus those were converted to a surface excess adsorption (N_{exc}) for comparison with experimental data. In the present study, the surface excess adsorption was calculated by $N_{\rm exc} = N_{\rm abs} - \rho_{\rm b} V$, where $\rho_{\rm b}$ is the bulk density of gas, and V is the volume of the internal pore spaces of the SWCNT bundle model. The pore volume was estimated by geometric calculation.



Figure 5. α_S plots of N₂ adsorption isotherms on (a) LA-SWCNT and oxLA-SWCNT, (b) SG-SWCNT and oxSG-SWCNT. The solid lines are used to evaluate the pore structure parameters shown in table 1.

The overall adsorption, $n \pmod{g^{-1}}$, on bundled SWCNTs is split into the sum of adsorptions on groove sites, $n_{\text{simul}}^{\text{groove}}$, interstitial sites, $n_{\text{simul}}^{\text{interstitial}}$, and internal sites, $n_{\text{simul}}^{\text{internal}}$ [37, 38];

1

$$n = S_n n_{\text{simul}}^{\text{groove}} + \eta (n_{\text{simul}}^{\text{interstitial}} + n_{\text{simul}}^{\text{internal}})$$
(8)

$${}^{\text{groove, interstitial}}_{\text{simul}} = \sum w_{d_t} n^{\text{groove, interstitial}}_{\text{simul}, d_t}$$
(9)

$$n_{\rm simul}^{\rm internal} = \sum \alpha_{d_t} w_{d_t} n_{\rm simul, d_t}^{\rm internal} \tag{10}$$

where S_n is the external surface area (m² g⁻¹) of the SWCNT sample, η is the purity (mass fraction) of SWCNT, w_{d_t} is the mass fraction of SWCNT, and α_{d_1} is the mass fraction of open-SWCNTs, with diameter d_t , respectively. $n_{\text{simul},d_t}^{\{\text{groove, interstitial}\}}$ and $n_{\text{simul},d_t}^{\text{internal}}$ are the simulated excess adsorptions on groove or interstitial sites and internal sites, respectively, of a homogeneous bundle of a SWCNT diameter d_t . In this study, we chose the (10, 10) and (11, 11) SWCNTs of which diameters are $d_t = 1.356$ and 1.491 nm. The diameters are close to that evaluated for LA-SWCNT. The summations in equations (9) and (10) were taken over $d_t = 1.356$ and 1.491 nm. S_n , η , w_{d_t} , and α_{d_t} are the fitting parameters in order to reproduce an experimental adsorption isotherm by the least-squares method. For the groove site, the unit of adsorption amount is $mmol m^{-2}$, and for the interstitial and internal site, the unit of adsorption amount is mmol g^{-1} . We neglected the relatively large interstitial site arising from packing defects [36, 39].

In the grand canonical ensemble, volume, temperature, and adsorbate chemical potential are fixed, and thus we need to obtain the pressure of the bulk fluid as a function of the chemical potential at the same temperature to compare with experimental isotherms. In this study, we also performed Monte Carlo simulations with the FH effective potential in the canonical ensemble (FH-MC), which was combined with the Widom test particle insertion method [40] to determine the excess chemical potentials of the quantum hydrogen isotopes at 77 and 40 K. Pressure of the quantum hydrogen isotopes was calculated simultaneously during the FH-MC simulations.

4. Results and discussion

4.1. Characterization of the entangled structure of SWCNTs

Figure 2 shows TEM images of LA-SWCNT and SG-SWCNT. Mean diameters evaluated by the TEM analysis are 1.37 ± 0.25 nm and 2.85 ± 0.72 nm for LA-SWCNT and SG-SWCNT, respectively. As can be seen in the TEM images, LA-SWCNTs are well associated with each other, while SG-SWCNTs do not have an ordered bundle structure, but an irregular one. The irregular assembly of SG-SWCNT is attributed to presence of geometrical defects as well as its broad diameter distribution. The TEM analysis of SG-SWCNT reveals that the tube walls are geometrically more defective than those of LA-SWCNT; the defects in SG-SWCNT hinder a well-associated structure. It is expected that SG-SWCNT has defect-induced adsorption fields between the tubes comprising an assembly. The defect-induced pores are distinguishable from the one-dimensional interstitial sites.

