Optimization of metal dispersion in doped graphitic materials for hydrogen storage

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The noncovalent hydrogen binding on transition-metal atoms dispersed on carbon clusters and graphene is studied with the use of the pseudopotential density-functional method. It is found that the presence of acceptorlike states in the absorbents is essential for enhancing the metal adsorption strength and for increasing the number of hydrogen molecules attached to the metal atoms. Particular configurations of boron substitutional doping are found to be very efficient for providing such states and thus enhancing storage capacity. Optimal doping conditions are suggested based on our calculations for the binding energy and ratio between metal and hydrogen molecules.

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I. INTRODUCTION

Recently, the need for clean alternative energy sources that can replace fossil-based fuels is increasingly urgent because of global warming as well as problems related to oil supply. Hydrogen has been considered a strong candidate as an alternate fuel source as it is recyclable without emitting carbon dioxide. A critical issue for hydrogen energy is how to develop proper storage systems and methods that can operate at ambient conditions with enough gravimetric capacity.[1,2] In recent years, transition-metal-dispersed materials have been studied actively for high-capacity hydrogen storage.[3–7] The metal-hydrogen binding energy and ratio look very promising with respect to the capacity and release temperature. However, the issue of structural stability and the poor reversibility in transition-metal (TM) dispersion are some major concerns in developing hydrogen-storage materials of this kind. Problems arise because of the strong tendency of TM atoms to cluster.[8,9] For example, it was shown that aggregated Ti atoms are energetically more stable than well-separated individual Ti atoms in fullerene molecules.[8] Recently pyridinelike N defect on graphene was found to be very effective to avoid such TM aggregation problem.[7] Clear understanding of the process and mechanism of metal dispersion, clustering, and subsequent hydrogen binding is still required for developing TM dispersion-based hydrogen-storage systems.

In this paper, we present a systematic approach to address this issue and to determine the optimal conditions for metal binding, metal-hydrogen ratios, and for preventing metal clustering. We chose sp_2-like bonded carbon materials including graphene and coronene molecules as model materials to study. These materials serve not only as prototypes for this but also as building blocks of porous structures that can host metals and hydrogen molecules. We are particularly interested in the effect of charge transfer between dopants, metal atoms, and hydrogen molecules for metal dispersion and hydrogen adsorption. We believe that the analysis and main conclusions presented here are not limited to these particular structures but can be applied to other materials.

II. COMPUTATIONAL METHODS

All calculations are performed with the spin-polarized first-principles total-energy method as implemented in the Vienna *ab-initio* simulation package.[10] The projector augmented wave pseudopotentials are used as provided in this package. The electron exchange correlation is treated within local-density approximation (LDA),[11] which is reliable for covalent bonding and static Coulomb interactions.[6,12,13] For a cross-check, we repeated part of calculations with the generalized gradient approximation (GGA) in the form of Perdew-Burke-Enzelhof-type parametrization.[14] Overall trends in the GGA calculations are found to be similar to those obtained using LDA while the adsorption energies of H_2 molecules to transition metals are half the LDA values.[6,12,13] Presented below are the LDA results unless specified otherwise. The cut-off energy for the plane-wave-basis expansion is chosen to be 29.4 Ry and the atomic relaxation is carried out until Helmann-Feynman forces acting on atoms are less than 0.01 eV/Å. In order to simulate an isolated coronene molecule in the plane-wave-basis scheme, we choose a simple-cubic supercell with a lateral size of 15 Å.

III. RESULTS AND DISCUSSION

First we take coronene as substrate that can be considered as a model for a graphene fragment, and Sc, Ti, and V atoms as metal dispersoids, as shown in Fig. 1. The binding energy of Ti(E_b^{Ti}) on coronene, for example, is calculated to be about 2.17 eV, which is smaller than the Ti-Ti dimer binding energy of 2.40 eV in our calculations. This indicates that Ti atoms would prefer aggregation to atomic dispersion on

