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Simulation Studies of the Damaging Effect of Molecular Hydrogen gas on Double Walled Carbon Nanotubes

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ABSTRACT

The hydrogen damage in the double walled carbon nanotubes (DWCNTs) was studied through molecular simulation.The simulation performed in the measuring domain has the dimensions of about 20×20×13 A. Our calculations revealed that the partial pressure of the hydrogen gas between the two walls is 180 atm and this pressure is equal to hydrogen density of 7.6 mol/L.This simulation procedure showed that the partial amount of the hydrogen molecules gas at first dissociated and then penetrate to the external wall of DWCNT.This approach is similar to hydrogen embrittlement on metals surface.

Key words: Double Walled Carbon Nanotubes, Molecular, Measuring domain.

INTRODUCTION

Recently different storage technologies have been explored to develop a secure and cheap method to save hydrogen[1,2].Undoubtedly, the surface texture of carbonaceous materials is one of the mostimportant factors for hydrogen storage.Pores with two or three times the diameter of a hydrogen molecule were illustrated as the optimum dimension for hydrogen storage, because high gas density was acquired in the fine pores from the calculated results[3-7].

Carbon nanotubes are novel carbonswhich attracted great interest among the scientific society owing to a wide range of characteristicsincluding electronic, mechanical and other properties[8-13].

Nowadays, there has been a good deal of experimental and theoretical interest in the possibility of hydrogen storage in single walled carbon nanotubes (SWNTs), multi-walled carbon nanotubes (MWNTs) as well as carbon nanofibers[14-21].

It is usually approved that the majority of hydrogen adsorbed in SWNTs was physical adsorption on theirinside surface, as well as in the interstitial sites between nanotube bundles[22-28].

It has been found that hydrogen must initially find uncoveredgraphene edges where it dissociates into atomic hydrogen. These sites would then prepare path ways for the atomic hydrogen to migrate inward tooccupy the space between the basic planes[29-35].

This event resembles hydrogen damage in metal structures. Hydrogen damage is a general term which includes: Hydrogen Blistering and Hydrogen Embrittlement. Hydrogen blistering and embrittlement are results of the hydrogen penetration into a metal.The consequence islocal distortion and in extremecases complete destruction of the vessel wall[36-41].

In the past several years various experimental[42,43] and theoretical[44,45] works have been devoted to hydrogen adsorption on carbon nanotubes[46-48].

Considerable researches have been performed about carbon nanotube due to its versatile applications in the fields such as drug delivery[49,50], supercapacitors[51-53],gas adsorption[54-56] chemical[57-59] and electrochemical[60-62] sensors. There are several magnificent books[63-65] and reviews[66-68] that describe synthesis, processing, characterization and applications of carbon nanotubes[69-71].

In the present work the structural damage of double walledcarbon nanotubes when treated with high pressure molecular hydrogen gas have been investigated by simulation approach[72-74].

Molecular gasadsorption simulation

The physisorption of hydrogen was studied in an array fragment including 48 carbons. The investigation was carried out on double walled carbon nanotube with chirality (10, 0),Length 13 A and a=5A, b=10A (a and b are inner and outer radius of cylinder, respectively), Fig.1.

It was assumed that C-H bonds were located on the terminal of carbon nanotube. ThreeH_2molecules were supposed to be located between two walls of carbon nanotubes. The calculated pressure of hydrogen molecules is about 180atmwhich is correspondingtohydrogen gas density of about 7.6mol/L.

The hydrogen adsorption in double walled carbon nanotubes arrays was investigated by molecular simulation.The double walled carbon nanotubestructurewassimulated by Nanotube Modeler3 package and then simulation was completed by Gausian09computationalpackage[75-79].

The calculations showed thatat P=180atm and T=300K two hydrogen molecules were adsorbed by external wall of double walled carbon nanotube and one hydrogen molecule has been dissociated as shown Fig. 2(b) andthetworesulted hydrogen atoms deformed the external wall of the double walled carbon nanotube as indicated in Fig.2(d).Results of the above-mentioned simulation are illustrated in table 1.

