

Ab initio study of dihydrogen binding in metal-decorated polyacetylene for hydrogen storage

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Using first-principles calculations based on the density-functional theory, we perform a detailed study of the dihydrogen (H_2) binding in *cis*- and *trans*-polyacetylene decorated with transition metal atoms. First, we investigate the origin of metal-dihydrogen bonding and observe the hybridization of e_g (t_{2g}) orbitals of the Ti atom with the σ (σ^*) orbitals of the H_2 molecules in octahedral geometries, which is consistent with the Kubas model. Second, using a statistical model parametrized by the results of *ab initio* calculations and experimental data, the adsorption and desorption of molecular hydrogens are calculated at ambient temperature and pressure. We find that the *usable* capacity at ambient conditions is dramatically reduced from the maximum capacity, the zero-point energy affects the storage capacity significantly, and the optimal binding energy of H_2 molecules under practical conditions is ~ 0.3 eV/ H_2 . Third, we examine the effects of the aggregation and intercalation of the Ti atoms on H_2 adsorption.

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I. INTRODUCTION

Hydrogen storage in solid state materials is one of the most essential requirements for commercialization of hydrogen vehicles with the fuel cell. The U.S. Department of Energy (DOE) has established the target for hydrogen storage capacity of candidate materials to be used on-board vehicles. The targets for gravimetric and volumetric capacity of hydrogen to be achieved by the year 2015 are 9 wt % and 81 kg/m³, respectively.¹ Although much effort has been devoted to storing hydrogen in metal and chemical hydrides, there have so far been no promising materials for hydrogen storage because of poor reversibility.²⁻⁴ In the last decade, nanostructured materials such as carbon nanotubes (CNTs) and metal-organic frameworks have received a great deal of attention due to the potential for high-capacity storage (large surface area), fast kinetics (adsorption and desorption in the form of molecular hydrogen), and enduring media (good reversibility).⁵⁻⁸ However, the nanostructured materials have up to now fallen short of expected capacity near room temperature and ambient pressure owing to the small binding energy of hydrogen to the nanomaterials (~ 0.07 eV).⁹⁻¹¹ In order to reversibly store (i.e., both adsorb and desorb) hydrogen under such conditions, it was suggested that the binding energy of hydrogen should lie in the energy window of $\sim 0.2-0.6$ eV,^{11,12} and numerous studies in search of nanomaterials enhancing the binding energy of hydrogen have been carried out.¹¹⁻²⁰

Recently, we have reported a first-principles study on the combinatorial search for optimal hydrogen-storage nanomaterials among transition metal-decorated polymers of many different kinds,¹³ where each transition metal atom adsorbs multiple H_2 molecules with the binding energy of $\sim 0.2-0.6$ eV/ H_2 . In particular, metal-decorated *cis*- and *trans*-polyacetylene (PA) may store a large amount of hydrogen that can meet the DOE target of 9 wt %. In this paper, we carry out a more detailed study on dihydrogen (i.e., H_2 molecule) binding in *cis*- and *trans*-PA decorated with transition metal atoms. We select Ti and Sc atoms for decorating atoms because Ti and Sc atoms can adsorb more hydrogen

molecules than other transition metal atoms and are the lightest (hence advantageous in gravimetric capacity) among them. A single Ti (Sc) atom bound on the side of *cis*- and *trans*-PA adsorbs up to five (five) and four (five) H_2 molecules, respectively. We will show that the origin of bonding between the metal atom and H_2 molecules is the hybridization of d orbitals of the Ti with σ and σ^* orbitals of H_2 which is consistent with the Kubas bonding model.²¹ Optimal binding energy of the H_2 molecule at practical working conditions is found to be around 0.3 eV and the zero-point energy (ZPE) reduces the usable capacity significantly. We also investigate effects of the aggregation and intercalation of the Ti atoms on hydrogen adsorption.

II. COMPUTATIONAL DETAILS

The present study was performed using first-principles spin-polarized electronic structure calculations based on the density-functional theory.²² The plane-wave-based total energy minimization²³ with the Vanderbilt ultrasoft pseudopotential²⁴ was employed with the generalized gradient approximation (GGA) of Perdew, Burke, and Ernzerhof (PBE).²⁵ The kinetic energy and the relaxation force cutoff were 35 Ry and 0.001 Ry/a.u., respectively. When the unit cell length of polymer we chose was 8.9 Å, the Monkhorst-Pack k -point scheme²⁶ was used with 7 k -points with 0.016 ($2\pi/\text{Å}$) spacing. We tested the convergence of the results as the number of k -points increased up to 10. The minimum number of k -points for desired accuracy in our systems was 4. For periodic supercell calculations, the distance between polymers was maintained over 10 Å.

