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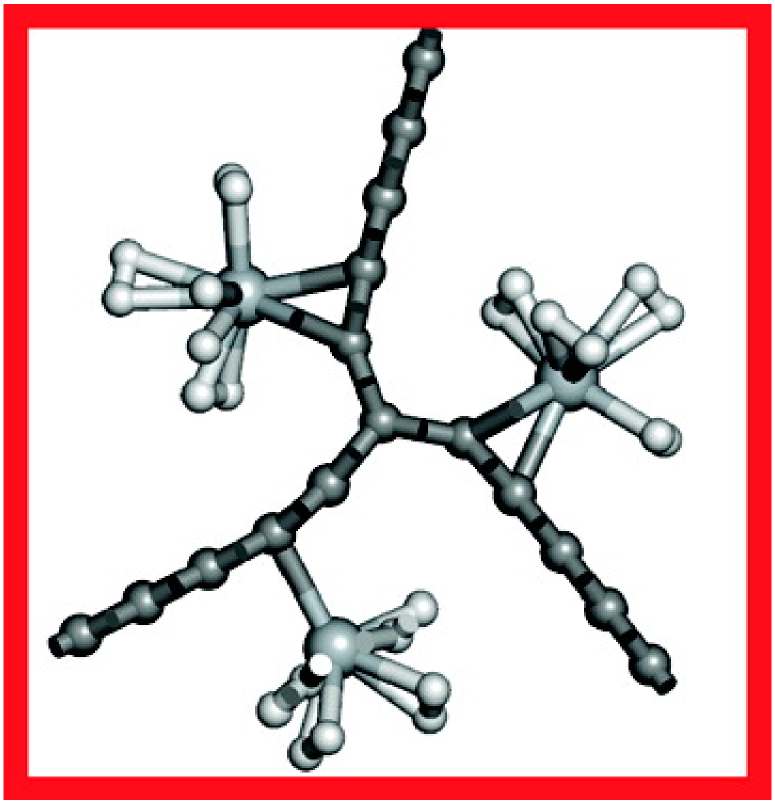

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Computational Study of Hydrogen Storage Characteristics of Covalent-Bonded Graphenes

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Abstract: We performed first-principles calculations to investigate the hydrogen storage characteristics of carbon-based 3-D solid structures, called covalently bonded graphenes (CBGs). Using the density functional method and the Møller−Plesset perturbation method, we show that H_2 molecular binding in the CBGs is stronger than that on an isolated graphene with an increase of 20 to ~150% in binding energy, which is very promising for storage at ambient conditions. We also suggest that the CBGs of appropriate size can effectively work as frameworks for transition metal dispersion. The adsorption properties of hydrogen on the metal atoms dispersed inside the CBGs are also presented.

Recently, there has been extensive research on the development of exploitable hydrogen energy. It is clean and recyclable and will hopefully substitute fossil-based fuels, helping to resolve the issue of global warming, not to mention the energy problem itself.[1−3] One of the most challenging problems in this field is to store hydrogen with a sufficient gravimetric as well as volumetric capacity. To overcome the technical limit associated with storing hydrogen in its gaseous phase, recent research has focused on solid-phase storage.[2] The overall requirements for practical room-temperature operation of hydrogen storage are summarized as an adsorption energy of about 30 kJ/mol per H_2 and a gravimetric capacity of 6 wt % or higher.[3−5] In addition, the host materials should be stable over many hydrogen uptake−release cycles.

Earlier, nanostructured materials such as carbon nanotubes have attracted great attention as they were expected to have a large surface area with decent chemical reactivity.[6] Unfortunately, subsequent studies showed that carbon-based nanomaterials do not possess such a great capacity as was earlier claimed. The weak binding energy of hydrogen on the materials was shown to be the origin of low capacity at ambient conditions. This indicates that the nanostructure by itself does not necessarily lead to desired storage characteristics and that chemical or structural modifications in the nanostructures should be incorporated for improving storage capacity.[4,5] Other approaches such as dispersing transition metal atoms on nanostructures have also been suggested in recent literature for increasing the binding energy and storage capacity.[7−9] However, an immediate concern about such metal-dispersed nanostructures is the stability against metal clustering.[10] If the stabilization of the dispersed metal atoms is not properly dealt with, the suggested structures would be of little practicality.