In the measuring domain of dimensions 20×20×13 A, we placed an array of 76 atoms,(48 carbon atoms plus 24 hydrogen atoms)and 3 hydrogen molecules,Fig 1.

The simulation was carried out until optimization was approached,after which from the molecular properties, the macro parameters were determined.Within the framework of this study partial dissociation of hydrogen molecules and penetration of hydrogen atoms into external wall of double walled carbon nanotube was assumed to be similar toembrittlementphenomenonin metals[80-82].

RESULTS AND DISCUSSION

Atomic hydrogen (H) is the only species capable of penetratinginto metals and alloys. Molecular hydrogen (H2) does not penetrate into metals and alloys[36].It can be assumed that similar process is occurred during penetration of hydrogen into the surface of DWCNTs[83-85].

Simulation procedure showed final location of hydrogen molecules related to the DWCNT which yielded most stable state of the

Table 1: The calculation summary of simulation and optimization procedure

Calculation type	Basis set	E(RHF) (a.u.)	RMS Gradient Norm (a.u.)
FOPT	B3LYP	-1834.3	0.057

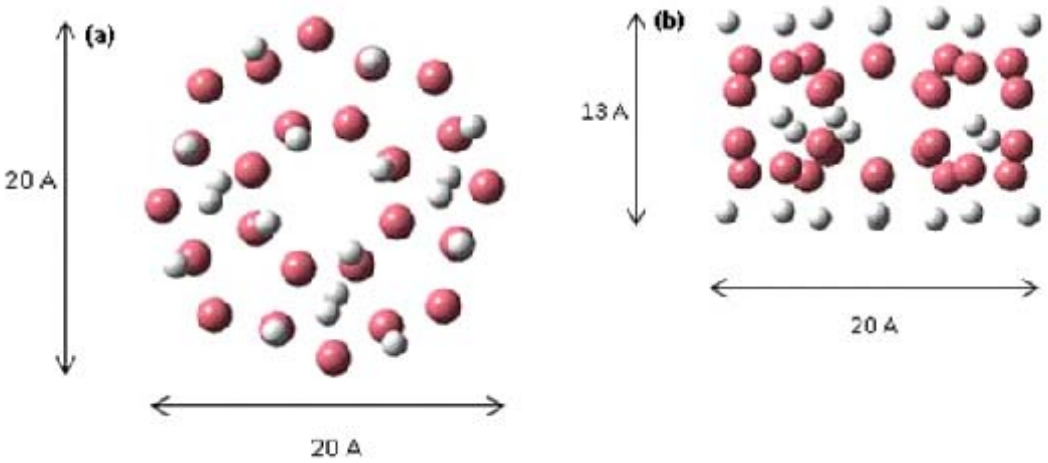

Fig.1: First system configuration used for optimization by the Gaussian09 package, (a) top view and (b) side view. Arrows indicate the dimension of the simulated system

