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Calcium-Decorated Carbyne Networks as Hydrogen Storage Media

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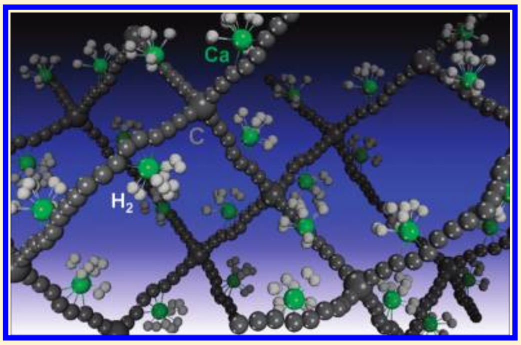
ABSTRACT: Among the carbon allotropes, carbyne chains appear outstandingly accessible for sorption and very light. Hydrogen adsorption on calcium-decorated carbyne chain was studied using ab initio density functional calculations. The estimation of surface area of carbyne gives the value four times larger than that of graphene, which makes carbyne attractive as a storage scaffold medium. Furthermore, calculations show that a Ca-decorated carbyne can adsorb up to 6 H_2 molecules per Ca atom with a binding energy of ~0.2 eV, desirable for reversible storage, and the hydrogen storage capacity can exceed ~8 wt %. Unlike recently reported transition metal-decorated carbon nanostructures, which suffer from the metal clustering diminishing the storage capacity, the clustering of Ca atoms on carbyne is energetically unfavorable. Thermodynamics of adsorption of H_2 molecules on the Ca atom was also investigated using equilibrium grand partition function.



KEYWORDS: Carbyne, carbon chain, calcium, hydrogen storage, density functional theory

Ubiquitous carbon allotropes can be ranked by the coordination number of their structures, the number of nearest neighbors to each C atom, as diamond, graphite, nanotubes and fullerenes, graphene and possible foam-like sp^2-networks, and then monatomic chains of carbyne (we stop short of including diatomic molecule C_2 which does not constitute a material and is rather unstable). In this series, less coordinated structures are more open for adsorbing other species, thus showing greater effective surface area (e.g., none for a bulk diamond but as great as ~2630 m^2/g for graphene). This openness combined with low weight, make carbon structures unique for adsorption of gases general and for hydrogen in particular.

Lack of efficient storage material is one of the major problems on the way to successful use of hydrogen as "green" alternative fuel for vehicles. The Department of Energy (DOE) has set the hydrogen gravimetric capacity target of 6.5 wt % in the perspective materials for industrial usage.[1] Recently, lot of efforts have been devoted to investigating carbon nanostructures such as nanotubes,[2] sheets (graphene[3,4]), and molecules (fullerenes[5]) as effective hydrogen adsorbents. However, physical sorption in these systems generally requires cryogenic temperature because of too small binding energy of ~0.05 eV, which makes it impractical for vehicular usage. Desirable binding energy should lie in a range of 0.2−0.4 eV per H_2 for the ambient condition storage.

On the other hand, carbon nanostructures decorated by transition (Sc or Ti)[6,7] and alkali (Ca)[8−12] metal atoms have shown the potential for hydrogen storage because these structures adsorb up to 6 H_2 molecules per metal atom with a binding energy of ~0.2−0.6 eV.[6−12] For example, Ca-decorated graphene,[10] edge-decorated graphene nanoribbons,[11] and carbon nanotubes[12] display the maximum gravimetric density of 8, 5, and 5 wt % respectively. The metal atoms in such organometallic complexes play the main role of adsorbing hydrogen molecules, whereas the graphitic materials serve as host for them. So, a decrease in the dimensions of the host material is expected to increase the gravimetric capacity as well as volumetric capacity of hydrogen following the density increase of Ca atoms per volume or per C atom. From this point of view, the thinnest possible carbon nanostructure, namely, carbyne which is a single chain of carbon atoms may be utilized as a host material because of its perfect one-dimensional geometry (and consequently, greater surface area). For decorating metal atom, Ca atom is expected to be the best because it has low weight and is less-aggregating element[10,11] (and is low-cost).

