Engineering the ligand states by surface functionalization: A new way to enhance the ferromagnetism of CrI₃

Hongxing Li¹, Zi-Peng Cheng¹, Bin-Guang He¹, and Wei-Bing Zhang∗

¹ Hunan Provincial Key Laboratory of Flexible Electronic Materials Genome Engineering, School of Physics and Electronic Sciences, Changsha University of Science and Technology, Changsha 410114, People’s Republic of China

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The newly discovered 2D magnetic materials provide new opportunities for basic physics and device applications. However, their low Curie temperature (T_C) is a common weakness. In this paper, by combining magnetic Hamiltonian, Wannier functions and first-principle calculations, we systematically study the magnetic properties of monolayer CrI₃ functionalized by halogen. The magnetic exchange coupling (EX) and magnetic anisotropy (MA) are found to increase significantly by X (X=F, Cl and Br) atom adsorption, and increase along with the coverage of X atom. In the frame work of superexchange theory, the enhanced EX can be ascribed to the reduced energy difference and increased hopping strength between Cr d and I p orbitals, due to the states of I ligand are engineered by X adatom. Besides, the X adatom may provide additional ferromagnetic superexchange channel. Finally, the CrI₃ that one side is fully adsorbed by F atoms is found to be a room temperature ferromagnetic semiconductor with T_C=650 K. Our results not only give an insightful understanding for the enhancement of ferromagnetism of CrI₃ by atom adsorption, but also propose a promising way to improve the ferromagnetism of 2D magnetic materials.

I. INTRODUCTION

Magnetism in two-dimension (2D) is an interesting topic for several decades, due to the novel physical phenomena and promising applications in low-dimensional devices. In 2017, the intrinsic ferromagnetism is discovered for the first time in atomically thin layers of CrI₃ and Cr₂Ge₂Te₆. which provide new platforms for the study of low-dimensional magnetic phenomenon and spintronics device. For example, the photominescence of monolayer CrI₃ is spontaneous circularly polarized, in which the helicity is determined by the magnetization direction. The van der Waals magnetic tunneling junctions that composed by multi-layer CrI₃ demonstrate giant tunneling magnetoresistance.

Unfortunately, the Curie temperature (T_C) is always very low, especially the 2D semiconductor ferromagnet, as a result of its low carrier concentration and few ligands. For instance, T_C of monolayer CrI₃ and bilayer Cr₂Ge₂Te₆ are 45 K and 28 K, respectively. The ultra-low T_C means the sample must be cooled to a very low temperature to maintain the long-ranged magnetic order, which is very expensive and inconvenient. To overcome this obstacle, many strategies, including electrostatic doping and strain, are adopted to improve the T_C. Especially, Huang et al. propose a new general strategy to improve the T_C of CrI₃ by isovalent alloying, and they revealed that the enhancement can be ascribed to the reduced virtual exchange. Our previous work also demonstrates the ferromagnetism of CrI₃ can be enhanced in vdW heterostructure, as a result of interlayer charge transfer.

Since a large part of atoms expose to the surface, the properties of 2D materials are very sensitive to surface functionalization. There are many works about the effects of surface functionalization on the electronic structure and topological properties of 2D materials. Recently, this method has been used to modify the magnetism of 2D magnetic materials. C. Frey et al. functionalize MXene surface by different nonmetal elements, finding that the magnetic order and magnetic anisotropy vary with elements. This is because the nonmetal atoms bond with magnetic ions directly, and then the spin-orbit coupling and electron localization of magnetic ions are manipulated. Upon metal atom adsorption, owing to carriers doping, both magnetic coupling and magnetic anisotropy of CrI₃ and Cr₂Ge₂Te₆ can be tuned. However, the carriers doping also transfer the semiconductors to metals, which limit their applications.

