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## New Ti-decorated B<sub>40</sub> fullerene as a promising hydrogen storage material

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The newly found B<sub>40</sub> is the first experimentally observed all-boron fullerene and has potential applications in hydrogen storage. Here we investigate the binding ability and hydrogen storage capacity of Ti-decorated B<sub>40</sub> fullerene based on DFT calculations. Our results indicate that Ti shows excellent binding capability to B<sub>40</sub> compared with other transition metals. The B<sub>40</sub> fullerene coated by 6 Ti atoms (Ti<sub>6</sub>B<sub>40</sub>) can store up to 34 H<sub>2</sub> molecules, corresponding to a maximum gravimetric density of 8.7 wt%. It takes 0.2–0.4 eV/H<sub>2</sub> to add one H<sub>2</sub> molecule, which assures reversible storage of H<sub>2</sub> molecules under ambient conditions. The evaluated reversible storage capacity is 6.1 wt%. Our results demonstrate that the new Ti-decorated B<sub>40</sub> fullerene is a promising hydrogen storage material with high capacity.

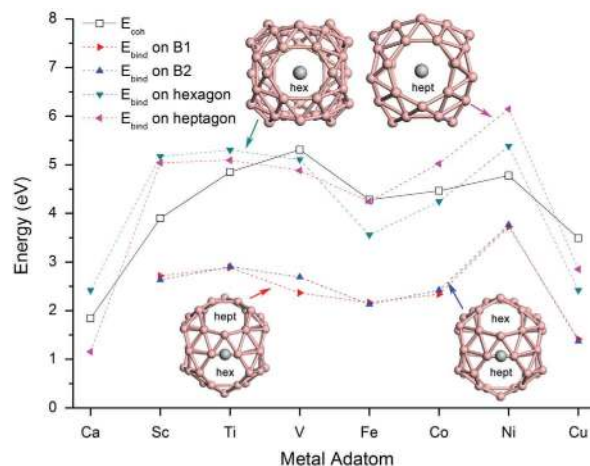
Hydrogen has long been considered as a clean, abundant and efficient energy carrier<sup>1,2</sup>. Developing appropriate storage media is of the importance for practical application of hydrogen energy. As an earth-abundant element, boron is widely applied for hydrogen storage with its chemical hydrides and nanostructural forms<sup>3</sup>. Boron-based chemical hydrogen storage materials such as borohydrides (e.g., LiBH<sub>4</sub> and NaBH<sub>4</sub>) are promising compounds because of their high hydrogen capacities<sup>4–6</sup>. However, due to kinetic and/or thermodynamic limitations, the chemical hydrides suffer from poor reversibility<sup>7</sup>, there are still difficulties in practical application of borohydrides<sup>8</sup>. An efficient solution is to find suitable all-boron nanostructures as replacement.

Since the bulk boron cannot be found in nature, the design and synthesis of bulk boron allotropes still keeps challenging to theoretical and experimental chemists. It attracts more interest on all-boron fullerenes after the theoretical prediction of B<sub>80</sub> fullerene<sup>9</sup>, which is a hollow cage-like cluster resembling the C<sub>60</sub>. It is revealed that all of the boron allotropes are based on different arrangements of B<sub>12</sub> icosahedrons<sup>9,10</sup>. After that, various types of boron fullerene nanostructures were proposed and simulated by theoretical calculations, such as B<sub>32+8n</sub> (from B<sub>32</sub> to B<sub>80</sub>)<sup>11</sup>, B<sub>32+6n</sub> (from B<sub>32</sub> to B<sub>56</sub>)<sup>12</sup>, 80n<sup>2</sup> boron fullerenes series (from B<sub>80</sub> to B<sub>2000</sub>)<sup>13</sup>, B<sub>100</sub><sup>14</sup>, etc.

Boron fullerenes are seen as efficient hydrogen storage media since they are light-weight and have the capability to bind with metal adatoms. Combined with the fact that isolated transition metal (TM) has the ability to bind a certain number of hydrogens in molecular form, theoretical simulations on hydrogen adsorption by metal-adsorbed boron fullerenes were reported<sup>15–17</sup>. By density functional theory (DFT) calculations, Li *et al.*<sup>16</sup> declared that Ca-coated B<sub>80</sub> fullerene can store up to 8.2 wt% H<sub>2</sub> with an adsorption energy of 0.12–0.40 eV/H<sub>2</sub>. Before that, Zhou *et al.*<sup>17</sup> reported the hydrogen adsorption on alkali-metal (Na, K) doped B<sub>80</sub>. They found that B<sub>80</sub>Na<sub>12</sub> and B<sub>80</sub>K<sub>12</sub> show fairly low adsorption energies (0.07 eV/H<sub>2</sub> and 0.09 eV/H<sub>2</sub>), indicating that alkali-metal is unsuitable for hydrogen storage. So far, all the theoretical investigations are based on the “proposed” boron fullerenes. Their applications in hydrogen storage may be unfeasible due to the uncertainty of the adsorbents.

