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Effects of charging and electric field on graphene functionalized with titanium

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Abstract
Titanium atoms are adsorbed to graphene with a significant binding energy and render diverse
functionalities to it. Carrying out first-principles calculations, we investigated the effects of
charging and static electric field on the physical and chemical properties of graphene covered
by Ti adatoms. When uniformly Ti covered graphene is charged positively, its
antiferromagnetic ground state changes to ferromagnetic metal and attains a permanent
magnetic moment. Static electric field applied perpendicularly causes charge transfer between
Ti and graphene, and can induce metal–insulator transition. While each Ti adatom adsorbed to
graphene atom can hold four hydrogen molecules with a weak binding, these molecules can be
released by charging or applying electric field perpendicularly. Hence, it is demonstrated that
charging and applied static electric field induce quasi-continuous and side specific
modifications in the charge distribution and potential energy of adatoms absorbed to
single-layer nanostructures, resulting in fundamentally crucial effects on their physical and
chemical properties.

(Some figures may appear in colour only in the online journal)

1. Introduction

Titanium, a light transition metal atom with unfilled 3d shell, is among the few kinds of atoms which make rather strong bonds to graphene. Therefore, the interaction of Ti with graphene and carbon nanotubes has been a subject of active study [1–4]. In nanoelectronic applications, a conductive Ti film on graphene serves as a medium or interface for the contact of other materials to graphene [5–7]. When adsorbed, Ti atoms can render various functionalities to graphene, such as metallicity and magnetic properties. Additionally, owing to its specific electronic configuration and interaction with carbon atoms, Ti is playing an important role in the hydrogen economy aiming at a renewable energy source [8]. Carbon based materials complexed with Ti adatoms have been shown to form a recyclable medium for high capacity hydrogen storage with proper kinetics near room temperature [2, 9–15]. Other specific atoms like Li and Ca adsorbed to graphene

can also yield high storage capacity [16, 17]. For example, it was shown that in the double-sided (2×2) Ti coverage of a graphene layer each Ti adatom can hold four H_2 molecules and thus this complex attains 7.8 wt% storage capacity [2]. The Dewar–Kubas interaction [18] between Ti/graphene complex and H_2 molecules is weak and enables the release of stored hydrogens near or above the room temperature.

In this paper we showed that physical and chemical properties of graphene functionalized with Ti adatoms can be modified either by charging or by applying a static electric field. Graphene, which becomes an antiferromagnetic metal when uniformly covered by Ti atoms undergoes a metal–insulator transition when a static electric field is applied perpendicularly. The magnetic ground state of Ti/graphene complex can be changed by charging. Both charging and applied electric field can change the interaction between Ti and H_2 molecules, which are weakly bound to Ti

adatoms. For specific values of excess electronic charge and electric field, H_2 molecules are released. While Ti/graphene complex is chosen as a prototype system, charging and perpendicular electric field induce quasi-continuous and side specific modifications in various single-layer nanostructures with fundamentally crucial effects.

2. Methodology

Our predictions are obtained by performing first-principles calculations within density functional theory [26, 27] using a linear combination of numerical atomic orbitals (LCNAO). We used the double ζ polarized basis set and the exchange–correlation functional is approximated by the Perdew, Burke and Ernzerhof functional [28] within the generalized gradient approximation. A 150 Ryd mesh cutoff is chosen and the self-consistent field calculations are performed with a mixing rate of 0.1. The Brillouin zone is sampled with a Monkhorst–Pack mesh [29] with $(5 \times 5 \times 1)$ **k**-points, whereas we use $(45 \times 45 \times 1)$ **k**-points in specific systems. Core electrons are replaced by norm conserving, nonlocal Troullier–Martins pseudopotentials [30]. Geometry optimizations are performed by the conjugate gradient method by allowing all the atomic positions and lattice constants to vary. The periodic boundary conditions (PBC) are used within the supercell geometry and the vacuum spacing between graphene layers in adjacent supercells is taken as 15 Å. The convergence for energy is chosen as 10^{-5} eV between two consecutive steps. In atomic relaxations, the total energy is minimized until the forces on atoms are smaller than 0.04 eV Å^{-1}. Numerical calculations are carried out using the SIESTA package [31, 32].

