



# Hydrogen adsorption on hexagonal silicon nanotubes

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## ABSTRACT

We present a first-principles study of geometrical structure and energetics of hydrogen adsorbed on hexagonal single-walled silicon nanotubes (SiNTs). The adsorption behaviors of hydrogen molecules on SiNTs are investigated. The binding energies for the most stable physisorbed configurations are calculated to be less than 0.1 eV. The energy barriers are also investigated for dissociation of H<sub>2</sub> molecules. Finally, we consider encapsulation of H<sub>2</sub> molecules in SiNTs. The possibility of SiNTs as hydrogen storage materials is discussed.

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## 1. Introduction

Due to their novel quantum mechanical phenomena as well as various potential applications, carbon-based low-dimensional nanostructures such as carbon nanotubes and graphene have attracted much attention. In fact, the recent synthesis of graphene provided foundation for new devices. Nevertheless, silicon is still one of the most important materials even in the field of nanoscience. Si-based nanowires and nanotubes have recently been investigated theoretically and experimentally [1–5].

Bai et al. [3] suggested that Si nanotubes (SiNTs) could form by the top-to-top stacking of square, pentagonal and hexagonal silicon structures and showed using ab initio calculations that the pentagonal and hexagonal SiNTs may be locally stable in vacuum. They provided a computational evidence for the existence of such one-dimensional silicon nanostructures, although those structures have not been observed experimentally yet. Very recently, the stability and related electronic structure of their hexagonal SiNTs with some defects were investigated [6].

Under ambient conditions, Si nanostructures may be passivated or oxidized. To consider the possibility of SiNTs as a hydrogen

storage material along with hydrogen passivation, we focus in this paper on the interaction of hydrogen with pure SiNTs without defects. Here, we study adsorption behaviors of hydrogen molecules on and in the SiNT. The binding energies and the energy barriers are also calculated.

## 2. Calculation methods

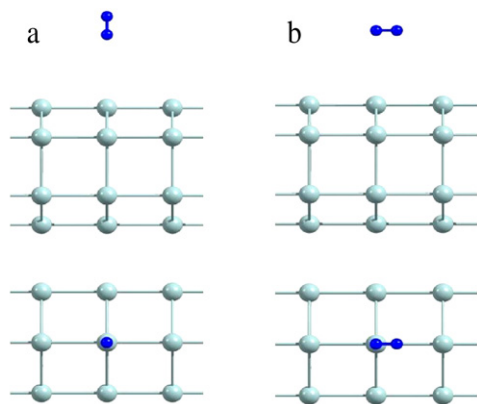
We have performed the density functional theory (DFT) calculations within generalized gradient approximation (GGA) and local density approximation (LDA) using the Vienna ab initio simulation package (VASP) [7,8]. The cutoff energy is set to 200 eV and the atoms are represented by ultrasoft pseudopotentials as provided with VASP [9]. To investigate a hydrogen molecule adsorbed on the SiNT, we consider hexagonal SiNTs having 48 silicon atoms and vacuum region between SiNTs about 10 Å perpendicular to the tube axis. For the Brillouin-zone integration we use a  $1 \times 1 \times 15$  grid in the Monkhorst–Pack special  $k$ -point scheme. To study the reaction energy barriers for dissociation and encapsulation of a hydrogen molecule on the SiNT, we use the nudged elastic band (NEB) method [10].

## 3. Results and discussion

First, we calculate the total energy of a SiNT with a hydrogen molecule adsorbed at both the GGA and LDA levels. To find the

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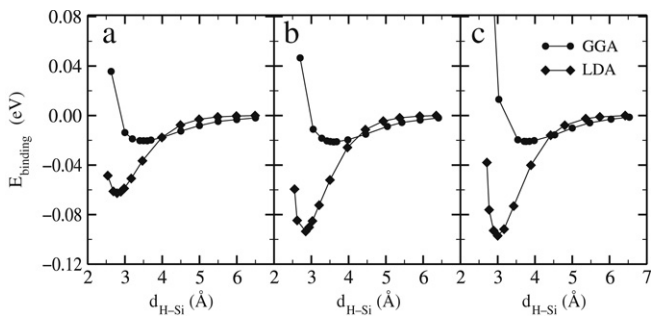


**Fig. 1.** Structures of hexagonal SiNTs with  $H_2$  molecules adsorbed on the atop site where the H–H bonds are (a) perpendicular and (b) parallel to the tube axis, respectively.

**Table 1**  
Relative energies (in units of meV/molecule) of adsorption sites

Site	Atop		Bridge		Hollow	
	Perp.	Parallel	Perp.	Parallel	Perp.	Parallel
GGA	0	4.2	0.6	2.3	0.6	5.0
LDA	35.4	51.4	4.5	15.3	0	15.7

The energies are referred to the lowest energy in each case of GGA and LDA.



