

# Ca-Coated Boron Fullerenes and Nanotubes as Superior Hydrogen Storage Materials

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Received January 13, 2009; Revised Manuscript Received March 6, 2009

## ABSTRACT

A comprehensive study was performed on hydrogen adsorption and storage in Ca-coated boron fullerenes and nanotubes by means of density functional computations. Ca strongly binds to boron fullerene and nanotube surfaces due to charge transfer between Ca and the B substrate. Accordingly, Ca atoms do not cluster on the surface of the boron substrate, while transition metals (such as Ti and Sc) persist in clustering on the B<sub>80</sub> surface. B<sub>80</sub> fullerene coated with 12 Ca atoms can store up to 60 H<sub>2</sub> molecules with a binding energy of 0.12–0.40 eV/H<sub>2</sub>, corresponding to a gravimetric density of 8.2 wt %, while the hydrogen storage capacity in a (9,0) B nanotube is 7.6 wt % with a binding energy of 0.10–0.30 eV/H<sub>2</sub>. The Ca-coated boron fullerenes and nanotubes proposed in this work are favorable for reversible adsorption and desorption of hydrogen at ambient conditions.

Hydrogen has widely been recognized as an ideal alternative energy carrier for fossil fuels due to its merits of being nonpolluting and abundant in nature.<sup>1–3</sup> One bottleneck in developing a hydrogen economy is to find feasible and safe storage materials that can store hydrogen with high gravimetric and volumetric density and that can allow hydrogen adsorption and desorption to be operated under ambient conditions.<sup>4–6</sup>

Metal-decorated carbon nanostructures, a kind of hydrogen sorbents, have been proposed to satisfy the above requirements.<sup>7</sup> To achieve the reversible hydrogen uptake and release at ambient conditions, the ideal H<sub>2</sub> binding energy should be in the range of 0.2–0.4 eV/H<sub>2</sub>,<sup>8</sup> which is intermediate between the physisorbed and chemisorbed states. By density functional theory (DFT) computations, Zhao et al.<sup>9</sup> showed that Sc-coated B-doped fullerenes C<sub>48</sub>B<sub>12</sub>[Sch]<sub>12</sub> can store up to 8.77 wt % H<sub>2</sub> with the binding energy of ~0.3 eV/H<sub>2</sub>, while Yildirim et al.<sup>10</sup> found that up to 8 wt % of hydrogen can be stored in Ti-coated single-walled carbon nanotubes. In these pioneering studies, transition metal (TM) atoms were assumed to be homogeneously distributed on the substrate. However, it is very difficult, if not impossible, to realize these predicted uniformly coated homogeneous monolayers experimentally, since TM atoms

tend to form clusters on the surface of carbon nanostructures, and consequently the hydrogen storage capacity drops dramatically.<sup>11–15</sup> To avoid the perplexing clustering problem, Shevlin and Guo<sup>16</sup> proposed to firmly emplace the TM atoms in a carbon matrix by defecting the support, while Sun et al.<sup>17</sup> proposed to utilize Li atoms to coat C<sub>60</sub> uniformly, taking advantage of the larger binding energy between Li and C<sub>60</sub> than the cohesive energy of lithium bulk metal; however, the rather weak H<sub>2</sub> adsorption energy is a concern.