In the present work, by employing of first-principle calculations, we functionalize monolayer CrI₃ by the congeners of I, namely X=F, Cl, Br and I. We find X adatom bonds with I atom of CrI₃ strongly. The magnetic exchange coupling (EX) and magnetic anisotropy (MA) of monolayer CrI₃ will be enhanced by the adsorption of F, Cl and Br atoms, and increase with the coverage. To understand the underlying mechanism, the magnetic Hamiltonian and Wannier function calculations are carried out. At last, we fully functionalize one side of CrI₃ by F atom, finding this system is a room temperature 2D ferromagnetic semiconductor.

II. CALCULATION METHOD

All our spin-polarized calculations were performed on Vienna ab initio simulation package (VASP) based on density functional theory. The ion-electron in-
The lattice parameter of CrI$_3$ consider four possible sites on monolayer CrI$_3$ and the interaction among them can be neglected. The distance between adjacent adatoms is 14.06 Å, so the artificial interactions between the images of slabs can be neglected. Brillouin zone sampling was performed by a 7×7×1 Γ-center mesh. The Wan-nier functions calculations were implemented by Wannier90 Code.[27] The single-atom adsorption is modeled by adsorbing one halogen (X=F, Cl, Br and I) atom on 2×2 supercell of CrI$_3$, and the corresponding coverage is 8.3% monolayer. The lattice parameter of CrI$_3$ is optimized to be 7.03 Å, so the distance between adjacent adatoms is 14.06 Å and the interaction among them can be neglected. To determine the most stable adsorption configuration, we consider four possible sites on monolayer CrI$_3$, namely the top of Cr atom (TCr), top of I atom (TI), hollow site (H), and top of hollow site (H’), as shown in Fig. 1(a). The adsorption energy $E_{ad}$ of adatom is calculated by

$$E_{ad} = E_{CrI_3} + E_X - E_{tot}$$  (1)

Where $E_{CrI_3}$, $E_X$ and $E_{tot}$ are the energies of monolayer CrI$_3$, isolated X atom and the adsorbed system X@CrI$_3$. By this definition, the positive value of $E_{ad}$ suggests the adsorption is energetically favorable, while the negative value manifests an energy consumed adsorption. We find that all X atoms have largest positive $E_{ad}$ at TI site. However, the largest $E_{ad}$ decreases monotonically from F to I, as the reduced electronegative. The results indicate all the X atoms can absorb on CrI$_3$ stably. Bader charge analysis is used to calculate the charge transfer between CrI$_3$ layer and X adatom. The electron is found to transfer from CrI$_3$ to X atom, which is similar to the situation that X atom adsorbs on MoS$_2$. However, CrI$_3$ transfers more electron to X adatom than MoS$_2$ at the same GGA-PBE level. For example, F adatom gets 0.614 e from CrI$_3$, while it is just 0.572 e from MoS$_2$. The large magnitudes of adsorption energy and charge transfer indicate the covalent bonds are formed between I and X atoms. Interestingly, the length between Cr atom and the I atom that bonds with X adatom decreases from 2.747 to 2.696 Å, which means the Cr-I bond is strengthened by the adsorption of X atom.

The spin-polarized band structures are calculated to understand the electronic properties of X@CrI$_3$. As we can see in Fig. 2 in the gap region, there are two localized bands. One is close to conduction band (marked as LC), and the other one is near valance band (marked as LV). The distance between LC and LV decreases from F to I. Even so, the systems are still semiconductors. It should be noted that the spin direction of LV is downward, which is opposite to the upward spin of valence band.

![Figure 1](image)

**FIG. 1.** (a) The schematic diagram of the adsorption sites on monolayer CrI$_3$. (b) The adsorption energy $E_{ad}$ of X adatom at difference site, the inset is the optimized atomic structure of TI configuration. The pink, blue and purple balls represent the I, Cr and X adatom.

