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Transition Metal Decoration In Planar Nanostructures

6.1 Introduction

The safe and convenient storage of molecular hydrogen is a crucial target in the transition to a hydrogen-based energy economy. Among many different approaches to achieve this end, one is that of storing hydrogen in nanostructure materials. Significant attention is being focused on nanostructure materials, such as fullerenes and nanotubes especially of carbonic compounds, as possible candidate structures for hydrogen storage. These nanostructures, due to their high surface-to-bulk ratio, constitute a class of materials that presents a great potential for this clean energy alternative. Several works on metal decorated nanostructures for hydrogen storage have been reported in the literature. However if we look at the practical implementation of these kinds of structures for hydrogen storage, it has a very limited success. This is because of the question of stability of most of these nano-structures and the relatively high desorption temperature for hydrogen storage. Apart from these, there are several outstanding issues that need to be resolved viz.; (a) metal clustering on the surface, (b) ambiguity of exohedral versus endohedral decoration of metal atom in nano-structure, (c) barrier height effect for hydrogen desorption for endohedral storage of hydrogen, and lastly (d) subcritical utilization of fullerene or nanotube surface affecting the volumetric efficiency of hydrogen storage.

Over the past few years, metal decorated carbon nanotube (CNT), boron nitride nanotube (BN-NT) and fullerene or cage structures of carbon and B-N held the central stage of attraction for hydrogen storage in nano-structure materials. It is expected that
the planar form of these structures would be interesting as well. In fact, significant amount of effort is being devoted on designing metal decorated planar nano-structures for hydrogen storage.\textsuperscript{11-14} But all the earlier works discussed selective metal decorations on the graphene surface which is difficult to achieve experimentally when metal atoms are sputtered on graphene surface that led to prevention of metal clustering. In this work, we have embarked upon such a case of random non-selective Ti-metal decoration on both sides of graphene as well as BN-sheet with a focus on its potential use for storage of $H_2$ molecules.

Here we propose two novel conjecture to circumvent the problem of metal clustering on the surface either by (a) chemical modification of the graphene like carbon network or (b) by introducing vacancy in the pristine graphene sheet. We have shown here, that with introduction of B and N in the pure graphene like carbon network (i.e.; by chemically modifying the graphene sheet), different chemical orderings of hexagons in a B-C-N composite planar nano-structure, viz.; $BC_4N$-sheet, metal clustering can completely be prevented. Remarkably, our first-principles calculation shows that this Ti decorated $BC_4N$ sheet can store up to 8.42 wt\% of hydrogen in molecular form, which is more than the DOE (Department of Energy) target of 6 wt\%. Using \textit{ab initio} molecular dynamics simulation, we have shown that at 300 K the system remains stable with all four $H_2$ attached with Ti, while at 500 K hydrogen gets released in molecular form from the $Ti@BC_4N$ sheet without breaking the structure. We believe that these results are useful to realize the potential of B-C-N composite planar structure as promising hydrogen storage materials. An alternative approach to avoid metal clustering on a homogeneous graphene sheet is to introduce single C-atom vacancy into the graphene sheet. We have investigated a spin polarized density functional model calculation on a graphene sheet comprising of 3d transition metal (TM) adsorbed on a defect, implanted on the sheet that has a periodic repetition of C-atom vacancy. This TM decorated vacancy modulated graphene sheet is capable of storing 5.6 wt\% of molecular hydrogen which shows nice desorption at a temperature starting only at 400 K.

6.2 Computational Methods

All the planar structures in our study have been modeled in terms of supercells of suitable
dimensions in x- and y-directions and a layer of vacuum on either side. For graphene and BN sheet, we have taken a 32-atom cubic supercell with dimensions 9.8Å x 9.8Å x 12.0Å; while for the BC$_4$N sheet, the supercell consists of 24 B, 96 C, 24 N atoms in a 25.6Å x 14.9Å x 12.0Å cubic cell. Electronic structure and total energies were calculated with the Vienna \textit{ab initio} simulation package (VASP),\textsuperscript{15} based on DFT.\textsuperscript{16,17} Projector-augmented wave (PAW) potentials\textsuperscript{18} were employed for the elemental constituents; viz. H, B, C, N, Sc, Ti, V, Mn, Fe and Co potentials, which contained one, three, four, five, three, four, five, seven and eight valence electrons, respectively. The GGA calculation was performed with the Perdew-Wang\textsuperscript{19,20} exchange-correlation potential. The k-points mesh was generated by the Monkhorst-Pack method\textsuperscript{21} and all results were tested for convergence with respect to the mesh size. In all calculations, self-consistency was achieved with a 0.1 meV convergence of total energy. For high precision calculation we used a cutoff energy of 600 eV for plane wave basis. For obtaining the optimized ground state geometry,\textsuperscript{22,23} atomic forces were converged to less than 0.001 eV/Å by conjugated gradient (CG) minimization.

