Titanium-capped carbon chains as promising new hydrogen storage media

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The capacity of Ti-capped *sp* carbon atomic chains for use as hydrogen storage media is studied using first-principles density functional theory. The Ti atom is strongly attached at one end of the carbon chains via d-p hybridization, forming stable TiC_n complexes. We demonstrate that the number of adsorbed H₂ on Ti through Kubas interaction depends upon the chain types. For polyyne (n even) or cumulene (n odd) structures, each Ti atom can hold up to five or six H₂ molecules, respectively. Furthermore, the TiC₅ chain effectively terminated on a C₂₀ fullerene can store hydrogen with optimal binding of 0.52 eV/H₂. Our results reveal a possible way to explore high-capacity hydrogen storage materials in truly one-dimensional carbon structures.

1 Introduction

To develop economical hydrogen energy, carbon nanostructures with sp^2 -like bonding functionalized by transition metal (TM), ¹⁻⁶ alkali metal (AM)^{7,8} and alkaline-earth metal (AEM) atoms⁹ have been expected to be promising storage materials due to their light weights and large surface areas. Recently, Iijima et al.¹⁰ transformed graphene to single sphybridized carbon chains containing 16 carbon atoms. In addition, chains with metal atoms connected to the ends have been previously generated, ¹¹ and their magnetic, electronic, and transport properties have been studied extensively.^{12,13} These results inspired us to consider whether metal-capped carbon atomic chains are efficient hydrogen storage media. In this study, we conduct theoretical studies of high-capacity hydrogen storage media consisting of a Ti atom capped on two kinds of atomic carbon chains, cumulene (with double C-C bonds) or polyyne (with alternating singlet and triplet bonds). The number of adsorbed H₂ molecules is only determined by the type of chain. Each Ti atom in TiC₅ and TiC₈ can bind up to six and five H₂ molecules, respectively, corresponding to storage capacities of 10 wt % and 6.5 wt %. The average binding energy of H₂ molecules on TiC₅ (TiC₈) is 0.59 eV/H_2 (0.57 eV/H_2), which is between the physisorption and chemisorption energies.

2 Computational method

Numerical calculations were performed using spin-polarized density functional theory (DFT) with the Perdew-Wang (1991) exchange-correlation function, ¹⁴ as implemented in the DMol³ package (Accelrys Inc.).¹⁵ A double numerical atomic orbital augmented by *d*-polarization functions (DNP) was employed as the basis set. In the self-consistent field calculations, the electronic-density convergence threshold was set to 1×10^{-6} electron/Å³. Geometric optimization was performed with convergence thresholds of 10^{-5} Ha for the energy, 2×10^{-3} Ha/Å for the force, and 10^{-4} Å for the atomic displacements. We performed normal-mode analysis of the obtained structures to ensure that the structures optimized without any symmetry constraints were true minima of the potential-energy surface.

3 Results and discussion

We first consider the bonding energetics of a single Ti atom at one end of the C_n (n=5-16) chains. The binding energies of Ti, shown in Fig. 1(a), are much larger than those of Ti on sp^2 hybridized carbon materials,^{2–5} and the adsorption strengths are thus strong enough to maintain stable Ti- C_n structures at room temperature. Moreover, the Ti binding energies exhibit an interesting odd-even oscillatory behavior, consistent with the trend of Mulliken charge [see Fig. 1(a)]. This behavior suggests that the bonding between the Ti atom and carbon chains has a significant ionic characteristic. In addition, the configurations of Ti C_n complexes exhibit significant differences for odd or even values of n. For instance, the C-C distances in Ti C_5 , depicted in Fig.1(b), are rather uniform. In contrast, the bond lengths of Ti C_8 alternate, consistent with

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 σ - π bonding [Fig. 1(c)]. Contour plots of the total electronic charge density confirm these bonding patterns.



Fig. 1 (a) Mulliken charge and binding energy of TiC_n as a function of the number of carbon atoms. The optimized bond lengths (in Å) and the contour plot for the total electronic charge density of (b) TiC₅ and (c) TiC₈. The large and small balls represent the Ti and C atoms, respectively. Calculated partial density of states (PDOS) of (d) TiC₅ and (e) TiC₈ in units of state/eV. The solid black lines and dotted blue lines represent the C-2*p* and Ti-3*d* states, respectively. Insets of (d) and (e) show the bonding orbitals (the two colors denote \pm signs of the wave function) corresponding to states indicated by black arrows.

