Energetics and kinetics of Ti clustering on neutral and charged C_{60} surfaces

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Using *ab initio* spin density functional theory, we investigate the energetics and kinetics of Ti clustering on both neutral and charged C_{60} surfaces. We compare the formation energy of sparsely dispersed zero-dimensional (0D), compact single-layered two-dimensional (2D), and clustered three-dimensional (3D) Ti_N configurations as a function of cluster size ($N \leqslant 12$) and further study the transformation kinetics between them. We find that 0D configuration is always less stable than that of 2D and 3D configurations and 0D to 2D transformation involves in a single Ti diffusion process with kinetic barrier of $\leqslant 0.7$ eV. On the other hand, there exists a critical cluster size (N_C) of $N_C = 5$, below which 2D layers are preferred to 3D clusters. Hole- or B-doping greatly enhance the Ti-fullerene interaction and lead to stronger dispersion of Ti atoms. Even so, for moderate charge doping (less than seven holes) the critical size of Ti atoms on neutral C_{60} surprisingly remains unchanged or only slightly increases to $N_C = 6$ by B-doping. However, we find that the formation of 3D clusters may be hindered by a high kinetic barrier related to the process of single Ti atoms climbing up a single Ti layer. This barrier is ~ 1 eV or even 1.47 eV for B-doped C_{60} surfaces which is high enough to stabilize larger 2D structures ($N \geqslant N_C$) at low temperatures. These findings may prove to be instrumental in stabilizing transition metal coated nanostructures and especially homogeneously Ti-coated fullerenes, which are believed to be a very promising material for hydrogen storage. © *2008 American Institute of Physics*. [DOI: 10.1063/1.2981043]

I. INTRODUCTION

Hydrogen is considered as a promising and environmentally friendly energy carrier for renewable energy. The commercialization of hydrogen fuel has been hampered by the lack of a safe, effective, and cheap storage media.[1–3] Carbon-based materials,[4,5] such as graphite and carbon nanotubes (CNTs), have been suggested as good candidates for hydrogen storage because of their light weight and large surface area. However, it turns out that in these carbon sp^2 structures the hydrogen binding energy originating from van der Waals interactions between the respective inert components is very weak and of the order of ~ 0.08 eV/H_2. As a consequence, under near ambient conditions the hydrogen storage capacity is only ~ 0.1 wt %,[6] which is far below the gravimetric target of 6 wt % proposed by the U.S. Department of Energy.[7]

Recent theoretical studies showed that hydrogen binding to the surface of transition metals (TMs), especially Ti doped carbon-based nanostructures[8–10] and organic molecules[11–13] is much stronger than to pristine carbon structures. The hydrogen binding energies of 0.1–0.6 eV/H_2 fall in the desirable range of being suitable for practical applications under near ambient conditions.[14] Theoretical calculations demonstrated that the reversible hydrogen storage capacity reaches up to 8.77 and 7.7 wt % on TM-doped fullerenes[8] and CNTs,[9,10] respectively. In these proposed carbon nanostructures the TM atoms are sparsely distributed on the surface of fullerenes or CNTs. In this paper we define this configuration as zero-dimensional (0D), and we identify the close-packed single layer on the curved surface as two-dimensional (2D) structure, and a multilayered cluster as three-dimensional (3D) structure. The question remains whether such a sparse 0D TM distribution is experimentally achievable. It has been shown experimentally that among many TMs only Ti can evenly coat the surface of single walled CNTs (SWCNTs).[15,16] Also, fullerenes doped with Ti and V appear to be stable.[17] However, so far there is no experimental evidence showing it is actually possible to coat the surface of CNTs or fullerenes with sparsely distributed (0D) layer or a single homogeneous (2D) of Ti atoms. In fact, the transmission electron microscopy images of metal coated SWCNTs clearly demonstrated that Ti atoms coat over CNTs in the form of closely packed multilayers or clusters rather than a homogeneous single layer.[15,16] The mass spectrum of Ti-coated C_{60} clusters[17] indicates that Ti atoms form 2D or 3D clusters on fullerene surfaces rather than 0D. A previous theoretical calculation suggested that a single Ti layer on a CNT is energetically stable and the shape of the CNT is strongly distorted by the Ti layer.[18] On the contrary, another theoretical calculation concluded that a 3D Ti cluster is energetically much more favorable than that of 0D by comparing the formation energies of 12 Ti atoms in a sparse distribution and

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in a partial-icosahedron cluster on C_{60}.[19] However, there are no theoretical studies which thoroughly discuss this topic. In order to determine whether a given atomic configuration is achievable or not, both energetics and kinetics of the formation process on an atomistic level have to be considered.