Carbyne was first synthesized in 1959[13] by oxidative dehydropolycondensation of acetylene using copper catalyst. The longest carbon chains made by laser vaporization of graphite are ~200 Å,[14] and the longest isolable carbon chains of ~20−60 Å synthesized very recently.[15] Also recently, carbyne was observed trapped inside the carbon nanotubes[16,17] after the irradiation of graphene ribbons,[18,19] or critical straining of carbon nanotubes[20,21] and graphene nanoribbons.[22−24] Despite an earlier notion that carbyne can only exist at high temperature (2600−3800 K),[25] recent studies show that carbon films consisting of carbyne,[26,27] or carbyne oligomers,[15] can be fabricated at room temperature. The room-temperature synthesis of carbyne, as well as demonstrations of formation of carbyne chains from carbon nanomaterials, suggest the possibility of fabrication of carbyne. Moreover, it was found that carbyne can be stabilized by

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intercalation of metal ions[13] and the stability of carbon chains decorated with various metal atoms was theoretically investigated.[28]

This motivates us to investigate the stability of such carbon chains decorated with the Ca atoms (Ca—carbyne), and especially their ability to store hydrogen. We performed the analysis of Ca—carbyne complexes and found that the most stable configuration is the carbyne with Ca atoms adsorbed next to carbon bonds (not near a single C). It was further found that carbyne with neighboring Ca atoms located on the chain opposite sides is more favorable by energy; also important is that we found that Ca atoms do not tend to cluster (unlike recently reported transition metals decorating carbon nanomaterials). Calculations show that the Ca—carbyne complexes adsorb up to 6 molecules H_2 per Ca atom, with the desirable binding energy for reversible storage and the hydrogen storage capacity can reach up to ~8 wt %. We also investigated the thermodynamics of adsorption of H_2 molecules on the Ca atom using equilibrium grand partition function.

All calculations were carried out using density functional theory in the framework of generalized gradient approximation (GGA) in Perdew—Burke—Ernzerhof[29] parametrization with periodic boundary conditions using Vienna ab-initio Simulation Package.[30−32] Projector-augmented wave method along with a plane wave basis set with energy cutoff of 400 eV was used. To calculate equilibrium atomic structures, the Brillouin zone was sampled according to the Monkhorst—Pack[33] scheme with a k-point density 0.08 $Å^{-1}$. To avoid spurious interactions between neighboring structures in a tetragonal supercell, a vacuum layer of 14 Å in all nonperiodic direction was included. Structural relaxation was performed until the forces acting on each atom were less than 0.05 eV/Å. For the analysis of binding mechanism, we calculated all-electron partial density of states using Gaussian'03 package.[34]

First, we analyze the stability of Ca—carbyne complex by evaluating the binding energy of Ca atoms to the carbon chain

$$E_{\mathrm{bind}}(Ca) = \frac{[E_{\mathrm{C}} + nE_{\mathrm{Ca}} - E_{\mathrm{C-Ca}}]}{n} \qquad (1)$$

where $E_{\mathrm{C-Ca}}$, E_{C}, and E_{Ca} are the total energies of the calcium—carbyne system, carbyne, and an isolated calcium atom, respectively, and n is the number of Ca atoms in the unit cell. The calculations of Ca—carbyne complexes were carried out within a unit cell with the fixed lattice parameter taken from the pristine carbyne, as both experimental and theoretical studies on carbyne were carried out with the fixed chain ends.[18−24] This allows us comparison of the results with the literature, to lend additional support to the conclusions.

On the basis of general chemical intuition, the optimal position of a Ca atom is at a bridge site of the carbyne (C—C) bonds as at this position it optimally binds to the adjacent carbon atoms. In another position, with the Ca near a single carbon atom, the Ca atom disturbs the π-system creating a high energy radical. We confirmed this hypothesis by performing several calculations with respect to position of a single Ca atom and found that Ca atom indeed prefers to bridge the C atoms. Therefore, for further analysis we use this structure, Figure 1a.