To elucidate the nature of the bonding, the projected density of states (DOS) shown in Fig. 1(d) illustrates the bonding orbitals of the C_5 (C_8) and Ti atom result from the hybridization of the carbon chain π orbitals and the Ti-*d* orbitals. The C-p and Ti-d hybridization is evidently stronger in TiC₈ than in TiC₅, in accordance with the larger binding energy of TiC₈. Since odd-numbered and even-numbered free chains have full and half-occupied HOMOs (highest occupied molecular orbitals), respectively, different states are responsible for the bonding of the Ti atom to C_5 or C_8 . From the isosurface plots of these states [Fig. 1(d)], it is clearly that the LUMO (a linear combination of degenerate $\pi_{p_x}^*$ and $\pi_{p_y}^*$ antibonding orbitals) of C₅ hybridizes with two Ti-d orbitals to create a new π -symmetry bond. However, for TiC₈ there is an overlap between one Ti-*d* orbital and the $\pi_{p_y}^*$ antibonding state of C₈. As mentioned above, the bonding mechanisms for TiC₅ and TiC₈ seem to be very similar to the Dewar coordination.¹⁶

The stability of the TiC_5 and TiC_8 complexes was further tested by normal mode analysis, and no negative mode was

found. However, it remains to be shown whether it is possible to realize linear C_n -Ti chains experimentally. To address this issue, we calculated the minimum-energy path (MEP) for different reaction processes with the nudged elastic band method to determine the energy barrier.¹⁷ The image number considered is 16 to ensure that the obtained MEP is correct. In Figs. 2(a) and 2(b), the MEPs show that a single Ti atom is attached to the right end of C_5 and C_8 without any energy barrier. The other end is free and ready to be attached to any other structure with a high surface-to-volume ratio. The main Ti vibrational frequencies, 623 cm^{-1} in TiC₈ and 359 cm^{-1} in TiC₅, correspond to the stretching modes of C-Ti. These characteristic modes will provide a reference for the Raman/IR spectra of the synthesized materials. To this end, a monatomic carbon chain, realized by removing the carbon atoms from the graphene through energetic electron irradiation inside a transmission electron microscope, ¹⁰ can be used as the initial material in the fabrication process.



Fig. 2 Variation in the total-energy difference of a Ti atom attached at a distance *d* from the right free end of the carbon chain.

Now we investigate the interaction between these complexes and hydrogen molecules. The first H₂ molecule is found to dissociate on both TiC₅ and TiC₈ complexes and bind atomically to Ti, with interatomic H distances of 3.003 Å [Fig. 3(a)] and 2.748 Å [Fig. 3(b)], respectively. Such a dissociation is observed in most TM-hydrogen binding [Ref. 2] due to excessive charge transfer from the TM to the antibonding σ^* state of H₂. Additional H₂ molecules, however, bind molecularly around the Ti atom, since the charge transfer per H₂ molecule is not enough to destabilize the dihydrogen state when more hydrogen molecules are added to the system.

For TiC₅, several initial configurations of the second H₂ molecule were considered in the search for the lowest energy structure. The structure in which one of the H₂ molecules binds as a dihydride is 0.09 eV higher in energy than the structure in which both H₂ molecules bind in molecular form [Fig. 3(a)]. We continue to introduce successive hydrogen molecules near the Ti atom. Surprisingly, it is energetically favorable for the TiC₅ complex to adsorb 6 H₂ molecules, corresponding to a ~10 wt % gravimetric density. A close examination of the geometry of the TiC₅(H₂)₆ configuration shows that the adsorbed hydrogen molecules are divided into two sets

[Fig. 2(a)]. First, the molecule on the top binding site, which is vertical to the carbon chain axis, has a bond length of 0.808 Å and the largest bonding energy, 0.82 eV. Second, the H-H bonds of the side H₂ molecules lie almost parallel to the chain axis, with the lower H atoms of each H₂ molecule tending to tilt toward the chain. The bond lengths between the Ti and the lower (upper) H atoms are 1.910 Å (1.970 Å). The side molecules are more weakly bound, with a binding energy of 0.54 eV/H₂ and an elongated H-H bond distance of 0.810 Å, on average. All of these features suggest that different bonding mechanisms (to be discussed below) for the two sets of H₂ molecules on TiC₅.