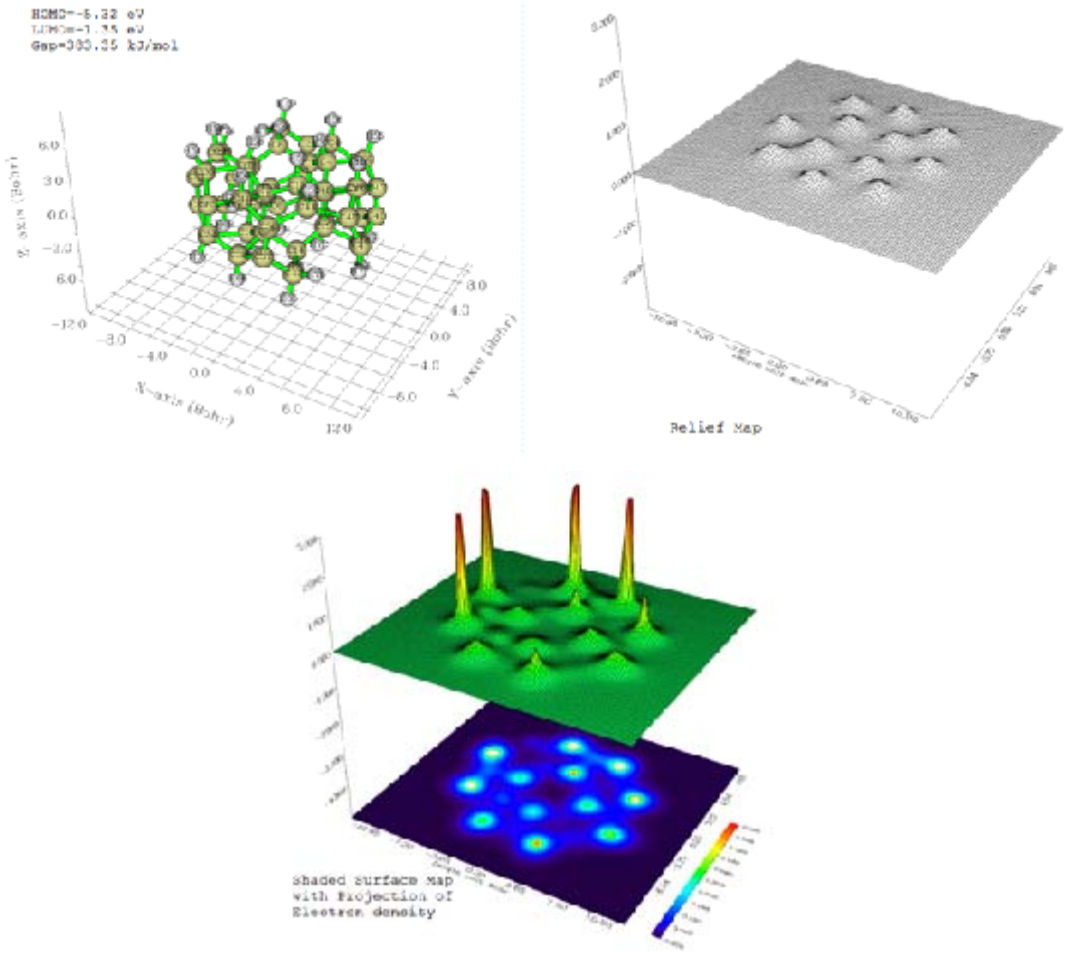

Fig. 2: Several system configurationsof electron density

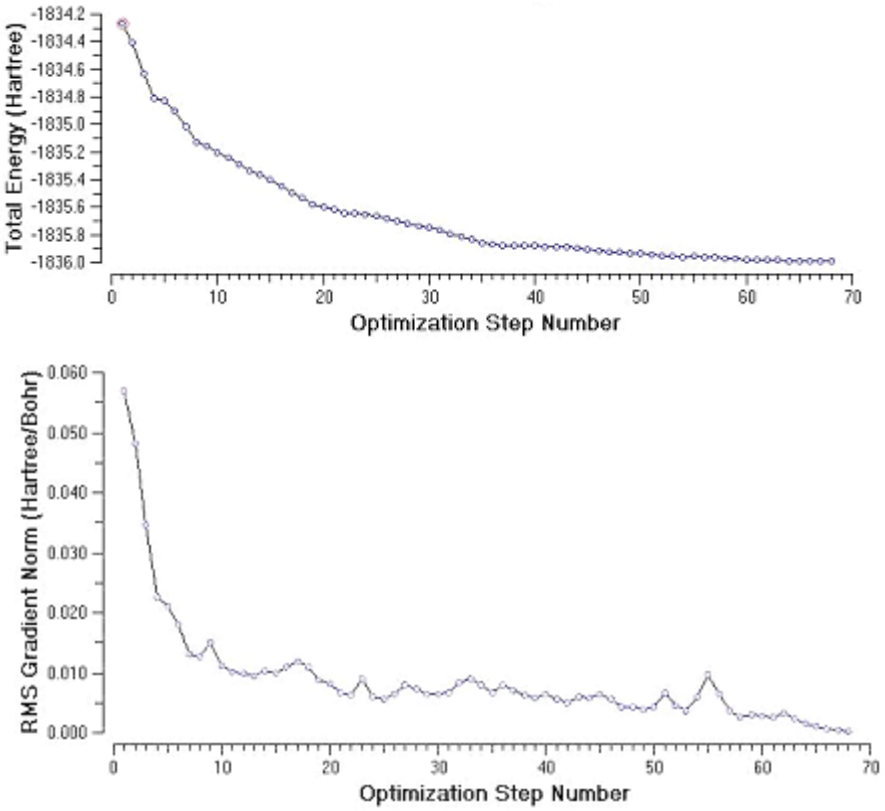

Fig. 3: Total energy (a) and RMS gradient (b)change during optimization step

system with minimum energy of approximately-1834.3hartree, Fig.3.

The simulation results showed that at 300K inside of the double walled carbon nanotube, two factors are critical for hydrogen adsorption:

1) Distance of the hydrogen gas molecules from the walls of nanotube before penetration
2) Partial dissociation of hydrogen molecules and embrittlement in carbonnanotube surface.

The pressure of hydrogen gas molecules between the walls of DWCNT was calculated to be about 180atm, but according Heisenberg uncertainty principle, in this space, measurement of pressure is limited by equation of the type:

$$\Delta x.\Delta P_x \geq \frac{h}{4\pi}$$

Where Δx is the uncertainty in the distance between the walls of DWCNTwhich is equal to 5A andΔP_x is the uncertainty in a particular component of momentum that calculated according to the following equation:

$$\Delta P_x = \Delta(m\overline{V_x}) = \frac{\Delta E_{kx}}{2m} = \frac{h}{4\pi\Delta x}$$

Where m is mass of hydrogen molecule ($m=3\times10^{-24}$), so that uncertainty in the kinetic energy of molecular hydrogen is given by:

$$\Delta E_{kx} = \frac{mh}{\pi\Delta x} = 6.98\times10^{-12}$$

According to the perfect gas model, the internal energy of the gas is equal to its kinetic energy, therefore:

$$\Delta E_{kx}=\frac{1}{3}E_k, E_k=U=\frac{3}{2}kT$$

Since the Equation of State for perfect gas is, $PV_m=NAKT$ therefore the uncertainty in kinetic energy of the gas is:

$$\Delta E_{kx}=\Delta(\frac{PV_m}{2N_A})$$