We analyze the binding mechanism of Ca atom to carbyne in this configuration. In Figure 1b,c, the total density of states for pure carbyne (Figure 1b) and the partial density of states for the Ca—carbyne (Figure 1c) are shown. The 4s orbitals of the Ca atom play the main role in binding of Ca to carbyne. It is easy for Ca atom to donate the s electrons due to their relatively low ionization potentials[35] which leads to delocalization of the orbitals (Figure 1c). Also, the 3d orbitals of Ca atom and a small fraction of the 4p orbitals participate in bonding. There is a clear indication of charge transfer from s orbitals of Ca atom to carbyne π-system and from carbyne π-system to the d orbitals of the Ca atom forming donor—acceptor bond along with the shift of the Fermi level of the pure carbyne DOS. This bonding leads to a distortion of carbon sp hybridization (angles equals to 160° which are smaller than typical 180° of sp state, but larger than 120° of sp^2 state) and bending of whole carbon chain (Figure 1a). Electron transfer from Ca to carbyne results in a positive charge on Ca atom (Mulliken charge +0.64e).

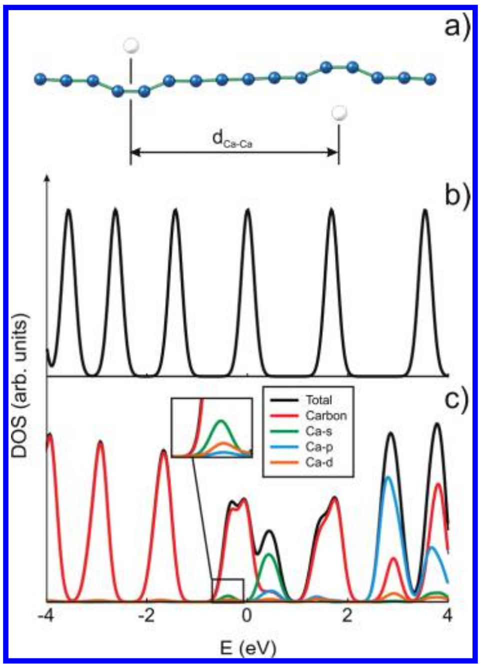

Figure 1. (a) Structure of a o-Ca—carbyne complex where two Ca atoms adsorb on carbyne with distance $d_{\mathrm{Ca-Ca}}$ = 10.3 Å; (b) the density of states (DOS) of carbyne and (c) Ca—carbyne complex. The total DOS is presented by black line. The partial DOS of carbyne is presented by red line. The partial DOS of 4s, 4p, and 3d Ca atom is presented by green, blue, and orange lines respectively. Energy of top of valence band is taken as zero.

For the second Ca atom, we tested two possibilities with the neighboring Ca atoms that were located either at the same side of the carbyne (s-Ca—carbyne) or at the opposite sides (o-Ca—carbyne). Among various geometries of adsorbed Ca it was found that the above two configurations are the most favorable. The dependence of Ca binding energy upon the distance between the Ca atoms displays nonmonotonous oscillatory behavior, Figure 2. At small Ca—Ca distance (~2.6 Å), the binding energy of the Ca atom for the s-Ca—carbyne is increased to 1.9 eV from 1.6 eV at the Ca—Ca distance of ~5 Å because of the attractive interaction of the nearest Ca atoms. In contrast, at the Ca—Ca distance of ~5 Å, the binding energy is reduced to 1.6 eV because of distortion of the carbyne frame by the Ca adsorption. Further increasing the Ca—Ca distance leads to increase of the binding energy. The binding energy of the Ca atom saturates to about 2.0 eV when the distance exceeds 17 Å, Figure 2. The saturated value is somewhat lower than the binding energy of 1.9 eV when the Ca atoms are close to each other, essentially meaning that the metal atoms should not cluster on carbyne. This is due to the competition between several effects: distortion of the carbyne chain, a short-range chemical attraction and