Besides TM doping, another way to enhance hydrogen binding on fullerenes is to make use of the charging effect.[20] The charge states of fullerenes can be controlled by ion/electron bombardment, laser desorption, chemical doping, electrochemical doping, etc.[20–26] The hydrogen binding energy on both positively and negatively charged fullerenes increases quadratically with the net charge. Therefore, the hydrogen binding energy of 0.18–0.32 eV/H_2 with a hydrogen storage capacity as high as 8.04 wt % can be achieved on a charged fullerene.[20] The enhancement is attributed to the polarization of hydrogen molecules by the high electric field generated near the surface of a charged fullerene, which is delocalized due to the delocalization of the extra charges.

Our main goal of this paper is to understand to what extent and under which circumstances Ti coating on fullerenes is stable against clustering. In order to address this issue, we systematically compare the formation energies of 0D, 2D, and 3D Ti configurations on C_{60} surfaces and study the transformation kinetics between them. This study bridges the gap between theoretical idea of using Ti-coated fullerenes as hydrogen storage media and experimental production of the theoretically designed systems.

This paper is organized as follows. In Sec. II we present the modeling and calculation methods used in this study. In Sec. III we present data and results. In Sec. III A we explore the energetics of Ti clusters as a function of cluster size (N), i.e., the number of Ti atoms ($N \leqslant 12$), on neutral and charged C_{60} surfaces. There, our goal is to compare the structural stability of different Ti configurations of 0D, 2D, and 3D. In Sec. III B we extend this study to B-doped C_{60}. Section III C discusses the kinetics associated with transformations from 0D to 2D and from 2D to 3D Ti configurations on neutral and charged C_{60} surfaces. The kinetic barriers of different processes are compared to each other. Section IV is for discussion and conclusion.

II. MODELING AND CALCULATION METHODS

Our *ab initio* spin density functional calculations were performed using the Vienna Ab-initio Simulation Package (VASP),[27] with the exchange-correlation potential described by the Perdew–Wang version of gradient generalized approximation.[28] We employed the projector-augmented wave pseudopotentials[29,30] to describe the interaction between ion cores and valence electrons. The energy cutoff for the plane-wave basis set was 400 eV. All considered structures were relaxed, without any constraints, until the force on each atom was less than 0.01 eV/Å.

For selected cases, we compared spin-polarized results with non-spin-polarized results. We found that spin-polarized calculations are necessary for these systems with unsaturated TMs. For instance, the total magnetic moment of the 0D sparse configuration of 12 Ti atoms above 12 pentagons of C_{60} is $30\mu_B$, and the energy difference between spin-polarized and non-spin-polarized results is ~5 eV. For each structure, we considered different spin coupling between the Ti adsorbates and chose the state with the lowest energy as the ground state. The energy barrier calculations were performed by using the Nudged Elastic Band (NEB) method[31–33] with a climbing image as implemented in VASP. We inserted four replicas between the initial and final states and relaxed the atomic positions until the atomic force acting on the images is less than 0.01 eV/Å in magnitude.

In calculating the energy of a charged cluster, a uniform background charge was introduced to keep the system charge neutral within a supercell. The spurious electrostatic interactions due to the introduction of the uniform background charge, and that associated with the long-range interaction between different supercells, were corrected with monopole and multipole terms using the schemes implemented in VASP.[34–36] We carefully monitored each correction component with respect to the supercell size. We choose a $22 \times 22 \times 22$ Å cubic supercell and energy convergence has been carefully checked. If C_{60} is charged with more than two electrons, fictitious states, stemming from spurious interactions between adjacent charged images due to periodic boundary conditions, appear near the Fermi level and cause unphysical effects for highly negatively charged fullerenes.[20] Therefore we limited our studies to C_{60}^q systems with $-2 \leqslant q \leqslant 6$, where q is the net charge of the system. The Ti_N cluster binding energy per Ti atom (E_b) on the surface of C_{60} is defined as $E_b = [E(C_{60}) + N \times E(Ti) - E(Ti_N C_{60})]/N$, where $E(Ti_N C_{60})$ is the total energy of the $Ti_N C_{60}$ complex and $E(C_{60})$ and $E(Ti)$ are the energies of an isolated C_{60} and a Ti atom, respectively. A positive E_b corresponds to an exothermal adsorption process.