Recently, an all-boron fullerene-like cage cluster B<sub>40</sub><sup>−</sup> was produced and observed<sup>18</sup>. Its neutral counterpart B<sub>40</sub> exhibits the fullerene-like cage (D<sub>2d</sub> symmetry) and is calculated to be the most stable structure among the B<sub>40</sub> allotropes. The relevant theoretical simulation indicates that B<sub>40</sub> fullerene is thermally

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**Figure 1.** The binding energy ( $E_{\text{bind}}$ ) of single metal adatom on different binding sites of  $B_{40}$ , 8 different metal adatoms are used as comparison. B1 and B2 represent the B-B bridge sites around hexagon and heptagon, respectively. The “hex” and “hept” are marked to denote the location of hexagons and heptagons. Pink ball: boron atom, grey ball: metal atom.

stable at temperature as high as 1000 K<sup>18</sup>. This is the first experimental evidence for the existence of all-boron fullerene.

For the hydrogen storage materials, transition metal (TM) atoms are important components due to their strong attraction to hydrogen molecules<sup>19–22</sup>. Among the TMs, titanium (Ti) is regarded as an ideal binding metal in nanomaterials since it takes great advantages in hydrogen storage, which has been concluded<sup>16</sup>. Because of the outstanding performance in hydrogen storage, Ti-decorated nanostructures have been widely reported<sup>19,23–32</sup>. However, previous computational researches on hydrogen storage of  $B_{80}$ <sup>16,17</sup> indicated that Ca is the appropriate adsorbate for boron fullerene due to the stable adsorption and high storage capacity. So which kind of metal atom would be the best adsorbate for  $B_{40}$  as hydrogen storage material? Here we perform DFT calculations on the binding capability of different metal atoms (Ca and TM: Sc, Ti, V, Fe, Co, Ni, Cu) decorated  $B_{40}$  fullerene. The simulations on hydrogen storage by metal-decorated  $B_{40}$  fullerene are also carried out.

## Results and Discussion

The surface of  $B_{40}$  fullerene contains 48 boron triangles, embedded by 4 heptagonal rings and 2 hexagonal rings. The hexagons are planar while the heptagons are non-planar. We placed metal atoms on different sites of surface of  $B_{40}$  and calculated the binding energy ( $E_{\text{bind}}$ ) following

$$E_{\text{bind}} = -\frac{1}{n} [E_{nM@B_{40}} - nE_M - E_{B_{40}}] \quad (1)$$

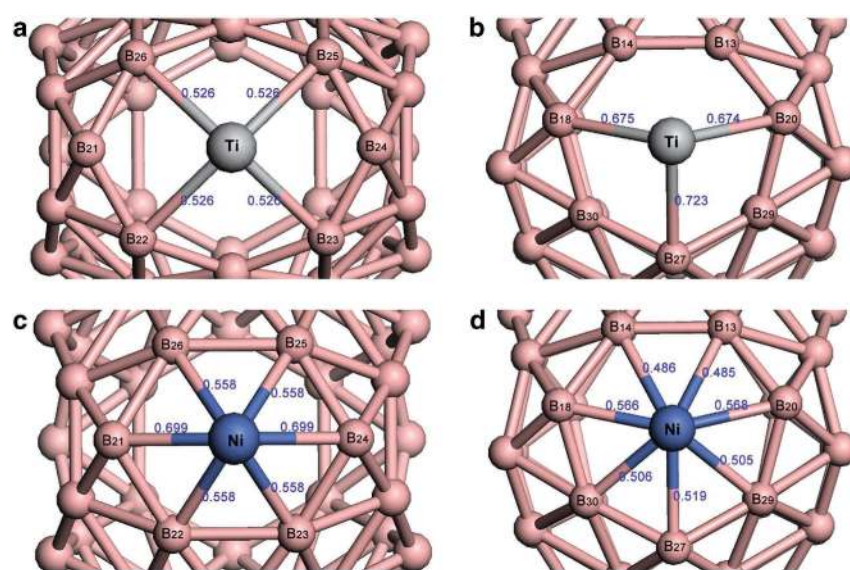
where  $n$  is the number of metal adatom coated on  $B_{40}$ .  $E_M$ ,  $E_{B_{40}}$  and  $E_{nM@B_{40}}$  stand for the total energies of metal adatom,  $B_{40}$  and the metal-coated  $B_{40}$  complex, respectively. We first calculated the binding energies of single metal atom on different binding sites of  $B_{40}$ , including the centers of hexagon and heptagon, as well as the B-B bridges around hexagon (B1) and heptagon (B2). We take 8 different metal adatoms (Sc, Ti, V, Fe, Co, Ni, Cu, and Ca) for comparison. As shown in Fig. 1, the centers of hexagon and heptagon are confirmed as the energy-favorable sites due to the significantly higher  $E_{\text{bind}}$  than sites B1 and B2. Ca atoms even cannot stably bind to the B-B bridges. To avoid the metal adatoms forming cluster on surface of  $B_{40}$ <sup>23,33</sup>, the metal species should meet the requirement that the binding energies are higher than their corresponding crystalline cohesive energies ( $E_{\text{coh}}$ )<sup>19,34</sup>.