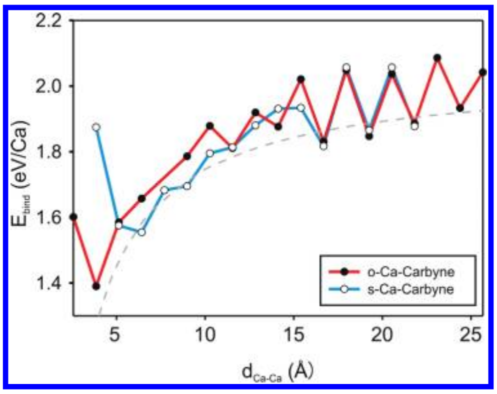

Figure 2. The dependence of Ca binding energy upon the axial distances between neighboring Ca atoms on the o-Ca−carbyne and the s-Ca−carbyne. The lines with filled and empty circles correspond to opposite and same position of the Ca atom relative to carbyne, respectively. The gray dotted curve is fitted by Coulomb repulsion energy (q^2/r) in o-Ca−carbyne where r is the distance between the Ca atoms and q is the charges of the Ca ion (+0.64e).

Table 1. The Calculated Additional or Average Binding Energy of H_2 Molecules (eV/H_2) on the Each Ca Atom of the o-Ca−carbyne Complex

number of H_2	1	2	3	4	5	6
additional binding energy	0.24	0.31	0.32	0.16	0.23	0.07
average binding energy	0.24	0.28	0.29	0.26	0.26	0.22

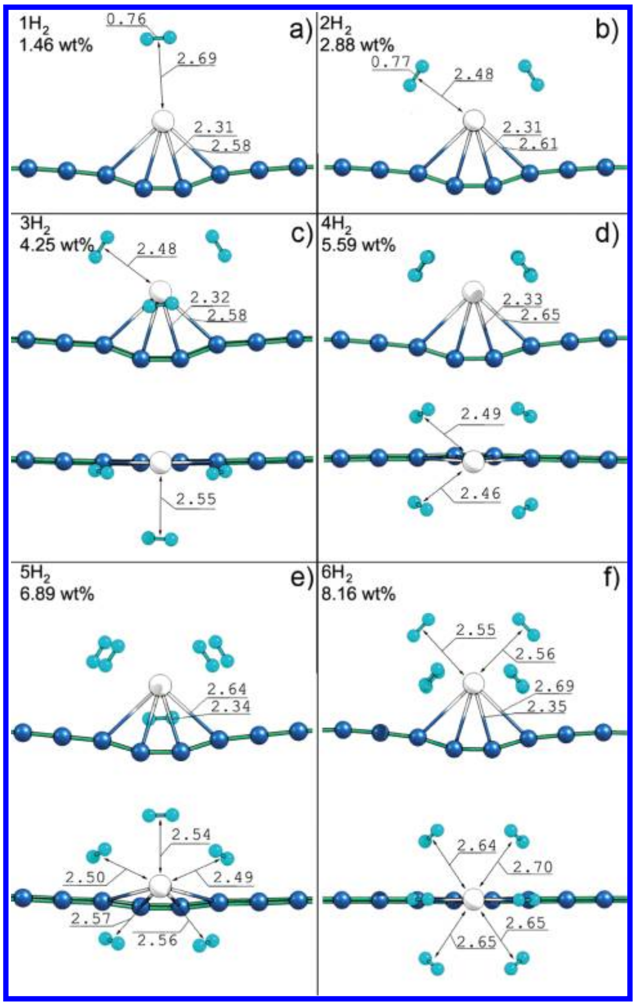

Figure 3. The atomic structures of carbyne decorated with a Ca atom with different H_2 attachment (a) $1H_2$, (b) $2H_2$, (c) $3H_2$, (d) $4H_2$, (e) $5H_2$, and (f) $6H_2$. The number of adsorbed H_2 molecules on the each Ca atoms, the weight percentage, Ca−H_2 distances (Å) are shown.