We also perform \textit{ab initio} molecular dynamics (MD) simulations using Nose algorithm\textsuperscript{24} in order to investigate the stability of the optimized structures and desorption of hydrogen molecules from Ti@BC$_4$N sheet and TM@Vacancy-Graphene respectively. For Hirshfeld charge analysis we have used Dmol\textsuperscript{3} code,\textsuperscript{25} where exchange and correlation terms are treated within generalized gradient (GGA) functional by Perdew \textit{et. al.}\textsuperscript{26} Core electrons were treated in a non-relativistic all-electron implementation of the potential. A double numerical quality basis set with polarization function (DNP) was considered.

\section*{6.3 Results And Discussion}

\subsection*{6.3.1 Ti@Graphene And Ti@BN-sheets For H-storage: Advantages And Shortcomings:}

We first consider Ti adsorption on a supercell of graphene and BN-sheet. In this context it should be mentioned that in nanotubes or fullerenes, the endohedral versus exohedral decoration of the metal atom encounters the problem of surmounting a rather large barrier height.\textsuperscript{9} However, for a sheet it is feasible to adsorb metal atoms on both sides of the surface with negligible energy barrier.\textsuperscript{11,14} The optimization was carried out by placing Ti at different locations and the results suggest that for both the sheets, Ti prefers to get
adsorbed on the centre of a hexagon. Further interaction of hydrogen molecules shows that the Ti is capable of binding $4H_2$ molecules in case of both graphene and BN-sheet. After the adsorption of a Ti on one side, we place another Ti on the opposite side of the sheet. The results show that the second Ti can be attached below the centre of the same hexagon for both these systems. The binding energy of the second Ti is of course less than the first Ti, as expected, but interestingly, it is also capable of storing additional $4H_2$ molecules in case of graphene [Figure 6.1 a] and $2H_2$ molecules in case of BN-sheet [Figure 6.1 b]. In case of BN sheet, further adsorption of $H_2$ leads to its dissociation into atomic hydrogen.

Finite temperature \textit{ab initio} molecular-dynamics (MD) simulations [2ps time period and time step 1 fs] have also been performed for $Ti_2@\text{graphene} + 8H_2$ and $Ti_2@BN - \text{sheet} + 6H_2$ in the temperature range of 0-300 K and 300-800 K in steps of 100K. Our results show that at 300 K both the systems are stable with all the $H_2$ molecules attached with Ti atoms, while at around 700-800 K, the hydrogen get desorbed from the Ti@graphene and Ti@BN-sheet 62.5 \% and 58.0 \%, respectively. It may be argued that 2ps MD is statistically insufficient to estimate desorption temperature accurately; however the most important outcome of this MD simulation is that hydrogen can be extracted from the system without breaking the Ti-C in case of Ti@graphene and Ti-B or Ti-N bonds in case of Ti@BN-sheet. Further, the time step is 1fs in the temperature range of 100 K, which is sufficient to break the geometry of the structure even from this 2ps MD simulation calculation, if the system is unstable. In order to estimate the gravimetric efficiency of these systems, we have
attempted to fully cover both sides of the respective sheets with Ti atoms. However, due to stronger Ti-Ti interaction, Ti atoms agglomerate to form clusters on the surface. In case of Ti@graphene, the strength of the Ti-C bond depends on the transfer of the electrons from Ti-3d/4s to C-2p resulting in $Ti^+$ ions. With two sided Ti-decoration [Figure 6.2 a, b], the magnitude of charge transfer reduces due to effective sharing of a single C atom by 6 Ti atoms (3 above the surface, 3 below the surface), and consequently the strength of the Ti-C bond decreases at the cost of Ti-Ti clustering on one side of the graphene. The same scenario was found in case of BN-sheet. Based on these results we infer that these kinds of planar structures can serve as potential hydrogen storage material provided we could successfully prevent metal clustering on the planar structure.

Till date, very few attempts have been made to prevent metal clustering on the surface of a nanostructure with the introduction of suitable additional dopant atoms, albeit at the cost of system stability and further reduction in gravimetric efficiency of the system. Another way to achieve this without compromising with system stability as well as gravimetric efficiency is by introducing B and N into the graphene network and thereby forming a B-C-N composite planar nano-structure. In particular, since $BC_4N$ nanotube has already been synthesized as a stable nanotube, we decided to flatten the structure and hence produced $BC_4N$ planar structure.
6.3.2 Chemical Modification Of Graphene: B-C-N Composites

