



A First Principles Study of Hydrogen Interaction with Ca decorated SiCNT

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Abstract: Hydrogen storage poses limitations in maximizing the use of hydrogen as an energy source for industrial applications. The search and realization of lightweight materials which can store significant amount of hydrogen in its condensed form, at ambient conditions, is still a continuing challenge for researchers today. A first principles study on the viability of calcium decorated silicon carbide nanotube (SiCNT) as a hydrogen storage material was conducted. Silicon carbide strongly enabled Ca decoration, evident on calcium's large binding energy of -2.83 eV on the hollow site of the nanotube. Calcium's low cohesive energy and strong binding with SiCNT may prevent the metal decoration to form clusters with other adsorbates. Bader charge analysis also revealed that there is a charge transfer of 1.45e from Ca to SiCNT resulting to calcium's cationic state that may induce charge polarization to a nearby molecule such as hydrogen. Hydrogen molecule was then allowed to interact with the metal adsorbate where it indeed exhibits charge polarization, induced by the electric field emanating from calcium's cationic state. This resulted to a significant binding energy of -0.22 eV. Results reveal that Ca on SiCNT can be a promising candidate for a hydrogen storage material.

Key Words: Hydrogen energy; Density Functional Theory

1. INTRODUCTION

Hydrogen storage remains to limit the use of hydrogen fuel cell systems due to the low density of hydrogen which requires large containments for it to be stored in the gas phase. The search for plausible candidates for hydrogen storage with a significant gravimetric percentage capacity is still a continuing challenge for researchers today. This problem motivated researchers to investigate on different ways of storing hydrogen in the condensed form and one of which is storing it in materials such as nanostructures. Nanostructures seemed to be good candidates for H₂ storage

due to its light weight property but it manifests low binding energy with hydrogen molecule which makes storage at ambient conditions still a challenge (Mpourmakis et al., 2006). Recently, metal decorations on nanostructures revealed an improvement on their hydrogen storage capability specifically on hydrogen's binding energy (Banerjee et al., 2011; Ivanovskaya et al., 2001; Banerjee et al. 2012). But due to these metals' high cohesive energy, they tend to cluster and thus decreasing the amount of hydrogen it can hold (Krasnov et al., 2007; Sun et al., 2005). Because of this problem, This study proposes a metal decorated nanotube as a possible hydrogen storage material with calcium as the adsorbate,

given that it has a much lower cohesive energy compared to transition metal decorations, adsorbed on silicon carbide nanotube which has a reactive surface that may easily facilitate sidewall decorations.

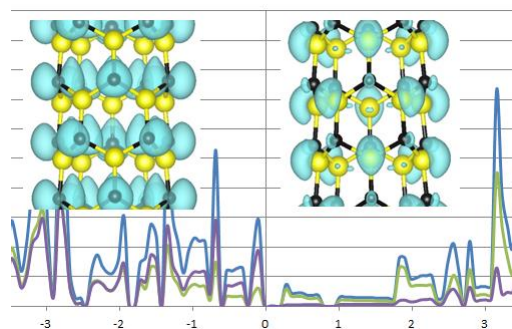
2. COMPUTATIONAL METHODS

Spin Polarized DFT calculations are performed as implemented in the Vienna Ab initio Simulation Package (VASP). The electron exchange correlation is treated within generalized gradient approximation by Perdew-Burke-Ernzerhof. The cut off energy for the basis set is chosen to be 500 eV. The atomic relaxation is carried out until the Hellmann-Feynman forces of atoms are less than 0.01 eV/Å. Monkhorst-Pack scheme with 1 X 1 X 8 special K-points is used for Brillouin zone sampling. An 18 X 18 X 10.5 Å supercell was used to model the 5,0 nanotube which encloses two unit cells of the system. The binding energy is calculated as $E_b = E_{tot} - (E_0 + E_{ad})$ where E_{tot} is the total energy, E_{ad} and E_0 are the energies with and without the adsorbate respectively.