Coulomb repulsion of positively charged calcium ions. The attractive interaction leads to gain in the binding energy of the Ca atom when two Ca atoms are close. On the other hand, at this position they induce energetically unfavorable distortions in the host material. Overall the distortion effect and Coulomb repulsion (gray curve in the Figure 2) dominate over the attraction between the Ca atoms, making the clustering process energetically unfavorable. This is an important result as most of the metal atom decorated systems suffer from the clustering, detrimental for storage capacity.[6] Also it should be noted that the binding energy ∼2.0 eV is larger than the binding energy of Ca atoms to a fullerene (1.3 eV[8] or 1.21 eV in our calculations), armchair carbon nanotubes (1.27 eV[9], or 1.20 eV in our calculations) and comparable with the binding energy of Ca atom to the narrow zigzag carbon nanotube (2.64 eV[9], 2.73 eV in our calculations) because of the higher localized charge transfer due to the pure one-dimensional nature of carbyne. The results are similar to those for the o-Ca−carbyne except that at the small axial distance between the Ca atoms (2.6 Å) the binding energy of the Ca atom is even smaller than in the corresponding s-Ca−carbyne. In the case of o-Ca−carbyne, Ca atoms are located at the opposite sides of the carbyne chain thereby reducing the interaction. The binding energies of Ca atom in both s-Ca−carbyne and the o-Ca−carbyne become nearly same when the Ca−Ca distance exceeds 17 Å, and the interactions between the Ca atoms as well as between the distorted chain areas become negligible. The molecular formula of the optimized structures with the Ca−Ca distance of ∼10 Å for hydrogen storage purpose can be written as $(C_8{\bullet}Ca)_n$ where n is a large integer.

Computations show an oscillatory behavior in the Ca binding energy, apparently originating from the fact that there are two nonequivalent C−C bonds in carbyne. Carbyne exists in two phases: (i) energetically favorable polyyne phase with alternation of triple (1.24 Å) and single (1.34 Å) bonds by Peierls distortion, called α-carbyne, and (ii) cumulene-type double bonds, as β-carbyne.[36] Ca atom binds stronger to the "single" bonds than to "triple" ones. Because of the strain induced by the adsorption of the Ca atoms, the C−C bonds become practically equal, $d(C{\equiv}C) = 1.29$ Å and $d(C{-}C) = 1.30$ Å.

Now we turn to the hydrogen adsorption on the Ca−carbyne, investigated here for the example complex with the Ca−Ca distance 10.3 Å. The binding energy of nth H_2 molecule E_{bind} is defined as $E_{bind}(nH_2) = E((n-1)H_2) + E(H_2) - E(nH_2)$, where $E(nH_2)$ and $E((n-1)H_2)$ are the total energies of the Ca−carbyne complex with adsorbed n and $n-1$ of H_2 molecules, respectively, and $E(H_2)$ is the energy of an isolated H_2 molecule. The results of H_2 adsorption on the Ca−carbyne complex are summarized in Table 1 and Figure 3. The hydrogen molecules bind to Ca atoms via the Kubas interaction[37] which lies in between the strong chemical and weak physical binding. The addition of each H_2 molecule leads to increase of the distance between the H_2 molecule and the Ca atom accompanied with a very small increase of the distance between the Ca atom and the carbyne (from 2.31 to 2.35 Å). The calculated binding

Table 2. **Calculated Surface Area of Graphene, Carbyne, and Carbon Atom with Specific Surface Area (SSA) and Accessible Surface Area (ASA) Methods for Comparison, and Their Adsorption Capacities of Hydrogen**[a]