**Ti decoration On $BC_4N$ Sheet**

The ground state structure and properties of Ti decorated (6,6) armchair $BC_4N$ nanotube have already been reported, and their suitability for hydrogen storage studied.\(^9\) Here we have simply opened up this nanotube to realize a planar structure [Figure 6.3 a] by selectively substituting the C-atoms in graphene with B and N in such a way the local structural unit of $BN_3$ and $NB_3$ are linked with a B-N bond [Figure 6.3 b]. Such a $BC_4N$ sheet turns out to be semiconducting with a band-gap of 0.8 eV [Figure 6.4 a]. Moreover, our first-principles MD simulation predicts that the $BC_4N$ sheet has a high thermal stability (up to 900K). $BC_4N$ planar sheet has 7 different kinds of hexagonal sites which have different affinities for binding Ti on the surface [Table 6.1]. To ensure the most preferred location of Ti, we have optimized the Ti on different hexagonal faces of $BC_4N$ sheet and compared the relative stability. Subsequently, we decorate all these preferred hexagons on one side of the $BC_4N$ sheet, and repeat the same decoration with Ti atoms on the opposite side. Interestingly, for the second surface the preferred hexagon is not the same as that of the first surface. Table-1 summarizes our results for the first Ti optimization in the first surface. We see that for the first surface, 1B5C and 6C are the most stable hexagons. When we fill all those hexagons of one side of BC4N sheet with Ti atoms and started searching the preferred hexagons in the opposite side.

![Figure 6.3](image-url)

Figure 6.3: (a) Ball and stick model of pure $BC_4N$ sheet. (b) In ground state configuration of $BC_4N$ sheet, $B - N_3$ and $N - B_3$ is connected by a B-N bond, which gives the structure some extra stability under high temperature.
[second surface], quite expectedly this turns out to be the 2B1N3C face [see Table 2 in S.I.] which is energetically second lowest in Table-1. This is because when all the 6C and 1B5C hexagons are filled with Ti on one side, it is easier for a Ti to go towards the energetically second lowest hexagon (Table -1) of the sheet on the opposite side. In our supercell sheet structure, we have total eighteen 6C, six 1B5C and twelve 2B1N3C hexagons. So all total 36 Ti atoms can be accommodated in this BC4N sheet and we have confirmed that this fully covered structure is stable without any clustering of Ti atoms in either of the side of the sheet. This is an important observation. The reason for such non-clustering is because of the fact that with different hexagonal combination, the probability of Ti occupancy in all the hexagons are not same and consequently Ti can fully transfer its charge to the C atoms on its preferred hexagon to make strong Ti-C bonds as compared to the Ti@graphene or Ti@BN-sheet. To illustrate this fact we have performed Bader Charge Analysis of all the systems, viz., Ti36@graphene, Ti36@BN – sheet and Ti36@BC4N-sheet. The total charge associated with different Ti atoms according to Bader partitioning in Ti36@graphene, Ti36@BN – sheet and Ti36@BC4N-sheet have been shown in Figure 6.5. Since Ti-atom has 4 outermost valence electrons [4s23d2], any value of charge state less (more) than 4 indicates that the Ti becomes cationic (anionic). It is clearly evident from Figure 6.5 that in case of both Ti36@graphene and Ti36@BN – sheet, the charge states of different Ti atoms fluctuate around the value 4. In contrast, for Ti36@BC4N – sheet, the charge states of all the Ti ions are significantly lower (i.e. highly cationic state), indicating strong charge transfer from Ti to the host substrate material (i.e. BC4N-sheet). Such a consistent non-fluctuating charge state of all

Table 6.1: BE value of Ti atom for estimation of the preferred hexagon in one side of the BC4N-sheet. $N_{hex}$ is denoted as the total no of a particular type of hexagon in the BC4N-sheet.

<table>
<thead>
<tr>
<th>Different hexagonal Faces</th>
<th>$N_{hex}$</th>
<th>Binding Energy in eV/Ti atom</th>
</tr>
</thead>
<tbody>
<tr>
<td>6C</td>
<td>18</td>
<td>-2.09</td>
</tr>
<tr>
<td>1B-5C</td>
<td>6</td>
<td>-2.09</td>
</tr>
<tr>
<td>1N-5C</td>
<td>6</td>
<td>-1.73</td>
</tr>
<tr>
<td>2B-1N-3C</td>
<td>12</td>
<td>-1.96</td>
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<tr>
<td>2B-2N-2C</td>
<td>12</td>
<td>-1.34</td>
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<tr>
<td>2N-1B-3C</td>
<td>9</td>
<td>-1.28</td>
</tr>
<tr>
<td>1B-1N-4C</td>
<td>6</td>
<td>-1.76</td>
</tr>
</tbody>
</table>
the Ti ions decorating the \( BC_4N \)-sheet helps preventing metal clustering on the surface, thereby facilitating efficient storage of molecular hydrogen. This reiterates our conjecture that introduction of different chemical orderings of hexagons serves as a panacea to the problem of metal clustering. From a comparison of the partial densities of states of pure \( BC_4N \) and \( Ti@BC_4N \) [Figure 6.4 a and b], we observe that the partially occupied Ti-peak appears in the gap of the semiconducting \( BC_4N \). The lower energy shoulder of the occupied Ti-DOS coincides with a newly formed hump arising out of C-2p [see Figure 6.4 b]. This hybridization between Ti-3d/4s and C-2p leads to a strong Ti-C bond, as compared to the Ti-Ti bond, which in turn plays a crucial role to avoid Ti-clustering on the surface.