III. RESULTS AND DISCUSSION**A. Dihydrogen binding in transition metal-decorated *cis*-polyacetylene**

Figure 1(a) shows *cis*-polyacetylene. A single Ti atom is bound to *cis*-polyacetylene with the binding energy of 2.4 eV and the distance between the Ti atom and the nearest carbon atoms is 2.25 Å in Fig. 1(b). Up to five hydrogen molecules

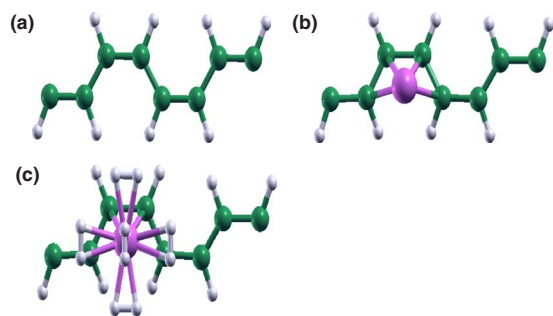


FIG. 1. (Color online) Atomic structures of dihydrogen binding to a single Ti attached on *cis*-polyacetylene. Green, pink, and white dots indicate carbon, titanium, and hydrogen atoms, respectively. (a) Pristine *cis*-polyacetylene. (b) A single Ti is attached on *cis*-PA. (c) Five H_2 molecules are adsorbed on the Ti atom.

are attached to a Ti atom as shown in Fig. 1(c). In the case of one adsorbed H_2 molecule, the bond length of the H_2 molecule is elongated from 0.75 to 0.83 Å. As the number of adsorbed H_2 molecules increases, the degree of the bond length elongation slightly decreases and the binding energies of H_2 molecules to the Ti atom range from 0.42 to 0.58 eV/ H_2 . We denote the structure of a single Ti-decorated *cis*-polyacetylene as *cPA-Ti- nH_2* where n is the number of adsorbed H_2 molecules, and other structures also follow this notation. The structure of *cPA-ScH* adsorbs up to five hydrogen molecules and the binding energies of H_2 molecules in *cPA-ScH- nH_2* range from 0.16 to 0.28 eV/ H_2 as n varies. Table I shows the binding energy per H_2 molecule in metal-decorated PA as a function of n .

We have calculated the binding energy of H_2 molecules with the local density approximation (LDA) as well. The binding energies of H_2 molecules for each H_2 adsorption number are approximately twice as large as those of the GGA calculation. Kim *et al.* reported that, in the case of boron and beryllium-doped fullerene, the LDA calculations agree much better with the quantum Monte Carlo (QMC) results than the GGA calculations.¹² On the other hand, Zhao *et al.* tested and confirmed that the binding energy with the GGA calculation in the case of dihydrogen binding to a $Cr(CO)_3(PH_3)_2$ molecule (containing the transition-metal Cr atom) is in good agreement with the experimental value.²⁷ We tend to think that the GGA is a better method than the LDA for a system involving transition metals such as Ti. The state-of-the-art methods treating the many-body exchange-correlation effects properly such as QMC calculations are

TABLE I. Calculated static binding energy per hydrogen molecule (eV/ H_2) for *cis*- and *trans*-PA decorated with Ti or Sc as a function of the number of adsorbed H_2 molecules.

Number of H_2 molecules	1	2	3	4	5
<i>cPA-Ti</i>	0.55	0.58	0.48	0.42	0.46
<i>cPA-ScH</i>	0.27	0.28	0.28	0.20	0.16
<i>tPA-TiH₂</i>	0.37	0.37	0.36	0.30	
<i>tPA-ScH</i>	0.34	0.37	0.29	0.25	0.21

necessary to obtain the binding energy of H_2 molecules more accurately in metal-dihydrogen complexes, but the QMC calculation for the entire system is beyond the scope of the present paper and is yet to be done.

Now, we investigate the origin of metal-dihydrogen bonding and analyze orbital hybridization. Figure 2 illustrates the projected density of states (PDOS) and the eigenfunctions for five hydrogen molecules attached to *cPA-Ti*. The optimized structure as depicted in Fig. 2(a) has a nearly octahedral symmetry, and hence five d levels of the Ti atom are basically split into e_g and t_{2g} levels. The PDOS plotted in Fig. 2(b) indicates that the metal-dihydrogen binding stems from the hybridization of the d orbitals of Ti and the s orbitals of H_2 . The eigenstate in Fig. 2(c) shows the hybridization of a linear combination of e_g orbitals ($3d_{x^2-y^2}$, $3d_{3z^2-r^2}$) with σ orbitals of H_2 molecules (even symmetry), and the state in Fig. 2(d) shows the hybridization of the $3d_{x^2-y^2}$ orbital with σ orbitals of H_2 molecules. The t_{2g} orbitals ($3d_{xy}$, $3d_{yz}$, and $3d_{zx}$) of the Ti atom are hybridized with the σ^* orbitals of H_2 molecules as illustrated in Figs. 2(e)–2(g). Therefore the e_g orbitals are hybridized only with the σ orbitals of H_2 molecules and the t_{2g} orbitals are hybridized only with the σ^* orbitals of H_2 molecules, supporting the Kubas model (based on electron donation and backdonation) for metal-dihydrogen complexes.²¹ The states at -0.9 and -0.3 eV shown in Figs. 2(f) and 2(g) exhibit hybridization among different orbitals, namely, the π^* -like state of polyacetylene, $3d_{yz}$ or $3d_{zx}$ of Ti, and the σ^* orbitals of H_2 molecules.