Here, we propose that regular or irregular combinations of sp^3-bonded carbon atoms and graphene fragments could lead to very stable porous carbon structures, which are advantageous for hydrogen molecular storage as well as for metal dispersion without clustering. We designate these structures as covalently bonded graphenes (CBGs) to distinguish them from solid graphite, which is solidified through a van der Waals type of weak intergraphene interaction.[11] Recently, a theoretical study was reported on hydrogen storage characteristics of layered graphene segments that can have a flexible interlayer distance.[12] The CBGs are instead 3-D graphitic materials and can be viewed as model systems of covalently bonded segments of nanoscale graphenes. Since the structural stability of variants of CBGs has been discussed in the literature,[13,14] here we focus mainly on their potential as host materials for hydrogen storage. Through first-principles calculations, we study H_2 molecular binding in CBGs to compare with those on isolated graphene. A more interesting feature of CBGs is their potential capability of fixing transition metal atoms, especially 3d elements. As the CBGs have sp^3-bonding at planar joints as shown next, the transition metal atoms are likely to be absorbed at the vertex

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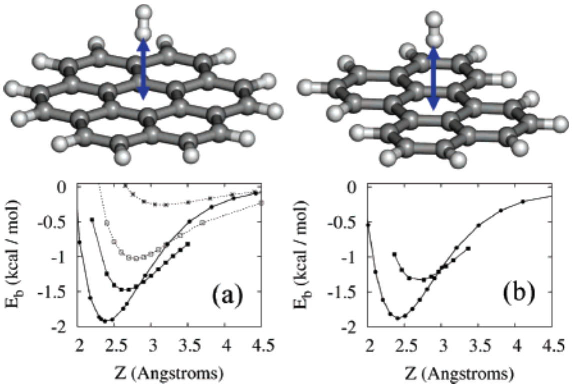

Figure 1. Binding energy curves of H_2 on (a) $C_{24}H_{12}$ and (b) $C_{20}H_{12}$ as a function of the distance Z from the center of the middle hexagon ring. The solid circles and solid squares are data of LDA/plane-wave and MP2/aug-cc-pVTZ calculations, respectively. The empty squares and stars are obtained from the calculations with MP2/6-311++G** and GGA/plane-wave, respectively. For solid squares in panels a and b, the aug-cc-pVTZ basis set is used for H_2 and six carbon atoms at the center, while other atoms in the substrate are described with the cc-pVTZ basis. Correction of the basis set superposition errors is performed by the counterpoise method.[23]

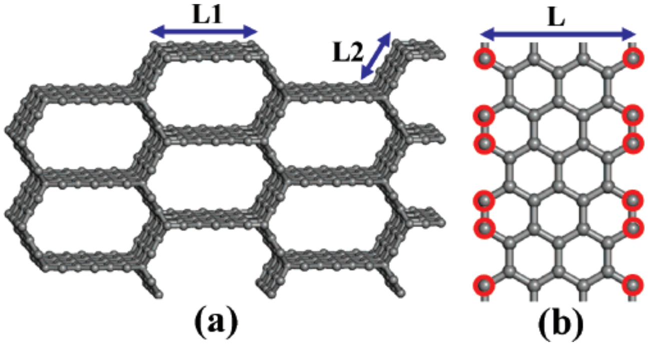

Figure 2. (a) Perspective view of CBG ($L1$, $L2$), with $L1$ and $L2$ denoting the unit of the sidewall length. (b) Width of the side plane, as denoted by L, is given as a half integer starting from 1. For this particular size, L is 3. Red circles indicate the sp^3-bonded carbon atoms that join other side planes to make 3-D graphitic structures.

sites of the CBGs, thereby reducing the possibility of clustering. We choose Ti as a representative 3d transition metal element for studying atomic dispersion and investigate the hydrogen-adsorption property on the metal atoms in the CBGs to estimate their storage capacity.

For computation, we used the Vienna ab initio simulation package (VASP).[15,16] The generalized gradient approximation (GGA) in the form of the PBE-type parametrization or the local density approximation (LDA) in the Ceperley−Alder form was employed for the exchange correlation of electrons.[17,18] The ionic pseudo-potentials are described via the projector augmented wave (PAW) method, and the cutoff energy for the plane-wave basis was set to be 500 eV.[19] Prior to presenting the main part of the computational results, we investigated the accuracy of our density functional calculations by comparing it with the Møller−Plesset second-order perturbation method (MP2) with various basis sets as implemented in the Gaussian 03 package (see Supporting Information). We also performed a single-point calculation with coupled-cluster singlets and doublets with perturbative triplet correction (CCSD(T)) to check the basis dependence.