Figure 6.4: Electronic Structure of (a) pure \( BC_4N \)-sheet (b) \( Ti@BC_4N \)-sheet (c) \( Ti@BC_4N \)-sheet+4\( H_2 \). (d) Orbital plot of \( Ti@BC_4N \)-sheet.
6.3: Results And Discussion

Figure 6.5: Total charge contained in different Ti atoms with Bader partitioning rule in $Ti_{36}@graphene$, $Ti_{36}@BN - sheet$ and $Ti_{36}@BC_4N - sheet$ respectively after Bader Charge analysis.

Hydrogen Storage In $Ti@BC_4N$-Sheet

Once we circumvent the problem of metal clustering of Ti atoms by different chemical ordering of hexagons, we focus our attention to study the interaction of hydrogen on it. The results reveal that like in case of $Ti@graphene$ or $Ti@BN - sheet$, each Ti atom placed on the $BC_4N$ sheet can adsorb up to 4 $H_2$ molecules irrespective of whether it is on 6C or 1B5C site. The sequential binding energy values of four hydrogen molecules on the Ti adsorbed (placed on 1B5C hexagon) $BC_4N$-sheet are estimated to be 0.55, 0.67, 0.42, 0.45 eV, respectively. Moreover, we note that these BE values are of similar magnitude when Ti is attached on the 6C or 2B1N3C hexagonal faces. It should be emphasized here that all the binding energy values from 1st to 4th hydrogen adsorption lie in the perfect energy window between physisorption and chemisorption. The large unoccupied peak of the Ti-3d/4s above the Fermi energy tells us that Ti atom in $Ti@BC_4N$ is in the cationic state and can accept electrons from other atoms [Figure 6.4 b]. As hydrogen molecules are added one after another, the vacant d-orbital of Ti gets gradually filled up, and as a result of that the unoccupied states of $Ti^+$ (as shown in DOS of $Ti@BC_4N$) becomes
de-populated in $Ti@BC_4N + 4H_2$ at the cost of the H-1s peak to grow [Figure 6.4 c]. This is also apparent from the molecular orbital plot [HOMO-2] of $Ti@BC_4N + 4H_2$ where we can clearly see that we need two unoccupied energy states, one for bonding with hydrogen and the other to bind the metal to the planar sheet [Figure 6.4 d]. We next consider

Figure 6.6: $16H_2$ adsorption in two adjacent hexagons [above and below] of $BC_4N$-sheet for two-sided 4Ti decoration [2 Ti above and 2 Ti below]. (d) Optimized structure of fully Ti decorated $BC_4N$-sheet for 144 $H_2$ adsorption [$Ti_{36}@BC_4N + 144H_2$].

two Ti atoms adsorbed on the consecutive 6C hexagons (or one 6C and the other nearest 1B5C hexagons) on one side and two Ti atoms on the nearest 2B1N3C hexagons on the opposite side. Now the interaction of hydrogen with this system shows that these four Ti atoms can hold total 16 hydrogen molecules as shown in Fig- 6(a). This is quite encouraging as far as molecular $H_2$ adsorption is concerned. Based on these results we estimate that with full Ti coverage, a total 144 $H_2$ molecules can be adsorbed on the $Ti_{36}@BC_4N$-sheet with a gravimetric efficiency of 8.42 wt% of hydrogen. To ascertain this conjecture, we have attempted to relax 144 $H_2$ molecules on the $Ti_{36}@BC_4N$ substrate [Figure 6.6].

Our calculations for the fully relaxed decorated structure indicate that the system should be capable of storing up to 8.42 wt% of hydrogen. After hydrogenation, we have per-

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1As the system consists of 468 atoms, this is computationally very difficult task of having all the 144 $H_2$ molecules to be adsorbed in molecular state into the system after full optimization. Even after final optimization we notice that few $H_2$ molecules are dissociated into 2H atoms, while a most of the 288 H atoms are attached close to the system in molecular form.

2There have been attempts to prepare ultra-thin graphitic sheet of thickness down to few atomic
formed an *ab initio* molecular dynamics (MD) simulation using a Nose thermostat.\(^{24}\) The \(Ti_2@BC_4N\)-sheet + 8\(H_2\) system was heated at 300K, 400K, 500K and 600K and allowed to equilibrate for 2ps at each temperature. The results show that about 75\% hydrogen desorbs from the \(Ti_2@BC_4N\)-sheet in the temperature range 500-600 K. Moreover, it should be mentioned that by carrying out the MD simulation for 2ps duration, it is difficult to achieve a statistically meaningful temperature, however by comparing with our earlier MD results on \(Ti_2@\text{graphene} + 8H_2\) or \(Ti_2@\text{BN} - \text{sheet} + 6H_2\), it suggest that the desorption temperature has been lowered for a B-C-N composite planar structure.