Figure 3 shows synchrotron XRD patterns of LA-SWCNT and SG-SWCNT. An XRD pattern of a trigonally packed SWCNT bundle, which is composed of a narrow diameter distribution, shows a characteristic diffraction pattern assignable to a two-dimensional triangular lattice of SWCNTs [41]. While the XRD pattern of LA-SWCNT shows the characteristic Bragg peaks, which can be assigned to the two-dimensional lattice of bundled SWCNTs, the characteristic Bragg peaks are absent in the XRD pattern of SG-SWCNT. It indicates that the entangled structure of SG-SWCNT is irregular and the assembly of SG-SWCNTs does not form any bundle structure such as seen in LA-SWCNT. The XRD pattern of SG-SWCNT also suggests a wide diameter distribution for the SG-SWCNT sample. The above insight is also confirmed by a mean diameter estimation from TEM observation, such as 1.37 nm and 2.85 nm [22] for LA-SWCNT and SG-SWCNT, respectively. The tube diameter of SG-SWCNT is distributed from 1 to 5 nm [22], therefore the diameter distribution of SG-SWCNT is much broader than that of LA-SWCNT.



Figure 6. Annealing effect of RBM frequency and the corresponding tube diameter for (a) the annealed LA-SWCNTs acquired with 2.33 eV (532 nm) excitation, (b) those acquired with 1.96 eV (632.8 nm) excitation, (c) and (d) are depicted for the annealed SG-SWCNTs acquired with 2.33 and 1.96 eV excitations, respectively. The dotted lines indicate RBM peak centers of the unannealed samples.

Figures 4 and 5 show N₂ adsorption isotherms and corresponding α_S plots, respectively, on LA-SWCNT, oxLA-SWCNT, SG-SWCNT, and oxSG-SWCNT at 77 K. The α_S plot is a comparison plot to a standard adsorption isotherm, providing pore structural information of a sample. Carbon black (#32b, Mitsubishi Kasei Co.), of which the geometrical surface can be regarded as a flat surface, is used for the standard sample in this study, so that a deviation of the α_S plot from linearity can be ascribed to a difference of adsorption field from that of the flat surface. Pore structure parameters evaluated by the BET and SPE methods [42] are summarized in table 1. It can be clearly seen in figure 4 that the oxidation treatments of both LA-SWCNT and SG-SWCNT enhance the adsorption amount of N₂, indicating that the accessible space

for N₂ is increased, mainly by the cap-removal. It results in an increase of the total surface area, a_{total} ; 4.7 and 1.8 times as large as LA-SWCNT and SG-SWCNT, respectively, are obtained by the oxidation treatments (table 1). The socalled f-swing is observable in the α_s plot of oxLA-SWCNT, resulting from the strong interaction potential field due to the internal site of SWCNTs. oxSG-SWCNT also shows a slight f-swing, however it is less prominent than that of oxLA-SWCNT. This can be ascribed to a difference of mean diameter between LA-SWCNT and SG-SWCNT; the narrower the diameter, the stronger the interaction potential field. An intriguing fact is that the α_s plots of both SG-SWCNT and LA-SWCNT show linearity, indicating that most of the accessible area for N₂ is regarded as a nearly flat surface. Since LA-



Figure 7. H₂ and D₂ adsorption isotherms at 40 K on (a) LA-SWCNT and oxLA-SWCNT, (b) SG-SWCNT and oxSG-SWCNT.



Figure 8. H₂ and D₂ adsorption isotherms at 77 K on (a) LA-SWCNT and oxLA-SWCNT, (b) SG-SWCNT and oxSG-SWCNT.