Figure 1a shows the calculated binding energy curves of H_2 on coronene ($C_{24}H_{12}$), which is taken as a model system for a graphene fragment, with the hydrogen molecule separated at a distance Z from the center of the carbon hexagon ring. The solid circles and stars are the data obtained with LDA and GGA using VASP, respectively. As commonly accepted, we observed that the binding energy calculated with LDA was much larger than the GGA value. A critical problem is that the medium-range dispersion interactions are not reliably described by the density functional method within both approximations.[20] The highly correlated CCSD(T) method is the most accurate and reliable method but is extremely expensive so that a single calculation of hydrogen binding on coronene, for instance, is essentially out of the reach of computational resources available to us. The MP2 method, another wavefunction-based method, is usually employed in practice to describe the interactions, while its accuracy should be tested with great care because of its sensitivity to the choice of basis set.[12,20]

Recently, Ferre-Vilaplana[21] reported a comprehensive study of the MP2 computations of the H_2−graphene interaction as compared to the CCSD(T) method. It was shown that MP2 with an aug-cc-pVTZ basis was practically the best choice in calculating the hydrogen−graphene physisorption energy with almost the same accuracy as CCSD(T) with a larger basis set such as aug-cc-pVQZ. Following this suggestion, we calculated the H_2 binding on coronene-like molecules with the MP2 method with several choices of basis set including the counterpoise correction of the basis set superposition error.[22] Solid squares in Figure 1a are data obtained at the MP2 level by using the aug-cc-pVTZ basis set for H_2 and six carbon atoms at the center and cc-pVTZ for other atoms in coronene. The squares are the calculated results with the 6-311++G** basis set for all atoms. We find that the binding energy depends quite sensitively on the size of the basis set, especially at the center of coronene. The basis set at the edge of the molecule is less relevant to the binding energy. In fact, we tested a reduced basis set by assigning 6-311G** to hydrogen atoms at the edge of coronene, and the binding energies were found to be basically the same as that with the aug-cc-pVTZ basis set. Here, we conclude that the 6-311++G** basis set is insufficient for H_2−graphene physisorption interactions. For comparison, we also performed CCSD(T) calculations with the 6-311++G** basis set for a smaller system to find that the binding energy of the hydrogen molecule does not converge to that obtained with a larger basis set.[23] On the other hand, the binding energy curves from LDA calculations closely and consistently follow those from MP2 using the aug-cc-pVTZ basis set with an overestimate of about 30 to ~40% in binding energy and an underestimate of about 9% in binding distance, which is also confirmed by similar calculations in $C_{20}H_{12}$ (Figure 1b). This indicates that the LDA calculation with the plane-wave basis set (LDA/plane-wave) is

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(23) We independently calculated the H_2 adsorption on benzene and found that the binding energy with CCSD(T)/6-311++G** is about 0.49 kcal/mol, which is only half of the CCSD(T)/aug-cc-pVTZ.[22]

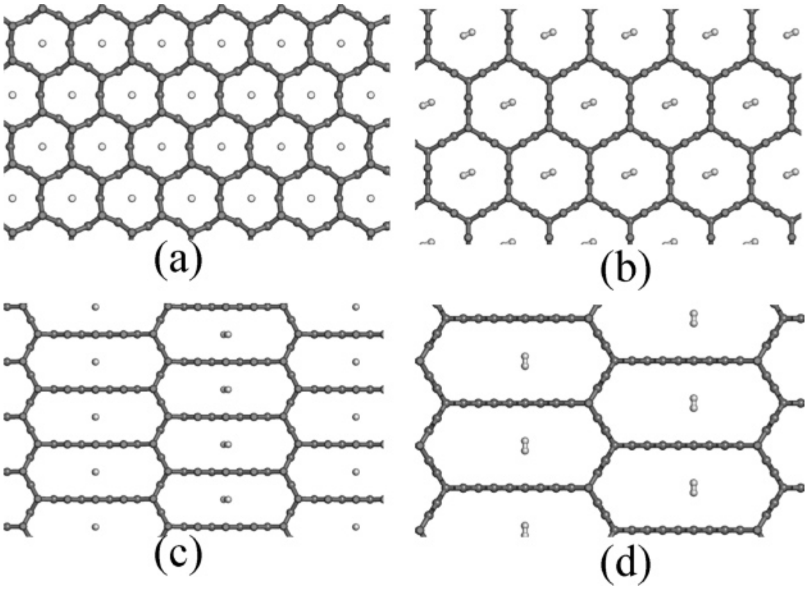

Figure 3. Optimized geometries for H_2 molecules adsorbed on (a) CBG(1, 1), (b) CBG(1.5, 1.5), (c) CBG(4, 1), and (d) CBG(4.5, 1.5), respectively. H_2 molecules are put in the middle of each cell in the CBGs.