III. ENERGETICS OF Ti CLUSTERS AND KINETICS OF THEIR FORMATION PROCESSES

A. Energetics of Ti_N clusters on neutral and hole-doped C_{60} surfaces

Figure 1(a) shows the three most stable configurations of a single Ti atom on the surface of C_{60}. The most stable adsorption site is above a hexagonal ring, with a binding energy of 2.50 eV, while the adsorption above a pentagonal ring and a carbon double bond is less favorable by 0.50 and 0.67 eV, respectively. On positively charged fullerenes ($q > 0$),[20–26] the Ti binding energy increases nearly linearly with the net charge as it is shown in Fig. 2(a). On the other hand, on negatively charged fullerenes ($q < 0$) (Refs. 20–26) the Ti binding energy remains similar to that of a neutral system. This is because Ti prefers to donate electrons to the fullerene cage since it is more electropositive than C. Therefore Ti can donate more electrons to a positively charged fullerene, resulting in a stronger Ti-fullerene interaction, while it donates less electrons to a negatively charged fullerene, compensating the charge effects. We would like to emphasize that unlike in the case of molecular hydrogen interacting with charged fullerenes where the binding energy enhancement originates from the polarization of hydrogen molecules,[20] Ti atoms directly form chemical bonds with the fullerene. The possible polarization of Ti atoms is negligible

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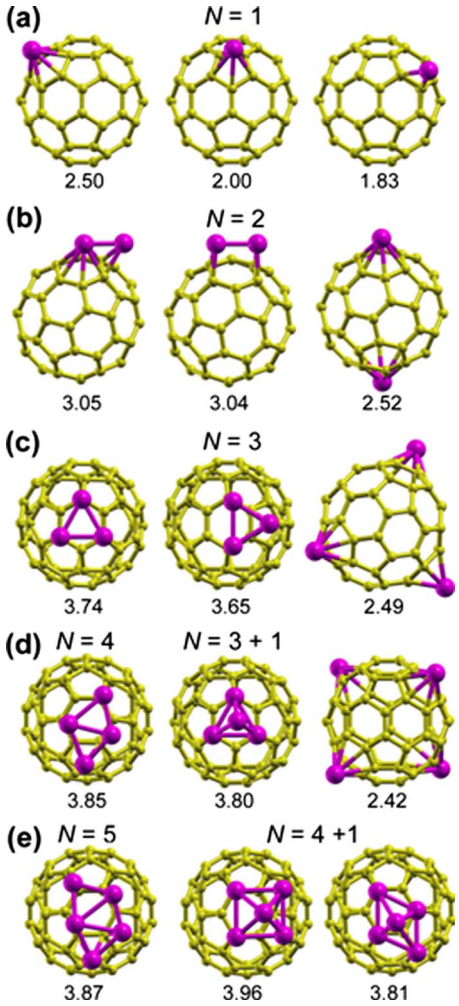

FIG. 1. (Color online) The lowest energy structures and the Ti binding energy per Ti (in eV) of neutral Ti_NC_{60} complexes for (a) $N=1$, (b) $N=2$, (c) $N=3$, (d) $N=4$, and (e) $N=5$. C and Ti atoms are denoted by yellow and magenta balls, respectively.

