A Molecular Dynamics Simulation of Hydrogen Storage with SWNTs

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The mechanism of efficient hydrogen storage (1) with SWNTs (2,3) was studied through classical molecular dynamics simulations. Most of reported molecular simulations (4,5) dealt with the adsorption of hydrogen to fixed SWNTs. Here, the motion of SWNTs connected as a bundle with van der Waals force was taken into account in order to estimate the reasonable adsorption between SWNTs.

Assuming the physical adsorption of hydrogen to the surface of SWNTs, potential forms between H_2-H_2 and C-H_2 were both expressed by Lennard-Jones functions. Each SWNT was regarded as rigid molecule and van der Waals potential between SWNTs was derived as Lennard-Jones (8-4) function by integrating potential between carbon atoms. As shown in Fig.1, 7 SWNTs were placed in a fully periodic system, so that a SWNT exactly continues in the longitudinal direction. The adsorption interior of each SWNT was calculated separately with shorter SWNTs.

During 500 ps simulation for 77K and 15 MPa, the adsorption was observed only outside of bundles as shown in Fig. 2(a). In order to realize the adsorption between SWNTs within reasonable simulation period, the van der Waals potential between tubes was once decreased. By reducing the van der Waals potential to 1/50, the hydrogen molecules rapidly intruded between SWNTs by expanding the bundle of SWNTs as shown in Figs. 2(b) and 2(c). By restoring the van der Waals force, the adsorption structure remained almost unchanged as in Fig. 3(b). The mean distance between SWNTs settled down to about 2.0 nm for (10, 10), and there were 1 or 2 layers of hydrogen molecules between SWNTs. Similar simulations were performed for (8,8) and (12,12) as shown in Fig.3. The number of finally adsorbed hydrogen molecules N_{Aout} is listed in Table 1. Here, N_{Aout} was almost proportional to the number of carbon atoms N_{C}, and the storage amount became about 5 wt % regardless of the tube radius. The number of absorbed hydrogen molecules in exterior of SWNTs was simply proportional to the exterior surface area of SWNTs.

In order to estimate the adsorption to the tube interior, a bit shorter SWNTs was simulated. Fig. 4 shows the final absorbed structure for about 15 MPa and 77 K. The number of absorbed hydrogen molecules was almost proportional to the volume of interior space as listed in Table 1. While the amount in weight percent of hydrogen adsorption inside SWNTs increased with increasing diameter, adsorption between tubes was almost constant. Total amount of hydrogen adsorption for 77K and 15 MPa system was predicted as 6.9, 7.7, and 8.1 wt % for (8,8), (10,10), and (12,12) bundles, respectively. These predictions were almost consistent with the experimental adsorption amount by Ye et al. (6).

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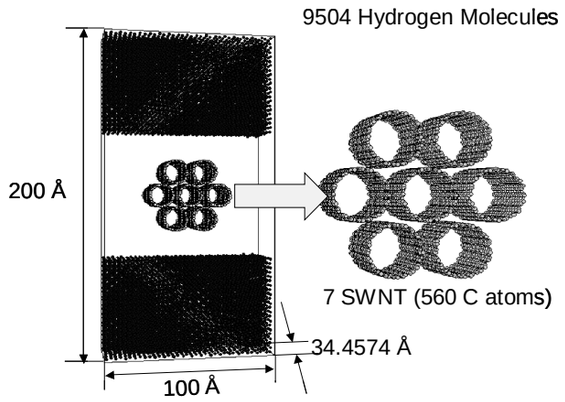
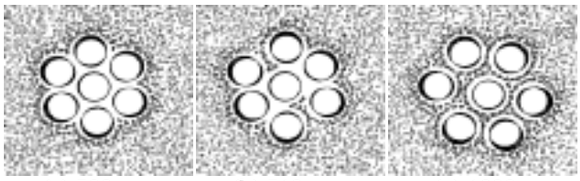
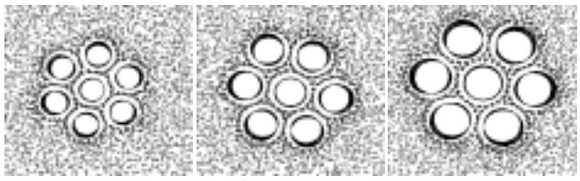


Fig. 1 Initial configuration of a bundle of (10,10) SWNTs.



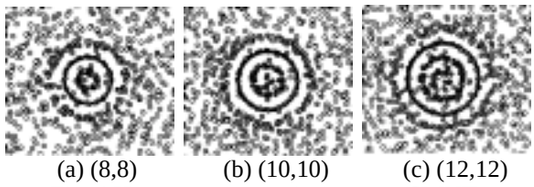
(a) 500 ps (b) 510 ps (c) 1000 ps

Fig. 2 Adsorption of hydrogen molecules between each SWNT. (a) Normal condition, (b), (c) After reducing the van der Waals interaction between SWNTs by 50 times.



(a) (8,8) (b) (10,10) (c) (12,12)

Fig. 3 Adsorption of hydrogen molecules for SWNTs with different diameters.



(a) (8,8) (b) (10,10) (c) (12,12)

Fig. 4 Hydrogen storage inside each SWNT.

Table 1 Final amount of hydrogen adsorption

Tube	p [MPa]	U [eV]	r [Å]	Outside N_{Aout}	Interior $N_{\mathrm{Ain}}/N_{\mathrm{C}}$	Total [wt %]
(8, 8)	15.0	-97.6	16.8	980	32/320C	6.88
(10, 10)	15.1	-105.6	20.0	1240	57/400C	7.65
(12, 12)	15.5	-116.0	22.3	1430	88/480C	8.12