Molecular and dissociative adsorption of multiple hydrgens on transition metal decorated C_{60}

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Recently we have predicted [Phys. Rev. Lett. 94, 175501 (2005)] that Ti-decorated carbon nanotubes can adsorb up to 8-wt% hydrogen at ambient conditions. Here we show that a similar phenomenon occurs in light transition-metal decorated C_{60}. While Sc and Ti prefer the hexagon (H) sites with a binding energy of 2.1 eV, V and Cr prefer double-bond (D) sites with binding energies of 1.3 and 0.8 eV, respectively. Heavier metals such as Mn, Fe, and Co do not bond on C_{60}. Once the metals are adsorbed on C_{60}, each can bind up to four hydrogen molecules with an average binding energy of 0.3-0.5 eV/H₂. At high metal coverage, we show that a C_{60} can accommodate six D-site and eight H-site metals, which can reversible adsorb up to 56 H₂ molecules, corresponding to 7.5 wt%.

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An efficient storage media for hydrogen is crucial for the advancement of hydrogen and fuel-cell technologies.1 Currently, a lot of effort is being devoted to engineering nanomaterials so that they dissociate H₂ molecules into H atoms and reversibly adsorb hydrogen molecules at ambient conditions.1–10 Much work has focused on carbon-based materials such as nanotubes,2–4,11 and metal hydrides such as alanates.13 It is found that, while the hydrogen-carbon interaction is too weak for hydrogen storage at ambient conditions,11 the metal-hydrogen interaction is too strong. Very recently we have shown14 a novel way to overcome this difficulty by forming artificial metal-carbide-like structures on single-wall carbon nanotubes (SWNT). From accurate first-principles calculations, we show that a single Ti atom adsorbed on a SWNT can strongly bind up to four hydrogen molecules.14 At large Ti coverage we find that a (8,0) SWNT can store hydrogen molecules up to 8-wt%, exceeding the minimum requirement of 6-wt% for practical applications. These results can be explained by a simple Dewar-Chatt-Duncanson model,15,16 where the interaction is caused by donation of charge from the highest occupied orbital of the ligand to the metal empty states and a subsequent back donation from filled d orbitals to the lowest unoccupied orbital of the ligand.

Here we show that a similar phenomenon occurs in light transition-metal decorated C_{60} molecules. We first discuss several possible adsorption sites for a single Ti atom on a C_{60} molecule. Then we show how a single Ti atom on a C_{60} can bind up to four hydrogen molecules via Kubas interaction.15,16 Multiple metal coverage cases, yielding up to 8-wt% hydrogen storage, are discussed next. Finally, we briefly describe the results for other transition metals from Sc to Co.

The energy calculations were performed within a plane-wave implementation17 of the Generalized Gradient Approximation18 to Density Functional Theory. We used Vanderbilt ultrasoft pseudopotentials19 treating the following electronic states as valence: Ti 3s, 3p, 3d, and 4s, C 2s and 2p, and H 1s. A cutoff energy of 350 eV was found to yield total energies converged to within 0.5 meV/atom. We used a cubic supercell of a = 16 Å for single-metal C_{60} systems and a = 20 Å for full coverage cases. We also made spin-polarized calculations for cases where the ground state of the metal-coated C_{60} is magnetic. Conjugate-gradient structural relaxations were considered to be converged when forces on atoms were smaller than 0.2 eV/Å.

Figure 1 shows the four possible adsorption sites on a C_{60} molecule that are considered in this study. The C_{60} molecule has the truncated-icosahedral symmetry with twenty hexagons (H), twelve pentagons (P), thirty C–C double bonds (D) between two hexagons, and sixty

(a) C_{60}Ti(H) (b) C_{60}Ti(P)

(c) C_{60}Ti(S) (d) C_{60}Ti(D)

FIG. 1: A single Ti atom adsorbed at hexagonal (H) (a) and pentagonal (P) (b) hollow sites, and single (S) (c) and double (D) (d) bond sites of a C_{60} molecule, respectively.
TABLE I: Calculated Ti–C and C–C bond distances, Mulliken charges, spins, and binding energies for a single Ti atom adsorbed at the four different sites of a C60 molecule shown in Fig. 1. For bare C60, the calculated double and single bond lengths are 1.44 and 1.38 Å, respectively.