Where $V_m=0.13$ L.mol^{-1}and$N_A=6.02\times10^{23}$. Therefore $\Delta P=6.5\times10^{13}$ atm. This huge uncertainty shows that microscopic and macroscopic pressures are very different.

CONCLUSION

Using the molecular optimizing simulation method, the pressure of the molecular hydrogen gasbetween the walls of DWCNT and average distance betweenhydrogen species and the surface of the DWCNT has been calculated.

The specific location of hydrogen molecules with respect to hexagonal rings of DWCNT wall is an indication of hydrogen penetration into carbon nanotube walls. In the previous works these centers referred to as "carbon islands"[86].

The calculated results reveal that hydrogen molecules are physisorbed on the center of carbon nanotube hexagonal ring. Exposed carbon edges as "carbon islands" have a significant contribution in hydrogen adsorption. Hydrogen adsorbed in the DWCNTs could not be entirely released from the surface of the carbon nanotube[87-89].

Hydrogen molecules dissociate inside of the center of hexagonandarechemisorbed by carbon atoms. This process causes hydrogen damage of carbon nanotube. A fraction of the pore structure of the DWCNTs was permanently destructed by hydrogen adsorption.

Based on the performed simulation, it seems that in physisorb and Chemisorb of hydrogen on double walled carbon nanotubes, internal wall is unperturbed but external wall is damaged by molecular and atomic hydrogen. This research proposed that the amount of adsorbed hydrogen is proportional to the outer diameter of DWNTs. These results are consistent with the previously reported works[44,45,90] although a complete study of this aspect is required.

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