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Combinatorial Search for Optimal Hydrogen-Storage Nanomaterials Based on Polymers

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We perform an extensive combinatorial search for optimal nanostructured hydrogen-storage materials among various metal-decorated polymers using first-principles density-functional calculations. We take into account the zero-point vibration as well as the pressure- and temperature-dependent adsorption-desorption probability of hydrogen molecules. An optimal material we identify is Ti-decorated *cis*-polyacetylene with reversibly usable gravimetric and volumetric density of 7.6 wt % and 63 kg/m^3, respectively, near ambient conditions. We also propose ''thermodynamically usable hydrogen capacity'' as a criterion for comparing different storage materials.

Hydrogen storage is a crucial technology to the development of hydrogen fuel-cell powered vehicles [1,2]. Recently, nanostructured materials have received special attention because of potentially large storage capacity (high gravimetric and volumetric density), safety (solid-state storage), and fast filling and delivering from the fuel tank (short molecular adsorption and desorption time) [3–5]. However, when the thermodynamic behavior of the gas under realistic environments is taken into account, the *usable* amount of hydrogen with these nanomaterials falls far short of the desired capacity for practical applications, and the search for novel storage materials continues worldwide [6–9]. It is to be emphasized that hydrogen storage in nanostructured materials utilizes the adsorption of hydrogen molecules on the host materials, and its thermodynamic analysis is distinct from that of metal or chemical hydrides. Each adsorption site on the nanomaterial behaves more or less independently, and the probability of hydrogen adsorption follows the equilibrium statistics, which is a smooth function of the pressure and temperature. There is no sharp thermodynamic phase transition between the gas and the adsorbed state of H_2, in contrast to the case of metal or chemical hydrides where an abrupt phase transition occurs at well-defined pressure at a given temperature [10].

With this caveat, a general formalism applicable to hydrogen adsorption on nanomaterials was derived in the present study from the grand partition function with the chemical potential determined by that of the surrounding H_2 gas acting as a thermal reservoir. As each site can adsorb more than one H_2 molecule, information on the multiple adsorption energy is necessary. (The situation is analogous to O_2 adsorption and desorption on hemoglobin, which can bind up to 4 O_2 molecules.) In the equilibrium of the H_2 molecules between the adsorbed and desorbed (gas) states, the occupation (adsorption) number f is obtained from $f = kT\partial \ln Z/\partial \mu$, 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. Here f per site is reduced to

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

where ε_l is the adsorption energy per H_2 molecule when the number of adsorbed molecules is l, and g_l is the multiplicity (degeneracy) of the configuration for a given l. The summation is over all different configurations up to the maximum number ($N_{\max}$) of adsorbed molecules.

Another important thermodynamic feature in the H_2 adsorption energetics is 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. (The zero-point vibration *within* the H_2 molecule, on the other hand, exists in both gas and adsorbed states and cancels out in the calculation of f.) The actual energy ε_l to be used in Eq. (1) is the static adsorption energy (usually calculated and reported in the literature) *minus* the zero-point vibration energy, which sums up to as large as 25% of the static adsorption energy according to our calculation, a value not to be neglected at all.

Considering these thermodynamic aspects, we paid attention to the fact that simple polymers decorated with light transition metal atoms may be superior to other recently reported nanomaterials such as Ti-decorated nanotubes [11] or Sc-decorated fullerenes [12] in terms of usable gravimetric and volumetric density. The basically one-dimensional nature of polymers is advantageous for compact storage, with a very small number of carbon atoms needed to accommodate a decorating metal atom which attracts hydrogen molecules. Furthermore, entangled chains of long polymers form a solid structure ideal for safe handling of the hydrogen. A systematic approach was employed to search for optimized high-capacity hydrogen-storage nanostructures based on polymers. For the supporting backbone materials, we first considered *trans*- and *cis*-polyacetylene (among linear carbon chains), polyaniline, polyphenol, poly para phenylene, and poly ether ether ketone (chains of hexagonal rings), and polypyrrole and polythiophene (chains of pentagonal rings). For decorating transition metals, we initially chose

all light transition metal elements starting from Sc in the periodic table. Various possible adsorption sites of the transition metal atoms were tested for each case. The maximum number of adsorbed H_2 molecules also varied (up to six) at different sites. In short, the total combinatorial number in our study exceeded 1000. In practice, we were able to reduce the number considerably by eliminating obviously unfavorable cases using a few test calculations of the adsorption energy and structural stability. Many kinds of pentagonal and hexagonal ring chains were ruled out. For decorating atoms, only Sc, Ti, and V atoms passed the first-round candidate screening test. Such a combinatorial search for the optimized material and geometry yielded a few promising nanostructures for hydrogen storage.