The binding energy E_b is calculated from the expression $E_b = E_T[\text{graphene}] + E_T[\text{Ti}] - E_T[\text{Ti/graphene}]$, in terms of the total energies of bare graphene and of free Ti atoms, and the structure optimized total energy of one Ti adatom adsorbed to each graphene supercell. All total energies are calculated in the same (4×4) supercell. $E_b > 0$ indicates a bonding structure.

3. Results

In the present study using PBC, a single Ti atom adsorbed to graphene is treated within the supercell geometry, whereby Ti–Ti coupling is minimized. The periodically repeating structures corresponding to one Ti atom adsorbed at different sites of the (4×4) supercell are optimized. The binding site of the Ti adatom, which is favorable energetically, is then determined as the one with minimum total energy. According to present calculations, a single Ti atom is adsorbed to the hollow site of graphene (i.e. above the center of hexagon) with a binding energy of $E_b = 0.9$ eV and with a magnetic moment of 3.52 μ_B. The height of the adsorbed Ti atom from the graphene plane is 2.37 Å. The minimum energy barrier to the migration of a single Ti adatom is ~0.30 eV and occurs along the direction from the hollow to the top site (i.e. on top of carbon atoms). While these values are calculated by adsorbing one Ti atom to each (4×4) supercell, the

ground state is antiferromagnetic for four Ti atoms uniformly adsorbed to each (4×4) supercell, whereby the magnetic coupling between adsorbed Ti atoms is allowed. Under these circumstances, the antiferromagnetic ground state is 90 meV more favorable energetically compared to the ferromagnetic state.

Having briefly discussed the interaction between the single Ti atom and graphene and the resulting bonding, we now examine the effects of charging and static electric field. Normally, periodic boundary conditions (PBC) realized by repeating charged supercells have a divergent electric potential energy. The resulting drawbacks and limitations have been the subject matter of several studies in the past. Additional background charge of opposite polarity has been added to neutralize the excess charge and hence to achieve the convergence of the electronic potential [19–21].

Another serious drawback is the dependence on the vacuum spacing between periodically repeating graphene layers. When charged negatively or subjected to a perpendicular electric field and treated using the plane wave basis set within PBC, the properties of systems such as Ti adsorbed on graphene can exhibit a spurious dependence on the vacuum spacing. This artifact arises due to the dipping of the electronic potential below the Fermi level at the middle of the vacuum spacing, which is larger than a value depending on Q or $\vec{E}$. Eventually, localized states are accommodated by the electrons from the Ti/graphene complex causing the electrons to spill into the vacuum. Such an artifact cannot arise for an actual situation, namely single Ti/graphene, which does not repeat periodically. It has been shown that one can hinder the vacuum spilling even at high charging or electric field by using localized basis set [22, 23] with PBC. Hence, this spurious dependence on the vacuum spacing will not occur in the present calculations using LCNAO. Throughout the paper, the positive $Q > 0$ (negative $Q < 0$) charging indicates depleted–removed (added–excess) electrons per (super)cell; $Q = 0$ corresponds to the neutral system. For bare graphene, it is possible to simulate electron and hole doping via adding or removing electrons from the system [23–25].

Similarly, electric field applied perpendicularly to the graphene, $\vec{E}$, is specified as positive if it is along the z-direction (or it is pointing towards the Ti adatom); otherwise $\vec{E}$ is specified as negative if it is in the opposite direction. Applied $\vec{E} > 0$ induces electronic charge transfer from the Ti adatom to graphene or vice versa for $\vec{E} < 0$. Since Ti atoms are situated 2.37 Å above the graphene plane, the static electric field applied perpendicularly to graphene gives rise to a potential difference, in which the electronic potential energy along the z-direction is strongly modified. Eventually, the charge distribution is modified by maintaining the charge neutrality of the whole system. Hence, specific physical and chemical properties of the Ti/graphene system undergo various changes.