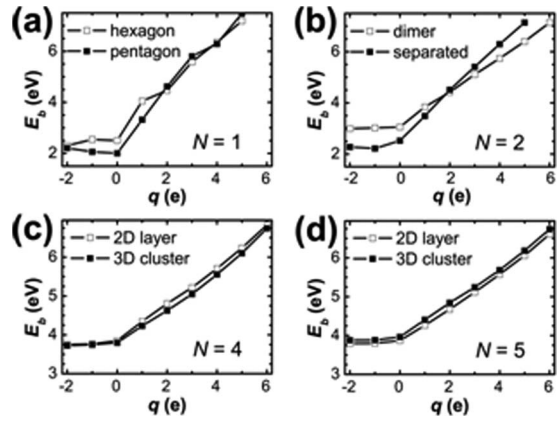

FIG. 2. The binding energies per Ti atom in the Ti_NC_{60} complexes as a function of net charge. (a) $N=1$. Binding energies of a Ti atom positioned on top of a hexagonal or pentagonal site. (b) $N=2$. Binding energies of a Ti dimer [left panel of Fig. 1(b)] and the separated distribution [right panel of Fig. 1(b)]. (c) $N=4$. Binding energies of 2D layer [left panel of Fig. 1(d)] and 3D cluster [middle panel of Fig. 1(d)]. (d) $N=5$. Binding energies of 2D layer [left panel of Fig. 1(e)] and 3D cluster [middle panel of Fig. 1(e)].

in its effect. Thus the Ti binding energy does not increase quadratically with the net charge unlike in the case of hydrogen molecules.[20]

Two Ti atoms prefer to dimerize rather than be separately distributed [see first two panels of Fig. 1(b)] because the Ti–Ti interaction is much stronger than the interaction with the fullerene. The Ti binding energy of two separately distributed Ti atoms [right panel of Fig. 1(b)] is similar to the binding energy of a single Ti atom. The energy difference between the dimer and the sparse distribution is 1.06 eV on a neutral fullerene surface. This difference decreases linearly as the number of holes on the fullerene increases, as presented in Fig. 2(b). If there are more than two holes ($q>2$) the relative stabilities are changed and the separated distribution becomes energetically more favorable than the dimer, i.e., the Ti-fullerene interaction becomes stronger than the Ti–Ti interaction. Three Ti atoms show a similar behavior; they prefer to form trimers on neutral C_{60} [first two panels of Fig. 1(c)] and for $q>3$ the sparse distribution [right panel of Fig. 1(c)] becomes more stable.

Here we note that the stability of the Ti_NC_{60} complex is dependent on adsorption sites and spin coupling as well. For instance, the three Ti atoms prefer to locate on top of the same hexagonal ring rather than on different rings in order to minimize the strains in the complex. The spin coupling between Ti atoms shows complicated behavior, which is determined not only by interactions between Ti atoms but also by their adsorption sites. The total magnetic moments of a Ti atom are $2.0\mu_B$, $4.0\mu_B$ and $0.0\mu_B$ for a Ti located above the hexagon, pentagon, and double bond, respectively. A Ti-trimmer has a net magnetic moments of $6.0\mu_B$ for a sparse distribution [right panel of Fig. 1(c)] and $2.0\mu_B$ for a compact-layer structure shown in the left panel of Fig. 1(c). Depending on its spin coupling, various magnetic states are possible and the energy differences between these states are typically less than 0.2 eV. In general, the ferromagnetic coupling between Ti atoms is always energetically preferred if Ti atoms are homogeneously and sparsely distributed on C_{60} surface, while the antiferromagnetic coupling is preferred for a compact configuration. In considering energetics we always choose a spin state with the lowest energy for each configuration.

For the Ti_4C_{60} complex, we denote 2D layer structures by $N=4$ and 3D clusters by $N=3+1$. Among all configurations, the layer structure shown in Fig. 1(d) is the most stable with a total energy gain of 0.22 eV relative to that of the 3D cluster. No changes in the relative structural stability between 2D and 3D structures are observed by changing the amount of net charge ($q\leqslant 6$); the Ti binding energies of the 2D layer and 3D cluster increase with nearly the same slope as the positive charge increases [Fig. 2(c)], indicating that extra charges have similar effects on both structures. In the case of five Ti atoms the 3D cluster ($N=4+1$) becomes more stable than the layer structure ($N=5$) [see Fig. 1(e)] and there is no change in the stability sequence of 2D layer and 3D cluster with respect to net charge [see Fig. 2(d)]. In general, if N is larger than or equal to the critical size ($N_C=5$), the 3D cluster is energetically more stable than the 2D layer independently of hole doping ($q\leqslant 6$).