SWCNTs form a well-bundled structure, which is evidenced by the TEM observation and the XRD pattern, the effective pore width of the interstitial sites can be estimated by the simple triangular lattice model; the effective pore width of the interstitial sites is ~ 0.45 nm for the (10, 10) SWCNT, of which the diameter is 1.37 nm (see supporting information available at stacks.iop.org/JPhysCM/22/334207/mmedia). This value is comparable to the classical size parameter of the N2 molecule $(\sigma_{\rm ff} = 0.3615 \text{ nm})$ [43]. The linear α_S plot of LA-SWCNT is explained by the steric exclusion of the N2 molecules against the interstitial site. Almost all the N2 molecules are adsorbed only on the external surface of the bundle; the groove sites do not have a deep interaction potential well for N2. For SG-SWCNT, the total surface areas ($a_{\text{total},\text{BET}} = 1190 \text{ m}^2 \text{ g}^{-1}$ and $a_{\text{total}} = 1010 \text{ m}^2 \text{ g}^{-1}$) are close to the geometrical surface area of a free-standing, closed-cap SWCNT (1380 m² g⁻¹) for an external surface of the (21, 21) SWCNT, of which the diameter is 2.85 nm (see supporting information available at stacks.iop.org/JPhysCM/22/334207/mmedia). It implies that

Table 1. Pore structure parameters of the SWCNT samples.

Sample	$a_{\text{total,BET}}$ ^a	$a_{\text{total}} ^{b}$	a_{ext}^{b}	v_p^{b}
	(m ² g ⁻¹)	(m ² g ⁻¹)	(m ² g ⁻¹)	(ml g ⁻¹)
LA-SWCNT oxLA-SWCNT SG-SWCNT oxSG-SWCNT	300 1100 1190 1920	300 1430 1010 1850	450 — 830	0.28

^a Total surface area evaluated by the BET method.

^b a_{total} , a_{ext} , and v_{p} are the total surface area, external surface area, and micropore volume evaluated by the SPE method.

each SG-SWCNT comprising the assembly does not tightly compact each other and most of the external surface is exposed to N₂ molecules, so that the α_S plot turns out to be almost linear.

The entangled structure and tube diameter distribution play an important role for the coalescence of SWCNTs induced by an annealing treatment under vacuo [44–46]. Coalescence



Figure 9. Simulated H_2 adsorption isotherms on the (10, 10) and (11, 11) SWCNT bundles at 40 K. The adsorption isotherms contributed from the groove, internal, and interstitial sites are distinctly shown. The integrated adsorption isotherms of the individual sites (denoted as Total) are also shown by the heavy solid and dotted lines for the (10, 10) and (11, 11) SWCNT bundles, respectively. The horizontal axis is denoted by (a) linear and (b) logarithmic scales.

of SWCNTs starts at a temperature higher than \sim 1600 K, leading to transformations to multi-wall carbon nanotube and graphitic structures at much higher temperatures (<2000 K). Since the frequency of the Raman-active Ag mode, the so-called radial breathing mode (RBM), inversely correlates to tube diameter [47], the effect of RBM frequencies against annealing temperature is examined. Figure 6 shows Raman spectra obtained with excitation energies of 1.96 eV (632.8 nm) and 2.33 eV (532 nm) in the RBM frequency region of the annealed LA-SWCNT and SG-SWCNTs at 1773, 1873, 1973, 2073, and 2273 K. The upper horizontal axis shown in figure 6 indicates the tube diameter evaluated by the following equation;