We can conjecture the maximum number of adsorbed H_2 molecules from the so-called 18-electron rule.^{15,28} The empirical rule states that the transition metal atom can adsorb up to the number (N_{\max}) of H_2 molecules until the total number of electrons associated with the metal atom becomes 18 (including the valence electrons of the metal atom and bonding electrons contributed from atoms chemically bonded to the metal atom). According to the rule, the maximum adsorption number of H_2 molecules is expressed as $N_{\max} = [(18 - n_v - n_\pi - n_b)/2]$, where n_v is the number of valence electrons of the metal atom, n_π is the number of π electron bonds between the supporting material (polymers) and the metal atom, n_b is the number of extra chemical bondings to the metal atom, and $[X]$ is the integer not exceeding X . We confirm the validity of this rule through our first-principles calculations in the present systems. In *cPA-Ti*, $n_v=4$, $n_\pi=4$, and $n_b=0$, so that we have $N_{\max}=5$. Likewise, in *cPA-ScH*, $n_v=3$, $n_\pi=4$, and $n_b=1$, so that we again have $N_{\max}=5$.

B. Dihydrogen binding in transition metal-decorated *trans*-polyacetylene

Figure 3 shows the Ti bonding to *trans*-PA and H_2 adsorption on Ti. A single Ti atom is bound to the side of *trans*-PA with the binding energy of 3.8 eV. The distance between the Ti atom and the nearest carbon atom is 2.16 Å. When one H_2 molecule is adsorbed on the Ti atom, the H_2 molecule is dissociatively bound on the Ti atom to become TiH_2 with the binding energy of 1.2 eV. When the first H_2 molecule is adsorbed on TiH_2 , the distance between the H_2 molecule and the Ti atom is 1.8 Å and the bond length of the H_2 molecule