Figure 1 indicates that Sc, Ti and Ni show higher binding energies with  $B_{40}$  than their cohesive energies, both on the centers of hexagon and heptagon. Thus Sc, Ti and Ni could be used as good adsorbates to decorate  $B_{40}$ . The average binding energies of 1–6 metal adatoms (Sc, Ti, and Ni) on different facets of  $B_{40}$  are listed in Table 1. When there are more than 4 Sc atoms, the Sc-coated  $B_{40}$  complexes will distort and cause instability of the fullerene-like substrate. Oppositely, the introduction of more Ti and Ni atoms will not affect the geometric structure of  $B_{40}$  significantly. When all of the hexagonal and heptagonal facets are coated by Ti or Ni atoms, the  $Ti_6B_{40}$  or  $Ni_6B_{40}$  complexes keep stable and provide high  $E_{\text{bind}}$ .

It is worth noting that due to the differences in valence electron configuration, Ni and Ti show significantly different bonding structures and binding energies with the different facets of  $B_{40}$ . By comparing the binding energies with equal number of metal atom in Table 1, it can be concluded that Ti is more energy-favorable on hexagon, while Ni is more energy-favorable on heptagon. To reveal the bonding

Metal adatom	Sc	Ti	Ni
$E_{\text{coh}}/\text{eV}$	3.90	4.85	4.44
$E_{\text{bind\_hex1}}/\text{eV}$	5.17	5.30	5.38
$E_{\text{bind\_hept1}}/\text{eV}$	5.04	5.09	6.14
$E_{\text{bind\_hex2}}/\text{eV}$	5.22	5.27	5.36
$E_{\text{bind\_hept2}}/\text{eV}$	5.24	5.29	6.07
$E_{\text{bind\_hex2hept2}}/\text{eV}$	–	5.58	5.69
$E_{\text{bind\_hept4}}/\text{eV}$	–	5.88	6.06
$E_{\text{bind\_6}}/\text{eV}$	–	5.83	5.81

**Table 1.** The average binding energies ( $E_{\text{bind}}$ ) of 1–6 metal adatoms (Sc, Ti, and Ni) on different facets of  $B_{40}$ , the cohesive energies ( $E_{\text{coh}}$ ) of the metal are shown as comparison<sup>47</sup>. The subscripts “hex” and “hept” indicate that the metal adatoms are adsorbed to the hexagonal and heptagonal facets of  $B_{40}$ , while the Arabic number indicates the number of metal adatoms that coated on the corresponding facet.  $E_{\text{bind}_6}$  means that all the 6 facets are decorated by the metal adatoms.