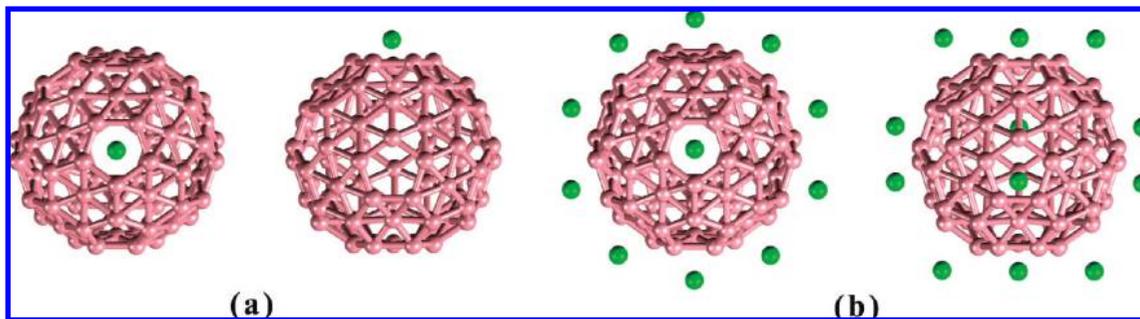
Note that, among the TM atoms examined so far, Ti overshadows all the others, since typically it has the best dihydrogen binding energies in the surveyed nanostructures.<sup>9–14,16,18–25</sup> A new star has just emerged: by DFT computations, Yoon et al.<sup>26</sup> found that the notorious clustering can be prevented in Ca coated C<sub>60</sub> system, and Ca<sub>32</sub>C<sub>60</sub> has a hydrogen uptake of >8.4 wt %; thus, Ca is superior to all the recently suggested metal coating elements. This finding was further supported by very recent reexamination by Wang et al.<sup>27</sup> and Yang et al.,<sup>28</sup> the computed hydrogen storage capacity is 6.2 wt % and 9 wt %, respectively.

Boron nanostructures, including fullerenes and nanotubes, may also be promising hydrogen storage media, since they are also light-weight. A fascinating finding in boron cluster research is the unusual high stability of B<sub>80</sub> discovered by Szwacki et al.<sup>29</sup> By DFT computations, they showed that B<sub>80</sub> fullerene is theoretically the most stable boron cage, which can be viewed as a B<sub>60</sub> polyhedron reinforced by extra

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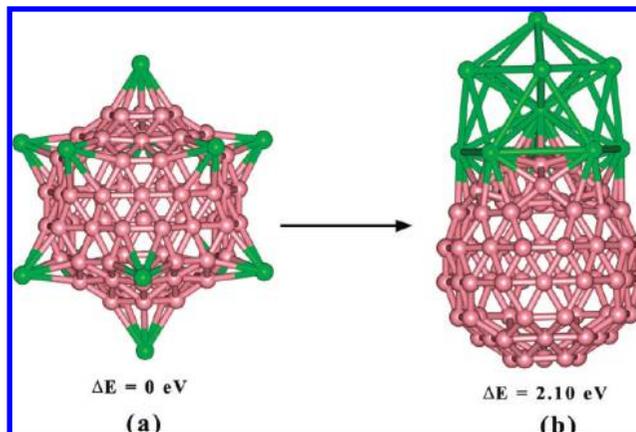


**Figure 1.** Top and side views of the optimized structures of (a) one Ca atom placed on B<sub>80</sub> fullerene and (b) 12 Ca atoms coating on B<sub>80</sub> fullerene.

atoms placed in the centers of all hexagons. Though adopting a slightly puckered cage with  $T_h$  symmetry,<sup>30–32</sup> instead of a perfect  $I_h$  cage, B<sub>80</sub> resembles the electronic properties of C<sub>60</sub> very well.<sup>33–35</sup> Boron nanotubes (BNTs)<sup>36</sup> were first predicted by Gindulytė et al. in 1998<sup>37</sup> and later synthesized experimentally in 2004.<sup>38</sup> However, the geometric structures of boron nanotubes have puzzled theoreticians for some time.<sup>36,39–42</sup> Inspired by the novel chemical bonding in B<sub>80</sub>, scientists<sup>40–42</sup> found that BNTs wrapped with the  $\alpha$ -sheet are remarkably more favorable than puckered triangular structures.<sup>39</sup> It is not a surprise that hydrogen adsorption in boron nanostructures attracted much research interest.<sup>43–45</sup> Especially, soon after Szwacki et al.'s finding,<sup>29</sup> Li et al.<sup>45</sup> reported that B<sub>80</sub>Na<sub>12</sub> and B<sub>80</sub>K<sub>12</sub> can store up to 11.2 wt % and 9.8 wt % H<sub>2</sub> with the binding energy of 1.67 and 1.99 kcal/mol (0.07 and 0.09 eV). However, the adsorption energy is so weak that hydrogen adsorption is in an unstable physisorption state at ambient conditions.