			H_2 uptake (wt %)	
material	method	surface area for H_2 (m^2/g)	$\varphi = 0.55$	$\varphi = 0.91$
graphene	SSA	2627	6.94	11.5
	ASA	2750	7.26	12.0
carbyne	SSA	10973	29.0	47.9
	ASA	13155	34.7	57.5
carbon atom	SSA	45933	121	201
	ASA	64298	170	281

[a] φ means a coverage fraction which is normalized to 1.

energy of H_2 molecules displays nonmonotonic behavior as the minimum is reached for the structure with three adsorbed H_2 molecules per Ca atom. Adding more H_2 molecules leads to slow decrease of the binding energy to 0.23 eV/H_2, for the adsorption of five H_2 molecules to a Ca atom, when the molecular formula of the Ca-decorated carbyne is $(C_8{\bullet}Ca{\bullet}5H_2)_n$. This means that the hydrogen storage capacity can reach 6.9 wt %, which satisfies the DOE requirement. The binding energy of the sixth H_2 adsorption (which would mean 8.16 wt % storage) drops to 0.07 eV/H_2 because of the increase of the repulsive interaction between the H_2 molecules. This maximum hydrogen storage capacity is much greater than the capacity (~5 wt %) of the Ca-decorated graphene nanoribbons[11] and carbon nanotubes.[12] Therefore, we conclude that Ca−carbyne complex can adsorb up to 5 H_2 molecules (per Ca) with sufficient energy and amount of hydrogen for using it as a storage material. We should mention that 6.89 wt % is the lowest limit of possible sorption of hydrogen on the Ca−carbyne complex because the GGA approach underestimates the binding energy of H_2 molecules. Also, increasing the density of Ca atoms along the chain could further enhance the hydrogen uptake.

To estimated now the upper limit of H_2 adsorption capacity of carbyne without Ca attachment, we used two measures: specific surface area (SSA)[38] and accessible surface area (ASA).[39] The SSA method is based on the geometrical calculation of the area whereas the ASA method is based on the Monte Carlo integration technique where the probe molecule is "rolled" over the framework surface. The details of the calculation of SSA and ASA can be found in the corresponding papers. For the calculation of SSA of carbyne, its surface is represented as a cylinder with radius 2.7 Å (distance of physical adsorption between carbon and hydrogen[40]). Obtained values of SSA and ASA of carbyne and graphene for comparison are shown in Table 2. The rough estimation of adsorption capacity of materials in assuming of monolayer adsorption of H_2 (with random[41] and hexagonal packing with coverage fraction 0.55 and 0.91, respectively) gives us the following numbers presented in Table 2. It can be seen from the table that whereas graphene looks promising as material storage, at the same conditions the carbyne area-based limit of adsorption is in the range of from ~30 to 60 wt %. Of course, such area-based evaluation ignores the weakness of the binding, and the values obtained refer to very low temperatures. In contrast, presence of Ca, as an anchor with stronger binding for H_2, makes the storage conditions more reasonable, as analyzed below.

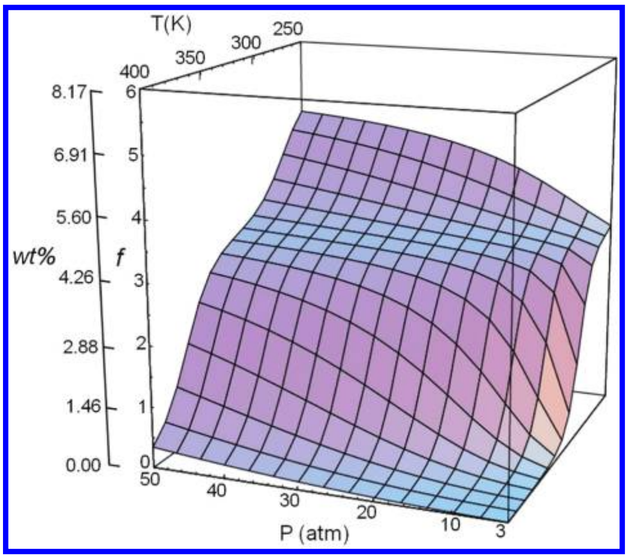

Figure 4. Occupation number (f) and the hydrogen storage capacity (wt %) as a function of the pressure and the temperature on the Ca−carbyne complex.