**TABLE I.** The calculated results. $d_{I-X}$, the distance between I and adatom, in Å. $\Delta \rho$, the charge transfer from CrI$_3$ to adatom, in e. $d_{Cr-I}$, the length of bond Cr-I in which I atom is attached by X adatom, in Å. $\angle_{Cr-I-Cr}$, the bond angle of Cr-I-Cr in which I atom is attached by X adatom, in degree. $M_X$ and $M_I$, the magnetic moment of X atom and I atom that bonds with X atom, $\mu_B$. In pristine CrI$_3$, $d_{Cr-I}$=2.747 Å, $\angle_{Cr-I-Cr}$=94.77°, and $M_I$ is -0.081 $\mu_B$.

| X   | $d_{I-X}$ (Å) | $\Delta \rho$ (e) | $d_{Cr-I}$ (Å) | $\angle_{Cr-I-Cr}$ (°) | $M_X$ (e) | $M_I$ (e) |
|-----|---------------|-------------------|----------------|------------------------|-----------|-----------|
| F   | 2.20          | 0.614             | 2.696          | 95.93                  | -0.377    | -0.331    |
| Cl  | 2.76          | 0.428             | 2.723          | 96.62                  | -0.290    | -0.374    |
| Br  | 2.93          | 0.341             | 2.729          | 96.63                  | -0.231    | -0.205    |
| I   | 3.07          | 0.231             | 2.798          | 95.03                  | -0.261    | -0.140    |

The extension of the isosurface of LV and LC around I atom is larger than F adatom, so the contribution of I atom to the localized band is greater than F adatom. By examining the shape of isosurface, we find LV around Cr atom is t$_{2g}$ feature. Furthermore, two lobes of d orbital connect with the p$_{\pi}$ orbital of I atom, confirming the bonding state. At the same time, F adatom bonds with I atom by p$_{\pi}$ hybridization. Different from LV, the LC is mainly contributed by Cr d$_{x^2-y^2}$ orbital. This is accordant with the fact that valence band...
FIG. 2. (a) (b) (c) and (d), the spin-polarized band structure of CrI$_3$ adsorbed with F, Cl, Br and I atom, respectively. Blue line is spin-up and red line is spin down. (e) and (f), the partial charge density of band LV and LC as demonstrated in (a). The isosurface is set to 0.001 e/Å$^3$.

To further understand the effects of X adatom on local electronic structures, we project the density of states to F adatom, I$_1$, I$_2$, Cr$_1$ and Cr$_2$ atoms in F@CrI$_3$, as illustrated in Fig. 3. The projected density of states (PDOS) of I$_2$, Cr$_1$ and Cr$_2$ atoms do not display obvious difference from pristine CrI$_3$. It suggests the states of these atoms suffer negligible influence from X adatom, as they not bond with X adatom directly. The PDOS of F adatom in spin-up and spin-down directions are asymmetric, which is consistent with the above finding that F adatom is spin polarized with net magnetic moment. In the PDOS of F adatom and I$_1$ atom, there are two intense resonant states located at -5.0 and -0.1 eV, confirming the strong hybridization between F and nearest neighbor I atom. However, the states of I$_1$ and I$_2$ demonstrate significant difference, for the intensity of occupied states of I$_1$ from -3.8 to -0.2 eV is much weaker than I$_2$, which reflecting different chemical environments. Therefore, by the adsorption of X atom, the states of ligand I atom that bonds with X adatom directly will be manipulated.