**Figure 2.** Bonding structures of single Ti- or Ni-decorated  $B_{40}$ : (a) Ti@hexagon, (b) Ti@heptagon, (c) Ni@hexagon, and (d) Ni@heptagon. Covalent M-B bonds are shown with the bond order values (digits in blue color).

rules, we performed Mayor bond order<sup>35</sup> analysis on single Ti- and Ni-decorated  $B_{40}$  fullerene, as shown in Fig. 2. Different binding conformations on hexagonal ring and heptagonal ring are named M@hexagon and M@heptagon, respectively. The bonding structures reveal that Ni covalently bonds with all the surrounding boron atoms, but Ti only forms 4 and 3 stable covalent bonds (with bond order value larger than 0.5) when binds to hexagon and heptagon respectively. Considering their valence electron configurations (Ti:  $3d^24s^2$ , Ni:  $3d^84s^2$ ), the rich valence electrons determine that Ni can form as much as 7 weak Ni-B covalent bonds, while Ti only forms up to 4 Ti-B covalent bonds due to its 4 valence electrons. Ti-B average bond length ( $\sim 2.17 \text{ \AA}$ ) is longer than Ni-B average bond length ( $\sim 2.0 \text{ \AA}$ ), which explains why the Ti-coated hexagon expands in Fig. 2(a) compared with Ni@hexagon in Fig. 2(c). However, the Ti-coated heptagon changes slightly, mostly due to its non-planar arrangement of boron atoms. Ti@hexagon shows higher stability than Ti@heptagon since there are more Ti-B covalent bonds. Similarly, Ni@heptagon is more stable than Ni@hexagon because of the 7 covalent bonds. This is the reason why Ti is more energy-favorable on hexagon while Ni is more energy-favorable on heptagon.

Another important finding is that the average binding energy is related with the number of metal adatoms on different facets. That is, for Ti-decorated  $B_{40}$  fullerene, the average binding energy increases as the number of Ti atoms on heptagon increases, and decreases as the number of Ti atoms on hexagon decreases. Differently, for Ni-decorated  $B_{40}$  fullerene, the average binding energy decreases as the number of Ni atoms increases for both binding sites. It can be inferred that there exists attractive interaction between the decorated Ti atoms, while the interaction between the coated Ni atoms is repulsive. In

N(H <sub>2</sub> )	Ti@hexagon			Ti@heptagon			
	E <sub>ads</sub> (eV/ H <sub>2</sub> )	ΔE (eV/ H <sub>2</sub> )	Ti-1 <sup>st</sup> H <sub>2</sub> (Å)	E <sub>ads</sub> (eV/ H <sub>2</sub> )	ΔE (eV/ H <sub>2</sub> )	Ti-1 <sup>st</sup> H <sub>2</sub> (Å)	Ti-2 <sup>nd</sup> H <sub>2</sub> (Å)
1	0.82	0.82	1.953	0.74	0.74	1.928	–
2	0.51	0.20	1.962	0.78	0.82	1.898	1.926
3	0.43	0.26	1.957	0.65	0.39	1.932	2.110
4	0.40	0.31	1.975	0.57	0.30	1.942	2.116
5	0.36	0.22	1.950	0.52	0.32	1.956	2.111
6				0.49	0.39	1.955	2.113

**Table 2.** Calculated average adsorption energies (E<sub>ads</sub>) and consecutive adsorption energies (ΔE) by the successive addition of H<sub>2</sub> molecules to Ti@hexagon and Ti@heptagon, as well as the distance between Ti atom and the first (Ti-1<sup>st</sup> H<sub>2</sub>) or second (Ti-2<sup>nd</sup> H<sub>2</sub>) added H<sub>2</sub> molecule.

summary, when all the hexagonal and heptagonal rings are embedded by metal atoms, the binding of Ti will be stronger than Ni, and also the strongest among the chosen metal species. The stable binding of Ti on B<sub>40</sub> leads to promising applications of the Ti-decorated B<sub>40</sub> fullerene. Here we consider it as a suitable candidate for hydrogen storage.

According to the well-known 18-electron rule<sup>19,36</sup>, the maximum number of adsorbed hydrogen molecules (N<sub>max</sub>) is limited by the valence electrons that participating in covalent bonds. For metal-decorated B<sub>40</sub> fullerenes we design here, the 18-electron rule can be specified as

$$2N_{\max} = 18 - n_v(M) - n_v(B_{40}), \quad (2)$$

where  $n_v(M)$  represents the valence electron number of the metal element,  $n_v(B_{40})$  represents the electrons contributed by B<sub>40</sub>, which is 4 for Ti@hexagon and 3 for Ti@heptagon. The N<sub>max</sub> is calculated to be 5 and 5.5 for Ti@hexagon and Ti@heptagon, which demonstrates that the single Ti-decorated B<sub>40</sub> can store up to 5 and 6 H<sub>2</sub> molecules when Ti atom binds to hexagon and heptagon, respectively. However, the N<sub>max</sub> is calculated to be 1 for Ni-decorated B<sub>40</sub> fullerene. Obviously the Ni-decorated B<sub>40</sub> fullerene is inefficient as hydrogen storage medium.

