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On hydrogen storage in metal-decorated *trans*-polyacetylene

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Abstract

We propose metal-decorated *trans*-polyacetylene as a hydrogen storage medium using first-principles calculations based on the density-functional theory. When a hydrogen atom in polyacetylene is replaced by a TiH_3 or ScH_2, one structural unit of TiH_3 (ScH_2) can maximally bind five (six) hydrogen molecules with the binding energy of about 0.20 eV/H_2. The molecular formula of the optimal structure is $(C_4H_2{\cdot}2TiH_3)_n$ ($(C_4H_2{\cdot}2ScH_2)_n$), where two out of four hydrogen atoms in the C_4H_4 unit in polyacetylene are substituted by $2TiH_3$ ($2ScH_2$) units. Theoretically, the gravimetric and volumetric densities of the maximally stored hydrogen molecules here are 12 (14) wt.% and 140 kg/m^3, respectively.

Keywords: Transition metal atoms; *trans*-Polyacetylene; Hydrogen storage; Density functional theory

Hydrogen storage is an essential technology for the commercialization of CO_2-free hydrogen powered vehicles [1]. The U.S. Department of Energy (DOE) presented hydrogen-storage requirements for use on board vehicles. The goals for the gravimetric and volumetric density of hydrogen are 9 wt.% and 81 kg/m^3, respectively by the year of 2015 [2]. For the last decade, nanostructured materials such as carbon nanotubes as a hydrogen storage medium have attracted much attention because of safe storage, high-capacity (large surface area), and fast kinetics [3,4]. However, through many attempts to conduct hydrogen storage in the materials, it has been revealed that the stored hydrogen capacity falls far short of the desired capacity near room temperature and ambient pressure [5,6] due to the small binding energy of the hydrogen molecule (∼0.07 eV) on these materials. In order to store reversibly hydrogen by adsorption to the materials at ambient conditions, the binding energy of the hydrogen to the storing media is required to be ∼0.3–0.4 eV.

Recently, it has been reported that a transition metal atom decorated nanostructured materials such as fullerenes and carbon nanotubes to be used as a hydrogen storage medium can bind several hydrogen molecules with the binding energy of ∼0.3 eV/H_2 by Kubas interaction [7–9]. More recently, we reported a first-principles density functional study on combinatorial search for optimal hydrogen-storage nanomaterials based on polymers among various metal-decorated polymers [10]. We found that the metal-decorated polymers can store a significant amount of hydrogen. In order to present more detailed information in this paper, we focus on hydrogen storage in metal-decorated *trans*-polyacetylene (tPA) polymer. We devise that a single TiH_3 (or ScH_2) replaces one hydrogen atom in polyacetylene and forms chemical bonding with the carbon zigzag backbone. Our first-principles calculation described below indicates that the Ti (Sc)-decorated *trans*-polyacetylene is stable, which will be denoted as a Ti–tPA (Sc–tPA) polymer. The Ti–tPA (Sc–tPA) polymer can adsorb five (six) H_2 molecules with the binding energy of 0.18 (0.16) eV/H_2 by non-classical bonding. The optimum Ti–tPA (Sc–tPA) polymer with the maximum density of metal decoration can store hydrogen molecules with the gravimetric density of 12 (14) wt.% and the volumetric density of ∼140 kg/m^3.

We carried out spin-polarized first-principles electronic structure calculations based on the density functional theory [11]. The plane-wave based total energy minimization [12] with the Vanderbilt ultrasoft pseudopotential [13] was performed. The generalized gradient approximation (GGA) of Perdew, Burke, and Ernzerhof (PBE) [14] was used in the calculations. The kinetic energy and the relaxation force cutoff were 35 Ry and 0.001 Ry/a.u., respectively. For periodic supercell calculations, the distance between polymers was maintained over 10 Å in all cases.

Fig. 1(a) and (b) shows polyacetylene and the Ti–tPA polymer. One hydrogen atom in polyacetylene is substituted by a