**Fig. 2.** Binding energy profile of  $H_2$  adsorbed on SiNTs at (a) atop site, (b) bridge site, and (c) hollow site, as a function of the Si–H distance.

most stable configuration, several adsorption sites are considered, depending on the position and orientation of H–H bond. The molecule can be located at the top of Si atom (atop), the bridge of Si–Si bond (bridge), and the center of Si square (hollow), respectively. For each adsorption type, the H–H bond can be perpendicular or parallel to the tube axis. Fig. 1 shows two possible configurations of the atop site.

The relative energies of adsorption sites are listed in Table 1. In GGA, the atop site with perpendicular H–H bond has the lowest energy (binding energy = 31 meV/ $H_2$ ), which is almost similar in energy to other perpendicular configurations. In fact, the energy variations are very small, so all configurations considered are within less than 10 meV in energy. On the other hand, in LDA, the energy variations are relatively large compared to the GGA case. The lowest energy configuration for LDA is that  $H_2$  is at the hollow site with perpendicular H–H bond, and its binding energy is 94 meV/ $H_2$ . The distance between  $H_2$  and the closest Si atom of SiNT is about 3.7 Å (GGA) or about 3 Å (LDA) for both the atop and hollow sites with perpendicular H–H bond. Calculated binding energies and bond lengths manifest that LDA overbinds compared to GGA.

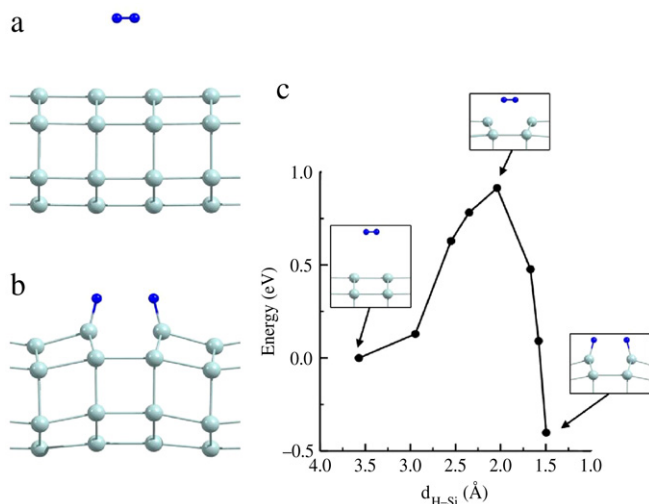
To better understand the binding behavior, we move the hydrogen molecule toward the relatively stable site, i.e., the perpendicular case of each adsorption type. Fig. 2 shows the binding energy of the hydrogen molecule as a function of its distance from the SiNT wall. In the calculation, the position of the hydrogen molecule is fixed, while those of all Si atoms in the SiNT

are relaxed. In GGA, the binding energy of hydrogen is about 0.02 eV and the binding distance between the hydrogen molecule and a Si atom is around 3.6–3.7 Å for all three cases shown in Fig. 2. On the other hand, in LDA, the binding energy and distance are somewhat varied: the binding energy is 0.06 eV for the atop site and about 0.1 eV for other two cases, and the binding distance is 2.8 Å for the atop and bridge sites and 3.0 Å for the hollow site. Since the position of the hydrogen molecule is fixed, the (LDA) binding energies from Fig. 2 are slightly smaller within  $\sim 0.01$  eV than the fully relaxed ones.