The binding energy of compact Ti configurations signifi-

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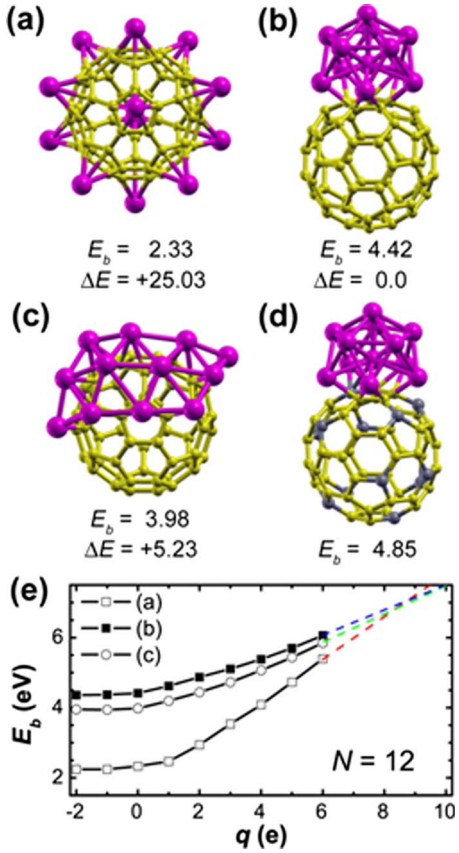

FIG. 3. (Color online) Three configurations of $Ti_{12}C_{60}$, (a) homogeneous distribution, (b) 3D cluster, and (c) 2D layer structure. E_b is the binding energy per Ti atom and ΔE is the total energy with respect to the energy of configuration (b). (d) Ti_{12} 3D cluster on $C_{48}B_{12}$ surface. B atoms are denoted by dark gray balls. (e) Binding energy per Ti atom as a function of net charge for $Ti_{12}C_{60}$ complexes shown in (a)–(c).

cantly increases with increasing cluster size because of a rise in the coordination number. On the other hand, the binding energy of the sparse distribution (0D) only slightly changes with the number of Ti atoms (as seen from Fig. 1). Therefore, the energy difference between the 0D configuration and the 3D cluster increases significantly with the number of Ti atoms and the sparse distribution becomes highly unstable at large N. The largest cluster we consider in this study is Ti_{12}. Twelve Ti atoms can form the 0D configuration by homogeneously occupying the 12 pentagon sites on C_{60} (Refs. 8 and 37) [Fig. 3(a)] or form the 3D cluster of a partial icosahedron frame[19] [Fig. 3(b)]. Besides these two geometries, we also consider the 2D layer structure which is shown in Fig. 3(c). The 0D distribution is less stable by 25.03 eV in total energy (ΔE) than the 3D cluster, in agreement with the result of Sun *et al.*[19] The energy difference of the 2D layer structure and the 3D cluster is much smaller; the 3D cluster is energetically more favorable by 5.23 eV in total energy. By hole doping, the total energy differences between the 0D distribution (or 2D layer) and the 3D cluster decrease with increasing net charge, as shown in Fig. 3(e). For instance, the total energy difference of the 0D and the 3D cluster at $q=5$ is 11.62 eV, which is smaller by 13.41 eV than that of the neutral state. By extrapolating the curves in Fig. 3(e), it can be seen that relatively highly charged states ($q \geqslant 9$) are required to reverse the stability of these two structures. The total energy difference between the 2D layer and 3D cluster decreases even slower with increasing net charge as shown in Fig. 3(e), and an even higher charge state is required to change the structural stability sequence. However, it is difficult to reach and maintain such high charge states.

B. Energetics of Ti_N clusters on boron-doped C_{60} surfaces

We now consider B-doped carbon fullerenes, where the charge neutrality of the system is maintained. Nevertheless, substitutionally doped boron induces a spatially localized hole, which generates a strong Ti-binding site. Therefore, effective role of B-doping turns out to be very similar to that of hole doping. As an example, we take $C_{48}B_{12}$, which is isoelectric to C_{60}^{12+} (Ref. 25). Here, the introduced holes are spatially localized at B sites and the TM binding energy increases on the B-doped C_{60} surface.