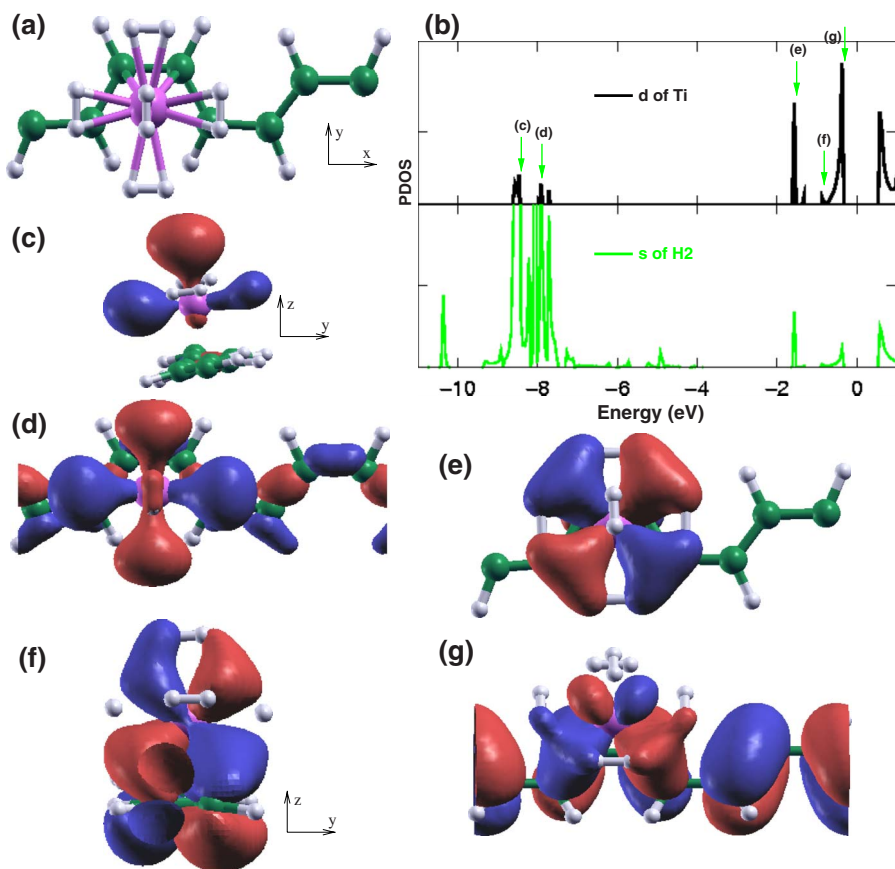


FIG. 2. (Color online) PDOS of the Ti atom and H₂ molecules, and eigenstates at the Γ point for five hydrogen molecules attached to a Ti atom in *cis*-PA. The Fermi level is set to zero. Green arrows indicate each state in the figure. (a) Optimized structure of five H₂ molecules attached to the Ti atom in *cis*-PA. (b) PDOS of the Ti atom and H₂ molecules for the optimized structure. (c)–(e) Electronic states with the isosurface value of ± 0.002 (a.u.)^{-3/2} at -8.6, -8.0, and -1.6 eV (two colors denote \pm sign of the wave function), respectively, and (f) and (g) are the isosurface value of ± 0.0005 (a.u.)^{-3/2} at -0.9 and -0.3 eV, respectively.

is elongated by 10%. The *t*PA-TiH₂ complex adsorbs up to four H₂ molecules with the average binding energy of 0.3 eV/H₂. As the number of adsorbed H₂ molecules increases, the degree of the bond-length elongation of H₂ molecules and the binding energy per H₂ are slightly reduced.

In the decoration with Sc, on the other hand, the initial structure should be *t*PA-ScH. The binding energy of the Sc atom is 2.0 eV and *t*PA-ScH adsorbs up to five H₂ molecules. The distance between the Sc atom and the nearest carbon atom is 2.20 Å. When the first H₂ molecule is adsorbed on ScH, the distance between the H₂ molecule and the Sc atom is 2.1 Å and the bond length of the H₂ molecule is elongated by 8%. The binding energy of adsorbed H₂ molecules is 0.21 eV/H₂ when five H₂ molecules are

attached to ScH. The number of adsorbed H₂ molecules in metal-decorated *trans*-PA also follows the 18-electron rule. In *t*PA-TiH₂, $n_v=4$, $n_\pi=4$, and $n_b=2$, so that we have $N_{\max}=4$. On the other hand, in *t*PA-ScH, $n_v=3$, $n_\pi=4$, and $n_b=1$, so that we have $N_{\max}=5$.

C. Optimum structures for hydrogen storage

We intend to design an optimum structure for the metal-decorated *cis*- and *trans*-PA as a host material for hydrogen storage. Here, we search for structures decorated with Ti atoms as compactly as possible, but without clustering of Ti atoms. We have found that the Ti atoms remain dispersed (i.e., no aggregation) and each Ti atom adsorbs H₂ molecules like a single Ti atom when two Ti atoms are separated at least by four carbon atoms away in the chain of the *cis*- and *trans*-PA. In order to store hydrogen as much as possible, the Ti atoms or TiH₂ units are attached to both sides of PA in the C₄H₄ unit. The unit of C₄H₄ is periodically repeated along the *x* axis which is the direction of the polymer chain. The molecular formulas of the optimal structures of Ti-decorated *cis*- and *trans*-PA can be written as (C₄H₄·2Ti)_{*n*} and (C₄H₄·2TiH₂)_{*n*}, respectively, where *n* is a large integer. When hydrogen molecules are maximally adsorbed on the structures as shown in Fig. 4, the molecular formulas of Ti-decorated *cis*- and *trans*-PA are (C₄H₄·2Ti·10H₂)_{*n*} and (C₄H₄·2TiH₂·8H₂)_{*n*}, and the maximum gravimetric capacity (G_{\max}) of the stored hydrogen is 12 and 10 wt %, respectively. In the case of Sc-decorated *cis*- and *trans*-PA, the

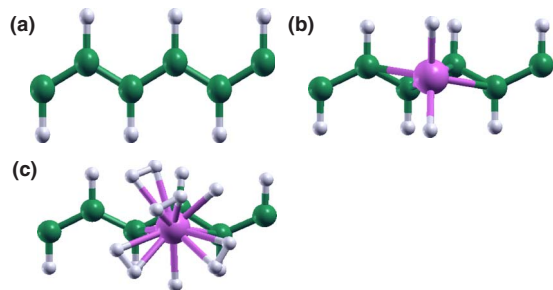


FIG. 3. (Color online) Atomic structures of dihydrogen binding in a single TiH₂ attached on *trans*-polyacetylene. (a)–(c) indicate pristine *trans*-polyacetylene, a single TiH₂ attached on *trans*-PA, and four H₂ molecules adsorbed on the TiH₂, respectively.