We employed spin-polarized first-principles electronic structure calculations based on the density-functional theory [13]. The plane-wave based total energy minimization [14] with the Vanderbilt ultrasoft pseudopotential [15] was performed. The generalized gradient approximation (GGA) [16] of Perdew, Burke, and Ernzerhof [17] 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.

The best candidate material we found in our search using the total energy calculations was *cis*-polyacetylene decorated with Ti atoms, whose structure after the H_2 molecule adsorption is presented in Fig. 1(a). The binding energy of a Ti atom on this polymer is 2.4 eV. The structure has about 2 wt% higher storage capacity than Ti-decorated *trans*-polyacetylene. (Since as-synthesized polyacetylene is of *cis*-type, it is in principle possible to attach Ti atoms to *cis*-polyacetylene, although *trans*-polyacetylene is a more stable structure.) N_{max} for this structure is five, and the H_2 molecules are compactly adsorbed on both sides of the polyacetylene plane. The molecular formula corresponding to this structure is $(C_4H_4 \cdot 2Ti \cdot 10H_2)_n$. The maximum gravimetric density (G_{max}) is defined by the weight ratio of $10H_2$ to $C_4H_4 \cdot 2Ti \cdot 10H_2$, which is 12 wt% as shown in Table I. G_{max} for other materials is calculated in the same way. We also present other important polymer geometries in Fig. 1 with the maximum number of H_2 molecules attached to the decorating Ti atoms. The calculated (static) adsorption energies per H_2 as a function of the adsorption number are presented in Fig. 2 for easy comparison among different materials. In *cis*-polyacetylene, for example, they are 0.55, 0.58, 0.48, 0.42, and 0.46 eV/H_2 for $l = 1, 2, 3, 4,$ and 5, respectively. As pointed out in previous works, the adsorption of a large number of H_2 molecules presumably occurs through the Dewar-Chatt-Duncanson coordination or Kubas interaction [18–20]. We found the elongation of H_2 molecules by ~10% through electron back donation from metal d orbitals to the antibonding hydrogen s orbitals, which supports these theories.

We chose to present in Fig. 2 the *static* adsorption energy, following the usual practice in the literature
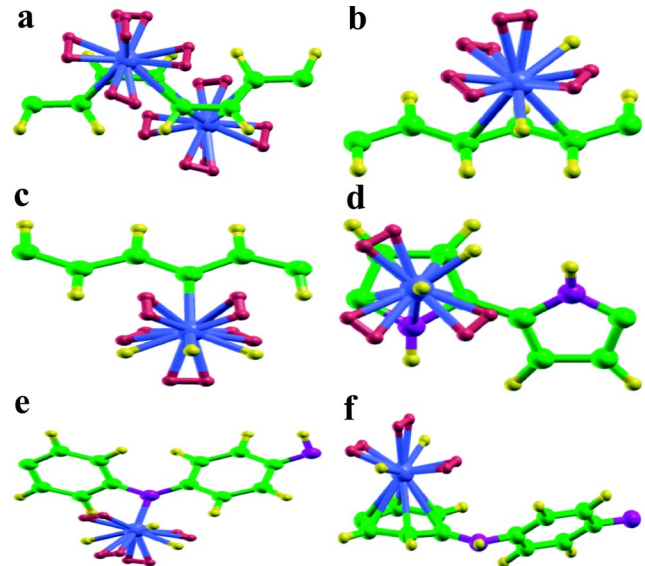

FIG. 1 (color online). Atomic structures of the Ti-decorated polymers with the maximum number of H_2 molecules attached to Ti atoms. Green, blue, purple, yellow, and red dots indicate the carbon atom, titanium atom, nitrogen atom, hydrogen atom composing the polymer, and the molecular hydrogen, respectively. (a) *Cis*-polyacetylene with five H_2 molecules attached per Ti atom. H_2's are shown on both sides of the (somewhat distorted) polyacetylene plane. In the rest (b)–(f), H_2's are shown only on one side of the polymer for visual clarity. (b) *Trans*-polyacetylene with Ti atoms located out of the plane of the polymer chain. (c) *Trans*-polyacetylene with Ti atoms in the plane of the chain. (d) Polypyrrole with Ti atoms out of the pentagonal plane. (e) Polyaniline with Ti atoms in the hexagonal plane. (f) Polyaniline with Ti atoms out of the hexagonal plane.

