Charge doping induced phase transitions in hydrogenated and fluorinated graphene

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Abstract

We show that charge doping can induce transitions between three distinct adsorbate phases in hydrogenated and fluorinated graphene. By combining ab initio, approximate density functional theory and tight binding calculations we identify a transition from islands of C₈H₂ and C₈F₂ to random adsorbate distributions around a doping level of ±0.05 e/C-atom. Furthermore, in situations with random adsorbate coverage, charge doping is shown to trigger an ordering transition where the sublattice symmetry is spontaneously broken when the doping level exceeds the adsorbate concentration. Rehybridization and lattice distortion energies make graphene which is covalently functionalized from one side only most susceptible to these two kinds of phase transitions. The energy gains associated with the clustering and ordering transitions exceed room temperature thermal energies.

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Low dimensional materials provide unique opportunities to manipulate their properties by chemical means. Graphene in particular is a zero band gap Dirac material which can be turned into a wide band gap insulator by hydrogenation\cite{1} or fluorination\cite{2,3}. Partially functionalized graphene offers a unique chance to tune optical and electronic transport properties between disordered Dirac material and insulating characteristics by varying the adsorbate concentration\cite{4} and the real space arrangement of the adsorbates\cite{3,4,5,6}. Similarly, electron correlation phenomena including magnetism\cite{9} and superconductivity\cite{10} can be expected to be most sensitive to adsorption patterns in chemically functionalized graphene. It is thus crucial to be able to tune real space arrangements of adsorbates for on-demand functionalization of graphene.

Interestingly, field theoretical studies suggested various structural phase transitions in dilute graphene adsorbate systems including instabilities towards Kekulé and sublattice symmetry broken patterns\cite{6,11,12,13,14}. It remained, however, unclear which of these transitions could be realized experimentally, particularly in situations with sizable adsorbate coverage (\(\sim 5\%\) to 20\%). In this letter, we show that adsorption patterns of hydrogen and fluorine atoms on graphene can be largely manipulated by charge doping. By combining ab initio density functional theory (DFT), the density functional tight binding scheme (DFTB) and tight binding calculations we find that charge doping can induce transitions between phases with homogeneous adsorbate distribution over the entire sample and separation into clean graphene and areas with maximum adsorbate coverage (Fig. 1). We furthermore find that in case of homogeneous adsorbate distribution, charge doping can trigger an ordering transition where the sublattice symmetry is spontaneously broken.

In general, the interplay of several mechanisms determines the stability of graphene derivatives: First, covalent adsorbates like H or F lift their C bonding partners out of the graphene plane and rehybridize them from \(sp^2\) to \(sp^3\). There are furthermore electronic energies associated with bond formation as well as electronically mediated interactions between adsorbates\cite{6,11,12,13,14,15}. We show that rehybridization and lattice distortion energies make graphene which is covalently functionalized from one side only most susceptible to the above mentioned phase transitions.

To study the influence of electron and hole doping on adsorption patterns of hydrogen and fluorine on graphene, we have investigated their stability by quantum mechanical simulations.
The dependence of adsorption energies $E_{\text{ads}}$ on adsorption patterns and charge doping has been calculated according to

$$E_{\text{ads}} = \frac{E_{G:X} - E_G}{n_X} - \frac{1}{2}E_{X_2}. \quad (1)$$

Here, $E_{G:X}$ is the energy of the doped graphene sheet with the adsorbed atoms X (X=H or F), $E_G$ is the energy of the doped graphene sheet of the same size without the adsorbates, $n_X$ is the number of adatoms, and $E_{X_2}$ is the energy of the adatom dimer. For all random adsorbate distributions considered below, each $E_{\text{ads}}$ presents an average over 20 configurations.

The quantum mechanical calculations for obtaining the total energies were carried out using the DFTB+ program package\textsuperscript{17} (version 1.2.2) with the parametrization sets mio-1-1\textsuperscript{18} for H-adsorption and pbc-0-3\textsuperscript{19} for F-adsorption. The doping has been simulated by employing the virtual crystal approach (VCA)\textsuperscript{20,21}. The various adsorption configurations have been relaxed until the forces on the atoms were smaller than $10^{-4}$ Hartree/Bohr. In order to check the reliability of the results, selected configurations have been recalculated using ab initio all electron DFT calculations as implemented in the FHI-AIMS code\textsuperscript{22} (version 081912) using the provided default tight basis sets for the atoms and the PBE exchange correlation functional. Here, the structures were relaxed using similar force criteria as used in DFTB+. For the k-point sampling we have used 4x4x1 and 2x2x1 Monkhorst-Pack meshes in the DFTB+ and FHI-AIMS calculations, respectively.