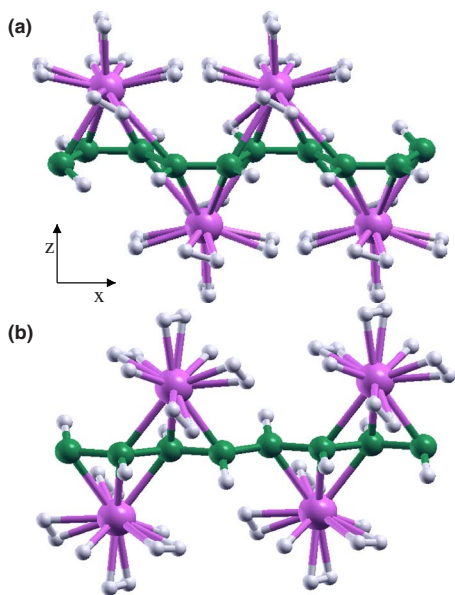


FIG. 4. (Color online) Maximum-capacity dihydrogen binding in optimal structures of Ti-decorated *cis*- and *trans*-polyacetylene. (a) *cis*-polyacetylene with the molecular formula $(C_4H_4 \cdot 2Ti \cdot 10H_2)_n$. (b) *trans*-polyacetylene with the molecular formula $(C_4H_4 \cdot 2TiH_2 \cdot 8H_2)_n$.

molecular formulas of optimum structures are $(C_4H_4 \cdot 2ScH \cdot 10H_2)_n$ in both cases and the stored capacity is 12 wt %. Next, we consider the volumetric capacity of the hydrogen. To calculate the maximum volumetric capacity of the hydrogen, the distances of aforementioned structures in the y and z directions are taken to be the van der Waals distance (~ 3.4 Å). The maximum volumetric capacity for optimal structures of Ti-decorated *cis*- and *trans*-PA is 100 and 80 kg/m^3 , respectively.

D. Hydrogen adsorption and desorption, and thermodynamically usable capacity

In hydrogen adsorption in nanostructured materials, its thermodynamic behavior is in sharp contrast to the phase transition in metal or chemical hydrides which are well-described by the van't Hoff equation.² The adsorption of hydrogen molecules should in general be described with the grand partition function.²⁹ Each adsorption site on nanostructured materials behaves more or less independently in the present case, and the probability of hydrogen adsorption at each site follows the equilibrium statistics as stated in Ref. 13. In the equilibrium of the H_2 molecules between the adsorbed and desorbed (H_2 gas as a reservoir) states, the adsorption number f is obtained from $f = kT \partial \log Z / \partial \mu$, where Z is the grand partition function, μ is the chemical potential of H_2 in the gas phase at given pressure p and temperature T , and k is the Boltzmann constant. When the phonon excitation is negligible, f per site is given by

$$f = \frac{\sum_{l=0} g_l e^{l(\mu - \varepsilon_l)/kT}}{\sum_{l=0} g_l e^{l(\mu - \varepsilon_l)/kT}}, \quad (1)$$

where $\varepsilon_l (<0)$ is the energy of adsorbed H_2 (with reference to H_2 at infinite distance) per H_2 molecule when the number of adsorbed molecules is l and g_l is the degeneracy of the configuration for given l . The summation is over the different number of adsorbed H_2 's up to the maximum (N_{max}). The adsorption number f is reduced to the well-known result

$$f = \frac{1}{1 + e^{-(\mu - \varepsilon)/kT}}, \quad (2)$$

when only one H_2 molecule adsorption is allowed per site without configurational degeneracy (i.e., $g_1=1$). If we designate the total number of adsorption sites as N , the total number of adsorbed H_2 's is fN . Then we can prove in this simplest case that the Helmholtz free energy is $fN\varepsilon + kTN \times [f \log f + (1-f) \log(1-f)]$, the enthalpy is $fN\varepsilon - kTN \times \log(1-f)$, and the chemical potential μ (=Gibbs free energy/ fN) = $\varepsilon + kT \log(f/1-f)$, which agrees with Eq. (2).

The zero-point vibrations of the H_2 molecules with respect to the host metal atom (e.g., Ti) on which H_2 's sit should be corrected for in the calculated binding energy. (Conventionally, the binding energy is defined to be positive, namely, $-\varepsilon_l$.) The actual binding energy ($-\varepsilon_l$) is the static binding energy (usually calculated and reported in the literature) *minus* the ZPE. We have calculated the ZPE for several configurations using the frozen phonon method.¹³ The ZPE obtained is approximately 20%–30% of the static (calculated) binding energy of the H_2 molecules. Therefore from now on, we will use the average value of the ZPE, namely, 25% of the static binding energy and subtract it from the static binding energy to obtain the true dynamic binding energy of hydrogen molecules.