at least qualitatively acceptable to describe the H_2−graphene interactions as it closely reproduces the binding curves obtained by more correlated methods. With this caveat in mind, we studied the hydrogen binding and metal dispersion in 3-D graphitic structures with the density functional method within appropriate exchange-correlation functionals.

Now, we introduce the structure of the CBGs. Figure 2a shows a typical CBG that consists of graphene strips of two different widths interconnected by the sp^3-bonded carbon atoms at the vertices. The width of the stripes is denoted by $L1$ and $L2$, and we designate this structure as CBG($L1$, $L2$). As the width of the graphene stripes is counted by the number of hexagonal rings from one sp^3-bonded edge to another, $L1$ and $L2$ are given as a multiple of one-half starting from 1. For example, the width of the stripe in Figure 2b equals three hexagons between the sp^3-bonded carbon atoms and is counted as $L = 3$. According to this naming scheme, the structure shown in Figure 2a becomes CBG(3, 1.5).

We first investigated the binding strength of one hydrogen molecule in CBGs of various sizes. The binding energies calculated with LDA of an H_2 molecule in CBG(1, 1), CBG(1.5, 1.5), CBG(4, 1), and CBG(4.5, 1.5) are 4.61, 3.92, 2.31, and 2.31 kcal/mol, respectively. This is a more than 20% increase in the binding energy as compared to that on a single graphene (∼1.84 kcal/mol as shown in Figure 1a) calculated with the same exchange-correlation functional. Figure 3 shows the optimized geometries of the corresponding H_2-adsorbed CBGs. As shown in Figure 1a, the H_2 binding distance on graphene is in the range of 2 to ∼3 Å. We expect an increase in binding energy when H_2 molecules are sandwiched between two graphene planes apart by such a distance. Our results indicate that the overall pore size is more important for the binding energy than the interplane distance alone.

In Figure 4a, we present the geometry for hydrogen molecules accumulated inside CBG(4.5, 1.5), which has a storage capacity of about 5 wt %. The average binding energy of hydrogen molecules at this storage capacity was found to be 2.31 kcal/mol per H_2. We note that the maximum storage capacity depends on the structure of CBG. If one of the side planes increases in length, for example, CBG(L, 1.5) with a sufficiently large L, the storage could reach up to 8 wt % with a similar binding energy. A key question is the possibility of synthesizing such regular structures of interconnected graphenes. It is worth emphasizing that the regularity in structures of the CBG presented so far is not truly necessary for holding hydrogen molecules. As an illustrative example, we show random-networked CBGs in Figure 4b. The aforementioned improvement of the H_2 binding energy should be sustained as long as the interlayer distances in the CBG structures are appropriately maintained. Chemical processes such as oxidation together with incorporating sp^3-bonds could lead to this kind of accumulated graphene plane with a separation of a few angstroms.[24] Another possibility is to use the graphene fragments or poly aromatic hydrocarbons to build the random-networked 3-D superstructures.[25]

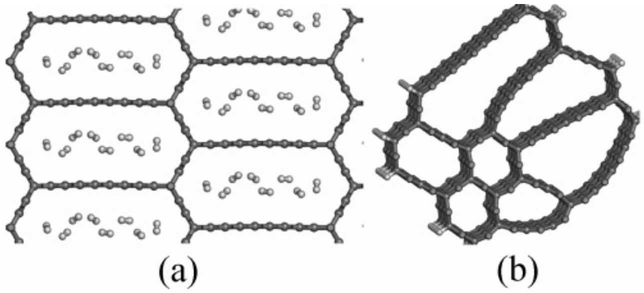

Figure 4. (a) Optimized geometry of CBG(4.5, 1.5) holding hydrogen molecules in its interiors. For this particular configuration of hydrogen molecules, the storage capacity is estimated to be about 5 wt %. (b) Illustrative view of random-networked CBGs.