Next, thermodynamics of adsorption of H_2 molecules on the Ca−carbyne complex was investigated. In equilibrium between H_2 gas and the H_2 molecules adsorbed on the Ca atom, the occupation number of H_2 molecules as a function of the pressure and temperature is as follows[42,43]

$$f = \frac{\sum_{n=0}^{N_{\max}} g_n n e^{n(\mu - \varepsilon_n)/kT}}{\sum_{n=0}^{N_{\max}} g_n e^{n(\mu - \varepsilon_n)/kT}} \tag{2}$$

where μ is the chemical potential of the H_2 gas, $-\varepsilon_n$ (>0) and g_n are the average binding energy of the H_2 molecules and the degeneracy of the configuration for a given adsorption number of the H_2 molecules n, respectively, $N_{\max}$ is the maximum number of attachable H_2 molecules per Ca atom, and k and T are the Boltzmann constant and temperature, respectively. Figure 4 shows the occupation number of H_2 molecules on the Ca atom as a function of the pressure and temperature, where the experimental chemical potential of H_2 gas[42] and the calculated binding energy (ε_n) obtained from our DFT-GGA calculations were used (Table 1). The occupation number f of H_2 molecules at 300 K and 30 atm is 3.98. This is attributed to the Gibbs factor ($e^{4(\mu-\varepsilon_4)/kT}$) for the binding of 4 H_2 molecules which dominates at 25 °C and 50 atm (adsorption conditions) where μ is −0.21 eV and ε_4 is −0.26 eV. The H_2 molecules at 100 °C and 3 atm (desorption conditions) are released as shown in Figure 4 because the Gibbs factors are negligible where μ is −0.39 eV. This analysis shows that roughly 4 of H_2 molecules out of 6 can be utilized upon the change of conditions, and therefore, the practical capacity between the adsorption and desorption is 5.59 wt %. We also calculate thermodynamically practical capacity between the above adsorption and desorption conditions for recently reported Ca-decorated graphene nanoribbon (GNR)[11] and Ca-decorated B-doped carbon nanotubes (CNTs).[12] The practical capacities are presented in Table 3 for comparison. This result shows that the practical capacity of the Ca−carbyne is

Table 3. Comparison for the Practical Capacity in Ca-Decorated Carbyne, Ca-Decorated Graphene Nanoribbons (GNR),[11] and Ca-Decorated B-Doped Carbon Nanotubes (CNTs)[12a]

	N_{max}	N_{ads}	N_{des}	N_{use}	maximum wt %	practical wt %
Ca−carbyne	6	3.98	0.01	3.97	8.16	5.59
Ca−GNR	5	1.02	0.00	1.02	5.13	1.07
Ca−B−CNTs	6	1.04	0.00	1.04	4.97	0.86

[a] N_{max} is the maximum number of H_2 molecules per Ca atom. $f \equiv N_{ads}$ is the number of adsorbed H_2 molecules per Ca atom at the condition of adsorption (50 atm-25 °C), and $f \equiv N_{des}$ is the number of adsorbed H_2 molecules per Ca atom at the condition of desorption (3 atm-100 °C). The usable number of H_2 molecules per Ca atom is obtained from $N_{use} = N_{ads} - N_{des}$.