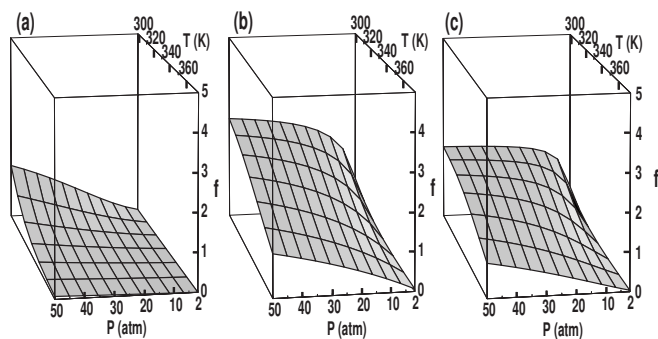


FIG. 5. Comparison of adsorption number-pressure-temperature (f - p - T) diagrams of H_2 in Ti- and Sc-decorated *cis*- and *trans*-polyacetylene. The ZPE is included in calculating the adsorption number f . The ranges of the pressure and the temperature cover typical conditions of H_2 filling and delivering from the storage tank. (a) Sc-decorated *cis*-polyacetylene. (b) Ti-decorated *trans*-polyacetylene. (c) Sc-decorated *trans*-polyacetylene. The plot for Ti-decorated *cis*-polyacetylene is in Ref. 13.

TABLE II. Usable capacity calculated from the adsorption number f . In the second column, “Yes” and “No” mean including and ignoring the ZPE in the binding energy, respectively. N_{ads} and N_{des} are the numbers of attached H_2 's per site at the condition of adsorption (30 atm-25 °C) and desorption (3 atm-100 °C), respectively. N_{use} is the practically usable number ($N_{\text{ads}} - N_{\text{des}}$) and N_{max} is the maximum number of adsorbed H_2 's. G is the gravimetric capacity.

Materials	ZPE	$N_{\text{ads}} - N_{\text{des}}$	$N_{\text{use}}/N_{\text{max}}$	$G_{\text{use}}/G_{\text{max}}$ (wt %)
Ti-decorated <i>cis</i> -PA	Yes	5.00–1.91	3.09/5	7.4/12
Sc-decorated <i>cis</i> -PA	Yes	0.86–0.00	0.86/5	2.1/12
Ti-decorated <i>trans</i> -PA	Yes	2.57–0.10	2.47/4	6.2/10
Sc-decorated <i>trans</i> -PA	Yes	1.90–0.05	1.85/5	4.4/12
Ti-decorated <i>cis</i> -PA	No	5.00–2.69	2.31/5	5.5/12
Sc-decorated <i>cis</i> -PA	No	2.76–0.00	2.76/5	6.6/12
Ti-decorated <i>trans</i> -PA	No	2.99–1.12	1.87/4	4.7/10
Sc-decorated <i>trans</i> -PA	No	2.02–0.90	1.12/5	2.7/12

To calculate the usable amount of hydrogen, the conditions of pressure and temperature at the time of adsorption (fuel filling) and desorption (delivering from the storage tank) should be decided. Before an agreement in the community is reached on the standards for such conditions, we provisionally choose the adsorption condition of 30 atm and 25 °C and the desorption condition of 3 atm and 100 °C. These conditions are determined based on practical situations in gas filling and vehicles operations as well as information available in the literature.^{1,30} The calculated thermodynamically usable capacity for metal-decorated structures is listed in Table II. The usable number (N_{use}) of hydrogen molecules per metal site is defined to be f ($p=30$ atm, $T=25$ °C) minus f ($p=3$ atm, $T=100$ °C). The usable capacity (G_{use}) is immediately obtained from N_{use} for each structure. In Fig. 5, the adsorption number f of hydrogen molecules per metal atom is plotted as a function of p and T . μ is obtained by interpolation of the experimental chemical potential³¹ in the temperature and pressure range of our interest as follows:

$$\mu = \mu_{\text{ideal}} - 0.00015(T - 186.5) \text{ (eV)} + 0.00065\{(\log_{10} p - 0.5)^2 - 0.25\} \text{ (eV)}, \quad (3)$$

where μ_{ideal} is the chemical potential of the ideal gas and the units of T and p are K and bar ($=10^5$ Pa), respectively. From Eq. (3), μ at 30 atm and 25 °C is -0.22 eV and μ at 3 atm and 100 °C is -0.38 eV, respectively. These μ values deviate only minutely from the ideal gas values of -0.21 and -0.36 eV. Degeneracy (g_l) of Ti-decorated *cis* (*trans*)-PA is 1 (3), 2 (3), 1 (2), 1 (2), and 1 for $l=1, 2, 3, 4,$ and 5 , respectively, and gives a minor correction to f .

In case of the Ti-decorated *cis*-PA, 3.09 H_2 molecules per Ti are desorbed among the five adsorbed H_2 molecules as presented in Table II, so that 1.91 H_2 molecules remain unused when p and T change from the adsorption condition to the desorption condition. This is ascribed to the fact that the binding energies of the first and the second adsorbed H_2 molecules are too large. In contrast, in the case of Sc-decorated *cis*-PA, the number of adsorbed H_2 molecules un-