$$\omega_{\rm RBM} = \frac{a}{d_{\rm t}} + b, \tag{11}$$

where $a \pmod{m}$ and $b \pmod{-1}$ are the coefficients that depend on environment which SWCNTs undergoes, and ω_{RBM} (cm^{-1}) and d_t (nm) are the RBM frequency and tube diameter, respectively. The coefficients a = 248 [48] and 227 [49] were used for LA-SWCNT and SG-SWCNT, respectively (for both samples, b = 0). The coefficient *a* for SG-SWCNT is close to that evaluated for a free-standing SWCNT [49, 50], agreeing with the results by nitrogen adsorption isotherms that assembled structures of SG-SWCNTs are not as tightly associated as that of LA-SWCNTs. For the RBM frequencies of LA-SWCNTs obtained by 2.33 eV excitation, the peak centered at $\sim 170 \text{ cm}^{-1}$ for unannealed LA-SWCNT shows a slight red shift on annealing at temperatures higher than 1773 K, and the peak intensity at 185 cm⁻¹ decreases as the annealing temperature increases. On the other hand, the Raman spectral feature around the RBM frequency of SG-SWCNTs is invariant until the annealing temperature reaches 1873 K. It indicates that LA-SWCNTs of relatively small diameter probably build into much larger tube due to their tightly packed bundle structure, for which intertubular C-C bonding may be easily induced by annealing treatment at the appropriate temperatures. The same tendency is observed for the RBMs obtained by the 1.96 eV excitation.

Consequently, the entangled structure of LA-SWCNT is very trigonally associated, forming bundles, whereas SG-SWCNT has a loosely-assembled structure, being almost separated from each other.

4.2. H_2 and D_2 adsorption on SWCNTs

Figures 7 and 8 show H₂ and D₂ adsorption isotherms on LA-SWCNT, oxLA-SWCNT, SG-SWCNT, and oxSG-SWCNT at 40 and 77 K, respectively. Irrespective of the SWCNT samples, the experimentally obtained adsorption amounts of D2 are larger than those of H₂ for every sample at 40 and 77 K. This phenomenon cannot be explained by the classical interaction potential theory, because it does not take into account any factor of mass or temperature. It is most likely ascribed to the quantum effect, which can be described by the Feynman-Hibbs effective potential shown in equation (2). It should be noted that the difference of the adsorbed amount is still observable at 77 K, indicating that the quantum effect plays an important role even at 77 K. It is expected that the unique entangled structures of LA-SWCNT and SG-SWCNT evidenced in section 4.1 should affect the adsorption behavior of H₂ and D₂. Therefore, these should be considered previous to discussion of H₂/D₂ selectivity. In order to provide further adsorption properties of H₂ and D₂ on the entangled structures of the SWCNTs, we examine the adsorption isotherms shown in figures 7 and 8 with the aid of the GCMC simulation results adopting the quantum effect.

As can be seen in figure 7, all adsorption isotherms of H_2 and D_2 at 40 K are Langmuirian, implying the presence of strong adsorption fields inducing micropore filling. It is worthwhile normalizing the adsorption amounts of H_2 at 0.1 MPa, n_{ad} , by the surface areas $(n_{ad}/a_{total} =$



Figure 10. Configurational snapshots collected from the GCMC simulated H₂ adsorption isotherms on the (10, 10) and (11, 11) SWCNT bundles at 40 K. Each lateral snapshot is highlighted on three adsorption sites; the interstitial, internal, and groove sites at the given pressures in (a)–(e). (a) $P = 10^{-8}$ MPa, (b) $P = 10^{-6}$ MPa, (c) $P = 10^{-4}$ MPa, (d) $P = 10^{-2}$ MPa, (e) $P = 10^{-1}$ MPa. (This figure is in colour only in the electronic version)