If a Ti atom is located on top of a hexagonal ring containing one or two B atoms, the binding energy is more than ~2 eV higher than that of Ti on pristine C_{60}. This high energy gain originates from a stronger hybridization between Ti and cage orbitals upon boron doping. After Ti adsorption, the charge on the B atom closest to Ti is increased by 0.05 electrons, indicating a local charge transfer from Ti to B atom. This promotes a strong hybridization between the delocalized Ti d orbitals and $C_{48}B_{12}$ orbitals (highest occupied molecular orbitals and lowest unoccupied molecular orbitals). For five Ti atoms, the 3D cluster ($N=4+1$ configuration) becomes slightly less stable than the 2D layer because the topmost Ti atom of the 3D cluster can hardly take advantage of the extra charge near B sites. Therefore, in this case the critical size takes the value of $N_C=6$. This phenomenon is closely investigated by comparing the occupation numbers of individual atomic orbitals, which were calculated by projecting the wavefunction onto spherical harmonics centered on individual atoms. We especially focus on the amount of charges of each Ti atom on $C_{48}B_{12}$ and on C_{60}. The amount of charges of a single Ti atom on $C_{48}B_{12}$ is smaller than that on C_{60} surface by $0.06e$ in 2D layer structure, i.e., the Ti donates more electrons to $C_{48}B_{12}$ comparing to the case of pristine C_{60}. On the other hand, in 3D clusters, the amount of total charge of the topmost Ti atom is almost the same for both pristine and B-doped cases, i.e., once Ti atom is at the second layer it mainly interacts with other Ti atoms and there is no significant interaction with carbon cages.

For neutral $Ti_{12}C_{48}B_{12}$ complexes, the average binding energy per Ti atom of the 0D configuration is 0.95 eV higher than on pristine C_{60}. However, there is no change in the relative stability between 2D and 3D structures for 12 Ti atoms; the 3D cluster is still the most favorable configuration. The total energy difference between the 0D distribution (or the 2D layer) and the 3D cluster is 18.83 (or 4.37) eV reduced by 6.20 (or 0.86) eV compared to that on pristine C_{60}. The average Ti binding energies of three $Ti_{12}C_{48}B_{12}$ complexes (0D distribution, 3D cluster, and 2D layer) as a function of net charge are similar to the corresponding

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$Ti_{12}C_{60}$ complexes. In the case of high charge states, $q>7$, the 0D is more favorable than the 3D cluster.

To summarize, the above calculations show that both hole doping and B-doping can help to stabilize both the 0D distribution and the 2D layer structure. Nevertheless, if $N>N_C$ (N_C being the critical size of the neutral complex) and $q<7$, energetically, the 3D Ti cluster is still the most favorable configuration. However, the total energy is not the only factor that determines whether a given configuration is likely to be observed, we also need to consider kinetic effects.

C. Kinetics of Ti_N cluster formations on neutral, hole-, and B-doped C_{60} surfaces

The transformation of 0D sparse distribution to 2D layer involves in a Ti atom diffusion on C_{60} surfaces. The diffusion barrier of a single Ti atom diffusing from a hexagonal to an adjacent pentagonal site on the surface of C_{60} turns out to be 0.78 eV, whereas the barrier in the reverse direction is only 0.28 eV. Therefore, it is relatively easy for a single Ti atom to diffuse from a pentagonal site to one of its adjacent hexagonal sites. The diffusion barrier between two adjacent hexagons on C_{60} turns out to be 0.71 eV.

To investigate the kinetics of 3D Ti cluster formation we assume that the Ti atoms are initially homogeneously deposited on the surface of pristine C_{60} forming mostly layer structures at low and medium coverages. The transformation process from a 2D layer to the energetically more favorable 3D cluster of $N \geqslant N_C$ always starts with a single Ti atom climbing up a single Ti layer. Using NEB methods, we calculate the energy barriers at the critical size $N_C=5$, i.e., the transition barriers from the $N=5$ to the $N=4+1$ structure for two possible transition mechanisms: direct hopping and position exchange as illustrated in Fig. 4(a). The energy barriers of these processes are 0.98 eV [see Fig. 4(b)] and 1.04 eV, respectively.

Next, we consider how hole doping affects the kinetics of the Ti-cluster formation. On a positively charged C_{60} surface, the Ti binding energy increases linearly with increasing net charge, while the kinetic barriers only change by a small amount. For example, the direct hopping barrier of the $N=5$ to $N=4+1$ formation process at $q=3$ is 0.93 eV, which is even smaller than the barrier of the neutral system ($q=0$). At a first glance this seems counterintuitive because one would expect that higher binding energies at the local minima result in a higher kinetic barrier. However, the homogeneously distributed extra charges enhance not only the Ti binding energies of local minima but also the binding energies of intermediate states as well. This results in a similar or even lower barrier height compared to that of the neutral system.