der the adsorption condition is very small due to too small binding energies and only 0.86 H_2 molecules per Sc are usable. The usable number of H_2 's depends on the binding energies ($-\epsilon_l$) at each adsorption number of H_2 molecules. In Fig. 6, we can see that the optimal binding energy of H_2 molecules under our adsorption and desorption conditions is ~ 0.3 eV including the ZPE correction (i.e., ~ 0.4 eV excluding the ZPE). Even if the maximum number of adsorbed H_2 's on the Sc-decorated PA is larger than that of Ti-decorated PA, the usable capacity of hydrogen in Sc-decorated PA is smaller because the binding energies of H_2 's come short of the optimal binding energy. The ZPE affects the usable capacity considerably as shown in Table II. In particular, the usable capacity of hydrogen in Sc-decorated *cis*-PA is dramatically reduced from 6.6 to 2.1 wt % because the binding energy of hydrogen molecules becomes far short of the optimal value when the ZPE is taken into account. In short, the usable capacity of hydrogen in practical situations could fall far short of the capacity we would expect from the maximum number of adsorbed H_2 molecules alone, and the optimal binding energy of H_2 molecules is ~ 0.3 eV/ H_2 , and the ZPE changes the hydrogen adsorption and desorption significantly.

E. Aggregation and intercalation of Ti atoms

It has been reported that the aggregation of Ti atoms on fullerenes influences the nature of the hydrogen binding to the Ti atom and reduces the storage capacity.³² In order to achieve a successful hydrogen storage using metal decoration, clustering of transition metal atoms should be suppressed. Recently, Jena *et al.* commented on clustering of Ti atoms for H_2 adsorption in *cis*-PA.³³ We study here the aggregation of Ti atoms in *trans*-PA. When a Ti atom is put on the position at 2 Å above another Ti atom bound on the *trans*-PA, the Ti atoms are aggregated, which is energetically more favorable by 2.3 eV than separated Ti atoms. Two H_2 molecules are attached to aggregated two Ti atoms in a dihydride form as shown in Fig. 7(a) when each H_2 is put on each Ti. Up to three H_2 molecules are consecutively attached

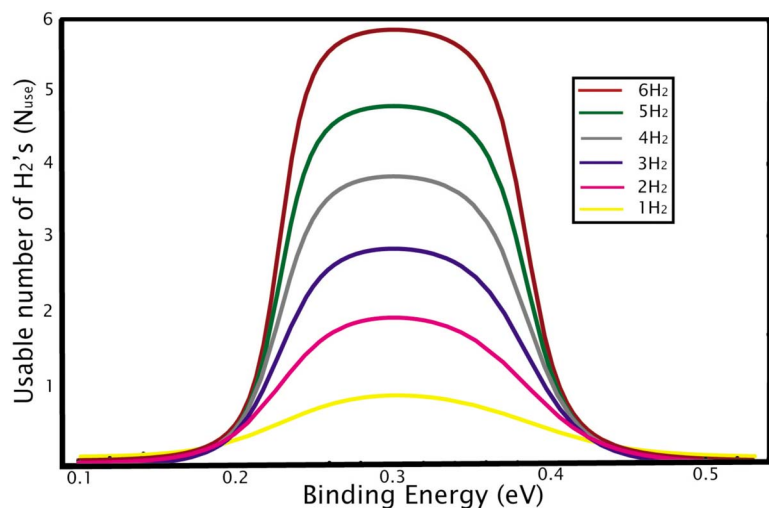


FIG. 6. (Color online) N_{use} ($N_{\text{ads}} - N_{\text{des}}$) is plotted as a function of the binding energy ($-\epsilon$) of H_2 's. Each color indicates a different N_{max} of adsorbed H_2 molecules. We choose $p=30$ atm and $T=25$ °C at adsorption and $p=3$ atm and $T=100$ °C at desorption. We assume that the binding energy ($-\epsilon_l$) is independent of l . The binding energy includes the ZPE and the degeneracy is neglected.

to one Ti atom of the 2TiH_2 complex in a dihydrogen form as depicted in Fig. 7(b) and the calculated binding energies of adsorbed H_2 molecules are 0.31, 0.37, and 0.20 eV/ H_2 for one, two, and three adsorbed H_2 molecules, respectively. The structure of the 2TiH_2 unit can adsorb up to seven H_2 molecules with the binding energy of 0.14 eV/ H_2 as shown in Fig. 7(c). The nature of the H_2 bonding differs from that of individually decorated metal atoms. In short, aggregation of the Ti atoms reduces the binding energies and the number of adsorbed H_2 molecules, and the usable capacity decreases accordingly.