<table>
<thead>
<tr>
<th></th>
<th>C60 Ti(H)</th>
<th>C60 Ti(F)</th>
<th>C60 Ti(D)</th>
<th>C60 Ti(S)</th>
</tr>
</thead>
<tbody>
<tr>
<td>d(Ti–C) (Å)</td>
<td>2.27</td>
<td>2.33</td>
<td>2.10</td>
<td>2.24</td>
</tr>
<tr>
<td>d(C–C) (Å)</td>
<td>1.42 / 1.45</td>
<td>1.44</td>
<td>1.52</td>
<td>1.48</td>
</tr>
<tr>
<td>Q(Ti) (e)</td>
<td>1.39</td>
<td>1.09</td>
<td>0.99</td>
<td>0.84</td>
</tr>
<tr>
<td>S(Ti)</td>
<td>0.99 Å</td>
<td>1.40 Å</td>
<td>1.13 Å</td>
<td>1.54 Å</td>
</tr>
<tr>
<td>Ebind (Ti) (eV)</td>
<td>2.098</td>
<td>1.633</td>
<td>1.837</td>
<td>1.220</td>
</tr>
</tbody>
</table>

C–C single bonds (S) which are between pentagon and hexagon carbon rings. We calculated the binding energy of a single Ti atom at these sites. The results are given in Table I along with relevant structural parameters. The binding energy is defined as

\[ E_{\text{bind}}(\text{Ti}) = E(C_{60}) + E_{\text{spol}}(\text{Ti}) - E_{\text{spol}}(C_{60} \text{Ti}), \]

where the \( E_{\text{spol}} \) energies are obtained from spin-polarized calculations. Hence, a positive binding energy indicates the system is stable.

Our results indicate that the H-site is the most stable configuration for C60Ti, with a binding energy of 2.1 eV. The D-site comes next with the shortest Ti–C bonds among the four possible configurations. In all cases, we have a charge transfer of about one electron to the C60 molecule. The S-site is the least stable adsorption site and therefore we do not consider it any further.

Figure 2(a) shows the energy variation, obtained from spin-unpolarized calculations, as a single H2 molecule approaches C60 Ti(D). The energy first decreases slowly as the hydrogen approaches the C60 Ti(D) complex. However, as the charge overlap gets large, the H2 molecule is attracted towards the Ti atom with a sharp decrease in energy. At this point, the H2 molecule is still intact with a significantly increased H–H bond length of 0.9 Å. The second pronounced decrease in energy is associated with the dissociation of the H2 molecule into two H atoms. At this point, the H–H distance increases up to 2.94 Å. The interaction between H2 and C60 Ti(D) is always attractive and therefore H2 is adsorbed onto the Ti atom without having to overcome any energy barrier. The final geometry is shown in the inset to Fig. 2(a).

In order to calculate the binding energy for this dissociative adsorption, we computed the total energies of the C60 Ti(D) and H2 reactants and the C60 Ti(D)H2 final product (dashed lines in Fig. 1(a)) from spin-polarized calculations. We obtained a binding energy of 1.16 eV (Fig. 2(a)).

Figure 2(b) shows the energy variation as two H2 molecules approach the TiH2 group, one from each side. As in the single-adsorption case, the energy always decreases, slowly at the beginning and very rapidly at the later stage when the two hydrogen molecules become strongly attached to the C60 Ti(D)H2 complex. We denote the final product by C60 Ti(D)H2–2H2. In the final configuration, the two H2 molecules were rotated by 90°, as shown in Fig. 2(b). The total energy change upon adsorption is about 0.65 eV (i.e., 0.325 eV/H2). Unlike in the first adsorption, the second and third H2 molecules do not dissociate, but display a rather elongated bond of 0.79 Å.