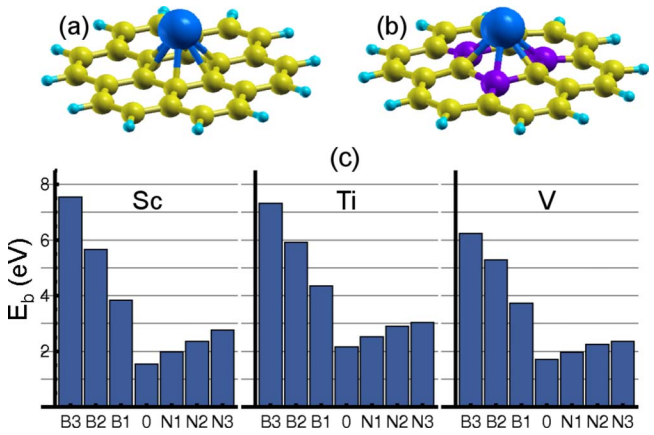

FIG. 1. (Color online) Optimized structure of Ti attached to (a) a pure and (b) a B-doped coronene molecule. Yellow, purple, and large blue balls represent carbon, boron, and titanium atoms, respectively. Saturating hydrogen atoms are depicted by small light-blue balls. (c) Calculated binding energies (E_b^{TM}) of transition-metal atoms (Sc, Ti, and V) on boron-doped or nitrogen-doped coronenes (each denoted by Bn or Nn with n being the number of B or N atoms in a carbon hexagon ring without forming B-B or N-N bonding).

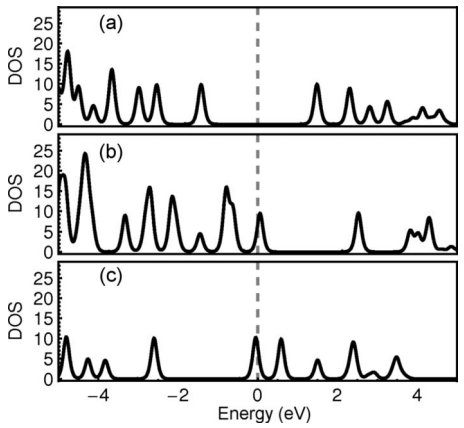

FIG. 2. Density of states of (a) a pure, (b) a B-doped, and (c) a N-doped coronene [$C_{21}B(N)_3H_{12}$] obtained after Gaussian convolution with an energy width of 0.05 eV of molecular levels. The Fermi level, set at the zero of energy, lies close to the HOMO (LUMO) state for B (N) doped coronene.

coronene or on similar structures. Roughly, the metal adsorption energy should be larger than the cohesive energy of the metal for atomic dispersion, as discussed in more details below. As TM-coronene binding is within the description of Dewar theory,[15] a change in bonding (or molecular levels) of coronene is necessary to enhance the metal adsorption energy. Boron or nitrogen is a natural choice to modify the molecular levels as they are easily incorporated for that purpose without changing the structure drastically. Figure 1 shows the optimized structures of Ti-bonded pure and B-doped coronenes together with calculated TM binding energies (E_b^{TM}) of Sc, Ti, and V. It is interesting to observe that each E_b^{TM} shows almost the same behavior of a significant enhancement in binding energy as the number of B atoms increases [see Fig. 1(c)]. On the other hand, nitrogen doping shows a modest change in the binding energy but appears comparatively ineffective.

We investigate in detail the molecular structures of pure and doped coronenes. Figure 2 shows the calculated density of states (DOS) of pure, B-doped, and N-doped coronene molecules. The empty p_z orbital of boron acts as a strong charge accepting center whereas nitrogen provides an extra electron. Upon B (N) doping, the Fermi-level shifts to the highest occupied molecular orbital (HOMO) [lowest unoccupied molecular orbital (LUMO)] level of the coronenes as shown in Figs. 2(b) and 2(c). It is well known that electronic charges transfer from TMs' d level to ligands at their binding, for example, in ethylene, fullerene, or carbon nanotubes.[3,4,15] One would expect that such charge transfers occur more efficiently when acceptorlike levels exist in the ligands, leading to stronger TM binding. For example, the valence charge of Ti on $C_{24-x}B_xH_{12}$ with $x=1$, 2, and 3 is found to decrease by about 0.18, 0.34, and 0.4 electron, respectively, from that of Ti on pure coronene while no clear correlation is found for nitrogen doping. The charge transfer would enhance the Coulomb interaction between metal and coronene. This explains at least qualitatively the observed trend in E_b^{TM} on B-doped coronenes and also the ineffectiveness of the N-substitutional doping for strengthening metal binding as shown above.