In contrast to simple hole doping, B-doping significantly increases kinetic barriers. The kinetic barrier of the $N=5$ to $N=4+1$ process on $C_{48}B_{12}$ increases to 1.47 eV [see Fig. 4(c)], which is 50% higher than the barrier on pristine C_{60}. This can be explained as follows. The holes introduced by B-dopants are localized near their respective B sites (unlike in the case of hole doping where extra charges are delocalized on the surface) and thus the Ti_5 cluster binds stronger near B-dopants. Especially, the charge-induced stabilization

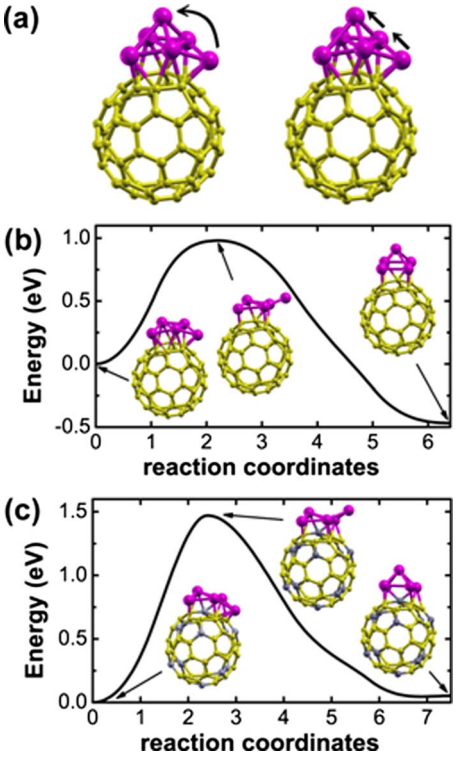

FIG. 4. (Color online) (a) Two possible mechanisms of 2D layer to 3D cluster transformation for Ti_5C_{60} complex, i.e., direct hopping (left) and position exchange (right). Both processes have similar kinetic barrier heights. Energy barriers of direct hopping for Ti_5C_{60} (b) and for $Ti_5C_{48}B_{12}$ (c).

effect on Ti configurations acts locally as discussed in Sec. III B. Consequently, the 2D layer, which is the initial state of the transformation process, and transitions states close to dopants are lowered in energy, while far away lying transition states and the 3D cluster state are not affected. Thus, the kinetic barrier of the transition process effectively increases. Figures 4(b) and 4(c) show how the kinetic barrier rises by ~0.5 eV due to the lowered energy of the initial state. Furthermore, due to the stronger interaction between Ti and B-dopants, the shape and the adsorption site of the Ti_5 2D layer and 3D cluster on $C_{48}B_{12}$ are different from those on pristine C_{60}. In fact, also the fullerene cage is slightly distorted by B-doping. Such changes in the geometry during the $N=5$ to $N=4+1$ process also contribute to a higher energy barrier. The increase in the kinetic barrier significantly reduces the probability of a 2D to 3D structure transformation on B-doped fullerene surfaces at a given condition.

IV. DISCUSSION AND CONCLUSION

In deciding an achievable, best (transition) metal coating configuration for use as hydrogen storage, there are two main factors to be considered: its structural stability as well as its chemical activities to hydrogen molecules.

In terms of structural stabilities, as discussed in the paper, both 2D and 3D Ti configurations are energetically much more stable than 0D configuration, which is due to high cohesive energies of Ti atoms. Thus, 0D structure can be preserved only if kinetic process prevents aggregation of Ti atoms. We found that diffusion of a Ti atom on C_{60} surface, a

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process required for 0D to 2D transformation, has a barrier height of $\leqslant 0.7$ eV, which is smaller than the energy barrier of 2D to 3D structure transformation, which is $\geqslant 1.0$ eV. This clearly shows that comparing to 0D structure, 2D layer is not only energetically more favorable but also kinetically easier to be preserved. In order to preserve 0D structure, on the other hand, all processes, which include Ti coating and fuel-cell operation, should be done at a very low temperature with very low metal deposition flux. The temperature should be low enough to prevent any Ti atoms to overcome the diffusion barrier of ~ 0.3 eV during the experimental time. We expect that boron doping helps to stabilize the 0D configuration by increasing Ti diffusion barrier, which has a similar mechanism of increasing adatom climbing up barrier in 2D to 3D transformation.

