HYDROGEN STORAGE IN HETEROJUNCTION CARBON NANOTUBES: MOLECULAR DYNAMICS STUDY

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Introduction

Hydrogen, a renewable and environmentally friendly energy resource, has drawn much attention in the past decades. Carbon nanotubes (CNTs) have been studied as potential candidates for hydrogen storage [1-3]. On the other hand, simulations have predicted low uptake of hydrogen on idealized SWNTs [4-7]. Y.C Ma et al [8] has explored a valid method to simulate the hydrogen storage in carbon nanotubes, e.g. non-equilibrium method, in which the hydrogen atom was given proper initial energy to collide with the carbon nanotube and high density of hydrogen was trapped into CNT.

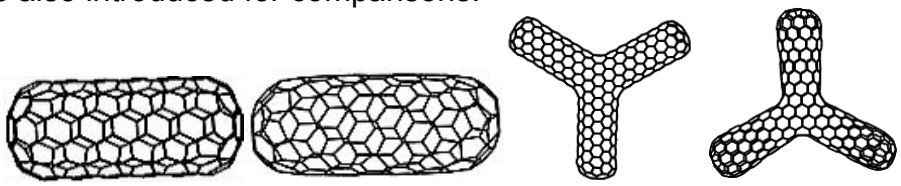
So far, all studies just focus on the straight CNTs, and the results show that the capacity of hydrogen storage depends on the type and morphology of the CNTs to great extent. Y-junction carbon nanotubes (Y-CNTs) have a peculiar morphology that is different from straight CNTs and are available now in large amount [9]. Unfortunately, the potential of using Y-CNTs for storing hydrogen has not been explored yet.

Here Y-CNTs and straight CNTs were introduced for molecular dynamics (MD) simulation studies of hydrogen storage. Topological defects were generated on each CNT or each branch to mimic the vacancy formed by the collision between the hydrogen atom with the CNT by randomly etching holes on CNT or Y-CNT. We hope that our preliminary results from MD simulations will shed some light on hydrogen storage in Y-CNTs in specific and also on the hydrogen storage in straight CNTs in general, thus will draw readership in fields of hydrogen storage and carbon science.

Models and Simulation methods

According to the models on the website (http://cnst.rice.edu), two ideal Y-CNTs were constructed, of which the branches are armchair (6,6) and zigzag (10,0) CNTs, respectively. In all cases, the length from one end to the center of Y-CNT is *ca.* 1.8 nm. For simplicity, they are termed as Y (6,6) and Y (10,0), of which the ends were capped

with half C_{60} and C_{72}. Two straight CNTs, e.g. (6,6) and (10,0) with the length of *ca*. 2.00nm were also introduced for comparisons.



A B C D

Fig.1 The models of ideal CNTS and Y-CNTs optimized with MM method (A - (6,6)(C_{180});B - (10,0)(C_{176}); C - Y (6,6)(C_{582}); D - Y (10,0) (C_{522}))

Fig. 1 shows the structures of two ideal Y-CNTs models and two ideal straight CNTs models optimized with molecular mechanics (MM) method. Topological defects were generated on the sidewall, on the pentagon of the top and on the heptagon of the crossing regions on each straight CNT and each branch of Y-CNTs. Therefore, there is one hole on one single CNT, but three holes on one single Y-CNT. Based on the structures with defects, molecular dynamics (MD) simulations were performed using *DISCOVER* module in *MATERIALS STUDIO* program package [10] to investigate the capability of hydrogen storage in each tube. *PCFF* forcefield, which is implemented in the program, is used. Unlike the previous work [4,6,7] in which the hydrogen molecules were treated as single-point structure less spherical particles, explicit atom model was used in the present study. The forcefield applied in the simulation studies use the Lennard-Jones (L-J) potential to describe the non-bonded interactions. And the deformations of Y-CNTs were allowed during the simulations. For each system studied in the present work, its structure was optimized before the main MD simulations, which makes the system's energy to be reduced to a minimum on the potential energy surface. The time step was taken as 1 fs for all MD simulations. *NVT* ensembles were adopted for simulations, where *N* represents the number of atoms, *V* is volume and *T* is temperature.

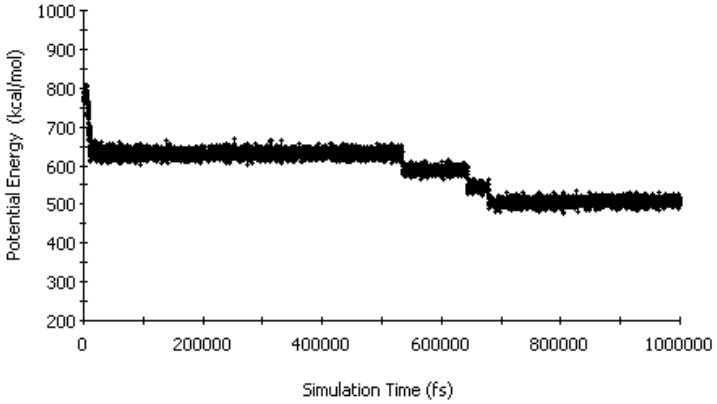


Fig.2 Relationship between the potential energy and the simulation time during the MD simulations about the hydrogen storage in straight (5,5) CNT after 1 ns at 298 K