A key issue in developing a metal-dispersed hydrogen-storage medium is the clustering of metal atoms, which is extremely troublesome for maintaining material stability and storage capacity. Despite previous demonstrations of promising hydrogen-adsorption properties of the TM-dispersed media, the metal clustering still remains as a challenging problem to solve.[8,9] Our calculations of metal binding on doped coronene present a plausible direction for addressing this issue. To provide a more explicit analysis, we calculate the binding energy of a metal dimer and two isolated metal atoms on a B-doped graphene sheet (with a composition of $C_{48}B_{12}$) as shown in Fig. 3. Remarkably, it is found that dimerized Sc and Ti on B-doped graphene are energetically unstable with respect to two separated atoms by about 1.35 and 0.52 eV, respectively, in terms of binding energy. In contrast, the dimerization is favored for V. On undoped

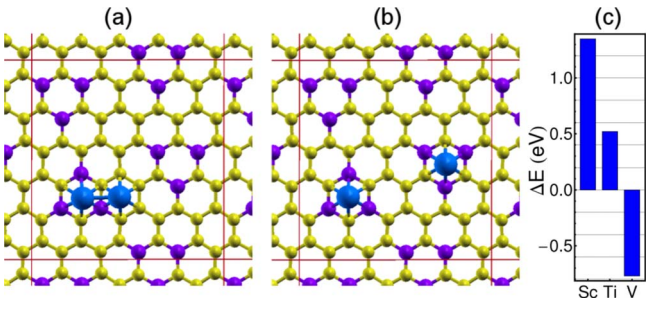

FIG. 3. (Color online) Two TM atoms on B-doped model graphene with a chosen unit cell [indicated by red rectangles in (a) and (b)] of $C_{48}B_{12}$ (a) in a dimer form or (b) as two separated atoms. (c) The energy difference between geometry (a) and (b) for Sc, Ti, and V. The plus sign in (c) indicates that the configuration (b) has a larger cohesive energy than that of the configuration (a) whereas the minus sign means the opposite.

graphene, on the other hand, the dimerization is strongly favored for all three TMs with energy gains of 1.90, 2.46, and 2.90 eV for Sc, Ti, and V, respectively. The cohesive energies (E_{coh}) of bulk TM are also calculated for comparison. We obtained 4.83, 6.50, and 6.66 eV for E_{coh} of Sc, Ti, and V, respectively, which are compared to the binding energies of individual atoms on B-doped graphene of 6.78, 6.72, and 5.47 eV, respectively. These calculated E_{coh} values are in good agreement with previous LDA results.[16] The large cohesive energy of V explains the stability of dimerization relative to two separated atoms. As a rule of thumb, the metal binding energy on absorbents should be larger than or at least similar to the cohesive energy of the metal for atomic dispersion. In this respect, transition metals of large cohesive energy should be ruled out for dispersion on graphitic structures. Our study suggests that dispersed strong binding sites should exist in absorbents for better metal dispersions, particularly at low metal coverage.

A critical and eventually encountered issue in hydrogen-storage research is the question of how to make bulk forms of the suggested materials without loss of the desired properties. Engineering such optimized graphitic fragments to build three dimensional porous structures is a demanding challenge. The B-doped graphenes have actually been synthesized experimentally[17,18] but detailed atomic structures were not characterized. The direct B-B bonding in graphene is known to be energetically unfavorable[19] (by about 1.0 eV with respect to two separated single boron atoms in graphene in our calculation). On the other hand, the second-nearest-neighbor boron atoms (B pair) are more stable than two single boron atoms by about 0.06 eV per B. Three boron atoms in the next-nearest neighbors (B triplet) are found unstable with respect to three separated B atoms (by about 0.17 eV per B). Calculated energetics provides a rough picture of boron formation; the B pairs start developing at low B concentrations, and a mixture of boron singles, pairs, and triplets are expected to form at elevated temperatures as B concentration increases. Again, as substitutional doping should be realized at highly nonequilibrium conditions, the kinetics would be a determining factor due to the small formation energy difference. Utilizing BN nanostructures as templates[20] or controlling individual fragmented graphenes[21] can also be a possible approach to develop proposed structures. While separated metal atoms are stable in B triplet configuration, TM is found to prefer the dimer form in B pairs with a small energy gain (about 0.19 eV for Sc). As the metal atoms are dispersed with non-negligible kinetic energies, the diffusion of TM atoms is of equal or more relevance to experiment for B-doping configurations. Figure 4 summarizes our calculations that show a Ti-diffusion energy barrier of about 1.13 eV to the second-nearest local minimum. This implies that, once atomistically bound, the Ti atoms will stay stable at the sites because of the diffusion energy barrier as well as the strong binding itself.