The superior hydrogen adsorption performance of Ca in Ca<sub>32</sub>C<sub>60</sub> and the very recent great progress in boron fullerenes and nanotubes prompted us to answer the following questions: What about the hydrogen adsorption in Ca and other TM-coated boron nanostructures? Do Ca and TM atoms cluster or not? In this work, we performed DFT computations to investigate hydrogen adsorption in Ca coated B<sub>80</sub> fullerene and (9,0) BNT to address the above issues.

All the computations were carried out within the DFT framework by using the Vienna *ab initio* simulation package (VASP).<sup>46</sup> The generalized gradient approximation (GGA) with the PW91 functional was adopted to treat electron exchange correlation,<sup>47</sup> and the electron–ion interactions were modeled by the ultrasoft pseudopotentials (USPPs).<sup>48</sup> Furthermore, we compared the GGA results with those of the local density approximation (LDA) with the CA functional when evaluating molecular hydrogen binding energies,<sup>49</sup> as previous studies showed that GGA underestimates the H<sub>2</sub> adsorption energy, whereas LDA overestimates the interaction,<sup>50,51</sup> though a high-level MP2 study showed that LDA results are significantly close to the MP2 results.<sup>52</sup> The energy cutoff for the plane-wave basis set was 360 eV with the supercell size of 25 Å along the  $x$ ,  $y$ , and  $z$  directions for B<sub>80</sub>-based systems and 25 × 25 × 10.08 Å<sup>3</sup> for (9,0) BNT, where the supercell length in the axial direction (10.08 Å) is twice the periodic length of the unit cell of (9,0) BNT. Five Monkhorst-Pack special  $k$  points were used for sampling

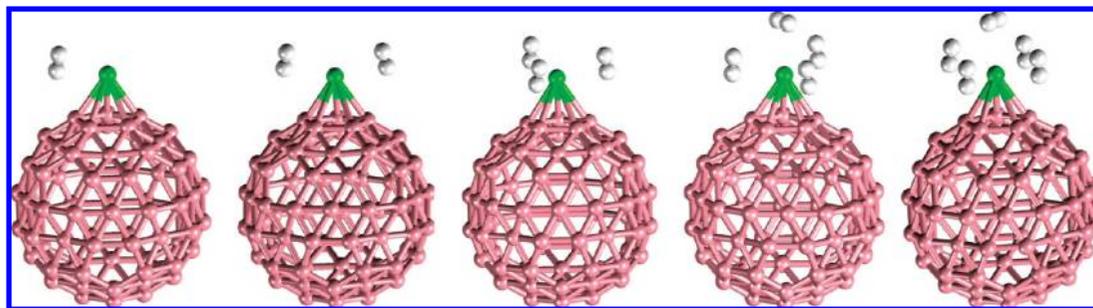


**Figure 2.** Two isomers of B<sub>80</sub>Ca<sub>12</sub>: (a) 12 Ca atoms located on pentagonal rings of B<sub>80</sub>, and (b) a Ca<sub>12</sub> cluster ( $C_{5v}$ ) on B<sub>80</sub>. The relative total energy,  $\Delta E$ , is referred to isomer (a).

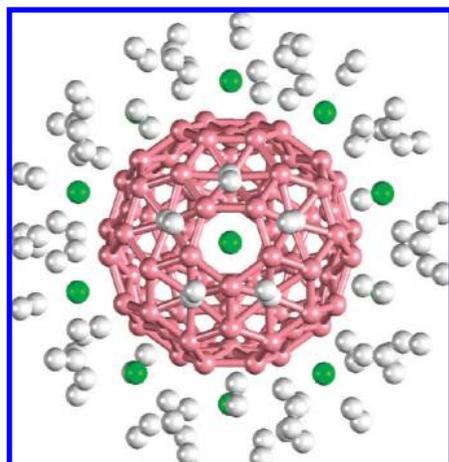
the 1-D Brillouin zone for BNT systems, and only the  $\Gamma$  point was adopted for B fullerenes. The convergence threshold was set as 10<sup>−4</sup> eV in energy and 10<sup>−3</sup> eV/Å in force. The positions of all the atoms in the supercell were fully relaxed during the geometry optimizations. The hydrogen adsorption energy is defined as  $E_a = E_{\text{host} - \text{H}_2} - E_{\text{host}} - E_{\text{H}_2}$ , where  $E_{\text{host} - \text{H}_2}$ ,  $E_{\text{host}}$ , and  $E_{\text{H}_2}$  are the energies of the complexed species, the separated host, and the H<sub>2</sub> molecule, respectively.

