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SiC Nanotubes: A Novel Material for Hydrogen Storage

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ABSTRACT

A multiscale theoretical approach is used for the investigation of hydrogen storage in silicon–carbon nanotubes (SiCNTs). First, *ab initio* calculations at the density functional level of theory (DFT) showed an increase of 20% in the binding energy of H₂ in SiCNTs compared with pure carbon nanotubes (CNTs). This is explained by the alternative charges that exist in the SiCNT walls. Second, classical Monte Carlo simulation of nanotube bundles showed an even larger increase of the storage capacity in SiCNTs, especially in low temperature and high-pressure conditions. Our results verify in both theoretical levels that SiCNTs seem to be more suitable materials for hydrogen storage than pure CNTs.

Hydrogen has been recognized as an ideal energy carrier, but for several reasons it has not been used yet. One of the major problems is the difficulty of finding efficient storage materials. Since 1997, when Dillon et al.¹ reported that carbon nanotubes (CNTs) can store hydrogen, numerous experimental and theoretical works have been performed in order to investigate hydrogen adsorption in CNTs and to improve the storage capacity of the tubes by doping them.² Nevertheless, most of these efforts failed to reach the DOE (Department of Energy) target of 6 wt % for commercial applications. It should be noted, however, that concerning those papers, which presented quite promising results, either

the results were resubmitted with lower weight percent values than the ones reported already or they have not been reproduced.

Nowadays, most of the scientists working on this field of research believe that the solution of this problem will come from the synthesis and development of new specific materials.^{3–5} From our previous work in the field of hydrogen adsorption in CNTs, even though we failed to find the “sponge” material for efficient adsorption capacity, we ended up in some conclusions that our results can be useful in designing novel materials suitable for hydrogen storage.^{6,7} By analyzing our results, we found that point charges upon the material’s surface can improve the storage capacity because they increase the binding energy of hydrogen. A

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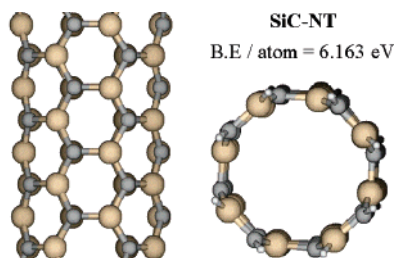


Figure 1. Side and top view of the most stable SiCNTs with alternating Si and C atoms found in ref 9.

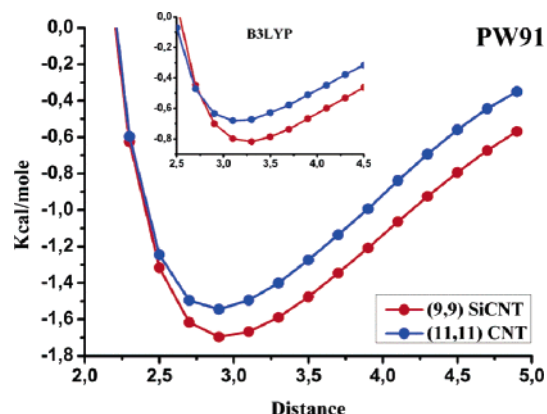


Figure 2. Potential energy curves of an H_2 vertical approach to the middle of a hexagon of the (9, 9) SiCNT's and (11, 11) CNT's outer walls.

charge-induced dipole interaction gives additional stabilization to the H_2 molecule.⁷

Additionally, in our previous theoretical study of silicon carbon nanotubes (SiCNTs),^{8,9} we found that between the two energetically stable forms of SiCNTs the one in which the Si and C atoms have alternating positions in the tube

wall is full of point charges (Figure 1). This happens because there is a continuous charge transfer of more than half an electron from Si to C. The tubules formation of these nanotubes, that had been first synthesized in 2001,^{10,11} together with the existence of point charges in their surface make them good candidate materials for hydrogen storage.

To investigate the hydrogen storage in SiCNTs, we implemented a multiscale theoretical approach: According to our strategy, first principle quantum chemical calculations were used for investigating the nature of the H_2 interaction with a single (9, 9) SiCNT. However, to obtain information for the weight percent of molecular hydrogen that can be stored in (9, 9) SiCNT bundles under different thermodynamic conditions, we have employed the well-established molecular simulation technique of grand canonical Monte Carlo (GCMC).¹² In addition, the quantum mechanical and the GCMC technique were carried out in the case of an (11, 11) CNT as well as CNT bundles, respectively, and the results obtained have been compared directly to those for the isodiameter (9, 9) SiCNT.

The ab initio calculations at the density functional level of theory (DFT) were performed to estimate the binding energy of an H_2 molecule at SiCNT walls. To treat our systems with high accuracy, without ending up in prohibitively large computations, we applied the cluster approximation. A curved coronene-like graphene sheet model from the corresponding (9, 9) SiCNT and (11, 11) CNT walls was separated and treated as an individual cluster. Aiming at the higher possible accuracy, we used two different basis sets to describe our system. The interacting region of hydrogen molecule together with the six nearest tube atoms were treated with a larger basis set (6-311++G**) than the other atoms of the cluster (3-21G). All of the calculations were