The doping and subsequent charge transfer between adsorbent and metal atoms can have profound effects on the hydrogen binding to the metal atoms. The metal-H_2 binding is mediated by static Coulomb interactions between the metal and hydrogen molecules.[22–25] A fractional-charge transfer occurs from metal to hydrogen molecules, occupying the antibonding σ^* state of H_2. As a result the hydrogen bond length is elongated, which is in turn indicative of the interaction. Excessive charge transfers, on the other hand, lead to the breaking of hydrogen-hydrogen bonding in H_2 and the dissociated hydrogen atoms make covalent bonds with metal atoms. For pure TM-hydrogen binding, such dissociation is frequently observed.[22–24] Controlling the charge state of metal-absorbent complexes will thus be a key to the optimization of metal-hydrogen binding energy and ratio. We expect that boron doping not only helps stabilize the dispersion of individual TM atoms but also reduces the hydrogen dissociation, leading to favorable molecular hydrogen binding to the metal. On the contrary, nitrogen doping would be ineffective in this respect as it introduces donorlike states. Figure 5 shows our calculated H_2 binding energies on metal-coronene complex with various doping ratio. It is interesting to find that increasing B-doping ratio in coronene significantly changes the hydrogen molecule adsorption behavior. First of all, the H_2 binding energy develops a uniform distribution as the B-doping ratio increases together with more hydrogen molecules being adsorbed. Dissociation of hydrogen is also reduced compared to pristine, single-B-doping cases, or the N-doping case. The uniformity of H_2 binding energies in B-doped metal-coronene complex is advantageous for practical purposes. There have been reports of boron-doping effects in selected cases[3] but an understanding of the doping on the molecular level is essential for developing desirable hydrogen-storage media. The N doping acts in a completely different way. Either a substantial fraction of H_2 tends to dissociate or the number of adsorbed hydrogen decreases as N-doping ratio increases, especially for Sc and Ti.

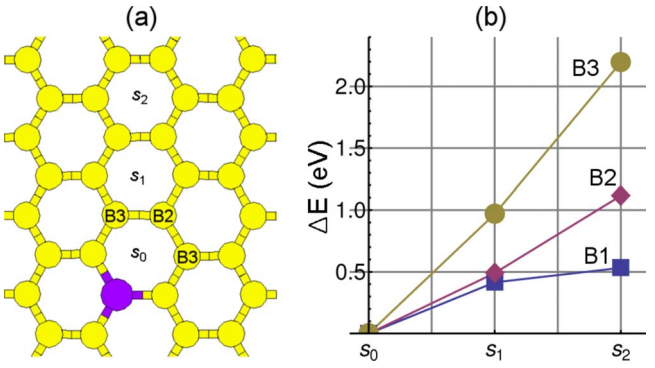

FIG. 4. (Color online) Diffusion energy barrier of a Ti atom on B-doped graphene. (a) s_0, s_1, and s_2 represent the local minimum sites of Ti adsorption, and B2 and B3 denote the sites for additional boron substitution of carbon in pair and triplet doping configurations, respectively. The dark gray (purple) circle is to show the initial boron substitution site (B1). (b) The total-energy difference (ΔE) of Ti adsorption on s_1 and s_2 relative to s_0 for single (B1), pair (B2), and triplet (B3) boron defects.