We now start to examine the effect of charging and electric field on the properties of the single Ti adatom, which is treated via the (4×4) graphene supercell with a Ti atom adsorbed at the hollow site. The side and top views of the atomic configuration are shown in figures 1(a) and
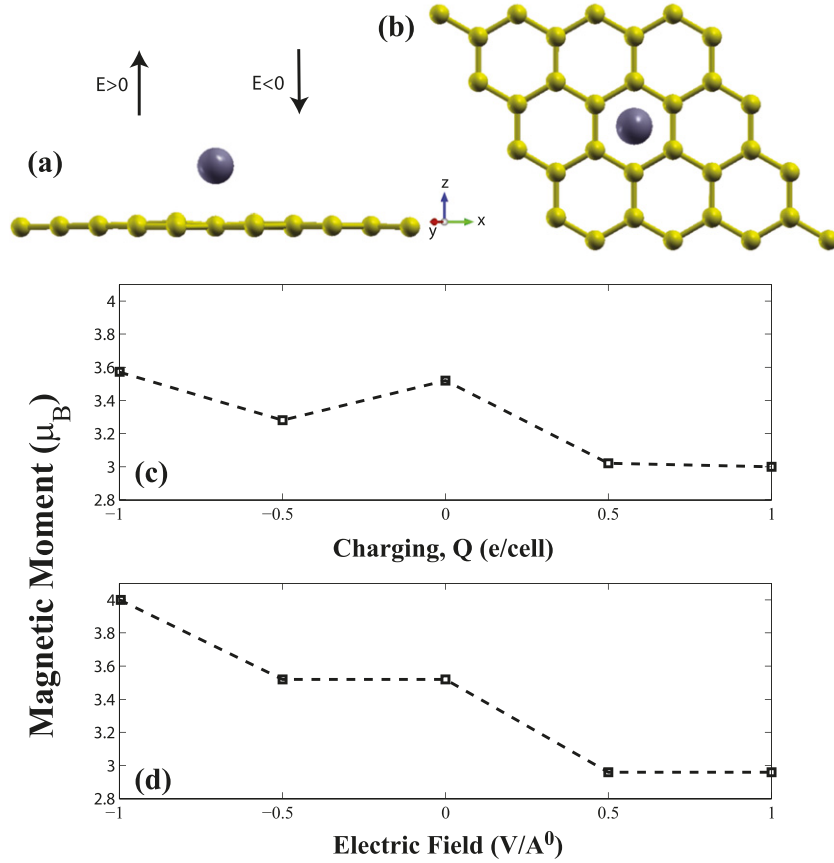
Figure 1. Variations of the calculated magnetic moment of the single Ti atom adsorbed to each (4 × 4) supercell of graphene with charging and applied perpendicular electric field. (a) Side view of the atomic configuration. Green/small, violet/large balls represent carbon and Ti atoms, respectively. (b) Top view. (c) Magnetic moment μ calculated as a function of charging Q. $Q > 0$ ($Q < 0$) corresponds to removed (excess) electronic charge. (d) Variation of the magnetic moment μ with the magnitude and direction of the static electric field, $\vec{E}$, applied perpendicularly. $\vec{E} > 0$ ($\vec{E} < 0$) is parallel (antiparallel) to the z-axis.

(b). In figure 1(c) we show the calculated variation of the magnetic moment with charging in the range of -1 e/cell < Q < $+1$ e/cell. The magnetic moment of the ferromagnetic state decreases to $\mu = 3$ μ_B/cell when 0.5–1.0 electrons are removed from the (4 × 4) supercell. Under excess electronic charge a reverse situation is observed, where the magnetic moment first decreases slightly for $Q = -0.5$ e/cell, then increases to $\mu = 3.6$ μ_B/cell for $Q = -1$ e/cell. The variation of μ is due to the accommodation of different electronic charges of Ti 3d states for different values of Q. A similar effect can be generated also by the static electric field as shown in figure 1(d). The magnetic moment decreases for the electric field pointing to the Ti adatom ($\vec{E} > 0$), since part of the equilibrium electronic charge on Ti is donated to the graphene, inducing charge depletion. The reverse situation results in an increase of the magnetic moment.