[11,12]. After subtracting zero-point vibration energies (25% of the static adsorption energy) for all structures, we obtained the true dynamic adsorption energy (ε_l) to be used in Eq. (1). For instance, the zero-point vibration energy per H_2 molecule for *cis*-polyacetylene was 0.09 eV for H_2 on top of the Ti atom and 0.12 eV for H_2 attached to the side [21]. We employed the experimental chemical potential in the literature [22] in the calculation of f. The degeneracy factor was approximated by the number of calculated local energy minima for given l. The largest g_l we found was 3, and, since the exponential factor $e^{l(\mu - \varepsilon_l)/kT}$ dominated, g_l's turned out to give a minor correction to the result. The occupation number f as a function of p and T for representative nanomaterials is presented in Fig. 3. The occupation-pressure-temperature (f-p-T) diagram of the nanomaterial storage in Fig. 3 is the counterpart of the widely used pressure-composition isotherms in metal hydride storage [10]. To obtain the usable amount of hydrogen, it is necessary to specify p and T at the time of adsorption (filling) and desorption (delivering from the storage tank). Since an internationally agreed-upon standard has not been set up, we propose to use the adsorption condition of 30 atm and 25 °C and the desorp-

TABLE I.   Hydrogen-storage capacity of representative nanomaterials from GGA calculations. PA, polyacetylene; PPY, polypyrrole; PANI, polyaniline; CNT, carbon nanotube. All are decorated with Ti except for Sc-decorated $C_{48}B_{12}$. -out means an out-of-plane configuration described in Fig. 1. 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 (2 atm-100 °C), respectively. N_{use} is the practically usable number ($N_{ads} - N_{des}$) and N_{max} is the maximum number of adsorbed H_2's. G and V are gravimetric and volumetric density, respectively.

Materials	$N_{ads} - N_{des}$	N_{use}/N_{max}	G_{use}/G_{max} (wt %)	V_{use}/V_{max} (kg/m^3)
cis-PA	5.00 − 1.84	3.16/5	7.6/12	63/100
PPY	3.00 − 0.05	2.95/3	4.9/5	33/34
PANI-out	3.00 − 0.96	2.04/3	4.1/6	31/46
$C_{48}B_{12}Sc_{12}$	2.68 − 0.02	2.66/5	4.7/8.8	23/43
CNT	1.95 − 0.35	1.60/3	4.1/7.7	Not available

tion condition of 2 atm and 100 °C, abbreviated to 30–25/2–100. These numbers, which may be revised in the future by consensus, are based on information in the literature [23,24] and reflect practical situations in gas filling and vehicle operations. 30 atm for adsorption and 1.5 atm for desorption were used in Ref. [24], but they did not take advantage of the temperature variation. We adopted an easily achievable temperature range of 25–100 °C here. Then, f at the condition of 30–25 minus f at 2–100 is the available number of H_2 molecules per site. These numbers are listed in Table I. For comparison, the same numbers for the Sc-decorated fullerene ($C_{48}B_{12}Sc_{12}$) [12] and the Ti-decorated carbon nanotube [11] are presented as well. We confirm that our results for the static adsorption energy of these materials agree with reported values [11,12]. When converted to the gravimetric density, Ti-decorated *cis*-polyacetylene stores usable H_2 molecules of 7.6 wt % out of the *maximum* density of 12 wt %, which is much greater than, say, the goal of 6 wt % by the year 2010 set by the Department of Energy (DOE) of the United States [23]. The Ti-decorated *cis*-polyacetylene is the best candidate material for hydrogen

storage in the list, better than that of Ti-decorated carbon nanotubes [11] or Sc-decorated fullerenes [12]. Note that 60% desorption of H_2 is achieved here at a temperature as low as 100 °C, which is considerably lower than the dissociation temperature of usual metal hydrides. If we were to slightly raise the desorption temperature to 130 °C, the usable gravimetric capacity of *cis*-polyacetylene would reach 9 wt %.

The volumetric density of the hydrogen storage is difficult to evaluate and not usually reported in the literature. To estimate the volumetric density, we assume that a hydrogen molecule adsorbed at the top of one unit cell and another adsorbed at the bottom of the next unit cell are separated by a van der Waals distance (∼ 3.4 Å). The calculated usable volumetric density is 63 kg/m³, which
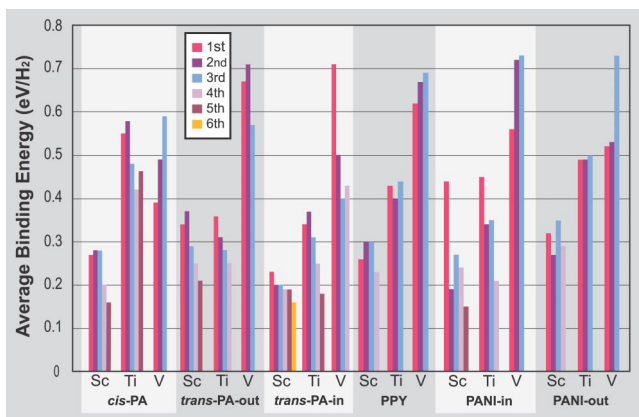