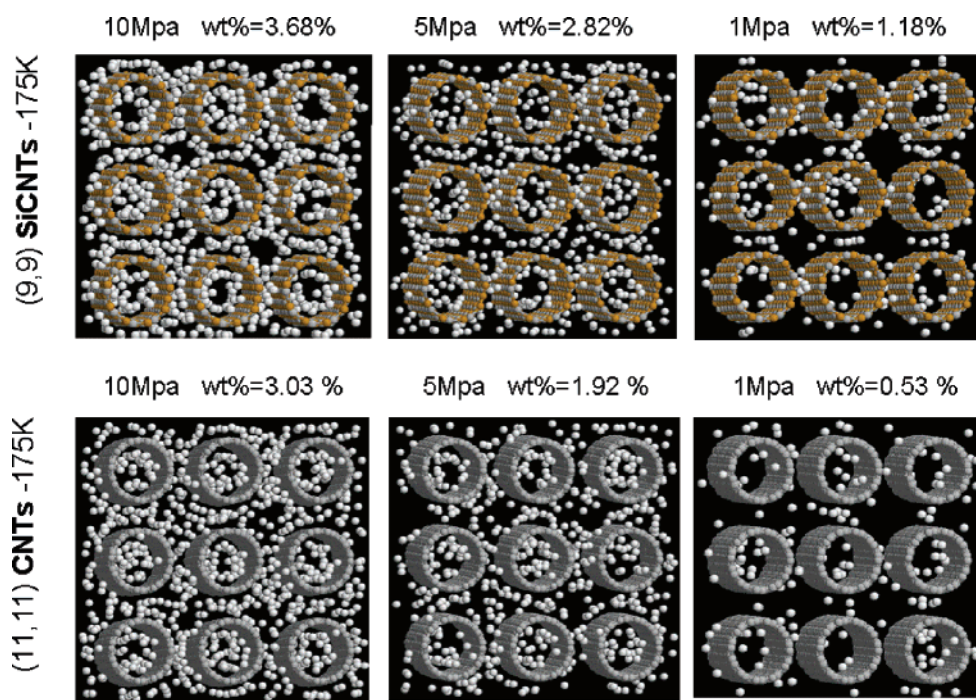


Figure 3. GCMC snapshots of the simulation box of the SiCNT (top) and CNT (bottom) bundles at 175 K and under 10, 5, and 1 Mpa pressure. Results for the weight percent of hydrogen in both systems are also given.

performed using the Gaussian 03 program package.¹³ To obtain a more accurate picture for the binding nature of hydrogen in SiCNTs, we performed the density functional calculations using two different functionals: B3LYP^{14,15} and PW91.¹⁶ The first hybridic functional gives more accurate geometric features, and the second exchange-correlation functional describes the dispersion forces better than B3LYP.¹⁷

A hydrogen molecule can approach the nanotube walls from inside and outside toward various binding sites (atoms, bonds, hexagons) and in many different orientations.¹⁸ All of these have been investigated in the case of an H₂ molecule approaching a (9, 9) SiCNT and a (11, 11) CNT. In Figure 2, we present the potential energy curve of the most important orientation obtained, which is the vertical approach of H₂ in the outer part of the tube walls and in the middle of a hexagon. Even though the two different DFT functionals are not in agreement considering the binding energy (PW91 gives almost double binding energy than B3LYP), both favor the H₂ binding to SiCNT over the CNT. The increasing in the binding energy is approximately 20% in the different binding sites. The reason is the partially heteropolar binding nature of the SiC bonds. The point charges on SiCNT's walls induce a dipole on the hydrogen molecule, resulting in more efficient binding.

As mentioned above, we used the grand canonical Monte Carlo (GCMC) simulations to obtain the weight percentage of hydrogen that can be stored in (9, 9) SiCNT bundles under different thermodynamic conditions. According to our simulation results, molecular hydrogen can be stored either internally or externally in the space between neighboring tubes. The amount of hydrogen that is stored is dependent on the attraction forces between the tube atoms and hydrogen molecules. The (9, 9) SiC tubes have diameters of 1.548 nm and heights of 2.0 nm. The simulation box is made up of three rows, of three tubes each, making up a total of 9 parallel nanotubes. The tube spacing is 0.7 nm, and the total volume of the box is 90.9 nm³. All of the interactions among hydrogen molecules as well as hydrogen and the atoms of the tubes are described by Lennard-Jones potentials. At first, we performed an NVT Monte Carlo simulation for the calculation of the excess chemical potential using the well-known Widom's test particle method; and then by the GCMC technique, we obtained density profiles of hydrogen inside and outside of the tube surface following the Metropolis' sampling scheme.¹⁹

At the top of Figure 3, we present three snapshots of the simulation box of the SiCNT's bundles at 175 K and under 10, 5, and 1 MPa pressure, respectively. At the bottom of the same Figure, we present the analogous snapshots for the isodiameter CNT. In these figures, the weight percent of the adsorbed hydrogen obtained in each case is presented. From this GCMC simulation, we can draw the general conclusion that at all of the thermodynamic states studied here, SiCNTs adsorb more hydrogen than CNTs. It is of particular importance to mention here that especially at low pressures (1 MPa) the storage capacity of SiCNTs is more than double compared to that of CNTs.

To conclude, our multiscale theoretical investigation of hydrogen storage in SiCNTs verifies that at both theoretical levels SiCNTs seem to be more suitable materials for hydrogen storage than pure CNTs at the aforementioned thermodynamic conditions studied. This encouraging theoretical outcome remains to be verified experimentally.

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