Figure 2(c) shows the energy evolution when a fourth hydrogen molecule approaches the C60 Ti(D)H2–2H2 system from the top. The energy again decreases continuously, indicating a zero-energy barrier. The final product, denoted by C60 Ti(D)H2–3H2, is shown in the inset. The fourth adsorption results in an energy gain of 0.433 eV/H2. The H–H distance of the top H2 is 0.85 Å. Several attempts to add a fifth hydrogen molecule at a
variety of positions failed, suggesting a limit of four H₂ per Ti. However, in view of a recent study showing that it is possible to attach twelve H atoms to a single transition metal, there might well be other transition paths that could yield more than four hydrogen molecules per C₆₀ Ti.

Next we discuss the adsorption properties of a Ti at the H-site of the C₆₀, as shown in Fig. 3. For the first H₂ adsorption, we find that the molecule does not dissociate, unlike in the case of Ti at a D-site (Fig. 2a). The reason is that the Ti atom is adsorbed very strongly at the H-site and, therefore, there is not enough charge left in the Ti to transfer to the σ* orbital of the hydrogen molecule and thus break it. The binding energy is about 0.58 eV and the H–H bond length 0.815 Å. Additional H₂ molecules can be adsorbed, without activation-energy barrier, up to four H₂ per Ti. The resulting system, which is shown in Fig. 3(b), is denoted by C₆₀ Ti(H₂)-4H₂. The final configuration is very symmetric, and all the hydrogen molecules benefit equally from the bonding with the Ti atom. The average binding energy per H₂ is about 0.465 eV, i.e. slightly smaller than that obtained for the first adsorption. We have also calculated the binding energy for the isomer C₆₀ Ti(H₂)₃H₂, where the first H₂ is bonded to Ti dissociatively. We find that this isomer is about 0.1 eV higher in energy than C₆₀ Ti(H₂)-4H₂.

The results for the adsorption of hydrogens at the P-site Ti are summarized in Fig. 4. The first adsorption is found to be dissociative without activation energy. The binding energy is about 0.615 eV, i.e. significantly smaller than that for Ti at the D-site (Fig. 2a), but the adsorption is still dissociative unlike for Ti at the H-site (Fig. 3(a)). The two isomers, C₆₀ Ti(P)H₂-3H₂ (Fig. 4(b)) and C₆₀ Ti(P)-4H₂ (Fig. 4(c)), are found to be almost degenerate and yield a binding energy of 0.45 eV/H₂.

Up to this point, we have discussed the interaction of H₂ with a single Ti atom bonded to a C₆₀, but clearly one can imagine attaching additional Ti atoms to a C₆₀, thereby increasing the hydrogen-storage capacity. In order to show the feasibility of this approach, we consider several cases. Figure 4(d) shows the full-coverage case where all the P-sites of a C₆₀ molecule host a Ti atom, each of which binds four H₂ molecules. The calculated binding energy is 0.492 eV/H₂, which is slightly higher than that of the single-coverage case of Fig. 4(c). A possible reason for this is that the C₆₀ distortes more in the single-coverage case than in the full-coverage one, which is more symmetric. In fact, we see the same effect in the binding energy of Ti atom at the P-site; we get 1.633 eV (see Table I) for a single Ti atom and 2.115 eV/Ti when there are Ti atoms at every P-site. These results are quite promising, as they suggest that it should be possible to synthesize the fully-covered systems. We note that early experiments have already indicated that it may be possible to coat C₆₀ with SWNTs by light-transition metals.