As shown in the supplementary material, the variations of the adsorption energies between different patterns as obtained from DFTB are very close to the DFT results for hydrogen adsorption. In case of fluorine adsorption DFTB generally overestimates the penalty for building sublattice polarized configurations with respect to sublattice symmetric configurations by approx. 0.2 eV/atom. However, this does not change our statements about the doping dependent phase transition between the sublattice polarized and sublattice unpolarized adsorption patterns qualitatively. These transitions should indeed occur at lower doping concentrations than predicted by the DFTB results. The absolute values of the adsorption energies are energetically too much favorable for H-adsorption and not favorable enough for F-adsorption with DFTB with respect to our ab initio DFT reference calculations. However, energy differences between
all patterns as well as trends with doping are reasonably described by our DFTB simulations. (See the supplementary material for a detailed comparison of the DFTB and DFT results.)

First, we consider the adsorption of H and F on one side of graphene. Previous DFT calculations showed that the C_8X_2-structures (Fig. 1C shaded area) correspond to the upper concentration limit for H/F single side adsorption on graphene. We thus compare E_{ads} for the ordered C_8X_2 structures to graphene with 10% adsorbed hydrogen and fluorine adatoms in fully random (X[1:1], Fig. 1A) and fully sublattice polarized but otherwise random (X[1:0], Fig. 1B) adsorption patterns in Fig. 2. At zero doping the C_8X_2 structures are by several 100 meV per atom more favorable than the X[1:1] or X[1:0] structures. This finding is in line with the tendency of H and F to aggregate when adsorbed on graphene.

The situation changes, however, drastically with charge doping. With increased doping level the adsorption energy decreases for the quasi random X[1:1] and X[1:0] patterns but not for the

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100% adatom coverage refers to one adatom per carbon atom.
Figure 2: Average relative binding energies (per adatom) for hydrogen (A,C) and fluorine adatoms (B) on graphene as function of charge doping for different adsorbate arrangements. (A,B) Single sided functionalization. (C) double sided hydrogenation. Energies are given with respect to the adsorption energy of C$_8$H$_2$ (A,C) and C$_8$F$_2$ (B) at zero doping. For the structure with random adsorbate distribution, each data point in (A,B,C) refers to an average over 20 different adsorption configurations with 20 hydrogen/fluorine atoms on a (10x10) graphene cell (200 carbon atoms). Error bars give the standard deviations.

C$_8$X$_2$-structures. Therefore, carbon-adatom bonds are strengthened in the X[1:1] and X[1:0] patterns according to the sign convention of Eq. (2). At doping levels above ±0.05 e/C-atom the X[1:1] configurations become more favorable than C$_8$X$_2$ with adsorption energy differences exceeding several 100 meV/X-atom. For H and F coverage on the order of 10%, charge doping can thus destabilize the separation into clean graphene and C$_8$X$_2$ islands. Doping therefore induces a phase transition from separated C$_8$X$_2$ islands to other adsorption patterns like the fully random X[1:1] pattern with energy gains largely exceeding room temperature.

We now turn to situations of doping beyond ±0.05 e/C-atom. With increasing charge doping, the adsorption energy difference between sublattice polarized X[1:0] and unpolarized X[1:1] patterns decreases and eventually even reverts sign. The fully sublattice polarized adsorption patterns become lowest in energy at electron and hole doping above ~ 0.1 e/C-atom for 10% hydrogen and fluorine coverage, respectively (Fig. 2A,B). This tendency towards sublattice ordering corresponds to the phase transition suggested in Ref. 6. Notably, for one-sided adsorption at strong charge doping, we find an energy gain of 60-100 meV/X-atom upon sublattice ordering. These binding energy differences clearly exceed room temperature thermal energies and suggest that a second doping induced phase transition between X[1:1] and X[1:0] structures should be, therefore, achievable even in room temperature experiments.
Clearly, the electron-hole asymmetry in the doping dependence of adsorption energies \(2A\) and \(B\) differs between randomly hydrogenated and fluorinated graphene, which reflects the difference in the polarity of the C-X bond.