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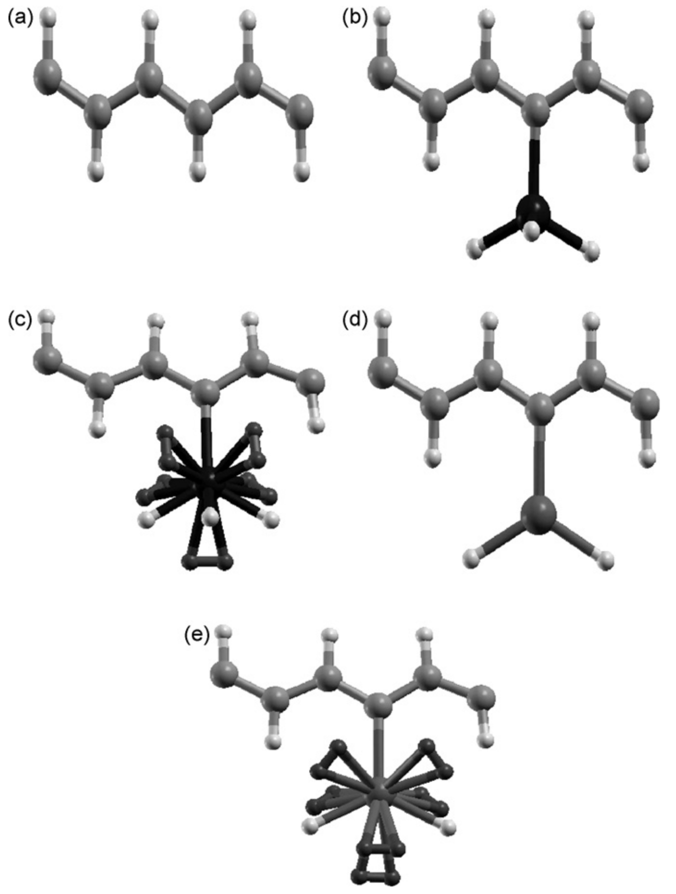

Fig. 1. Optimized atomic structures for *trans*-polyacetylene, TiH_3 or ScH_2 substituted for a hydrogen in the polyacetylene, and maximally adsorbed H_2 molecules to TiH_3 or ScH_2. (a) *Trans*-polyacetylene (tPA), (b) TiH_3 substituting a hydrogen atom in the polyacetylene, (c) Five H_2 molecules attached to TiH_3, (d) ScH_2 substituting a hydrogen atom in the polyacetylene and (e) Six H_2 molecules attached to ScH_2.

Table 1
Binding energy per hydrogen molecule (eV/H_2) for Ti–tPA and Sc–tPA polymers as a function of the number of adsorbed H_2 molecules

	Number of H_2					
	1	2	3	4	5	6
Ti–tPA	0.34	0.37	0.31	0.25	0.18	
Sc–tPA	0.23	0.20	0.20	0.19	0.19	0.16

TiH_3 in the Ti–tPA polymer and the structure is chemically stable because the Ti atom maintains the valence of 4. The Ti–C and Ti–H bond lengths are 2.06 and 1.72 Å, respectively. In Fig. 1(c), the five hydrogen molecules are maximally adsorbed on TiH_3 unit. The distance between Ti and H_2 is 1.86 Å and the H_2 bond length is elongated from 0.75 to 0.84 Å. As the number of adsorbed H_2 molecules increases, the H_2 bond length and the binding energy per H_2 are slightly reduced. In Fig. 1(d), a ScH_2 is substituted for a hydrogen atom in tPA. This structure is also chemically stable and Sc–C and Sc–H bond lengths are 2.25 and 1.80 Å, respectively. The bond lengths in the Sc–tPA polymer are longer than those in the Ti–tPA polymer. In Fig. 1(e), the distance between Sc and H_2 is 2.30 Å, which is significantly longer than the Ti–H_2 distance. The Sc–tPA polymer can maximally adsorb six hydrogen molecules per ScH_2 unit. As the number of H_2 molecules increases, the H_2 bond length and the binding energy per H_2 are slightly reduced as in the Ti–tPA case.

In Table 1, we list the calculated (average) binding energy per H_2 molecule as the number of H_2 molecules increases. The interaction, which is hybridization between the d orbital of the transition metal atom and the σ^* orbital of the hydrogen molecule, has been studied [9] and, recently, non-dissociative H_2 adsorption to a metal atom has been investigated [15]. The maximum number of adsorbed H_2 molecules, N_{max}, on a transition metal atom is known to satisfy the rule $N_{max} = (18 - n_v - n_c)/2$ [7,15], where n_v is the number of valence electrons of the metal atom and n_c is the number of conventional chemical bonding of the metal atom with other atoms. When TiH_3 is attached to C in the Ti–tPA, $n_v = 4$ and $n_c = 4$, so that we have $N_{max} = 5$. Our first-principles calculations show that five H_2 molecules are adsorbed to the Ti atom, confirming this empirical rule. In the Sc–tPA, $n_v = 3$ and $n_c = 3$, so that we have $N_{max} = 6$. Indeed, up to six H_2 molecules are found to be adsorbed to the Sc atom.