First, several possible sites were considered for the adsorption of a single Ca atom on B<sub>80</sub>. Ca atom prefers to bind strongly on top of the pentagonal ring of B<sub>80</sub>, similar to the case for the alkali metal atoms.<sup>45</sup> The Ca–B distance is ~2.59 Å with the binding energy of ~2.22 eV (Figure 1a). The Hirshfeld charge analysis shows that Ca carries a 0.77 lel positive charge, indicating that Ca atom is ionized and suggesting a possibility for molecular hydrogen adsorption due to the polarization mechanism.<sup>26</sup>

Then, we placed one Ca atom on top of each pentagon of B<sub>80</sub> to obtain Ca<sub>12</sub>B<sub>80</sub>, as presented in Figure 1b. After full relaxation, all 12 Ca atoms still bind separately on top of pentagons of B<sub>80</sub>. The bond length of Ca–B is ~2.65 Å, and the Hirshfeld charge analysis shows that Ca carries an average 0.39 lel positive charge in Ca<sub>12</sub>B<sub>80</sub>. The average binding energy of Ca in Ca<sub>12</sub>B<sub>80</sub> is 2.27 eV/Ca, which is a little larger than that in CaB<sub>80</sub> (~2.22 eV/Ca). To understand the higher binding energy of Ca<sub>12</sub>B<sub>80</sub>, we deleted B<sub>80</sub> from



**Figure 3.** Optimized configurations of Ca-coated B<sub>80</sub> fullerenes with one to five H<sub>2</sub> molecules at the GGA level.



**Figure 4.** Optimized configurations of five H<sub>2</sub> molecules on each Ca atom of Ca<sub>12</sub>B<sub>80</sub> at the GGA level of theory.

Ca<sub>12</sub>B<sub>80</sub> and computed the single-point energy of the residual 12 Ca atoms and found that the average energy of the residual 12 Ca atoms is  $\sim 0.04$  eV higher than the energy of a single Ca atom. The Ca atoms in Ca<sub>12</sub>B<sub>80</sub> still have some interaction energies at the average Ca–Ca distance of 6.50 Å (the corresponding value is 5.59 Å in Ca bulk metal (space group FM3-M<sup>53</sup>)). Thus, the rather higher Ca binding energy in Ca<sub>12</sub>B<sub>80</sub> is mainly due to the interaction among Ca atoms.

To check whether Ca atoms form clusters on the B<sub>80</sub> surface, we compared the relative stability of competing configurations consisting of 12 Ca atoms. As illustrated in Figure 2, the total energy of B<sub>80</sub> coated by 12 isolated Ca atoms (Figure 1b) is 2.1 eV lower than that of B<sub>80</sub> attached by the compact Ca<sub>12</sub> cluster (Figure S1 in the Supporting Information (SI)); moreover, the average binding energy (2.27 eV/Ca) of Ca in Ca<sub>12</sub>B<sub>80</sub> is much larger than the cohesive energy (1.82 eV/Ca) of the bulk Ca metal. This excludes the possibility of Ca clustering on B<sub>80</sub>. In contrast, we found that 3d transition metals, such as Sc and Ti, are

energetically more favorable to form clusters on the surface of B<sub>80</sub> (see Figures S2 and S3 in the SI). Therefore, from the prospect of hydrogen storage, Ca is more suitable than 3d transition metals to serve as coating atom on B<sub>80</sub>.