3. RESULTS AND DISCUSSION

SiCNT Electronic Structure

(5,0) SiCNT is a narrow gapped semi-conductor with a band gap of 0.2 eV which agrees with other studies (Wu and Guo, 2007; Zheng et al., 2010). Partial charge density (Fig.1) shows that the lowest unoccupied molecular orbital is mainly contributed by the pz orbital of silicon which makes SiCNT more reactive than carbon nanotube by having more electron acceptor states which indicates that the system can easily facilitate sidewall decoration.



$E-E_f(eV)$

Fig.1 : Density of states of SiCNT with the partial charge density profiles of the HOMO and LUMO

Ca adsorption on SiCNT

Four adsorption sites were identified where the potential energy as a function of separation distance were calculated (Fig. 2).

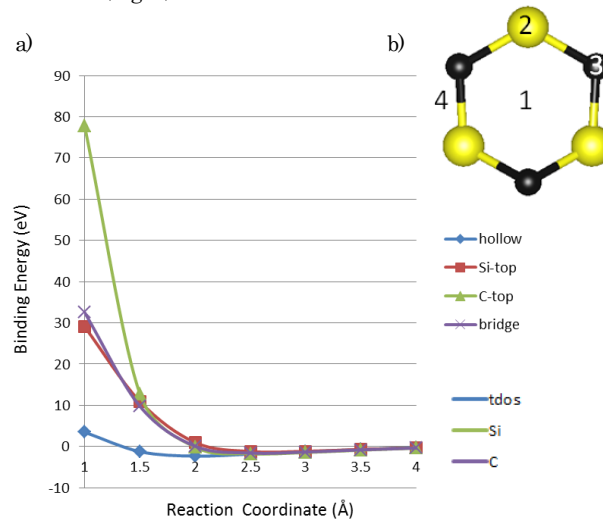


Fig.2: a) Potential Energy Curve as Ca approaches SiCNT
b) Ca adsorption sites: 1-hollow, 2-Si top, 3-C top, 4-bridge

Adsorption site	E_b (eV)
hollow	-2.83
Si-top	-2.68
C-top	-2.55
bridge	-2.60

Fig. 3: Optimized structure of Ca/SiCNT

Total energy calculations show that Ca preferred to adsorb on the hollow site of the nanotube with a strong binding energy of -2.83 eV (Table 1). Structural relaxation of Ca on other adsorption sites also show that calcium still tends to move towards the hollow site. The binding energy of calcium is found to be much greater than the cohesive energy of bulk calcium which may prevent the clustering between calcium decorations.

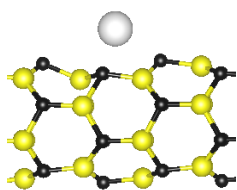


Table 1: Binding energy of Ca at different adsorption sites

Hydrogen Interaction

The study considered placing a hydrogen molecule on the surrounding sites of calcium to determine the effect of the calcium adsorbate to a nearby hydrogen molecule.

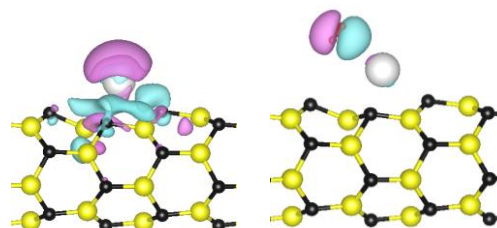


Fig. 4: Charge density difference profile of
a) Ca/SiCNT b) H_2 /Ca/SiCNT

Charge density difference profile (Fig. 6) shows how hydrogen exhibits charge polarization as it interacts with the calcium adsorbate. This is caused by the cationic state of calcium, with a bader charge of 1.45e, which can induce charge polarization to a hydrogen molecule. This interaction resulted to a binding energy of 0.22eV which is significant for storing H_2 at ambient condition.

4. CONCLUSION

In summary, the study showed that calcium adsorb strongly to SiC nanotube which may prevent clustering with other metal adsorbates. Calcium adsorption created a positively charged region surrounding the adatom which may induce charge polarization to a nearby molecule. Hydrogen molecule then interacts with Ca/SiCNT through induced charge polarization which resulted to a significant binding energy that may allow storage of H_2 at ambient conditions. Future work on multiple hydrogen interaction is already an ongoing study and will be the next phase of this research.

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