Next we treat the physical properties of a Ti/graphene complex consisting of four Ti atoms uniformly adsorbed to each (4 × 4) supercell. In figure 2 we present interesting sequences of transitions of electronic and magnetic properties induced by charging. As shown in figure 2(b) the Ti/graphene complex is an antiferromagnetic metal for $Q = 0$ and $\vec{E} = 0$. When a single electron is added to the system (i.e. $Q < 0$), the binding is weakened and the electronic charge on the Ti

adatom calculated by Mulliken analysis increases and the case is vice versa for $Q > 0$. Ti/graphene complex continues to be antiferromagnetic metal even if one electron is added to each supercell (corresponding to $Q = -1$ e/cell) as shown in figure 2(c). However, this complex changes to a ferromagnetic metal with $\mu = 0.198$ μ_B once one electron is removed (corresponding to $Q = 1$ e per (4 × 4) supercell) as shown in figure 2(c).

The effects of static electric field on the electronic and magnetic properties of the Ti/graphene complex are even more remarkable. The variation of the charge on the Ti adatom and resulting changes in the electronic structure of Ti/graphene complex are shown in figure 3 as a function of applied $\vec{E}$. The charge on the Ti adatom for a given $\vec{E}$ is calculated using Mulliken analysis. For positive values of $\vec{E}$ along the z-direction, the charge on the Ti adatom decreases with