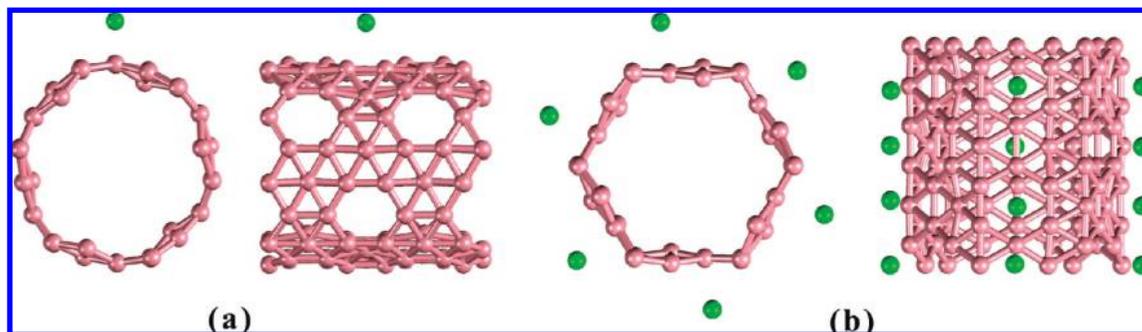
Next, we investigated the interaction between CaB<sub>80</sub> and hydrogen molecules. The adsorption energies and the equilibrium Ca–H and H–H distances are summarized in Table 1. Both GGA and LDA results are given for comparison. When one H<sub>2</sub> molecule is introduced to CaB<sub>80</sub>, the adsorption energy is  $-0.23$  eV for GGA and  $-0.53$  eV for LDA. It is widely regarded that LDA usually overestimates the dispersion interaction while GGA normally underestimates this effect and gives lower adsorption energies.<sup>50,51</sup> The real adsorption energy may lie between the GGA and LDA results. As shown in Table 1, the equilibrium Ca–H bond length is  $\sim 2.38$  Å. Meanwhile, the H–H bond is elongated from 0.75 Å (relaxed free H<sub>2</sub> molecule) to 0.78 Å due to the interaction between Ca and H<sub>2</sub>.

As more H<sub>2</sub> molecules approach CaB<sub>80</sub>, the average hydrogen adsorption energies, the distances between H<sub>2</sub> and Ca, and the H–H bond lengths change accordingly. As listed in Table 1, the binding energy is slightly reduced from  $-0.23$  to  $-0.20$  eV (GGA), which may be due to the steric repulsion when the number of H<sub>2</sub> molecules increases. A single Ca on B<sub>80</sub> can adsorb up to five H<sub>2</sub> molecules with a binding energy of  $\sim 0.20$  eV/H<sub>2</sub> at GGA and  $\sim 0.43$  eV/H<sub>2</sub> at LDA, similar to the case of Ca on C<sub>60</sub>.<sup>26</sup> Such optimal molecular hydrogen binding energies make hydrogen adsorption and desorption feasible at ambient conditions, which is critical for practical applications.

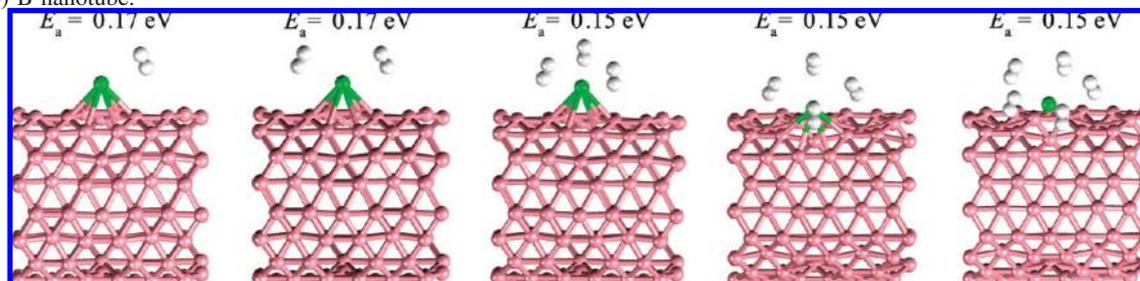
Up to five H<sub>2</sub> molecules can be adsorbed around each Ca atom in Ca<sub>12</sub>B<sub>80</sub> (Figure 4). The H–H bond length is in the range of 0.77 Å to 0.78 Å, and the average bond length between H<sub>2</sub> and Ca is  $\sim 2.40$  Å. The gravimetric density of H<sub>2</sub> stored in Ca<sub>12</sub>B<sub>80</sub> can reach 8.2 wt % with a binding energy of  $\sim 0.12$  eV/H<sub>2</sub> for GGA and  $\sim 0.40$  eV/H<sub>2</sub> for LDA,