In order to store many hydrogen molecules, there should be sufficient empty space around the TiH_3 or ScH_2 complexes. On the other hand, to increase the gravimetric and volumetric density of hydrogen, it is necessary to arrange the TiH_3 or ScH_2 units compactly. The optimum geometry of the Ti-decorated *trans*-polyacetylene together with maximally adsorbed H_2 molecules is shown in Fig. 2(a). In a unit supercell, two out of four hydrogen atoms in C_4H_4 are replaced by 2 units of TiH_3. This unit supercell is periodically repeated along the *x*-axis which is the direction of the polymer chain. The molecular formula of this structure can be written as $(C_4H_2{\cdot}2TiH_3)_n$ where the integer n is the total number of the proposed structural units. When five hydrogen molecules are stored per TiH_3, the molecular formula will be $(C_4H_2{\cdot}2TiH_3{\cdot}10H_2)_n$. The gravimetric density of the maximally stored hydrogen molecules in this case is 12 wt.%,

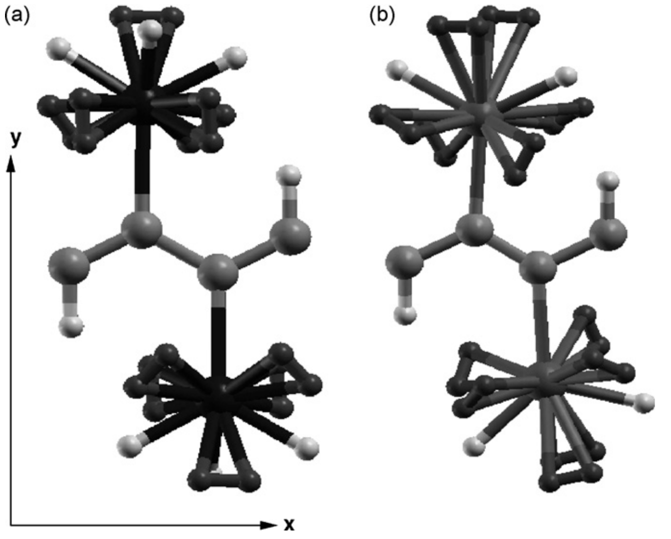

Fig. 2. Optimized atomic structures for maximally stored hydrogen to the structure of $(C_4H_2{\cdot}2TiH_3)_n$ or $(C_4H_2{\cdot}2ScH_2)_n$. (a) Maximally adsorbed H_2 in $(C_4H_2{\cdot}2TiH_3)_n$ and (b) maximally adsorbed H_2 in $(C_4H_2{\cdot}2ScH_2)_n$.

which is far beyond the DOE goal of 9 wt.% by the year of 2015.

We now consider the volumetric density of the hydrogen storage. Along the *z*-direction, the most compact arrangement is achieved when the distance between a hydrogen molecule adsorbed at the top of 1 unit cell and another one adsorbed at the bottom of the next unit cell (i.e., nearest neighbor in the *z*-direction) is approximately the van der Waals distance (∼3.4 Å). The same criterion of the van der Waals distance separation is adopted in the *y*-direction (between two parallel Ti–tPA polymer chains) in our estimation of the maximum volume density of the storage. We have found that there is a slight repulsive force between neighboring Ti–tPA polymer chains, which is quite desirable in order to avoid the agglomeration of the polymers into a solid cluster. The mutual repulsion among Ti–tPA polymers is the driving force to sustain the empty space to accommodate H_2 molecules. By attaching an end of each $(C_4H_2{\cdot}2TiH_3)_n$ polymer to the inner surface of the storage tank, the overall structure of the storage medium with a lot of empty space between fibers of the metal-decorated polymers may be maintained. The calculated maximum volumetric density of hydrogen molecules is ∼140 kg/m^3 which is again far above the DOE goal of 81 kg/m^3 by 2015. Another structure shown in Fig. 2(b) is $(C_4H_2{\cdot}2ScH_2{\cdot}12H_2)_n$, which is essentially the same as Fig. 2(a) except that TiH_3 is replaced by ScH_2 as mentioned above. At maximum storage of hydrogen ($6H_2$ per ScH_2), the volumetric density of the hydrogen molecules reaches ∼140 kg/m^3 again. We think that Ti-decorated structure has better chance of being used than Sc-decorated structure because, from a material point of view, Sc is rarer and harder to handle than Ti.

In conclusion, we have performed first-principles electronic structure calculations for hydrogen binding to *trans*-polyacetylene decorated by Ti and Sc atoms. The gravimetric and volumetric density of the Ti (Sc)-decorated polyacetylene are 12 (14) wt.% and ∼140 kg/m^3. Ti and Sc atoms can maximally adsorb five and six H_2 molecules, respectively. We propose the metal-decorated *trans*-polyacetylene described in this study as a promising hydrogen storage medium.

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