We furthermore considered hydrogenation from both sides. Here, full hydrogenation of graphene, i.e. 100% hydrogen coverage with H atoms binding to sublattices A and B above and beneath the graphene sheet, respectively, is possible and leads to the formation of graphane\(^{1}\). We consider two sided random hydrogen distributions at 10% coverage (i.e. 5% above and below), where H is either sticking to sublattice A only (H[1\(\bar{1}\):0]) or where it binds to sublattice A from above and B from below (H[1:1]). The adsorption energies follow a qualitatively similar trend with charge doping as in the case of single side functionalization (Fig. 2C). With increasing charge doping, hydrogen adsorption energies in the H[1\(\bar{1}\):0] and the H[1:1] configurations become more negative, while there is an increase in \(E_{\text{ads}}\) for graphane with charge doping. However, the formation of graphane is more favorable than random H[1\(\bar{1}\):0] or H[1:1] adsorption patterns over a much wider doping range than in the case of single side hydrogenation. Moreover, there is no doping induced transition towards a sublattice ordered H[1\(\bar{1}\):0] state in the doping range under investigation. The H[1:1] structure remains more favorable than the H[1\(\bar{1}\):0] state even up to doping levels of \(\pm 0.2\) e/C-atom. Therefore, doping induced adatom phase transitions are much easier realized in single side covalently functionalized graphene.

We now aim to identify the microscopic mechanisms behind the charge doping dependent emergence of different adsorbate patterns found above. There are two distinct contributions which determine the dependence of binding energies on doping and adatom patterns: first, adsorbate interactions mediated by the band structure energy of the graphene \(\pi\)-electron system\(^{6,11–16}\) and second strain and rehybridization energies. Only the latter contributions distinguish between adatom adsorption from one versus two sides. In the fully sublattice polarized patterns the energy difference between one and two-sided adsorption is almost an order of magnitude smaller than for patterns with equal sublattice population (c.f. 2A and C). The rehybridization and strain contributions are thus larger in situations, where both sublattices are covered. Previous DFT calculations on graphene with two hydrogen adatoms have shown that binding of two hydrogen atoms to two neighboring C atoms on different sides of the graphene sheet is by
0.5 eV more favorable than binding on the same side\textsuperscript{25}. For H pairs on second or third nearest neighbor positions the energy differences between single and double side adsorption are at least a factor of two smaller. Thus, the large strain and rehybridization energy differences in patterns with coverage of sublattices A and B originate from pairs (or also larger clusters) of hydrogen atoms, which bind to nearest-neighbor carbon atoms.

Figure 3: Density of states per unit cell of graphene with different levels of hydrogenation: pristine graphene, 10% hydrogenation with fully random H[1:1] and sublattice ordered H[1:0] configuration, and C\textsubscript{8}H\textsubscript{2}. The Fermi level of each configuration has been shifted to zero.

The band structure energy contribution to the adsorption energy differences can be estimated from the electronic density of states shown for the C\textsubscript{8}H\textsubscript{2}, H[1:1], and H[1:0] configurations in Fig. 3. In contrast to the other patterns, the spectrum of C\textsubscript{8}H\textsubscript{2} exhibits a gap which makes its formation favorable in the undoped case. Due to the gap, charge doping of C\textsubscript{8}H\textsubscript{2} is however associated with larger band structure energies than for the other two adsorbate configurations. Thus, C\textsubscript{8}H\textsubscript{2} clusters are destabilized and H[1:1] or H[1:0] patterns become more favorable at a certain doping level (c.f. Fig. 2). The electronic DOS of the H[1:1] structure is gapless around the Fermi level, while the H[1:0] structure exhibits large peak in the DOS at $E_F$. While the large DOS at $E_F$ in the undoped state of the H[1:0] pattern makes this pattern unstable against
structural (as well as possibly magnetic) reconstructions, doping of the H[1:0] pattern requires only small amounts of band structure energy. Therefore, the H[1:0] pattern becomes eventually most favorable at large doping.