**Table 1.** Average Adsorption Energies of H<sub>2</sub> on Ca-Coated B<sub>80</sub> Fullerene and the Corresponding Bond Lengths Computed at the GGA-PW91 and LDA-CA Levels of Theory

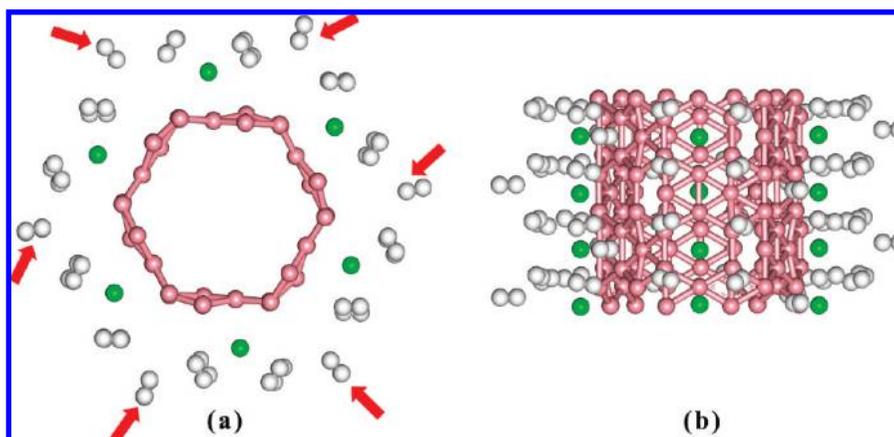
	$E_a$ (eV/H <sub>2</sub> )		$d_{\text{Ca-H}}$ (Å)		$d_{\text{H-H}}$ (Å)	
	GGA	LDA	GGA	LDA	GGA	LDA
B <sub>80</sub> CaH <sub>2</sub>	-0.23	-0.53	2.38	2.11	0.78	0.89
B <sub>80</sub> Ca(H <sub>2</sub> ) <sub>2</sub>	-0.21	-0.48	2.43	2.19	0.77	0.83
B <sub>80</sub> Ca(H <sub>2</sub> ) <sub>3</sub>	-0.21	-0.45	2.43	2.22	0.77	0.83
B <sub>80</sub> Ca(H <sub>2</sub> ) <sub>4</sub>	-0.20	-0.45	2.43	2.23	0.77	0.82
B <sub>80</sub> Ca(H <sub>2</sub> ) <sub>5</sub>	-0.20	-0.43	2.51	2.25	0.76	0.81



**Figure 5.** Top and side views of the optimized structures of (a) one Ca atom placed on a (9,0) B nanotube and (b) 12 Ca atoms coating on a (9,0) B nanotube.



**Figure 6.** Optimized configurations of Ca-coated (9,0) B nanotubes with one to five H<sub>2</sub> molecules. The corresponding average adsorption energies per H<sub>2</sub> were computed at the GGA level of theory.



**Figure 7.** Optimized geometry with five H<sub>2</sub> molecules around each Ca atom on a (9,0) B nanotube: (a) top view and (b) side view (at the GGA level of theory). The H<sub>2</sub> molecules at the hexagonal corner are indicated by red arrows.

which allows both adsorption of molecular hydrogen and its release at ambient conditions.

Boron nanotubes are also suitable substrates for Ca distribution and hydrogen storage. The optimized configuration of one Ca atom on a (9,0) B nanotube is depicted in Figure 5a; the Ca–B distance is  $\sim 2.62$  Å, Ca carries a 0.74 |e| positive charge (Hirshfeld charge analysis), and the binding energy of Ca is  $\sim 2.14$  eV. As shown in Figure 5b, when 12 Ca atoms coat on (9,0) BNT, the round tube is deformed into a hexagonal one, the bond length of Ca–B is  $\sim 2.66$  Å, Ca carries a 0.40 |e| positive charge (Hirshfeld charge analysis), and the average binding energy is  $\sim 2.10$  eV/Ca, which is slightly different from that of Ca-coated B<sub>80</sub>. the Ca[0012]defau