Some TMs produce too strong hydrogen binding sites in their 0D configuration, which results in either the dissociation of H_2 or a too strong H_2 binding energy and greatly reduces the hydrogen storage capacity at ambient conditions. Three-*d* TMs, for example, can hold two to four hydrogen molecules per atom,[8] where the dissociation of the first hydrogen molecule always occurs. A single Ti atom on C_{60} binds up to four dihydrogen molecules[8–10] and a Ti-dimmer binds 16 H atoms where 10 atoms remain in molecular form.[19] We also investigated the interactions between hydrogen molecules and the Ti 2D structures. Our study shows that the hydrogen binding to a small Ti cluster sensitively depends on the initial configuration of hydrogen near the cluster. The Ti-dimmer configuration we considered, for instance, can contain up to nine H_2 molecules with a binding strength of 0.44 eV/H_2 and only one H_2 molecule being dissociated. A Ti-trimmer binds 12 H_2 in molecular form with a binding energy of 0.28 eV/H_2 and a four Ti layer can bind 15 H_2 with 12 in molecular form, corresponding to a reversible storage capacity of $3H_2$/Ti. In summary, the hydrogen binding capacity of a small 2D Ti_N configuration ($N<5$) is as good as that of 0D. Therefore, we conclude that a small 2D Ti_N layer is the most interesting configuration for use as hydrogen storage, considering its structural stability and chemical activity.

Next, we discuss the materials consisting of finite number of organometallic complexes. There, the interactions between dipoles may prevent two TM atoms on two separated C_{60} from sticking to each other[5] but they may stick to each other depending on the material phase and strength of the induced dipole moments. The coalescence of two or more TM-decorated fullerenes by sharing metals will reduce their active sites available for hydrogen.[38] Such issues are the interesting topics to be addressed in the future studies.

In conclusion, we investigated the energetics and kinetics of Ti clustering on both neutral and charged C_{60} surfaces using *ab initio* spin density functional theory. First, we studied the energetics of Ti_N clusters as a function of the number of Ti atoms ($N\leqslant 12$). We found that there exists a critical cluster size, $N_C=5$, below which 2D layer structures are preferred to 3D structures. Hole- or B-doping greatly enhance the Ti-fullerene interaction. Even so, for moderate charge doping (less than seven holes) the critical size of Ti atoms on neutral C_{60} surprisingly remains unchanged or only slightly increases to $N_C=6$ by B-doping. However, we found that 3D cluster formation is hindered by a high kinetic barrier related to the process of single Ti atoms climbing up a single Ti layer. This barrier is ~ 1 eV or even 1.47 eV for B-doped C_{60} surfaces which is high enough to stabilize larger 2D structures ($N\geqslant N_C$) at low temperatures.

At higher temperatures this new effect may not be sufficient to prevent clustering of Ti atoms on C_{60} surfaces. However, other metals with a lower cohesive energy but also a strong interaction with the surface of C_{60} could produce homogeneously single-layer coated or sparsely coated fullerenes at higher temperature. There, charge effects might stabilize 2D layer structures to a much stronger extent and up to higher critical numbers. One candidate could be Sc. The fullerene binding energy of single Sc is almost the same as that of Ti,[9,10,39] while its cohesive energy is 3.90 eV,[40] about 1 eV smaller than that of Ti. Our study may prove to be instrumental in stabilizing TM coated nanostructures and especially homogeneously Ti-coated fullerenes, which are believed to be a very promising material for hydrogen storage.

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[37] We choose the configuration of 12 Ti occupying 12 pentagonal rings on C_{60} as a representative structure of a 0D, which is based on historical and practical reasons. Previous calculations showed that a C_{60} which contain 12 TM atoms occupying pentagonal ring on C_{60} is a promising hydrogen storage medium. In making C_{60} chemically active, Ti 0D structure seems a promising configuration, In this case it makes no significant differences in distributing 12 Ti atoms either on pentagonal or on hexagonal sites. For example, hydrogen binding capacities of two sites are similar. Our focus is whether the 0*D* structure can be stabilized energetically and kinetically. The energy difference between a Ti atom adsorbed on hexagon and pentagon site is 0.5 eV/atom, Nevertheless, 2D or 3D structure are significantly stable than any of those 0D structures.
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