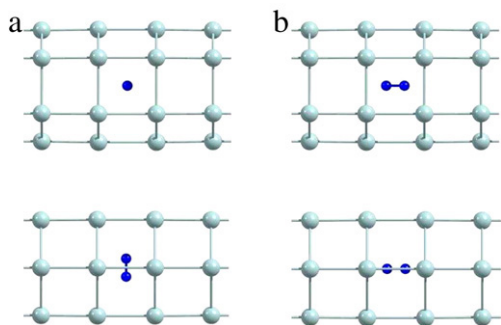
It is worthwhile to consider the possibility of SiNTs as hydrogen storage materials. Many studies of hydrogen-adsorbed nanostructures show that the binding energy for hydrogen storage should be about 0.3 eV [11–13]. However, the hydrogen molecule adsorbed on the SiNTs has a binding energy of 0.03 eV for GGA and at most 0.1 eV for LDA, respectively. Previous studies mentioned that the weak intermolecular (or nonbonding) bindings may be similar to the LDA results or some halfway between the LDA and GGA results [14]. Hence, the maximum value of the binding energy of  $H_2$  in the present system may be almost as large as 0.1 eV. Nevertheless, this binding energy is not enough for good hydrogen storage materials. On the other hand, it is understood that the weak nonbonding interaction (e.g., the van der Waals interaction) such as physisorption might not be well described by GGA or LDA [15–17]. Also, the van der Waals interaction due to polarization in metallic systems might be more important than in insulating or semiconducting systems. However,  $H_2$  has no electric dipole moment but has the electric quadrupole moment, so the polarization effect is expected to be very small for the  $H_2$  adsorption. Recently, Henwood and Carey reported that the binding energies of  $H_2$  on the metallic (9, 0) and the semiconducting (10, 0) CNTs are almost similar at several adsorption sites for LDA and GGA, respectively [18]. These CNT results may imply that the nonbonding interaction due to polarization in metallic SiNTs does not change our conclusion. Therefore, even taking both inaccuracy of GGA or LDA for the nonbonding interaction and the polarization effect into account, we believe that the binding energy cannot be larger than 0.2–0.3 eV, the required minimum binding energy for hydrogen storage.

We have considered the adsorption behaviors of the hydrogen molecule by varying its initial distance from the SiNT wall. In some specific cases (using GGA) where its bond is parallel to the tube axis and its distance is quite close ( $\sim 1.7$  Å) to the wall, the hydrogen molecule at the bridge site is dissociated into hydrogen atoms that are chemisorbed on nearby Si atoms. To find the activation energy barrier of the dissociation pathway from a physisorbed state [Fig. 3(a)] to this chemisorbed state [Fig. 3(b)], we use the NEB method [10]. We find that the bond of Si atoms with hydrogen attached is broken in the chemisorbed state. Fig. 3(c) shows that the energy barrier for dissociation is about 0.9 eV. The energy barrier for hydrogen dissociation on the SiNT is found to be lower than that on carbon nanotubes (CNTs): For the (5,5) CNT case, the energy barrier is 2.70 or 3.07 eV for two reaction paths [19], while that for the (3, 3) CNT is 2.7 eV [20]. On the other hand, a very small energy barrier of about 0.3 eV was also reported for the (3, 3) CNT [21].

Finally, we consider a hydrogen molecule encapsulated in a SiNT using GGA. Fig. 4 shows that the encapsulated hydrogen molecule is located at the center of the tube without dissociated. Encapsulation energy is defined as  $E(\text{encapsulation}) = [E(\text{SiNT}) + E(H_2)] - E(H_2@SiNT)$ , where  $E(\text{SiNT})$ ,  $E(H_2)$ , and  $E(H_2@SiNT)$  are the total energy of SiNT,  $H_2$ , and  $H_2@SiNT$ , respectively. The  $H_2$  encapsulation energy is calculated to be  $-1.28$  eV for both configurations shown in Fig. 4. The negative value means that the encapsulated state is higher in energy than the separate configuration of  $H_2$  and SiNT, and then  $H_2$  is hard to be encapsulated in SiNTs unless located in SiNTs by constraint. This



**Fig. 3.** Dissociation of  $H_2$ : (a) initial physisorbed state, (b) final dissociated state, and (c) the reaction pathway, as a function of the Si–H distance, from physisorbed to chemisorbed state showing a dissociation barrier ( $\sim 0.9$  eV).



**Fig. 4.** Hydrogen molecules encapsulated in SiNTs, where the H–H bonds are (a) perpendicular and (b) parallel to the tube axis, respectively.

encapsulation energy is larger by 1.31 eV than the adsorption energy of the most stable configuration on SiNTs. We consider pathways for penetration of the hydrogen molecule into the tip-opened SiNT. Using the NEB method [10], the energy barrier is calculated to be about 1.28 eV. Previous calculations shows that the penetration barrier into the open end of the (3, 3) CNT is about 3 eV [21]. This relatively larger value in the case of CNT compared to SiNT may be due to difference in bond strength of C–H and Si–H.

#### 4. Conclusion

We have investigated a hydrogen molecule adsorbed on SiNTs using DFT calculations. Our calculations show that  $H_2$  is the most stable at the atop site (GGA) or the hollow site (LDA) with the H–H bond perpendicular to the tube axis. However, since the binding energy variations are very small, at low temperature,  $H_2$  can adsorb practically at any possible sites considered. For the most stable physisorbed configurations, the binding energies are calculated to be less than 0.1 eV. Thus, it is found that pure SiNTs are not good for hydrogen storage. In addition, the activation energy barrier is calculated to be about 0.9 eV for dissociation of  $H_2$ .  $H_2$  is not likely to be encapsulated in SiNTs.

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