We use average adsorption energy (E<sub>ads</sub>) to evaluate the adsorption capability of the Ti-decorated B<sub>40</sub> fullerene. We also define consecutive adsorption energy (ΔE) as the energy gained by successive additions of H<sub>2</sub> molecules to evaluate the reversibility for storage of H<sub>2</sub> molecules. They are calculated based on the following formulas

$$E_{\text{ads}} = - \frac{1}{n} [E_{\text{Ti@B40} + n\text{H}_2} - E_{\text{Ti@B40}} - nE_{\text{H}_2}] \quad (3)$$

and

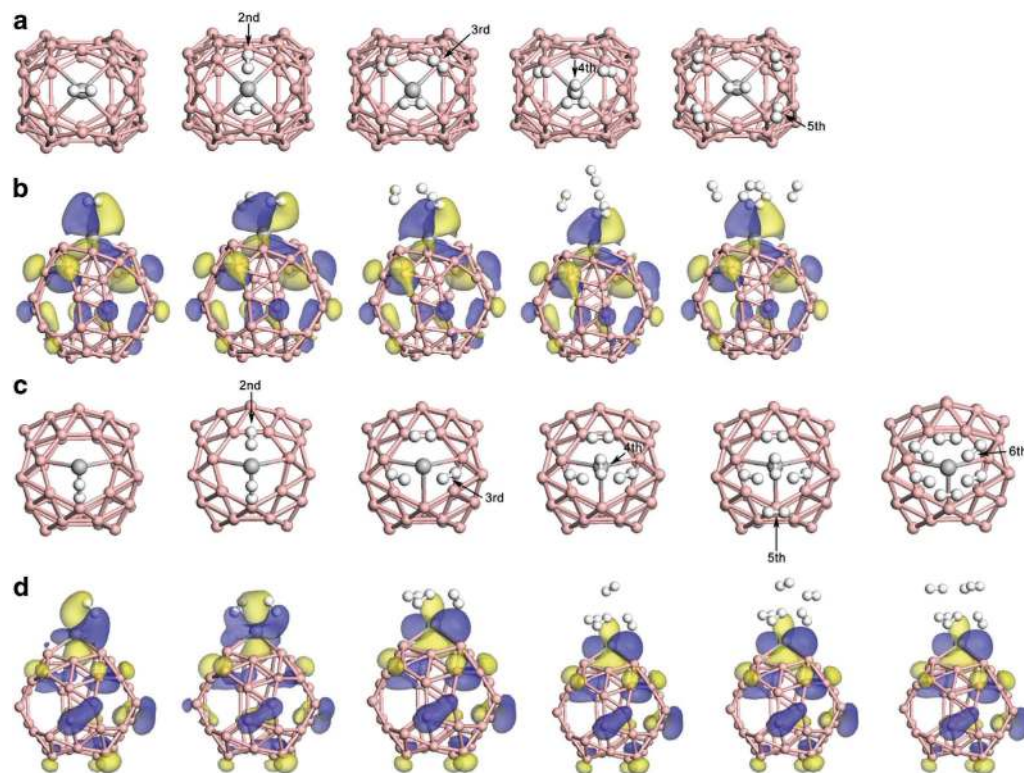
$$\Delta E = - [E_{\text{Ti@B40} + n\text{H}_2} - E_{\text{Ti@B40} + (n-1)\text{H}_2} - E_{\text{H}_2}] \quad (4)$$

where  $n$  stands for the number of adsorbed H<sub>2</sub> molecules.  $E_{\text{Ti@B40}}$  and  $E_{\text{H}_2}$  are the total energies of Ti-decorated B<sub>40</sub> and H<sub>2</sub> molecule.  $E_{\text{Ti@B40} + n\text{H}_2}$  and  $E_{\text{Ti@B40} + (n-1)\text{H}_2}$  are the total energies of Ti-decorated B<sub>40</sub> with  $n$  and  $(n-1)$  H<sub>2</sub> molecules, respectively. For efficient hydrogen storage at ambient conditions, the ideal adsorption energy should be in the range of 0.16–0.42 eV/H<sub>2</sub><sup>37,38</sup> to realize reversible adsorption and desorption. This energy range leads to intermediate between physisorption and chemisorptions<sup>16</sup>.