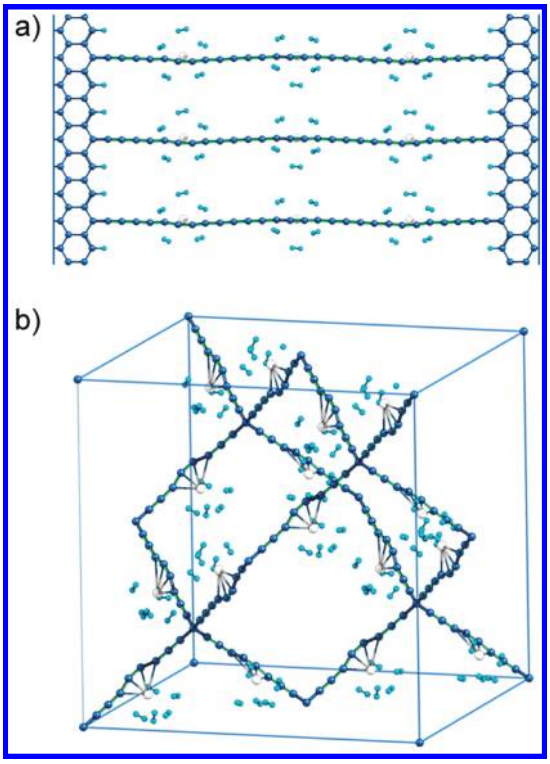

Figure 5. Fully relaxed atomic structures of (a) Ca-decorated carbyne-graphene and (b) Ca-decorated carbyne chain diamond-lattice with 5 H_2 adsorbed at each Ca atom.

significantly enhanced compared to the Ca−GNR and Ca−B−CNT and is close to the DOE target of 6.5 wt %.

The above analysis suggests the Ca−carbyne complexes as units for efficient room-temperature hydrogen storage. Very often, when isolated nanostructure such as fullerene or nanotube decorated with metal is proposed,[8,12] its realization in an extended-material form is omitted. An important question is then how such nanostructures can be assembled, at least in principle, into material-media, without sacrificing the H_2 capacity. In attempt to make such next step, we illustrate possible scalable media with two examples. It has been found that carbyne can be made by stretching from graphite or carbon nanotube edge,[14,18,20] and that 3D carbyne networks can be stabilized.[44] Following this, we design a structure consisting of carbyne and graphene ribbons (Figure 5a). Second example, inspired by the architecture of metal organic frames (MOF), is a diamond-lattice assembled from carbyne chains joined by sp^3-nodes ("meta-diamond", Figure 5b). Ca-decorated carbyne-graphene or meta-diamond in Figure 5 can adsorb 5 H_2 molecules per Ca atom with the binding energy of ~0.2 eV/H_2 (recomputed for the full primitive cells) and gravimetric capacity of ~6 or ~7 wt %, respectively. The gravimetric and volumetric capacities can be further estimated for different chain lengths, the number N of sp-carbon atoms in each chain. The gravimetric (volumetric) capacity of "diamond" from relatively short Ca-decorated carbon-chains N = 5, 6, 7, 8, and 9 are 8.9 (46), 8.1 (29), 7.3 (19), 6.8 (14), and 6.3 wt % (10 kg/m^3), but for $N \gg 1$ scale as $\sim N^0$ ($\sim N^{2-}$). Very recently, a diamond crystal consisting of carbon tetrahedrons has been predicted,[45] suggesting 3D structures where carbyne chains could be connected through carbon tetrahedron clusters-nodes. Stiffness of carbyne nano-beam, computed with the DFT methods, suggests that its room temperature persistence length l_p~100 Å[46] is sufficient to support the 3D-architectures of Fig. 5.

We have studied the calcium-decorated carbyne as a medium for hydrogen storage using ab initio calculations. Such "grape-vine" shaped complexes can uptake as much as ~8 wt % of hydrogen with a desirable binding energy of ~0.2 eV/H_2 for the effective reversible hydrogen storage. The rough estimate for surface area of pristine carbyne reaches up to ~13 000 m^2/g as well as H_2 maximum possible adsorption capacity ~50 wt %, which underscores the potential for storage. Despite a series of studies describing the methods for making carbyne, the structure is still considered as exotic. Recent experimental synthesis[15] and present work should stimulate further experimental efforts to synthesize this promising open-network material from light constituent elements.

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