On the other hand, when the second H_2 molecule is bound to TiC_8 , the structural configuration shown in Fig. 3(b) is more energetically favorable than its isomer (not shown) by 1.02 eV. As we add a third H₂ molecule close to the Ti atom, all of the hydrogen molecules are almost parallel to the chain and are bonded molecularly. Interestingly, the H-H bonds turn nearly perpendicular to the chain when the fourth H₂ molecule is attached. The maximum number of H₂ molecules that could be bound to the TiC_8 complex is 5, which corresponds to a hydrogen wt % of 6.5. Note that the adsorption of the fifth H_2 molecule does not affect the degree of the bond-length elongation of the side hydrogen molecules [Fig. 3(b)]. The H-H bond of the top H_2 molecule is 0.756 Å and the bond length between this H_2 molecule and the Ti atom is 2.334 Å, leading to an adsorption energy of 0.29 eV, which is only about half the value of the side molecules (0.66 eV).

Insight into the nature of Ti-H₂ bonding and the orientation of H₂ molecules can be gained from the DOS and molecular orbital (MO) analyses. The metal-dihydrogen binding of $TiC_5(H_2)_6$, shown in Fig. 3(c), stems primarily from the Kubas interaction.¹⁸ In the energy range from -10 to -6 eV (region I), the d orbitals of Ti are hybridized with the σ orbitals of the hydrogen molecules, resulting in charge transfer from the hydrogen to the metal. Region II of Fig. 3(c) highlights that the hybridization of the Ti-d orbitals with the H₂ σ^* -antibonding orbitals is responsible for keeping the side H₂ molecules parallel and the top H_2 molecule perpendicular to the TiC₅ chain. The isosurface plots of these states, as shown in Fig. 3(d), clearly confirm that the bonding is dominated by the overlap between the Ti-d and H₂-s states. To better understand the orientation of the side H₂ molecules, we also plotted the deformation charge in Fig. 3(a). The charge distribution around the lower H sites, marked in yellow, indicates that these H atoms lose a greater amount of charge. With the help of Mulliken charge population analysis, we identified that the upper H atom has a charge of 0.04 e, while the lower one carries 0.12 e due to charge transfer from H to the C atom. Thus, the distances between the Ti and the upper or lower H depend on the strength of the Coulomb interaction between the H and C atoms. The Kubas interaction is likewise found



Fig. 3 Optimized configurations of H₂ molecules adsorbed to the Ti atom on (a) C₅ and (b) C₈ along with the typical bond lengths (in Å). The large, medium and small balls represent the Ti, C and H atoms, respectively. The right panels of (a) and (b) show the deformation electron densities (molecular charge densities minus atomic charge densities) for the TiC₅(H₂)₆ and TiC₈(H₂)₅ complexes. The deformed density marked in blue corresponds to the region that contains excess electrons, while that marked in yellow indicates electron loss. The isovalue equals $0.1 \ e/Å^3$. (c) PDOS for six hydrogen molecules attached to the Ti atom on C₅. (d) Isosurfaces of major molecular orbitals corresponding to states in region I and II of panel (c). Panels (e) and (f) show the σ and σ^* orbitals, respectively, for the side hydrogen molecules hybridized with the Ti-*d* orbitals in TiC₈(H₂)₅. (g) The bonding orbital for the top hydrogen molecule.

in TiC₈(H₂)₅. Figure 3(e) shows that the Ti-*d* orbitals interact with the σ orbitals of the H₂ molecules. The hybridization between the Ti-*d* orbitals and the side H₂ molecules' σ^* antibonding orbitals plays a role in keeping them planar [Fig. 3(f)], in contrast to the situation in TiC₅(H₂)₆. The top hydrogen in TiC₈(H₂)₅ interacts with Ti rather weakly compared to the rest of the hydrogen molecules, as the relevant MO is more heavily polarized toward the C₈ than toward the H₂ [see Fig. 3(g)]. The Kubas interaction mentioned above leads to variations in the effective charge of the Ti atom. The Mulliken charge of the Ti atom varies from positive to negative as the number of hydrogen molecules increases. When the fifth (sixth) H₂ is adsorbed onto TiC₈ (TiC₅), the Ti atom carries -0.13 (-0.49) electrons.

The above results demonstrate that the interaction between

one Ti atom and the carbon chain is very strong, and the binding energy of H₂ on TiC_n is optimal for room temperature application. Now the question arises: can the storage performance of TiC_n be influenced by introducing another Ti? We first discuss the second Ti atom saturating the free end of TiC_n (n=5, 8). The binding energy for Ti to the TiC₅ (TiC₈) is 4.31 eV (4.39 eV), which is obviously much large than that of Ti on the sp^2 carbon nanostructures.^{2–5} However, further functionalization through Ti atoms bridging other C-C bonds makes the chain unstable, due to the fact that the small separation between Ti atoms leads to stronger Ti-Ti coupling. At the end, the linear chains are transformed to the clusters composed of C and Ti atoms, which is also confirmed by other theoretical studies.¹⁹ We therefore only consider two Ti atoms each capping one end of the C_n .