Given the structure and the number of available adsorbed hydrogen molecules, we now estimate the storage capacity of the materials studied here. Detailed information of kinetic processes together with equilibrium properties is necessary to draw meaningful numbers for storage capacity but here a simple estimation is presented to provide an upper bound of

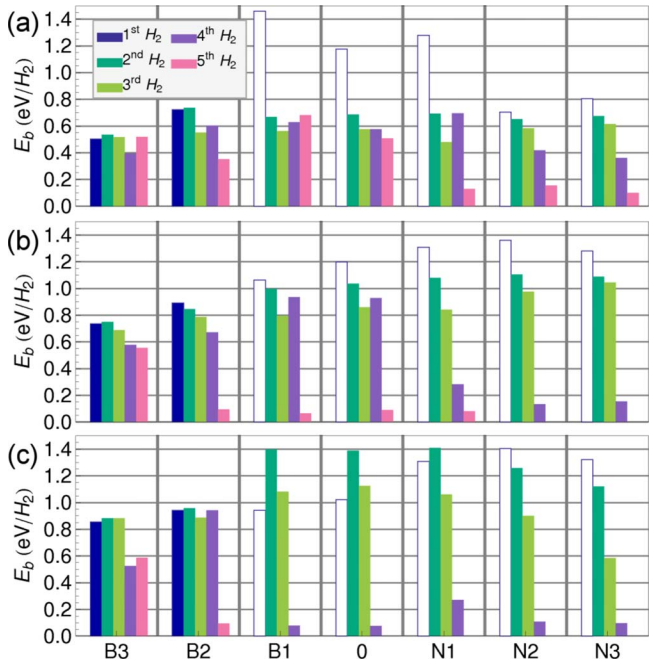

FIG. 5. (Color online) Hydrogen binding energy to B-doped or N-doped coronene-metal complex formed with (a) Sc, (b) Ti, and (c) V, respectively. The label in the abscissa is the same as in Fig. 1(c). The colored bars denote the net binding energy of hydrogen calculated by successively attaching the hydrogen molecules to the metal atoms as denoted in the enclosed legend in (a). First unfilled bars indicate the binding energy of hydrogen, for which the H-H bond distance is larger than 1.6 Å, a predefined dissociation limit. As B-doping ratio increases, we observe significant enhancements in H_2 adsorption including uniform adsorption energies, increased number of adsorbed H_2, and reduced H_2 dissociation. No such improvement is observed for N doping.

the capacity. The hydrogen-storage capacity of the structure is estimated to be about 4∼5 wt % depending on the transition metal. Utilizing both top and bottom sides of the structure in Fig. 3, Sc+B-doped graphene complex can store hydrogen up to 7.0 wt %. The hydrogen-adsorption energy of about 0.5 eV on average in Sc+B-doped coronene complex gives a release temperature of about 310 K as estimated from the Van't Hoff equation[26] with the zero-point energy taken into account. The zero-point energy amounts to about 25% of the total binding energy[5] and the release temperature would go up to 390 K if it is not considered. One caveat here is that the average binding energy and the release temperature should be understood within the error bar of current computational schemes. As LDA and GGA typically provide the upper and lower bounds of binding energy, respectively, the estimated release temperature may correspond to an upper bound of the true value. If we choose a thermodynamic condition of (T,p) for the release adsorption of about (100 °C, 2 atm) and (25 °C, 30 atm) as suggested in a recent report,[5] the actual capacity will be about 76% of the ideal maximum capacity. Interestingly, additional TM (Sc and Ti) binding on the other side of the graphene reduces the B-doping effect. This is due to a decrease in (average) charge transfer from the two TM atoms to the acceptor levels. The net metal-hydrogen ratio in this case also decreases from five to four H_2 per metal atom for Ti. This result supports the argument that the charge transfer from TM to absorbents is very crucial for hydrogen binding.

In summary, we have studied the metal dispersion and hydrogen binding properties on doped graphitic materials. It is found that the existence of acceptorlike states in absorbents is crucial in enhancing the metal binding and subsequent hydrogen adsorptions. We have shown that boron substitutional doping provides such states, leading to excellent doping conditions for hydrogen storage. Current analysis can be applied to other types of absorbents for designing hydrogen storage based on metal dispersion.

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