 $N_{\rm nor} \, \text{mmol} \, \text{m}^{-2}$), such that they are 0.016, 0.0099, 0.012, 0.014 mmol m⁻² for LA-SWCNT, oxLA-SWCNT, SG-SWCNT, and oxSG-SWCNT, respectively. The corresponding ratios of D₂ are 0.018, 0.011, 0.014, 0.016 mmol m⁻² for LA-SWCNT, oxLA-SWCNT, SG-SWCNT, and oxSG-SWCNT, respectively. Since the internal and interstitial sites of oxLA-SWCNT are accessible for the molecules, $N_{\rm nor}$ values, both of H₂ and D₂, for oxLA-SWCNT should be larger than those of LA-SWCNT due to the micropore filling in the internal and interstitial sites. However, both N_{nor} values of H₂ and D₂ for oxLA-SWCNT are smaller than those of LA-SWCNT by $\sim 40\%$. This can be attributed to pore-blocking in the vicinity of the entrance of the internal sites after completion of the monolayer adsorption and/or restricted diffusion of the molecules [3, 51]. On the contrary, oxSG-SWCNT shows a slight increase of the N_{nor} values, both of H₂ and D₂, from those of SG-SWCNT. The increase of the $N_{\rm nor}$ values are 17 and 14% for H₂ and D₂ adsorptions, respectively. It is plausible that the internal sites of oxSG-SWCNT are sufficiently accessible for the molecules. This can be ascribed to the difference of tube diameter for LA-SWCNT and SG-SWCNT; the mean diameters are 1.37 nm and 2.85 nm for LA-SWCNT and SG-SWCNT, respectively. OxLA-SWCNT has very strong adsorption sites in the internal tube spaces and the preadsorbed H₂ molecules near the pore entrance block further adsorption. The pore-blocking mechanism is rationalized by GCMC simulation of H₂ at 40 K, as shown in figure 9. A bundle of the (10, 10) SWCNTs and that of the (11, 11) SWCNTs, of which diameters are 1.356 and 1.491 nm, respectively, are used as the model structures of LA-SWCNT. Simulated adsorption isotherms of H₂ on three adsorption sites, that is, the interstitial site (denoted as Interstitial), internal site (Internal), groove site (Groove), and a sum of the individual sites (Total) are distinctly shown in figure 9. Corresponding configurational snapshots are depicted in figure 10. Adsorption on the interstitial site starts from $P = 10^{-9}$ MPa and $P = 10^{-6}$ MPa for the (11, 11) SWCNTs and the (10, 10) SWCNTs, respectively. It indicates that the interstitial site has the largest adsorption energy compared to other adsorption sites of the SWCNT bundles. As can be seen



Figure 11. Fitting of the simulated (a), (c) H_2 and (b), (d) D_2 adsorption isotherms at 40 K to experimental results for (a), (b) LA-SWCNT and (c), (d) oxLA-SWCNT.

around $P \approx 10^{-6}$ MPa, adsorption on the internal pore of the (10, 10) SWCNTs starts at much lower pressure than that of the (11, 11) SWCNTs, due to stronger adsorption field of the (10, 10) SWCNT. Monolayer adsorption is completed up to $P \approx 10^{-4}$ MPa, and filling of H₂ molecules in the internal space advances subsequently. Adsorption on the groove sites also starts from $P \approx 10^{-6}$ MPa, and a monolayer is formed up to $P \approx 10^{-2}$ MPa. Further adsorption on the groove sites proceeds with increasing pressure. According to the snapshot at P = 0.1 MPa, both for the (11, 11) and (10, 10) SWCNTs (figure 10), the size of the residual one-dimensional space of the monolayer adsorbed internal tube-space just fits a single H₂ molecule; inducing an intensive pore-blocking effect in oxLA-SWCNT at 40 K. The N_{nor} values of H₂ at 77 K are 0.0060, 0.0057, 0.0059, 0.0064 mmol m⁻² for LA-SWCNT, oxLA-SWCNT, SG-SWCNT, and oxSG-SWCNT, respectively. The $N_{\rm nor}$ values of D₂ at 77 K are 0.0064, $0.0062, 0.0063, 0.0070 \text{ mmol m}^{-2}$ for LA-SWCNT, oxLA-SWCNT, SG-SWCNT, and oxSG-SWCNT, respectively. The pore-blocking effect, even at 77 K, is still effective for oxLA-SWCNT.