More quantitatively, band structure energy differences can be described in terms of a tight-binding (TB) model $H = H_{\text{gr}} + H_{\text{imp}}$. Here, $H_{\text{gr}} = -t \sum_{i,j} c_i^\dagger c_j$ is the nearest-neighbor tight-binding Hamiltonian of graphene, where $c_i^\dagger$ ($c_i$) creates (annihilates) an electron at site $i$ and $t = 2.6$ eV is the nearest-neighbor hopping parameter. The adsorbates are taken into account through the Hamiltonian $H_{\text{imp}} = \varepsilon_d \sum_{i'} d_i^\dagger d_{i'} + V \sum_{i'} \left( d_{i'}^\dagger c_i + \text{h.c.} \right)$, where $d_i^\dagger$ ($d_i$) creates (annihilates) an electron at a defect level at a defect site with adsorbant ($i'$). The sum runs over all defect sites. The parameters $V = 6$ eV, $\varepsilon_d = 0$ for hydrogen and $V = 6$ eV, $\varepsilon_d = -2$ eV for fluorine have been fitted to our DFTB results and are in line with previous DFT calculations. The TB simulations were performed on supercells containing 1800 C-atoms and are averaged over 100 impurity configurations each.

The energy difference

$$\Delta E = E_{\text{ads}}(X[1:0]) - E_{\text{ads}}(X[1:1])$$

(2)

between sublattice polarized X[1:0] and unpolarized X[1:1] patterns as obtained from the DFTB and TB model are compared in Fig. 4A, B. While the TB results significantly deviate from the DFTB results for double sided hydrogenation, they reproduce the DFTB adsorption energy differences for, both, single side hydrogenation and fluorination, very well. The energy difference $\Delta E$ decreases with charge doping of any sign and changes sign at similar doping levels in DFTB and TB.

We furthermore evaluated the energy difference associated with the phase separation into graphene and C$_8$X$_2$ islands

$$E_{\text{sep}} = E_{G:X} - [(1 - 4c)E_G + 4c n_C E_{C_8X_2}]$$

(3)

for hydrogenated and fluorinated graphene at $c = 10\%$ coverage and various doping levels (Fig. 4C,D). The number of carbon atoms in the graphene sheets is indicated by $n_C$. There are clearly quantitative differences between $E_{\text{sep}}$ as obtained from DFTB and the TB model.
Figure 4: Adsorption energy differences $\Delta E$ (Eq. 2) between fully random X[1:1] and sublattice polarized X[1:0] configurations of H (A) and F adatoms on graphene (B). Solid lines are the DFTB results; TB dashed. In (A), the adsorption energy difference of hydrogen between sublattice unpolarized (H[1:1]) and polarized (H[11:0]) patterns is also shown for two side adsorption. (C,D) Energy gain $E_{sep}$ upon phase separation from X[1:0] or X[1:1] structures to C$_8$X$_2$ islands. The sample averaged H/F coverage is 10% in all cases.
Nevertheless, the TB models reproduce the doping levels, where the phase separation into graphene and C$_8$X$_2$ becomes less favorable than the X[1:1] or X[1:0] configurations, at least qualitatively correct. Also away from this phase transition, energy differences are at least captured qualitatively correct by the TB model.

The TB model is therefore used to extrapolate the DFTB results and to construct the charge doping and impurity concentration dependent phase diagrams of H and F adsorbed to graphene. To this end, we calculated total energies of graphene at several concentrations $c$ of adsorbed H and F, several charge doping levels $n$ and evaluated the phase separation energies $E_{sep}$ and energy gains upon sublattice ordering $\Delta E$ according to Equations (??) and (2). Thereby, we consider the electron doped case only, since the TB model of H on graphene is particle-hole symmetric and the tendency towards phase transitions in fluorinated graphene is strongest on the electron doped side.

As can be seen from Fig. 5A, the TB model suggests that the graphene-C$_8$H$_2$ phase separation occurs at sufficiently small charge doping ($n < 0.06$ e/C-atom) for all adatom concentrations ($c < 20\%$) considered, here. The energies associated with the phase separation can exceed room temperature thermal energies by more than an order of magnitude. The situation reverts around $n \sim 0.06$ e/C-atom. Here, the randomly hydrogen covered configurations appear more favorable by energies per unit cell which can again exceed room temperature already at adatom concentrations $c < 5\%$. Once the doping exceeds the adatom concentration ($n > c$), the sublattice symmetry broken H[1:0] structures become more favorable than the fully random H[1:1] configurations. For fluorine (5B) a qualitatively similar picture emerges. However, the tendency towards the destruction of the C$_8$F$_2$ islands and the sublattice ordering is stronger here.