Results and discussion

Firstly, MD simulations about the hydrogen storage in (5,5) CNTs (C_{180}) with etching hole

on the sidewall were performed to make a comparison with the literature [8]. It is found that the maximum number of hydrogen molecules in (5,5) CNTs is 44 at room temperature after 1ns, and the energy curve shown in Fig.2 is flat, indicating the system has reach the equilibrium state. The hydrogen amount is about 4.1%, which is close to the literature (*ca.* 4.7%) [8]. Similar simulations were carried out to examine the maximum number of H_2 molecules in Y-CNTs and straight CNTs with defects at 298 K and 80 K. The maximum number of hydrogen molecules and the weight percent of hydrogen (the ratio of the weight of hydrogen atom and carbon atom) for all cases were listed in Table 1.

Table 1 Maximum amount of H_2 in CNTs and Y-CNTs with defects at 298 K and 80 K

	298K			80K		
	Walll	Top	Connection	Wall	Top	Connection
(6,6) C_{180}	50	52		64	72	
wt%	4.63	4.81		5.93	6.67	
(10,0) C_{176}	50	51		61	66	
wt%	4.73	4.83		5.78	6.25	
Y (6,6) C_{582}	257	295	203	303	322	222
wt%	7.36	8.45	5.81	8.68	9.22	6.36
Y (10,0) C_{522}	220	241	186	258	278	225
wt%	7.02	7.69	5.94	8.24	8.88	7.18

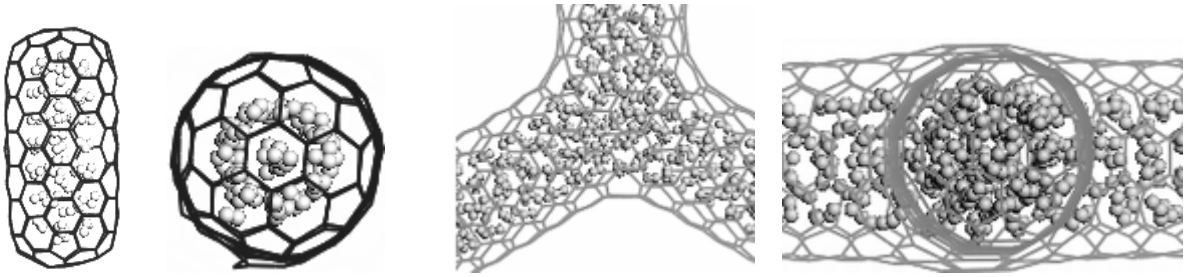


Fig.3 Side and top view of (6,6) and Y(6,6) carbon nanotube filler with hydrogen molecules after 500ps at room temperature

It can be clearly seen from Table 1 that the high density of hydrogen can be confined into (6,6) and (10,0) as well as Y (6,6) and Y (10,0) even at room temperature. The lower temperature can greatly increase the hydrogen content in these tubes, implying that the lower temperature favors to the hydrogen storage. It is surprised to find that hydrogen density in Y-CNTs is much higher than in straight CNTs. In other words, the hydrogen content will be significant increased when three straight CNTs were connected to form a Y-CNT. It might be due to the stable triangular structure of Y-CNTs. Here one thing should be mentioned that the hydrogen content in Y-CNTs with smaller diameter such as Y (4,4) is much lower. Therefore, Y-CNTs with larger diameter are necessary for hydrogen storage. It seems that the hydrogen content in the tubes with defects on the top is the highest but the lowest when the defect is on the connection. The chirality has no significant effect on the hydrogen density. It should be noted that hydrogen molecules

both in Y-CNTs and CNTs diffused along the branches and distributed uniformly during the simulations as can be seen in Fig.3, which is consistent with the literature [8,11]. It suggests that it is difficult for hydrogen molecules to adsorb to the inner wall of the tube, which makes some agreements with the literature [12]. The simulation results mentioned above make one to believe that high density of hydrogen molecules may be trapped in these tubes when the implanting method [8] is used, especially in Y-CNTs.

Conclusions

Comparative studies about the hydrogen storage in two Y-CNTs and two straight CNTs with defects of different positions were performed to investigate the potential of hydrogen storage in Y-CNTs by using molecular dynamics simulations. It is found that high density of hydrogen will be confined both in straight CNTs and Y-CNTs with defect of proper size. The hydrogen density in Y-CNTs is much higher than that in straight tubes, implying that Y-CNTs may be of potential for hydrogen storage. Furthermore, it seems that hydrogen content in CNTs with defect on the top is higher than on the wall or on the connection. The chirality of CNTs has no significant effect on the hydrogen density both in straight CNTs and Y-CNTs. In addition, the lower temperature is favorable for the hydrogen storage.

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