increasing magnitude of the electric field and the Ti/graphene complex remains metallic. In the reverse situation, namely for the negative electric field pointing downward, the charge on the Ti adatom increases with increasing magnitude of $\vec{E}$. The excess electronic charge on the Ti adatom is transferred from nearby carbon atoms of graphene and raises the electronic potential at the Ti atoms. Accordingly, the energies of the 3d orbitals of Ti raise in energy. As the charge on Ti increases
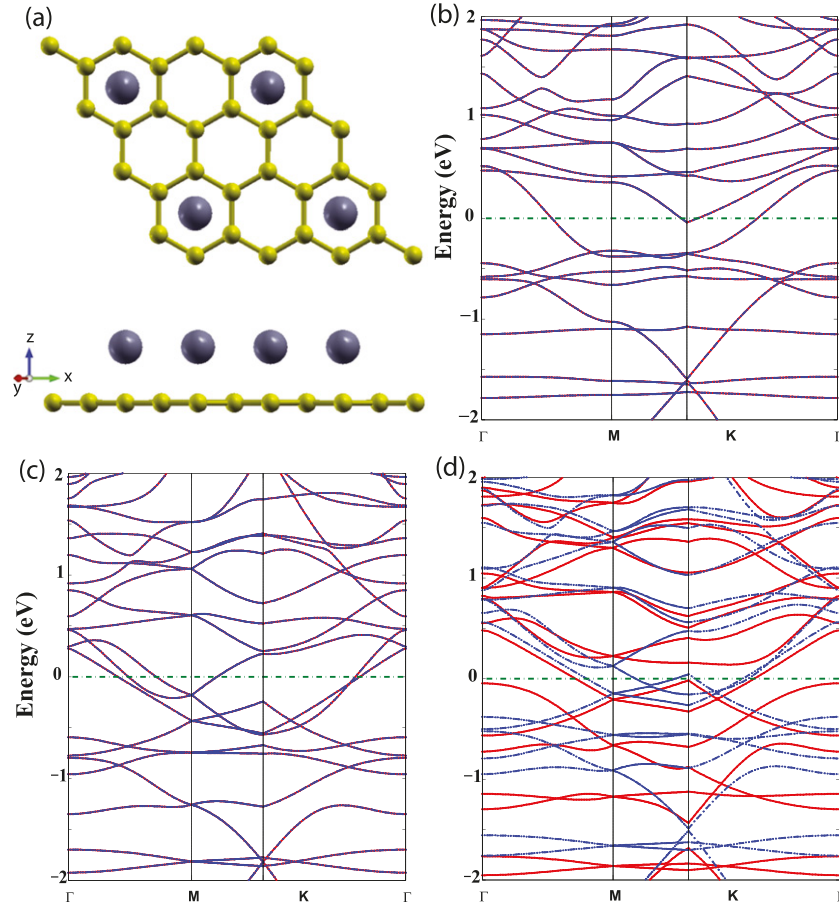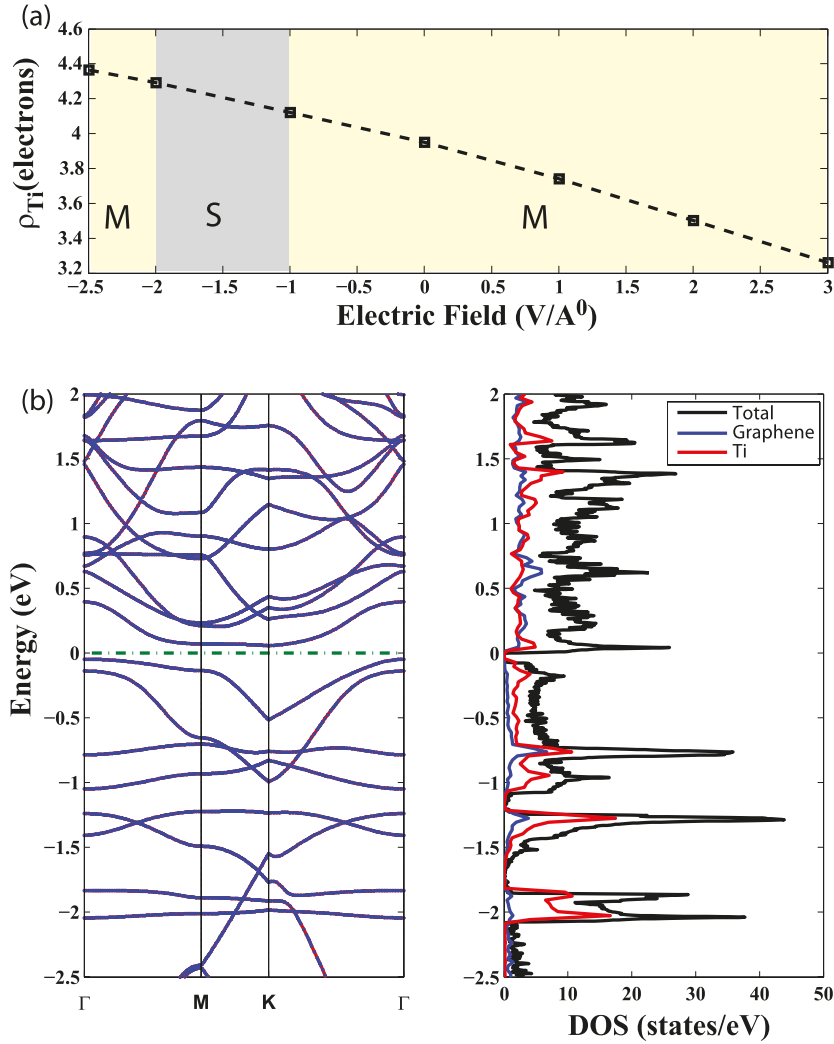
Figure 2. Changes in the electronic band structure of Ti/graphene complex induced by charging. (a) Top and side views of Ti/graphene complex consisting of four Ti atoms uniformly adsorbed to each (4×4) supercell. Green/small, violet/large balls represent carbon and Ti atoms, respectively. (b) The band structure of Ti/graphene complex described in (a) for $Q = 0$. The semimetallic bands of bare graphene changed to antiferromagnetic metallic bands upon the coverage of Ti atoms. (c) The same system as in (a), but one electron is added to each (4×4) supercell of Ti/graphene complex. Bands continue to be antiferromagnetic metal. (d) The bands changed to become ferromagnetic metal upon removal of one electron from each (4×4) supercell of Ti/graphene complex. Red and blue bands correspond to spin up and spin down states, respectively.