The binding energies of a hydrogen molecule on a Ca-coated (9,0) B nanotube are summarized in Figure 6. Just

like in the case of Ca-coated B<sub>80</sub> fullerene, we chose several initial configurations for H<sub>2</sub> molecules to search the lowest-energy configuration when optimizing the geometry of the complexes. Up to 5 H<sub>2</sub> molecules can be adsorbed on each Ca atom with a binding energy of  $\sim 0.15$  eV/H<sub>2</sub> (at the GGA level of theory). When one H<sub>2</sub> molecule is introduced to the substrate, the Ca–H bond length is  $\sim 2.47$  Å, and the H–H bond is elongated to  $\sim 0.77$  Å. As the number of H<sub>2</sub> on a Ca-coated (9,0) B nanotube increases, the average hydrogen adsorption energy decreases only slightly.

As five H<sub>2</sub> molecules are adsorbed around each Ca atom in (9,0) BNT (Figure 7), one H<sub>2</sub> molecule moves to the hexagonal corner (indicated by arrows in Figure 7a). The H–H bond length ranges from 0.76 Å to 0.77 Å, and the average distance between H<sub>2</sub> and the Ca atom is  $\sim 2.91$  Å, with a binding energy of  $\sim 0.10$  eV/H<sub>2</sub> at GGA and  $\sim 0.30$

eV/H<sub>2</sub> at LDA. Since one H<sub>2</sub> molecule escapes from the Ca atom, we place only four H<sub>2</sub> molecules around each Ca atom; however, one of the H<sub>2</sub> molecules still moves to the hexagonal corner of (9,0) BNT. The surface curvature in the hexagonal corner is large and leads to high sp<sup>3</sup> hybridization. The highly localized p<sub>z</sub> orbitals of B atoms<sup>50,54</sup> make the corner also even attractive for hydrogen molecules.

In summary, we investigated hydrogen adsorption on Ca-coated boron nanostructures. Ca can bind strongly to the surface of B<sub>80</sub> fullerene and boron nanotubes, thus avoiding the notorious clustering problem. B<sub>80</sub> fullerene coated with 12 Ca atoms can store up to 60 H<sub>2</sub> molecules with an average binding energy of 0.12–0.40 eV, corresponding to a gravimetric density of hydrogen storage of 8.2 wt %. The hydrogen storage capacity of a Ca-covered (9,0) B nanotube is 7.6 wt % with a binding energy of 0.10–0.30 eV. The strong interaction between Ca and boron fullerenes and nanotubes is attributed to the charge transfer. The optimal molecular hydrogen adsorption energies make reversible hydrogen adsorption and desorption feasible at ambient conditions. Ca-coated boron nanomaterials are superior media for hydrogen storage. Note that the hydrogen storage media proposed in this work are in the nanoscale; the hydrogen capacity will significantly decrease in macroscopic materials.<sup>55</sup> It is still a big challenge for further research to assemble the ideal media into suitable macroscopic materials for practical hydrogen storage. Porous structures similar to metal–organic frameworks (MOFs)<sup>56</sup> with Ca-coated B nanostructures as building blocks may be prospective for high gravimetric and volumetric hydrogen storage capacity.

**Acknowledgment.** This study was supported in China by the NSFC (50502021 and 20873067) and the 973 Program (2009CB220100), and in the USA by NSF Grant CHE-0716718, the Institute for Functional Nanomaterials (NSF Grant 0701525), and the U.S. Environmental Protection Agency (EPA Grant No. RD-83385601). This paper is dedicated to Prof. Walter Thiel on the occasion of his 60<sup>th</sup> birthday.

**Supporting Information Available:** The coordinates of the compact Ca<sub>12</sub> cluster as well as structures and relative total energies of B<sub>80</sub> coated with 12 isolated Ca, Sc, or Ti atoms, and B<sub>80</sub> attached to a Ca<sub>12</sub>, Sc<sub>12</sub>, or Ti<sub>12</sub> cluster. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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NL900116Q