Here GCMC simulated adsorption processes of H_2 and D_2 in the interstitial and internal sites, and on the groove sites

of the SWCNTs are compared with the experimental results on LA-SWCNTs and oxLA-SWCNTs. The GCMC simulated adsorption isotherms on the (10, 10) and (11, 11) SWCNTs in the bundle forms are used for comparison. Figures 11 and 12 show the experimental and simulated adsorption isotherms, which are fitted to the corresponding experimental adsorption isotherms, of H₂ and D₂ at 40 K and 77 K, respectively. Each simulated adsorption isotherm consists of three adsorption processes on the interstitial, internal, and groove sites. Though the simulated H₂ adsorption isotherms agree well with the experimental one both for LA-SWCNT and oxLA-SWCNT at 77 K, the simulation gives an overestimation around P = 10^{-5} - 10^{-4} MPa and an underestimation around $P = 10^{-7}$ -10⁻⁵ MPa at 40 K for LA-SWCNT and oxLA-SWCNT, respectively. Adsorption on the interstitial and internal sites occurs in the pressure ranges corresponding to these discrepancies. The overestimation for LA-SWCNT can be assigned to the pore-blocking effect, which in principle cannot be reproduced by GCMC simulation. The underestimation for oxLA-SWCNT should stem from the simple model of the cap-removal for opening the internal tube sites. It is well known that some geometrical defects, the so-called topological defects [52, 53], on the tube parts can be easily oxidized



Figure 12. Fitting of the simulated (a), (c) H_2 and (b), (d) D_2 adsorption isotherms at 77 K to experimental results for (a), (b) LA-SWCNT and (c), (d) oxLA-SWCNT.



Figure 13. Selectivity of D_2 over H_2 *S* (D_2/H_2) at 40 K evaluated from (a) the experimental adsorption isotherms and (b) the GCMC simulated adsorption isotherms. Selectivities contributed from the groove, internal, and interstitial sites are distinctly shown with those evaluated from the integrated adsorption isotherms.



Figure 14. Selectivity of D_2 over $H_2 S (D_2/H_2)$ at 77 K evaluated from (a) the experimental adsorption isotherms and (b) the GCMC simulated adsorption isotherms. The selectivities contributed from the groove, internal, and interstitial sites are distinctly shown with those evaluated from the integrated adsorption isotherms.

to provide nano-scale holes on the graphene wall [54]; the internal sites around the nano-scale holes should have deeper interaction potential wells for H_2 and D_2 . Accordingly, the bundle structure of oxLA-SWCNT has more intensive internal sites than the defect-free SWCNT model. The presence of defects, which is not taken into account in the simulation, can also explain a difference in the shapes of the experimental adsorption isotherms at 40 and 77 K; adsorption on the defect sites is less emphasized at 77 K, resulting in accordance with the simulated results, while enhanced filling near the defect sites is pronounced at 40 K.

4.3. Selectivity of D₂ over H₂ on SWCNTs

In order to predict the selectivity of D_2 over H_2 , S (D_2/H_2), both for the experimental and simulated results at 40 and 77 K, the ideal adsorption solution theory (IAST) [55] is applied to the single-component adsorption isotherms on LA-SWCNT, oxLA-SWCNT, SG-SWCNT and oxSW-SWCNT. The IAST provides approximate selectivities for a multicomponent system. However, it is applicable to estimate the selectivity of D_2 over H_2 for nanotube systems in good accordance with that evaluated from a binary mixture at moderate pressure, as discussed in detail by Challa *et al* [10]. We also discussed the accuracy of S (D_2/H_2) at 77 K by comparing with those predicted for a binary mixture and those predicted for a single-component system by using the FH-GCMC method; the deviations were less than 1.7% at low pressures [17].

A 1:1 concentration of the mixture of H₂ and D₂ in the bulk phase is assumed in the *S* (D₂/H₂) calculations. The detailed evaluation method of *S* (D₂/H₂) is described in the supporting information (available at stacks.iop.org/JPhysCM/ 22/334207/mmedia). Figures 13 and 14 show *S* (D₂/H₂) around $P = 10^{-5}-10^{-3}$ MPa for the experimental and simulated adsorption isotherms at 40 K and 77 K, respectively. The *S* (D₂/H₂) values of the unoxidized SWCNT samples