Taken together, our DFTB and TB calculations suggest the phase diagram shown in Fig. 1D. There is a phase separation into graphene and C$_8$X$_2$ at sufficiently small charge doping. For charge doping exceeding $n \sim 0.06$ e/C-atom the adatoms distribute over the entire sample, where sublattice symmetry breaking becomes favorable when the doping level exceeds the adatom concentration ($n > c$). In the vicinity of both transition lines more complex phase separated adsorption patterns might emerge. This can be seen from the concave shape of $E_{sep}$.
Figure 5: (A,B) Energy gains upon phase separation, $E_{\text{sep}}$ from fully random X[1:1] coverage to C$_8$X$_2$ islands for single hydrogenated (A) and fluorinated graphene (B). (C,D) Energy gains upon sublattice symmetry breaking (X[1:1]→X[1:0]) for hydrogenated (C) and fluorinated (D) graphene. Different curves refer to different charge doping levels between 0 and 0.2e/C-atom. Energy gains per unit cell are given.
at \( n \sim 0.06 \text{ e/C-atom} \) (Fig. 5A,B) as well as the steep increase in \( \Delta E \) as soon as \( c > n \) (Fig. 5C,D).

Hydrogen and fluorine adsorption on graphene are highly sensitive to external charge doping. Under which experimental circumstances could switching between different adsorption patterns be expected? Electrostatic doping allows to achieve carrier concentrations on the order of \( 10^{14} \text{ e/cm}^2 = 1 \text{ e/nm}^2 \approx 0.03 \text{ e/C-atom} \). According to our results, this alone is not enough to break the tendency towards graphene-C\(_8\)X\(_2\) phase separation. Chemical doping, for instance by means of alkali, earthalkali, or rare earth intercalation between graphene and its substrate, however, allows for electron doping up to \( \approx 0.1 \text{ e/C-atom} \). Thus, intercalated graphene samples are the most promising systems to explore the rich variation of covalently functionalized graphene systems with charge doping. In these electron doped systems particularly fluorine adatoms are highly susceptible to doping induced phase transitions.

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**Supplementary material**

As explained in the main article, the adsorption energies for the various hydrogen and fluorine adsorption patterns have been calculated using the total energies obtained by calculations with the DFTB+ program package. For every doping concentration and adsorption type (X[1:1] and X[1:0]) we considered 20 randomly generated configurations, which have been relaxed with the force criterion described in the main article. In order to test the reliability of the data, ab initio calculations for a few selected adsorption pattern had been carried out using the FHI-AIMS code.
As shown in Fig. 6, the absolute adsorption energies differ significantly from the DFTB values. Ab initio DFT calculations predict the hydrogen adsorption being unfavorable in the entire investigated doping range, while fluorine adsorption is favorable for all investigated doping levels. It is important to note, that the adsorption energies are calculated with respect of pristine graphene and isolated H\textsubscript{2} or F\textsubscript{2} molecules, which does not resemble the experimental conditions for hydrogenation and fluorination. In contrast to the absolute energies, the relative energies of the various configurations are very similar in both, DFTB and DFT. Both methods predict the C\textsubscript{8}X\textsubscript{2} configuration being less favorable at doping $\sim \pm 0.1$ e/C-atom. Also, both predict that the sublattice polarized configurations become more favorable than the sublattice symmetric ones beyond these doping concentrations. Figure 7 illustrates the relative adsorption energies taking the C\textsubscript{8}X\textsubscript{2} configuration as reference for each doping level. As can be seen, the prediction of DFTB about the doping level, at which the C\textsubscript{8}X\textsubscript{2} configuration gets less stable as the other investigated adsorption patterns is reliable. Furthermore, the DFTB prediction about the change in the stability order for the sublattice polarized and sublattice symmetric configurations is reliable as well.

![Figure 6: Adsorption energies for selected (A) hydrogen and (B) fluorine adsorption patterns as calculated by ab initio DFT and by the DFTB methods.](image-url)
Figure 7: Adsorption energies relative to the adsorption energy of the (A) C₈H₂ and (B) C₈F₂ configurations at various doping levels for selected configurations as calculated by the DFTB method and ab initio DFT method.

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