FIG. 2 (color online).   Calculated static adsorption (binding) energy per H_2 molecule for polymers decorated with Sc, Ti, or V atoms. The average binding energy per H_2 is plotted up to the maximum number of adsorbed H_2's allowed for each species. PA, PPY, and PANI stand for polyacetylene, polypyrrole, and polyaniline, respectively. -out and -in mean out-of-plane and in-plane configurations as previously shown in Fig. 1, respectively.
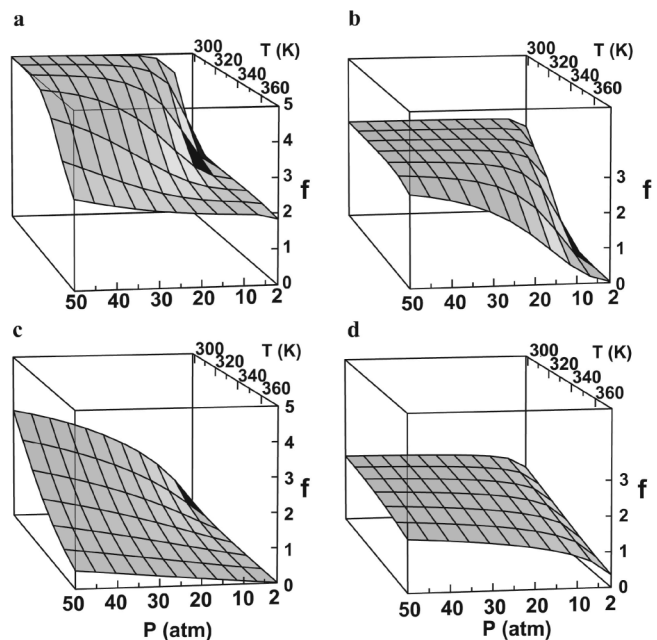

FIG. 3.   Occupation number-pressure-temperature (f-p-T) diagram of hydrogen storage in representative nanomaterials. The ranges of the pressure and the temperature cover typical conditions of filling and delivering from the storage tank. (a) Ti-decorated *cis*-polyacetylene. (b) Ti-decorated polypyrrole. (c) Sc-decorated $C_{48}B_{12}$. (d) Ti-decorated carbon nanotube.

is higher than the 2010 goal of 45 kg/m^3 set by the DOE of the United States [23].

So far, we have demonstrated an enormous potential of polymers as a hydrogen-storage medium. A serious problem yet to be overcome in practice is the attack of oxygen or other ambient gases. Polyacetylene is known to be especially vulnerable to it. One possible morphology to avoid oxidation is a dense matrix of polymer which is made permeable to H_2 but not to O_2. Clustering of decorating metal atoms is another obstacle in material fabrication [25]. In our simulation, which allowed for the relaxation of atomic positions, individually dispersed metal atoms did show local stability in linear polyaniline. However, how to suppress the aggregation of metal atoms in polymer matrices in general is a difficult question to be answered. As a brief summary of the experimental situation, we want to point out that hydrogen storage in polymer-dispersed metal hydrides was studied before [26]. It was hoped that the storage capacity of metal hydrides might be enhanced by incorporating a low-density polymer that could interact with the hydride on a molecular level and store additional hydrogen within the polymer structure. Although an increase in the hydrogen release was found, the maximum amount reached only 0.36 wt % in experiment. We believe that the low capacity is probably due to the poor morphology, i.e., too large (≥ 10 μm) Ti-polymer particles.

In summary, we have carried out first-principles electronic structure calculations for hydrogen binding to metal-decorated polymers of many different kinds. When the thermodynamic behavior of hydrogen molecules under realistic conditions is considered, the Ti-decorated *cis*-polyacetylene is found to have the highest usable gravimetric and volumetric density among nanostructures reported so far. We also propose the f-p-T diagram as a criterion for evaluating usable capacity at ambient conditions. It remains to be a challenge for experimentalists to fabricate a structure of individually dispersed Ti atoms on polymer as much as possible in order to achieve significantly improved storage capacity.

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