are larger than those of the oxidized ones, both at 40 and 77 K, because of the further contribution of adsorption on the interstitial sites at $P = 10^{-5} - 10^{-3}$ MPa. For example, S (D_2/H_2) values at 40 K for the (10, 10) SWCNT on the interstitial sites are larger than 10, on the other hand, those predicted for the integrated adsorption isotherms are This is because the internal and groove sites, of ~ 3 which the selectivities are much more moderate than those of interstitial sites, lower the intense selectivities as expected for the interstitial sites alone [2, 9, 10]. Experimental S (D₂/H₂) values of oxLA-SWCNT can be compared with those predicted for the simulated results of the integrated isotherms. The experimental S (D₂/H₂) values are lower than those of the (10, 10) and (11, 11) SWCNTs around $P = 10^{-5} - 10^{-3}$ MPa, both at 40 and 77 K, indicating the pore-blocking effect, which is expected to reduce the selectivities as predicted from the GCMC simulations. Since the simulations are conducted for the homogeneous SWCNT bundles, the simulated S (D₂/H₂) curves against pressure can be compared with oxLA-SWCNT, of which the bundle structure is similar to the model. The S (D₂/H₂) curves of SG-SWCNT cannot be simply ascribed to the simulated results because the assembled structures are hardly described by a simple model.

The highest *S* (D₂/H₂) curve among the experimental results is obtained for SG-SWCNT at 40 K. The maximum value of *S* (D₂/H₂) = 5 is obtained at $P = 10^{-5}$ MPa from which the *S* (D₂/H₂) gradually decreases, reaching *S* (D₂/H₂) = 3 at $P = 10^{-3}$ MPa. It is worth noting that the *S* (D₂/H₂) curve of SG-SWCNT is still observable even at 77 K, and more prominent than those of the other samples. *S* (D₂/H₂) = 3.8 at $P = 10^{-5}$ MPa is obtained for SG-SWCNT at 77 K, exceeding the simulated *S* (D₂/H₂) value for the interstitial sites of the (10, 10) SWCNT. Although the *S* (D₂/H₂) curve of SG-SWCNT at 40 K is far from the simulated curve of the (10, 10) SWCNT, it is comparable to that of the (11, 11) SWCNT. We deduce that strong potential sites, of which the effective pore widths should incorporate H₂

and D₂ while excluding N₂, are present in the assembly of SG-SWCNTs; diffusion of H₂ and D₂, even in such narrow sites, could proceed without the pore-blocking effect. On the other hand, the interstitial sites of LA-SWCNT, which are expected to exhibit a high selectivity, show a serious pore-blocking effect, as mentioned above. An exact structural model for the SG-SWCNT assembly remains unclear. However, topological defects, which are believed to be present in the SWCNT surface and induce, for example, kink structures in the straight wall of a SWCNT, could form some strong adsorption fields in the SG-SWCNT assembly. Furthermore, the calculated cohesive energy of a hydrogen atom on a so-called Stone-Thrower-Wales defect [56, 57], a kind of topological defect composing of pentagonal and heptagonal rings of carbon atoms, is lower than that of a hexagonal one [58]. The presence of these defects and the loosely packed assembly structure may play an important role in the high selectivity on the SG-SWCNT assembly.

5. Conclusion

We clearly verified the quantum molecular sieving effect on SWCNT with low temperature adsorption measurements and molecular simulations of H₂ and D₂. The entangled structure of LA-SWCNT is categorized as the well-ordered bundle form. SG-SWCNT has no well-defined bundle structure; SG-SWCNTs comprising an assembly are loosely associated with each other and strong adsorption fields, probably due to the presence of geometrical defects should enhance adsorption. The H₂/D₂ selectivity at 40 and 77 K was evaluated for LA-SWCNT, oxLA-SWCNT, SG-SWCNT, and oxSG-SWCNT. SG-SWCNT, both at 40 and 77 K, shows the highest selectivity among the samples used in this study. The high selectivity can be explained by its unique assembly structure, such as the loose assembly structure, which facilitates the diffusion of the molecules, and the presence of defects that may introduce strong adsorption fields on the nanotube surface. The low selectivity of LA-SWCNT against the GCMC simulated one is ascribed to the restriction of the diffusion of the molecules into the interstitial site accompanying the pore-blocking effect.

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