Although the CBGs provide an improved binding strength of H_2 over the pure graphite, the binding energy is still smaller than the requirement for the hydrogen storage operating at ambient conditions. The atomic dispersion of transition metal on light-element structures was suggested in some literatures to address this problem.[7−9] A critical issue in this approach is,

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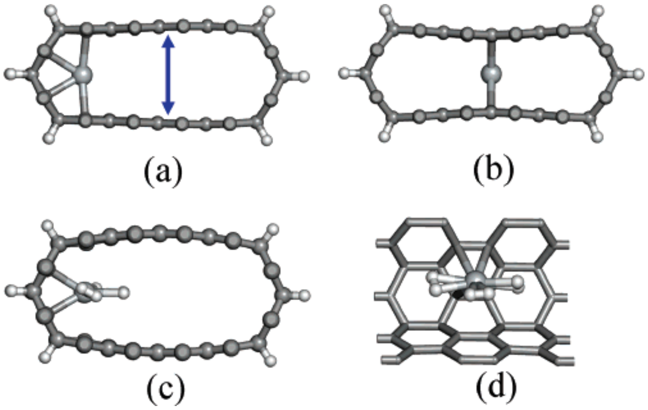

Figure 5. Optimized geometry of a single cell of CBG(4, 1) with Ti atoms attached at (a) the vertex and (b) the center site. The arrow in panel a measures the interwall distance of CBG. (c) Side view of three hydrogen molecules adsorbed on a Ti atom lying at the vertex site of CBG(4, 1). (d) Same as panel c but an enlarged side view from the other direction.

however, whether the dispersed metal atoms in such nanostructures would survive the clustering. In this regard, dispersing metal atoms inside a predefined superstructure can be effective for preventing metal clustering. Or the use of metal-embedded structures such as porous crystals consisting of titanium carbide clusters is another approach to possibly avoid the clustering problem.[26,27] Metal organic frameworks[28] have such structural characteristics, but the capability depends on their own chemical stability, which needs further assessment. We suggest that the CBGs could be optimal superstructures for the fixation of metal atoms. Our GGA calculations find that Ti atoms preferentially bind to the vertex of CBG due to the increased coordination number. Figures 5a,b show the optimized geometry for the Ti atom absorbed inside CBG(4, 1). To focus on individual cells in the CBG and also to reduce the computational load, we chose a pillar-shaped hexagonal unit of CBG with hydrogen passivation rather than the bulk CBG(4, 1). It is found in the GGA/plane-wave calculation that the binding energy of the Ti atom at the vertex (Figure 5a) is larger by about 13.84 kcal/mol than that at the center site (Figure 5b). This indicates that atomically dispersed transition metals would prefer the vertex sites in the CBG and are less likely to form a cluster unless the pore size is too large. We will elaborate on this issue below.

Next, we investigate the hydrogen binding characteristics on Ti-adsorbed CBG(4, 1). As GGA is shown to be more accurate than LDA in describing the interaction between hydrogen molecules and transition metals,[7−9] we use the GGA instead of the LDA to describe the interactions. Our total energy calculations show that three hydrogen molecules bind to one Ti atom at the vertex of CBG(4, 1), as shown in Figure 5c,d. Two hydrogen molecules are positioned along the axial direction of CBG with respect to the Ti atom, while the other one is attached to the Ti atom perpendicular to the axis. The H−H distance of the attached hydrogen molecule is found to be 0.81 Å, which corresponds to an about 7% increase from the H_2 bond length of 0.76 Å obtained with the GGA. For the two hydrogen molecules along the axial direction, the Ti−H distances are found to be 1.91 Å, whereas the Ti−H distance along the perpendicular direction is about 1.98 Å. The average binding energy of the three hydrogen molecules is calculated to be about 6.28 kcal/mol per H_2 with respect to isolated hydrogen molecules and the optimized titanium-dispersed CBG(4, 1).[29] Our calculations are in reasonable agreement with previous studies.[7−9] We note that the calculated binding energy is in the right range for storage operating at ambient conditions.