**Summary-1**

Graphene, BN and \(BC_4N\) planar structures, decorated with a 3d-Transition Metal viz. Ti, have been studied and compared from the point of view of efficient storage of molecular hydrogen. First-principles density functional calculations reveal that utilization of both sides of the sheet increases the gravimetric as well as volumetric efficiencies for hydrogen storage, as compared to those in functionalized nanotubes and fullerenes. The main bottleneck, however, is the problem of metal clustering on the surface while going for full coverage. In this work, we have shown how this metal clustering can be avoided in \(BC_4N\) sheet by chemical manipulation, without any other external means such as doping. We conclude from our studies that \(Ti_{30}@BC_4N\)-sheet is a stable structure that can be used for efficient hydrogen storage. Furthermore, this B-C-N nano-composite system is found to desorb \(H_2\) at temperature lower than those in graphene and BN sheet.

### 6.3.3 Vacancy Modulated Graphene Sheet

**TM-Doped Graphene Sheet With C-Vacancy**

The primitive cell of graphene consists of two carbon atoms as basis. We have used 4\(^2\)4 supercell comprising of 32 carbon atoms placed in a triclinic crystal of dimension 9.8\(\text{Å}\times 9.8\text{Å}\times 12\text{Å}\). It is possible to realize experimentally lattice defects in planar nanolayers, which in the limiting case leads to a single layer of graphene. For example, the so-called FLG (few layer graphene) reported by K. S. Novoselov *et. al.* *Science* **306**, 666 (2004) constitutes of a few layers (two, three, or more) of graphene. In view of the experimental shortcomings in producing a single layer planar structure, as considered in our present work, there is a possibility of reduction in gravimetric density in a multilayered planar structure.
structures such as graphene or Boron Nitride sheet. Recently there have been reports on vacancy generated defected graphene sheet. With a single C-vacancy (Vc) introduced in the graphene sheet, the total number of C-atoms in the sheet becomes 31 (Figure 6.7a). We have found that the binding energy (BE) of a single 3d TM dopant atom bonded to this vacancy generated defect lie in the range 4-8 eV which are consistently higher than the corresponding cohesive energies of the respective TM atoms, as shown in Fig. 2. Whereas the BE of the same TM atoms placed on top of the hexagon of a pure graphene sheet without any vacancy have been estimated and are found to lie in the range 1-1.4 eV (Figure 6.8) which are consistently lower than the corresponding cohesive energies of the TM atoms. Thus the increased BE in case of defected graphene sheet leads to prevention of metal clustering on the surface. In view of this, we have tried to do optimum TM coverage of the defected sheet. A 32-atom supercell of the graphene sheet can accommodate up to four such single C atom vacancies separated by a distance of ~6Å from each other. We have also verified from our MD simulation that a C28 sheet with 4 such vacancies remain stable up to a temperature of ~1000K. The formation energy/atom of pure graphene sheet (C32) is $E_{\text{form}} = [E_{\text{total}}(C32) - 32 \times E_{\text{total}}(C)]/32 = 7.91$ eV/atom while that of a single defect modulated Graphene sheet (C31) is $E_{\text{form}} = [E_{\text{total}}(C31) - 31 \times E_{\text{total}}(C)]/31 = 7.75$ eV/atom. These energies are comparable, indicating the stability of the defected sheet.
Figure 6.8: Binding energies of TM atoms located (a) at hexagon-top position of pure graphene sheet and (b) on the defect site of the defected graphene sheet. The cohesive energies of the respective TM atoms have been superposed for the sake of comparison.

Hydrogen Adsorption On TM@C31 For Single Side Doping (SSD)

We now estimate the H-adsorption in different 3d TMs anchored at the vacancy site on single side doped (SSD) defected graphene sheet. It is interesting to see that when a TM atom with less than half-filled (LTH) d-orbitals (let us call it $TM^1$ e.g. Sc, Ti, V) is attached to the defected site of the SSD graphene sheet C31, $H_2$ molecules get adsorbed with BE values ranging from 0.01 eV to 0.08 eV, which is much below the physisorption range. Whereas when a TM atom with half-filled or more than half-filled (MTH) d-orbitals (call it $TM^2$ e.g. Mn, Fe, Co) is doped onto the same site, it adsorbs $H_2$ molecules with much higher BE ranging from 0.5 eV to 0.82 eV. The difference of hydrogen adsorption capacity between the two classes of TM can be understood from the self consistent density of states (DOS) analysis of SSD Fe@C31 and Ti@C31 systems, as discussed later.
Hydrogen Storage Of TMs In Double Side Doped (DSD) Graphene Sheet \([TM^1@C31@TM^2]\)