Next, we studied the H₂ storage capacity of the TiC_nTi complex. The TiC₅Ti and TiC₈Ti can adsorb 12 and 10 H₂ molecules, respectively, with average binding energies of 0.53 and 0.55 eV/H₂. As shown in Figs. 4(a) and 4(b), the gravimetric densities of stored H₂ molecules for TiC_nTi becomes 13.3 and 9.4 wt % when *n*=5 and *n*=8, respectively. Analysis of the electronic structures of the TiC₅Ti-(H₂)₁₂ and TiC₈Ti-(H₂)₁₀ shows that the Kubas interaction between H₂ and TiC_n mentioned above also applies to the TiC_nTi complex. Note that introduction of the second Ti atom to TiC_n not only keeps the number of adsorbed H₂ per Ti on odd- or even-numbered chains, but also remains the binding energies of the H₂ with metal atoms .



Fig. 4 Geometries of (a) $TiC_5Ti-(H_2)_{12}$ and (b) $TiC_8Ti-(H_2)_{10}$. The large, medium and small balls represent the Ti, C and H atoms, respectively.

Because controlling the number of atoms per chain in the synthesis of carbon chains may be difficult with today's technology, it is important to know whether the results reported above for TiC_5 and TiC_8 are applicable to other Ti-capped carbon chains and how they vary with chain length. To this end, we have also studied the potential of the TiC_{15} and the TiC_{16} complexes as storage media, and we found that the number

of adsorbed H₂ molecules is six and five, respectively. The corresponding bond lengths of H₂ and Ti-H₂, as depicted in Fig. 5(a) and 5(b), are very similar to those in TiC₅(H₂)₆ and TiC₈(H₂)₅. Furthermore, the average binding energies of the H₂ molecules to TiC₁₅ and TiC₁₆ are, respectively, 0.54 and 0.59 eV/H₂, which are very close to the values found in the case of TiC₅(H₂)₆ and TiC₈(H₂)₅. The bonding mechanisms between Ti and H₂ presented above also hold for these chains. This suggests that the length of the chains does not affect the hydrogen adsorption performance. In summary, the finding that *a single Ti atom-capped, odd-numbered (even-numbered) carbon chain can bind up to six (five) hydrogen molecules* is very general.



Fig. 5 Geometries of (a) $TiC_{15}(H_2)_6$, (b) $TiC_{16}(H_2)_5$, and (c) a TiC_5 chain terminated on the C_{20} fullerene. (d) Optimized geometry of 6 H₂ molecules adsorbed on $C_{20}(TiC_5)$. The large, medium and small balls represent the Ti, C and H atoms, respectively.

While the above results are promising for isolated TiC_n systems, one can imagine terminating the other end of these complexes with suitable graphitic nano-objects. These new structures not only represent the typical interface in realistic nanostructures produced by cluster beam deposition.²⁰ Here we choose C₂₁ fullerene as the end-capping candidate, as it is the most frequently experimentally synthesized curved sp^2 system. An increasing amount of experimental²¹ evidence shows that these hybrid $sp+sp^2$ carbon-based systems (with linear chains connecting sp^2 -type fragments) exhibit unusual electronic and optical properties. Figure 5(c) illustrates that a TiC₅ chain can be effectively stabilized by termination on C₂₀. The calculated binding energy (with respect to the isolated TiC₅ plus the fully relaxed C₂₀) is 2.79 eV. As shown in Fig. 5(d), the TiC₅ assembled on the C_{20} structure can hold 6 H_2 molecules, with an average binding energy of 0.52 eV/ H_2 .

4 Conclusion

In conclusion, using all-electron DFT calculations, we have shown that each Ti atom adsorbed on even or odd-numbered carbon atomic chains can bind up to five or six hydrogen molecules, respectively. Note that the number of adsorbed H₂ molecules depends only on the type of chain. We propose that the TiC₅ chain terminated effectively on a C₂₀ fullerene can also store 6 H₂ molecules with an average binding energy of 0.52 eV/H_2 . Recent experiments have produced junctions between a single carbon chain and two fullerenes,²² which has provided a way to synthesis the $sp+sp^2$ system we proposed here. We hope that the theoretical results presented here will provide a useful reference for the design of high-capacity hydrogen storage materials in the laboratory.

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