It is a difficult task to find a way to suppress transition-metal clustering in the carbon chain structures. While it is

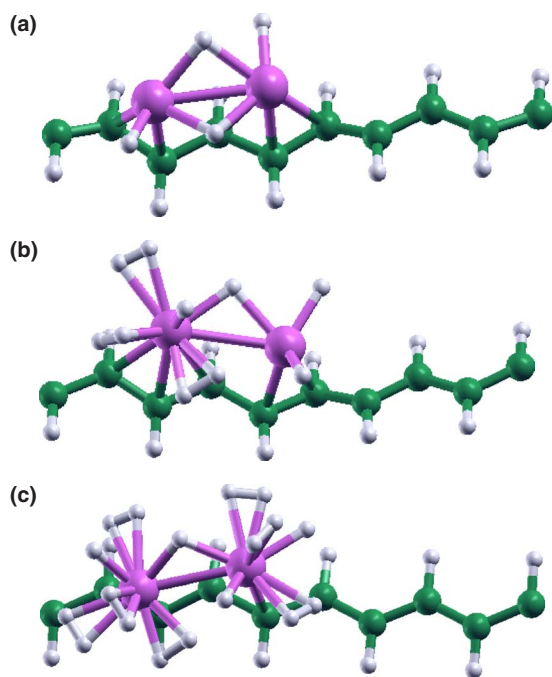


FIG. 7. (Color online) Dihydrogen binding in aggregated Ti atoms on *trans*-polyacetylene. (a) An aggregated structure of two TiH_2 on *trans*-PA. (b) The optimized structure of three hydrogen molecules attached to aggregated TiH_2 . (c) The aggregated structure adsorbs maximally up to seven H_2 molecules.

hard to avoid metal clustering on unsaturated conjugate chain structures (i.e., sp^2 -bonded carbons) such as polyacetylene, a combination of sp^2 and sp^3 carbon bonds [as exhibited, for example, in polybutadiene ($-\text{CH}_2-\text{CH}=\text{CH}-\text{CH}_2-$) $_n$] may suppress metal clustering because the saturated sp^3 carbon does not bind transition metal atoms and acts as a high potential barrier against the diffusion of metal atoms along the polymer. Then, the transition metal atoms may only be attached to the part of sp^2 -bonded carbon atoms which are separated by sp^3 -bonded carbons. Therefore there exists a possibility that individual metal atoms can bind H_2 molecules without metal clustering. Passivation by hydrogen on top of the Ti atom may also be necessary to protect Ti from further oxidation (or metallization).

We now study effects of Ti-intercalated *cis*- and *trans*-PA on H_2 adsorption. A single Ti atom is intercalated between two polymers as shown in Figs. 8(a) and 8(c). The binding energy of an intercalated Ti atom in *cis*- and *trans*-PA is 4.5 and 3.2 eV, respectively. Ti-intercalated *cis*- and *trans*-PA adsorb up to 4 H_2 molecules in both cases. Binding energies

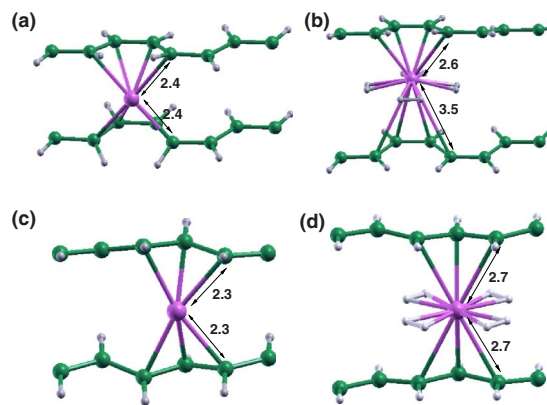


FIG. 8. (Color online) Dihydrogen binding in Ti-intercalated *cis*- and *trans*-polyacetylene. The unit of the presented bond lengths is angstrom. (a) A single Ti atom is intercalated between two *cis*-PA. (b) Four H_2 molecules are attached to Ti-intercalated *cis*-PA. (c) A single Ti atom is intercalated between two *trans*-PA. (d) Four H_2 molecules are attached to Ti-intercalated *trans*-PA.

of H₂'s for Ti-intercalated *cis* (*trans*)-PA are 0.54 (0.47), 0.22 (0.32), 0.16 (0.22), and 0.07 (0.17) eV/H₂ for adsorption of one, two, three, and four H₂'s, respectively. The binding energies of H₂'s are reduced, and therefore the usable capacity decreases. The decrease in the binding energy is ascribed to the increase of the distance between Ti and polymers by H₂ adsorption.

IV. SUMMARY

In summary, we have studied *cis*- and *trans*-PA decorated with Ti or Sc atoms as a hydrogen-storage medium using first-principles calculations. *cis*- and *trans*-polyacetylene decorated with Ti atoms bind up to five and four hydrogen molecules per Ti, respectively. It is observed that e_g and t_{2g} orbitals of the Ti atom are hybridized with the σ and σ^* orbitals of the H₂ molecules, respectively, in nearly octa-

hedral geometries. Optimal binding energy of H₂ molecules for practical applications is about 0.3 eV. The zero-point energy of adsorbed hydrogen molecules affects the usable capacity. Aggregation of metal atoms in PA may occur and affect the bonding nature of the hydrogen molecules and more intensive study in the future is necessary to overcome this problem. Intercalation of Ti atoms to PA is also found to reduce the binding energy of H₂ molecules.

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