Based on the above observation, we propose a novel conjecture of decorating the C atom vacancy from both the surfaces of the graphene sheet with a combination two different TM atoms, one with LTH \((TM^1)\) and the other with MTH \((TM^2)\) configurations (Figure 6.7 b). Our calculations reveal that the BE of the TM atoms at the Vc for this kind of double sided doping (DSD) is ideal for the storage of molecular hydrogen. In case of DSD, the BE of the TM atoms to the graphene sheet lies in the range of 4 eV to 5 eV, which eliminates the possibility of metal clustering at the surface. We use the nomenclature \(TM^1@C31@TM^2\) for such a system, for which the detailed adsorption and desorption properties of hydrogen molecules attached are listed in Table 6.3. It is to be noted that when the same TM atom is adsorbed above and below Vc, it does not yield a good hydrogenation. The hydrogen storage capacity of the TM dopants is mainly determined by the valence electronic configuration of the TM atoms in the combination. Table 6.3 shows that amongst all the different \(TM^1 - TM^2\) combinations, Fe-Ti serves...
the best from the perspective of gravimetric efficiency as well as desorption behavior. Fe adsorbs three $H_2$ molecules while Ti adsorbs two $H_2$ molecules. The hydrogenation follows a Kubas type interaction. The $H_2$ molecules retain their molecular structure and do not dissociate to form metal dihydride. The binding energy of the $H_2$ molecules is within 0.2-0.7 eV/$H_2$, which is in the molecular chemisorption range. In a way, a combination of TMs that have tendency to lose electrons to the defected host site, and thereby become cationic, is preferred for hydrogen storage. In Ti@C31@Fe, both Ti and Fe prefer to lose their valence electrons to the carbon atom to attain zero and half-filled valence configuration respectively. It has been observed that Sc@C31@Sc, Sc@C31@Fe, Ti@C31@Fe, Sc@C31@Co, Ti@C31@Co serve as prospective candidates for good hydrogenation. However, from the desorption point of view, Ti@C31@Fe (Table 6.3) turns out to be the best one. For full coverage, it is estimated that 4Ti@C28@4Fe structure can store 5.1 wt% of hydrogen. The desorption temperature of a hydrogen molecule is conventionally defined as the temperature at which the interaction between the $H_2$ molecule and the system becomes negligible. We assume that when the distance between $H_2$ molecule and TM is significantly large (i.e. say more than 3 Å), there is practically no interaction between the TM and $H_2$ molecule. Our 2ps ab initio molecular dynamics calculation with time step of 1 fs and 2000 SCF runs using Nose algorithm reveals that the system is stable at room temperature, while hydrogen desorption starts only at 400K (Table 6.3) and eventually with increase in temperature, other hydrogen molecules gets released from the system.

The interaction between two such TM modulated defected graphene sheet is interesting in view of the fact that there exists good inter-layer bonding between two layers of pure graphene. If TM modulated defected graphene sheet gets close to each other, they continue to remain separated by a distance of $\approx$3.4Å as in case of pure graphite. We have carried out model calculations with two such TM modulated layered structures of graphene sheet and found that the interaction of TM with vacancy i.e. Ti@Vc@Fe is much stronger compared to the interaction between the TMs facing two adjacent layers. It is to be noted that our calculation pertains to a single layer metal functionalized planar graphene sheet which is rather difficult to synthesize, although serious attempts are being made to realize a free standing graphene sheet. Incorporation of more than one layer is expected to affect the gravimetric efficiency.
Table 6.2: Hydrogen adsorption potential of various TM s in few specific combinations of the $TM^1@C31@TM^2$ system has been listed along with the BE and desorption temperature of the adsorbed $H_2$ molecules.