Figure 5(a) shows the case in which six Ti atoms are adsorbed at D-sites (i.e. sites on two-fold axes of the C₆₀ molecule). As in the case of full Ti(P) coverage, the binding energy per H₂ (0.592 eV) is slightly larger than that of the single-Ti case (0.559 eV). Interestingly, one can further add eight more Ti atoms at the hexagonal faces (i.e. those along the [111] directions), yielding a total of 14 Ti atoms per C₆₀. The fully hydrogenated case for this Ti coverage is shown in Fig. 5(b). The average binding energy is 0.522 eV/H₂, in remarkable agreement with the 0.305 eV/H₂ based on the energies for single coverage. This indicates that the 14 Ti atoms and 56 hydrogen molecules shown in Fig. 4(b) are not too close to each other, which in turn suggests that the system is able to host many titaniums and hydrogens. In fact, the configuration shown in Fig. 5(b), which has the chemical formula C₆₀ Ti₁₄ H₅₆, stores approximately 7.5 wt%
TABLE II: Calculated TM–C and C–C bond distances, Mulliken charges, spins and binding energies for a single TM atom (TM = Sc, Ti, V, etc.) adsorbed on a C_{60} molecule.

<table>
<thead>
<tr>
<th>Properties</th>
<th>C_{60}Sc(H)</th>
<th>C_{60}Ti(H)</th>
<th>C_{60}V(D)</th>
<th>C_{60}Cr(D)</th>
<th>C_{60}Mn(D)</th>
<th>C_{60}Fe(D)</th>
<th>C_{60}Co(D)</th>
</tr>
</thead>
<tbody>
<tr>
<td>d(TM–C) (Å)</td>
<td>2.29</td>
<td>2.27</td>
<td>2.18</td>
<td>2.09</td>
<td>2.30</td>
<td>2.28</td>
<td>2.26</td>
</tr>
<tr>
<td>d(C–C) (Å)</td>
<td>1.42/1.45</td>
<td>1.42/1.45</td>
<td>1.46</td>
<td>1.50</td>
<td>1.45</td>
<td>1.45</td>
<td>1.45</td>
</tr>
<tr>
<td>Q(TM) (e)</td>
<td>1.55</td>
<td>1.39</td>
<td>0.78</td>
<td>0.91</td>
<td>0.97</td>
<td>0.86</td>
<td>0.76</td>
</tr>
<tr>
<td>S(TM)</td>
<td>0.24 Å</td>
<td>0.99 Å</td>
<td>2.0 Å</td>
<td>2.35 Å</td>
<td>2.99 Å</td>
<td>2.53 Å</td>
<td>1.54 Å</td>
</tr>
<tr>
<td>E_{B}(TM) (eV)</td>
<td>2.127</td>
<td>2.098</td>
<td>1.308</td>
<td>0.760</td>
<td>-0.017</td>
<td>-0.130</td>
<td>-0.503</td>
</tr>
<tr>
<td>E_{B}(H_{2}) (eV)</td>
<td>0.300</td>
<td>0.454</td>
<td>0.497</td>
<td>0.239</td>
<td>-0.002</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

indicating that the C_{60}TM complex is not stable. We also found that the other transition metals are able to adsorb hydrogen in a way that is similar to that discussed above for Ti. The last line in Table II indicates the average binding energy per H_{2} in C_{60}TMH_{2}–3H_{2} configurations. It increases from 0.3 eV/H_{2} for Sc to 0.5 eV/H_{2} for V. Then, it decreases to 0.24 eV/H_{2} for Cr, and finally the complex becomes unstable for heavier transition metals.

In conclusion, we have used state-of-the-art first-principles calculations to show that light transition-metal decorated C_{60} molecules exhibit remarkable hydrogen storage properties. Metals bonded on the D-site dissociate the first H_{2} molecule without any activation-energy barrier, and then reversibly bond three more hydrogen molecules. However, metals adsorbed at the H-sites bind four hydrogen molecules without dissociating any of them. Combining these two binding sites, we show that a single C_{60} is able to bind up to 56 H_{2} molecules, corresponding to 7.5- wt% H-storage capacity. These results, along with our previous work on Ti-decorated SWNT,\textsuperscript{14} suggest a new direction towards high-capacity hydrogen storage materials by decorating nanostructured systems with light transition-metal. The transition-metal–hydrogen bond is explained by the Dewar-Chatt-Duncanson model,\textsuperscript{15,16} and has the right strength for room temperature reversible hydrogen storage.

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