The calculated E<sub>ads</sub> and ΔE are summarized in Table 2. With all of the ΔE larger than 0.2 eV/H<sub>2</sub>, our simulations confirm that the maximum adsorption numbers of H<sub>2</sub> molecules can reach 5 for Ti@hexagon and 6 for Ti@heptagon, respectively. For H<sub>2</sub> adsorption on Ti@hexagon, the first H<sub>2</sub> molecule exhibits significantly larger adsorption energy than the following H<sub>2</sub> molecules. Addition of the second to fifth H<sub>2</sub> molecule gains energies within 0.2–0.3 eV per H<sub>2</sub>, and they are adsorbed around the first H<sub>2</sub>, as shown in Fig. 3(a). Our analysis on the Ti-H<sub>2</sub> distance reveals that for the Ti@hexagon, the first added H<sub>2</sub> molecule keeps a close distance to the Ti atom (1.950 ~ 1.975 Å in Table 2). Particularly, affected by the 4 surrounding H<sub>2</sub> molecules, the 1<sup>st</sup> H<sub>2</sub> molecule of 5 H<sub>2</sub> molecules adsorbed Ti@hexagon will be closer to the Ti atom. Moreover, as shown in Fig. 3(b), the first H<sub>2</sub> molecule always shares the highest occupied molecular orbital (HOMO) with the adsorbent, indicating the strong chemical adsorption between the first H<sub>2</sub> molecule and Ti@hexagon.

The case of adsorption on Ti@heptagon is different. As we can see in Table 2, the first and second H<sub>2</sub> molecules both show strong binding to the Ti atom. This can be attributed to the extra 3d electron of Ti, which doesn't participate in forming covalent Ti-B bond. Figure 3(d) indicates that the Ti 3d orbital overlaps with the H 1s orbital when there is one or two H<sub>2</sub> molecules adsorbed. With the addition of third H<sub>2</sub> molecule, the overlapping between Ti and H<sub>2</sub> is interrupted. From the addition of 3<sup>rd</sup> to 6<sup>th</sup> H<sub>2</sub>





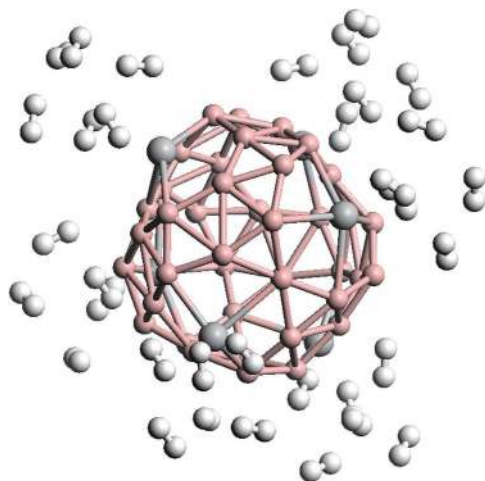
**Figure 3.** (a) & (c) Top view of successive addition of H<sub>2</sub> molecules on Ti@hexagon & Ti@heptagon. (b) & (d) HOMO distributions on Ti@hexagon & Ti@heptagon with H<sub>2</sub> molecules adsorbed, the HOMO isovalue is set as 0.03 e/Å<sup>3</sup>. Pink ball: B atom, grey ball: Ti atom, white ball: H atom.

molecule, the HOMOs only distribute on surface of Ti@heptagon, indicating the weakening of the H<sub>2</sub>-Ti interaction. On the other hand, distances between Ti and the first two H<sub>2</sub> molecules become significantly larger with the addition of 3<sup>rd</sup> to 6<sup>th</sup> H<sub>2</sub> molecules, which is consistent with the HOMO analysis. Addition of the third to sixth H<sub>2</sub> molecules gains consecutive adsorption energies within 0.3–0.4 eV per H<sub>2</sub>, which also meets the requirement for reversible uptake and release of H<sub>2</sub> molecules.

As displayed in Fig. 3, it should be pointed out that either the geometric structures or the distribution of HOMOs of the adsorption substrate (Ti-decorated B<sub>40</sub> fullerene) keep stable and are little changed with the increasing of adsorbed H<sub>2</sub> molecules, revealing the high stability of Ti-decorated B<sub>40</sub> fullerene. The geometric and electronic structure of the substrate is little affected by the addition of H<sub>2</sub> molecules, which is important for the realization of reversible hydrogen storage.