an indirect energy band gap is opened for -2 V Å$^{-1} < \vec{E} < -1$ V Å^{-1}. The band gap $E_g = 0.1$ eV for $\vec{E} = -1$ V Å^{-1}; it increases to 0.2 eV for $\vec{E} = -1.5$ eV, but diminishes for $\vec{E} = -2$ V Å^{-1}. The states at the edges of the valence and conduction band originate mainly from Ti. For other values of $\vec{E}$, the Ti/graphene complex is a metal with conduction bands crossing the Fermi level. This is an important result showing that a metal–insulator transition can be induced by an electric field applied perpendicular to the Ti/graphene plane. Interestingly, despite all the effects of the applied electric field between $\vec{E} = -2.5$ and $+2.5$ V Å^{-1} the magnetic state of Ti/graphene remained antiferromagnetic. It should be noted that a perpendicular field breaks the symmetry also between top and bottom sides of bare graphene leading to interesting implications. For example, the symmetry whereby the work function is normally equal at the two surfaces of graphene is destroyed by the perpendicular field. In the presence of adatoms like Ti, the energies of states associated with adatoms can be shifted upwards or downwards relative to the energies of graphene depending on the direction of the field.

This way the couplings of adatom states with graphene are changed, tuning the electronic state. These features associated with perpendicular field can be utilized for various device applications.

Finally, let us consider the effect of charging and applied electric field on the chemical properties of the Ti/graphene complex and how the bindings with H$_2$ molecules are affected. The interaction between a Ti adatom on graphene and H$_2$ molecules is very special and originates from the complex charge donation between carbon and Ti 3d orbitals and back donation upon H$_2$ adsorption [18]. These complex rearrangements of charges give rise to weak chemical binding between the Ti/graphene complex and H$_2$ molecules, so H$_2$ molecules attached to Ti adatoms can be released near/above room temperature. Due to induced charge rearrangements, each Ti adatom holding four H$_2$ molecules is affected by charging and by applied $\vec{E}$. The configurations calculated for various Q and $\vec{E}$ values are shown in figures 4(b)–(f). For positively charged Ti/graphene with $Q = 1.0$ e/cell, H$_2$ molecules remain bound to Ti adatoms. One of the bound H$_2$ molecules is desorbed under excess electronic charge of $Q =$

Figure 3. Effects of static electric field, $\vec{E}$, on the Ti/graphene complex consisting of four Ti atoms uniformly adsorbed to each (4×4) supercell of graphene. (a) Variation of the charge on the Ti adatom calculated with Mulliken analysis versus $\vec{E}$. Positive values of the field correspond to $\vec{E} \parallel z$-direction. The character of the Ti/graphene complex is changing from metal (M) to semiconductor (S) and from semiconductor to metal again with varying values and direction of applied $\vec{E}$. (b) The energy band structure of the Ti/graphene having a band gap for $\vec{E} = -1.0$ V Å^{-1} and corresponding total and partial density of states (DOS). The zero of energy is set to the Fermi level.

-2.0 e/cell. The applied electric field parallel to the z-axis leads to transfer of electrons from Ti to graphene and results in an effect similar to excess charge causing desorption. Only one H_2 molecule can desorb under $\vec{E} = +1$ V Å^{-1}. However, when the applied electric field exceeds $+1.5$ V Å^{-1}, Ti as well as H_2 molecules are desorbed from graphene.

A perpendicular field in the range of $\vec{E} = 1.0 - 2.0$ V Å^{-1} is high and hence one can anticipate that it can cause damage to the graphene layer. In the previous theoretical and experimental studies electric fields are used to modify graphene + adatom complexes which are in the same range or higher than the field in the present work [33–35]. For example, it was shown that electric field of $\vec{E} = 10$–20 V Å^{-1} applied in terms of Gaussian shaped pulses by femtosecond lasers can deoxidize graphene oxide without damaging the graphene layer [33]. Also, a similar setup is used in the exfoliation of graphite using a femtosecond laser. The application of field for

a very short time hinders the generation of non-equilibrium phonons, causing damage through heating. For the same reason carbon nanotubes transporting very high current do not burn easily. In a recent theoretical study, electric field of $\vec{E} = 1.0$ V Å^{-1} is used for the dissociative adsorption of hydrogen molecules on graphene [34]. Electric fields in similar ranges are used to create currents for the reduction of graphene oxide [35]. Also, high local fields or currents can be applied through the tip of a scanning probe microscope without damage to the substrate.