<table>
<thead>
<tr>
<th>system name $TM^1@C31@TM^2$</th>
<th>no. of $H_2$ attached with $TM^1$</th>
<th>no. of $H_2$ attached with $TM^2$</th>
<th>BE of $H_2$ adsorbed to $TM^1$</th>
<th>BE of $H_2$ adsorbed to $TM^2$</th>
<th>desorption of $H_2$ from $TM^1$</th>
<th>desorption of $H_2$ from $TM^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sc@C31@Sc</td>
<td>3</td>
<td>3</td>
<td>-0.18, -0.18, -0.17</td>
<td>-0.17, -0.20, -0.19</td>
<td>200K-300K</td>
<td>200K-300K</td>
</tr>
<tr>
<td>Ti@C31@Ti</td>
<td>2</td>
<td>1</td>
<td>0.14, 0.18</td>
<td>0.08</td>
<td>Below 300K</td>
<td>Below 200K</td>
</tr>
<tr>
<td>V@C31@V</td>
<td>1</td>
<td>1</td>
<td>0.12</td>
<td>0.07</td>
<td>Below 200K</td>
<td>Below 200K</td>
</tr>
<tr>
<td>Mn@C31@Mn</td>
<td>1</td>
<td>2</td>
<td>0.57</td>
<td>0.44, 0.69</td>
<td>600K</td>
<td>500K-750K</td>
</tr>
<tr>
<td>Fe@C31@Fe</td>
<td>1</td>
<td>2</td>
<td>0.32</td>
<td>0.47, 0.59</td>
<td>400K</td>
<td>500K-650K</td>
</tr>
<tr>
<td>Sc@C31@Ti</td>
<td>3</td>
<td>2</td>
<td>0.11, 0.18, 0.16</td>
<td>0.06, 0.08</td>
<td>Below 300K</td>
<td>Below 200K</td>
</tr>
<tr>
<td>Sc@C31@Mn</td>
<td>3</td>
<td>3</td>
<td>0.18, 0.17, 0.19</td>
<td>0.86, 0.67, 0.72</td>
<td>200K-300K</td>
<td>400K-750K</td>
</tr>
<tr>
<td>Sc@C31@Fe</td>
<td>3</td>
<td>3</td>
<td>0.11, 0.14, 0.08</td>
<td>0.38, 0.59, 0.77</td>
<td>Below 300K</td>
<td>500K-850K</td>
</tr>
<tr>
<td>Sc@C31@Co</td>
<td>2</td>
<td>3</td>
<td>0.14, 0.12</td>
<td>0.31, 0.69, 0.87</td>
<td>Below 200K</td>
<td>400K-950K</td>
</tr>
<tr>
<td>Ti@C31@Mn</td>
<td>1</td>
<td>3</td>
<td>0.21</td>
<td>0.42, 0.66, 0.74</td>
<td>300K</td>
<td>500K-800K</td>
</tr>
<tr>
<td>Ti@C31@Fe</td>
<td>2</td>
<td>3</td>
<td>0.29, 0.43</td>
<td>0.28, 0.49, 0.69</td>
<td>400K-500K</td>
<td>400K-700K</td>
</tr>
<tr>
<td>Ti@C31@Co</td>
<td>2</td>
<td>3</td>
<td>0.18, 0.21</td>
<td>0.19, 0.45, 0.81</td>
<td>200K-300K</td>
<td>300K-900K</td>
</tr>
<tr>
<td>V@C31@Mn</td>
<td>1</td>
<td>3</td>
<td>0.04</td>
<td>0.53, 0.68, 0.74</td>
<td>Below 200K</td>
<td>500K-800K</td>
</tr>
</tbody>
</table>
Figure 6.10: Total and partial (site-projected) densities of states (DOS) plots for Ti/Fe decorated defected graphene sheet for the following cases: (a) three C-atoms around the defect site, before and after Ti adsorption (b) same as (a) for Fe adsorption (c) Ti@C31 SSD after hydrogenation (d) Fe@C31 SSD after hydrogenation (e) Ti@C31@Fe DSD before hydrogenation (f) Ti@C31@Fe DSD after hydrogenation. In all the DOS plots 0 marks the Fermi level \( E_F \). All the unoccupied state lies above \( E_F \) while the occupied states lies below it. See text for details.
It is worth mentioning here that FeTiHx alloys constitute a family of bulk hydride that has been well studied both experimentally and using first-principles calculation. However, a simple Ti-Fe hetero-dimer binds hydrogen in atomic form, with binding energy of -1.8eV for Fe-H and -1.6eV for Ti-H. These fall in atomic chemisorption range, and hence it is not suitable for hydrogen storage. The interesting finding from our present study is that on putting Fe and Ti on defected graphene sheet, desorption kinetics is substantially improved along with other desirable features for hydrogen storage.

**Electronic Structure And Charge Transfer For SSD [TM@C31] And DSD [TM^1@C31@TM^2]**

From our Hirshfeld charge analysis, we observe that in a pure graphene sheet [C32], all the C atoms are charge neutral and have a homogeneous charge state of zero. However, on removing one C atom and thereby creating a defect (vacancy) in the graphene sheet, the three C atoms neighboring the defect site, call it C1, C2 and C3 (Figure 6.7 a), attain a charge state of +0.005 each (Table ??). Thereafter, when the TM atoms are inserted at the defect site, they lose their valence electrons to the C atoms and thereby become cationic (Ti+ and Fe+). For DSD with Ti and Fe, the net charge state of Ti becomes +0.5 while that of Fe becomes +0.18 (Table 2). Now when the hydrogen molecules are introduced, they lose electrons to the TM atoms and the C-atoms at the defect (via TMs). The TM atoms gain electron and attain a charge state of 0.27 and ≈ 0 for Ti and Fe respectively. Most of the unoccupied Fe orbitals take part in hydrogen bonding, while only a part of the unoccupied Ti orbitals contribute. As a result of this, Ti adsorbs two H2 molecules by gaining some electronic charge but still shows a remnant charge state of +0.275.