To check if the first adsorbed H<sub>2</sub> molecule will dissociate into two hydrogen ions on centered Ti atom and form dihydride complex, as mentioned in similar work<sup>19,22,24,25,27</sup>, we also modeled the dihydride contained complexes (B<sub>40</sub>TiH<sub>2</sub>) as initial configurations and performed full geometry optimization. Our simulation results (as displayed in **Figure S1**) show that the dihydride complex is less stable than our determined local minimum (about 1.10 eV higher in total energy). Meanwhile, singlet state should be considered as the ground state for dihydrogen adsorbed Ti@B<sub>40</sub> complexes due to the higher stability. The dihydrogen molecule with a slight elongation of H-H is determined as the local minimum for adsorption of the first H<sub>2</sub> molecule on Ti-decorated B<sub>40</sub>.

To look insight of the influence of B<sub>40</sub> in adsorbing hydrogen, we checked all the possible adsorption sites of undecorated B<sub>40</sub> for H<sub>2</sub> adsorption. Calculation results show that the B<sub>40</sub> fullerene itself is unsuitable for H<sub>2</sub> adsorption with E<sub>ads</sub> ranges from 0.15 eV to 0.20 eV (as listed in **Table S1**). All of the distances from the adsorbed H<sub>2</sub> to B<sub>40</sub> surface are larger than 2.8 Å, indicating the nature of weak physisorption. To see whether the H<sub>2</sub> molecule will transfer from Ti to B<sub>40</sub> when adsorbs to Ti-decorated B<sub>40</sub>, the possibility of H<sub>2</sub> adsorption onto B<sub>40</sub> in Ti-decorated B<sub>40</sub> (Ti<sub>6</sub>B<sub>40</sub>) is also checked. Our simulations elucidate that comparing with the H<sub>2</sub> adsorption on Ti atoms, the H<sub>2</sub> adsorption on B<sub>40</sub> is rather weaker with E<sub>ads</sub> around 0.2 eV (**Table S1**). Adsorption energies of H<sub>2</sub> on B<sub>40</sub> in Ti<sub>6</sub>@B<sub>40</sub> complex enhance slightly compared with the undecorated one (for the same adsorption site), indicating that the decoration of Ti atoms won't improve the adsorption performance of B<sub>40</sub> for H<sub>2</sub> much. For our modeled Ti<sub>6</sub>B<sub>40</sub> complexes, the Ti atoms exhibit high attraction for hydrogen molecules due to the high localization of FMO on them, as shown in **Figure S2**. This localization won't be significantly affected by the increasing H<sub>2</sub> molecules, making the transfer of H<sub>2</sub> molecule to B<sub>40</sub> difficult to happen.



**Figure 4.** The optimized structure of  $\text{Ti}_6\text{B}_{40}$  complex with 34  $\text{H}_2$  molecules adsorbed. Pink ball: B atom, grey ball: Ti atom, white ball: H atom.

Based on the calculation results of hydrogen adsorption on single Ti-decorated  $\text{B}_{40}$ , we constructed and optimized the adsorption configuration of  $\text{H}_2$  molecules on  $\text{Ti}_6\text{B}_{40}$  complex. As shown in Fig. 4 (the atomic coordinates of the optimized  $\text{Ti}_6\text{B}_{40}$  and  $\text{Ti}_6\text{B}_{40}$  with 34  $\text{H}_2$  molecules adsorbed are listed in **Table S2** and **S3**), up to 34  $\text{H}_2$  molecules are adsorbed around the Ti atoms [named  $\text{Ti}_6\text{B}_{40}(\text{H}_2)_{34}$ ]. Our calculated gravimetric density of hydrogen stored by  $\text{Ti}_6\text{B}_{40}$  can reach 8.7 wt%, with an average adsorption energy of 0.37 eV/ $\text{H}_2$ . As we have mentioned above, the first  $\text{H}_2$  molecule on Ti@hexagon and the first two  $\text{H}_2$  molecules on Ti@heptagon have stronger binding with the Ti atoms than the following  $\text{H}_2$  molecules. We measured the average distance between the  $\text{H}_2$  molecules and the corresponding Ti atoms for  $\text{Ti}_6\text{B}_{40}(\text{H}_2)_{34}$ . For  $\text{H}_2$  adsorption on hexagon-embedded Ti atoms, the average distance of the 1<sup>st</sup>  $\text{H}_2$  molecules to Ti atom is 1.952 Å, almost the same distance with the occasion of 5  $\text{H}_2$  molecules adsorbed Ti@hexagon. However, for  $\text{H}_2$  adsorption on heptagon-embedded Ti atoms, the average distances of the 1<sup>st</sup> and 2<sup>nd</sup>  $\text{H}_2$  molecules to Ti atom are 2.052 Å and 2.358 Å, respectively. The values are significantly larger than the occasion of 6  $\text{H}_2$  molecules adsorbed Ti@heptagon, indicating the repulsive interaction from  $\text{H}_2$  molecules on other facets. Analysis on  $\text{H}_2$ -Ti distance demonstrates that the increase of  $\text{H}_2$  molecule mainly affects the hydrogen adsorption on heptagon-embedded Ti atoms, which is the origin of reduction of the average  $\text{H}_2$  adsorption energy.