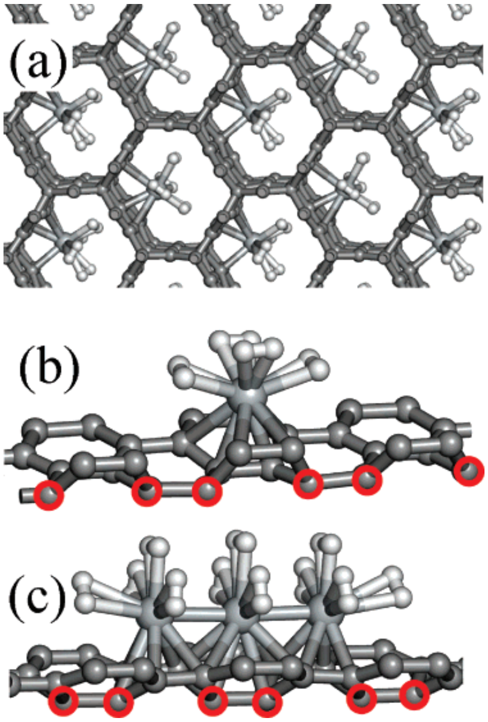

Figure 6. (a) Perspective view of CBG(1.5, 1) with titanium atoms affixed at the vertex sites and hydrogen molecules on titanium. Here, four hydrogen molecules are attached to each Ti atom. Enlarged side views of (b) four hydrogen molecules adsorbed on the Ti atom and (c) 11 hydrogen molecules on the titanium trimer affixed to the vertex sites of CBG (1.5, 1). The red circles in panels b and c denote the sp^3-bonded carbon atoms.

In CBG(4, 1), the distance between the two parallel side walls ($L = 4$) is about 4.7 Å as indicated by the arrow in the Figure 5a. In this case, the space inside the framework of CBG(4, 1) is not large enough to accommodate the maximum number of hydrogen molecules for each Ti atom. It is possible that larger CBGs are better in holding more hydrogen molecules per Ti atom at the vertex sites. On the other hand, larger CBGs may have drawbacks of metal aggregation. We investigate the metal dispersion characteristics in various CBGs and find that the Ti atoms tend to aggregate even at the vertex sites when the pore size of CBGs increases.[10] We note that the overall size of pores affects the aggregation more than the lateral size does. Noting these features, we need a tradeoff for the optimal size of CBG that provides enough room for H_2 storage but reduces the chance of metal aggregations. For example, CBG (1.5, 1) can satisfy such a requirement. Through the total energy calculations, we find that the 1-D atomic chain structure is the only allowable form of aggregations of titanium atoms inside CBG (1.5, 1). It

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(29) The binding energies of each hydrogen molecule with respect to remaining structures, namely, $E_b = E_{tot}[nH_2/\text{Ti-CBG}] - E_{tot}[(n-1)H_2/\text{Ti-CBG}] - E_{tot}(H_2)$, are also calculated. Here, nH_2/Ti-CBG indicates the titanium-affixed CBG structure with n H_2 molecules adsorbed. The binding energy is 6.00, 4.84, and 8.07 kcal/mol for the first ($n = 1$), second ($n = 2$), and third ($n = 3$) H_2 molecules, respectively.

is also found that a single Ti atom in CBG(1.5, 1) can hold four H_2 molecules, as illustrated in Figure 6a,b, consistent with previous work.[30] Since the periodicity along the axial direction of the CBG is incommensurate with the optimal Ti−Ti distance, it is difficult within plane-wave basis schemes to calculate infinitely long Ti atom chains lying inside CBGs. We address the hydrogen storage characteristics of the metal chains inside CBG by studying the hydrogen binding on titanium trimers. Figure 6c shows a titanium trimer inside CBG(1.5, 1) that binds 11 H_2 molecules. This result indicates that a long titanium chain can bind three H_2 molecules per Ti atom. If such Ti atom chains are incorporated inside the bulk CBG(1.5, 1), the storage capacity could reach up to 4 wt %.

In summary, we suggest that incorporating sp^3-bonded carbon atoms at the edges of graphenes leads to stable porous carbon structures (CBGs) that possess promising characteristics for hydrogen storage. Our calculations show that H_2 molecules bind to CBGs with an enhanced binding energy of about 20% or more as compared to that on pure graphite. The CBGs of appropriate size are shown to be capable of holding transition metal atoms effectively without aggregation. We show that the Ti atoms absorbed at the vertex of the CBG have a larger binding energy by about 13.84 kcal/mol than those at other sites. The hydrogen-adsorption property on the Ti atoms inside the CBGs in this study indicates that the CBGs can be good carbon-based frameworks for hydrogen storage with their capacity reaching 4 wt % or higher depending on their pore size and the length of the metal chains.

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Supporting Information Available: Frisch, M. J. et al. *Gaussian 03*, revision C.02; Gaussian, Inc.: Pittsburgh, PA, 2004. Complete reference is given. This material is available free of charge via the Internet at http://pubs.acs.org.

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