We have plotted the self consistent total DOS of three C atoms neighboring the defect of C31 (3C@hole) and compared it with the same after Ti/Fe adsorption (Figure 6.10 a and b) at the defect site (i.e. Ti@C31 and Fe@C31). It can be observed that in both cases, there are large unoccupied peaks of the metal atoms (red color peaks for Ti and blue color peaks for Fe) appearing at the cost of the disappearance of the unoccupied peak (black color peak) of 3C@hole of pure C31. This implies electron transfer from metal to the C atoms neighboring the hole in case of SSD. After full H2 adsorption in SSD Ti@C31 (Figure 6.10 c), the unoccupied peaks of Ti is still retained, while in case of SSD Fe@C31
Table 6.3: Hirshfeld charge distribution analysis of various TM decorated defected graphene structures. Negative sign implies electrons gained while positive implies to electrons lost by the atom (unit of charge is electron)

<table>
<thead>
<tr>
<th>System</th>
<th>C1</th>
<th>C2</th>
<th>C3</th>
<th>Ti</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>C31</td>
<td>+ 0.005</td>
<td>+ 0.005</td>
<td>+ 0.005</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Fe @C31</td>
<td>- 0.050</td>
<td>- 0.050</td>
<td>- 0.050</td>
<td>-</td>
<td>+ 0.240</td>
</tr>
<tr>
<td>Ti@C31</td>
<td>- 0.128</td>
<td>- 0.128</td>
<td>- 0.128</td>
<td>+ 0.530</td>
<td>-</td>
</tr>
<tr>
<td>Ti@C31@Fe</td>
<td>- 0.126</td>
<td>- 0.150</td>
<td>- 0.126</td>
<td>+ 0.500</td>
<td>+ 0.180</td>
</tr>
<tr>
<td>Ti@C31@Fe+5H₂</td>
<td>- 0.110</td>
<td>- 0.120</td>
<td>- 0.110</td>
<td>+ 0.270</td>
<td>- 0.006</td>
</tr>
</tbody>
</table>

The unoccupied peak nearly vanishes (Figure 6.10 d). The point to be noted here is that the presence of unoccupied level does not necessarily suggest the possibility of further electron transfer and hence H₂ adsorption. Coming to DSD Ti@C31@Fe (Figure 6.10 e), we observe that the unoccupied Ti-peak increases (compared to SSD Ti@C31) and shifts closer to the Fermi level, while the unoccupied Fe-peak decreases (compared to SSD Fe@C31), which desirably improves the provision of Ti in H₂ (than SSD Ti@C31) adsorption and decreases the same for Fe (than SSD Fe@C31). After H₂ adsorption (Figure 6.10 f), electron gets transferred from H₂ to the unoccupied Fe and Ti levels.

From the charge density plots of Ti@C31@Fe (Figure 6.11), we observe that Fe is

Figure 6.11: The charge density contour plots [in unit of electrons/(a.u.)³] for the DSD configuration of Ti@C31@Fe in two orthogonal planes: (a) passing through the graphene sheet; (b) passing through Ti and Fe perpendicular to the graphene sheet.
surrounded by a dense charge cloud passing through it and the dimpled carbon sheet. However, Ti is having relatively much weaker charge cloud around it (Figure 6.11 b). Comparing the cationic states of $Ti^+$ and $Fe^+$ in SSD versus DSD (Table ??), we observe that the differential change in Ti (0.52 to 0.50) is much less compared to the Fe (0.24 to 0.18). This indicates $Fe^+$ becoming less cationic in DSD configuration, which gets reflected in Figure 6.11b, by the dense electron cloud surrounding the Fe atom. It can be concluded that in DSD defected sheet with Ti and Fe, Ti loses most of its charge while Fe loses a part of its charge to the neighboring C atoms.

6.3.4 Summary-2

In summary, we have implemented DFT based first principles calculation to investigate the hydrogenation properties of defected graphene sheet modulated by 3d-TM atoms. The TM dopant atoms adsorbed above and below the defect site, were found to have an extra bonding to the sheet, which led to elimination of the clustering of the TM dopants. We observe that when the combination is composed of a 3d $TM^1$ of valence electron configuration less than half filled and another 3d $TM^2$ of valence electron configuration more than the half filled, an optimum wt % at room temperature can be realized. Amongst all possible $TM^1$ and $TM^2$ that we have tried to decorate the defected graphene sheet, Fe-Ti qualifies as the best possible combination satisfying both the criteria of a good gravimetric efficiency of hydrogen storage along with a favorable desorption kinetics. The fully decorated 4Ti@C28@4Fe structure was found to retain up to $\approx$5.1 wt % of H2 at room temperature. Hydrogen desorption started only at 400K, while by 600K most of the $H_2$ molecules were released without breaking the structure resulting in an energetically reversible kinetics.

6.4 Conclusion

We have investigated hydrogen storage in metal decorated graphene like planar structures by means of density functional calculations. We found that metal-clustering on the surface of the planar structure is the biggest challenge. Moreover, on a homogeneous planar sheet like graphene or BN sheet, the hydrogen desorption temperature is too high to realize those in practical usage. In order to circumvent this, we have prescribed here two specific
conjectures, i.e.; either by chemically modifying the graphene sheet as summarized in summary-1 or by introducing defects in the homogeneous carbon network as summarized in summary-2.
Bibliography