4. Conclusions

In conclusion, graphene and other carbon based nanostructures complexed by Ti adatoms are potential materials suitable for diverse applications. For example, depending on the Ti coverage, semimetallic graphene can become a metal and attain magnetic properties. In this paper we showed that
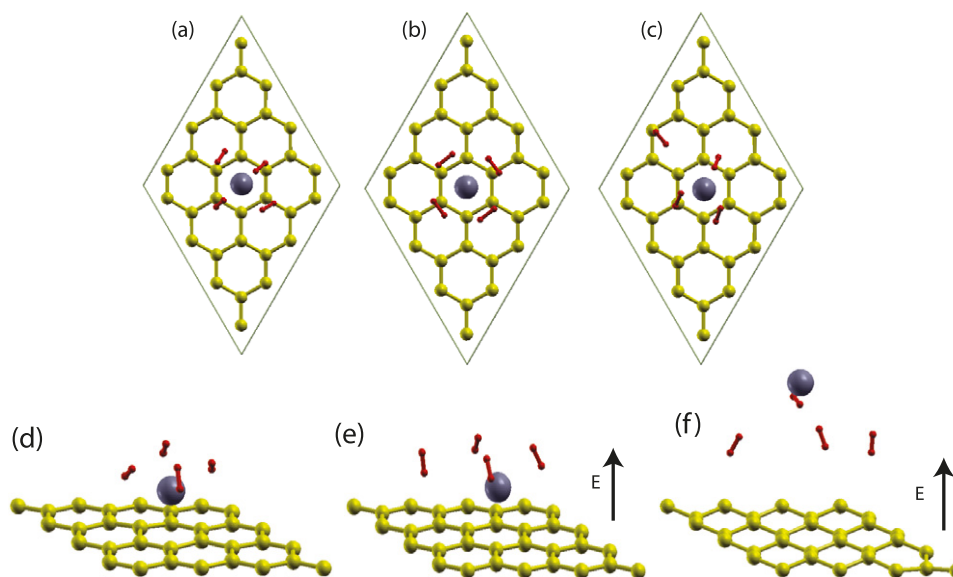
Figure 4. (a) Top view of the binding configuration of four H_2 molecules weakly bound to a Ti adatom on graphene for $Q = 0$. (b) The configuration of four H_2 molecules around a Ti adatom when one electron is removed from the system, (i.e. $Q = 1$ e/cell). All H_2 molecules remained bound to the Ti adatom. (c) The configuration corresponding to $Q = -2$ e/cell shows that one H_2 molecule is released. (d) Side view of (a) corresponding to $Q = 0$, and $\vec{E} = 0$. (e) $Q = 0$, but $\vec{E} = 1$ V Å^{-1}, where a single H_2 is released. (f) $Q = 0$, but $\vec{E} = 2$ V Å^{-1}, where Ti as well as H_2 molecules are desorbed. Green/small, violet/large balls and red dumbbells represent, respectively, carbon, Ti atoms and H_2 molecules. Calculations are performed on the (4×4) graphene supercell.

further to these functionalities achieved through Ti adsorption, Ti/graphene complexes can acquire additional functionalities upon charging or exerting a static perpendicular electric field. In view of their quasi-continuously varying values and directions, these external effects provide a number of options for tuning the physical and chemical properties. Not only Ti, but also other 3d transition metal atoms adsorbed to graphene and to other carbon based materials are expected to be affected by these external effects. As for the questions of how these external effects are exerted on a Ti/graphene complex, we note that local charging via an STM tip, parallel gate voltage or graphene placed in a quasi-homogeneous electric field can be used to produce similar effects.

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Acknowledgments

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