Evaluating from our calculation results on successive addition of  $\text{H}_2$  molecules, among the 34 adsorbed  $\text{H}_2$  molecules on  $\text{Ti}_6\text{B}_{40}$ , 24 of them have moderate adsorption energies within the range of 0.2–0.4 eV/ $\text{H}_2$ , corresponding to a reversible storage capacity of 6.1 wt%. It is notable that the bonding type and geometric structure of the  $\text{B}_{40}\text{Ti}_6$  complex is also little affected by the adsorption of  $\text{H}_2$  molecules. The favorable consecutive adsorption energy assures the reversible storage of hydrogen molecules under ambient conditions.

$\text{B}_{40}$  is a newly discovered boron nanostructure and also the first experimentally observed all-boron fullerene. Here we performed computational investigations on hydrogen storage capacity of Ti-decorated  $\text{B}_{40}$  fullerene. Comparative calculations reveal that, among the chosen metal species, Ti exhibits the strongest binding on surface of  $\text{B}_{40}$ . Ti-decorated  $\text{B}_{40}$  fullerene exhibits strong adsorption and high capacity for  $\text{H}_2$  molecules. Single Ti decorated  $\text{B}_{40}$  fullerene can store up to 5 and 6  $\text{H}_2$  molecules for Ti@hexagon and Ti@heptagon, respectively. All of the adsorption happens on Ti atom, and  $\text{B}_{40}$  shows weak capability in adsorbing  $\text{H}_2$  molecules. This leads to a maximum storage capacity of 34  $\text{H}_2$  molecules for  $\text{Ti}_6\text{B}_{40}$  complex with an average adsorption energy of 0.37 eV/ $\text{H}_2$ , corresponding to a gravimetric density of 8.7 wt%. The consecutive adsorption energy of  $\text{H}_2$  molecules within the range of 0.2–0.4 eV/ $\text{H}_2$  assures the reversible storage of 6.1 wt% under ambient conditions. Our computational investigations confirm that the Ti-decorated  $\text{B}_{40}$  fullerene is favorable for hydrogen adsorption, which makes it promising as a new hydrogen storage material.

## Methods

Density functional theory (DFT) calculations are carried out by DMol<sub>3</sub> program<sup>39,40</sup>. The generalized gradient approximation (GGA) functional by Perdew and Wang (PW91)<sup>41</sup>, along with a double numerical basis set including p-polarization function (DNP), is applied for the geometry optimization and property calculations. Dispersion-corrected DFT (DFT-D)<sup>42–44</sup> scheme put forward by Ortmann, Bechstedt, and Schmidt (OBS)<sup>45</sup> is used to describe the van der Waals (vdW) interaction. DFT semi-core pseudo-potentials (DSPPs)<sup>46</sup> are employed to efficiently treat with the core electron of TM element after Ca. Self-consistent-field (SCF) convergence tolerance is set to  $1 \times 10^{-6}$  Ha. The convergence threshold

values are specified as  $1 \times 10^{-5}$  Ha for energies,  $2 \times 10^{-3}$  Ha/Å for gradient, and  $5 \times 10^{-3}$  Å for displacement, respectively.

Reliability of PW91/DNP level in treating metal-boron system has been proven by Zhou *et al.*<sup>17</sup> in calculating the binding of alkali-metal (AM) on B<sub>80</sub> fullerene as well as the hydrogen storage capacity of B<sub>80</sub>-AM complexes. The incorporation of DFT-D scheme further improves the accuracy in evaluating weak interactions.

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## Author Contributions

Y.L. developed the main idea and supervised the project. H.D. performed all the calculation work and analyzed the results. H.D., T.H., S.L. and Y.L. wrote the paper.

## Additional Information

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