In CrI$_3$ sheet, ligand I atom bonds with magnetic Cr atom and is spin polarized in antiparallel direction. Interestingly, the spin polarization of X adatom is parallel to the I atom, and antiparallel to Cr atom. Consequently, the total magnetic moment of CrI$_3$ supercell is reduced by 1 $\mu_B$. It should be noted that the calculation cannot achieve the state that the magnetic moment of X adatom is antiparallel to I (parallel to Cr), even if we set this state initially. The magnetic moment $M_I$ of I atom in pristine CrI$_3$ is -0.081 $\mu_B$. However, for the I atom that bonds with F adatom, this value increases to -0.377 $\mu_B$. This phenomenon may be due to the charge transfer from I atom to X adatom, which leaves behind unpaired electrons at I atom. On the other hand, the transferred electrons pair with the electrons of X atom and reduces the magnetic moment $M_X$. For example, the magnetic moment of F adatom is -0.29 $\mu_B$, which is small than the 1 $\mu_B$ of isolated F atom. To further extract the exchange splitting $\Delta_{\uparrow\downarrow}$ of I atom in CrI$_3$, we calculate the difference between on-site energies of spin-up and spin-down Wannier orbitals in local coordinates. In pristine CrI$_3$, $\Delta_{\uparrow\downarrow}^{p_x(p_y)}=0.023$ eV and $\Delta_{\uparrow\downarrow}^{p_z}=0.068$ eV. However, for the I atom that bonded with F adatom in F@CrI$_3$, the $\Delta_{\uparrow\downarrow}$ for $p_x$, $p_y$ and $p_z$ are 0.560, 0.854 and 0.148 eV, which are increased by an order of magnitude. Thus the stability of the magnetism of ligand I atom in CrI$_3$ can be enhanced by X adatom.

As the MA is crucial in 2D magnetic material, we calculate the MA energy $E_{MAE}$ by

$$E_{MAE} = E_x - E_z$$

Where the $E_x$ and $E_z$ are the total energy of X@CrI$_3$ when magnetism direction points to x and z directions. The results are plotted in Fig. 4(a). We can see the $E_{MAE}$ of X@CrI$_3$ (X=F, Cl and Br) are 7.61, 8.02 and 8.43 eV.
FIG. 4. The exchange energy $E_{AFM} - E_{FM}$ (blue) and magnetic anisotropy energy $E_x - E_z$ (red) of X@CrI$_3$. (b) The exchange interaction parameters in CrI$_3@F$ as shown in (c).

6.90 meV, which are larger the 5.18 meV of 2×2 CrI$_3$. However, I adatom reduces the $E_{MAE}$ to 4.30 meV.

To determine the ground magnetic order, the EX energy $E_{EX}$ is calculated by

$$E_{EX} = E_{AFM} - E_{FM}$$

(3)

Where $E_{AFM}$ and $E_{FM}$ are total energy of X@CrI$_3$ at Neél antiferromagnetic and ferromagnetic state. As we can see in Fig. 4(a), similar to $E_{MAE}$, the $E_{EX}$ of X@CrI$_3$ (X=F, Cl and Br) is much larger than the pristine CrI$_3$. For example, the $E_{EX}$ of F@CrI$_3$ is 339.1 meV, almost twice as much as the 182.4 meV of 2×2 CrI$_3$. On the contrary, $E_{EX}$ of I@CrI$_3$ is 155.4 meV, which is smaller than the pristine CrI$_3$. Upon the adsorption of X adatom, both atomic and electronic structures of CrI$_3$ change. In order to clarify which fact plays the primary role in the regulation of ferromagnetism in CrI$_3$, we calculate the $E_{EX}$ and $E_{MAE}$ of unrelaxed F@CrI$_3$, and they are 342.7 and 8.4 meV, respectively. On the contrary, if we remove the F adatom from the relaxed F@CrI$_3$, then the $E_{EX}$ and $E_{MAE}$ are calculated to be 183.5 and 5.0 meV, which are very close to pristine CrI$_3$. Hence the modulation of magnetism of CrI$_3$ that caused by adatom is mainly due to the change of electronic states.

In the above we find X adatoms modulate the states of the bonded I atom pronoucneced, while exert very little influence on other atoms. In monolayer CrI$_3$, the states of I ligands play crucial role in the formation of ferromagnetism. As a consequence, the ferromagnetism in CrI$_3$ may be changed locally. To confirm this, based on a ferromagnetic state, we flip the magnetic moment of one Cr atom and calculate the energy change $\Delta E$. As illustrated in Fig. 4(d), the moments of Cr1, Cr2 and Cr3 are flipped successively. In Heisenberg model, the magnetic exchange energy can be expressed as $E = -\sum_{(ij)} J S_i \cdot S_j$, where J is exchange coupling parameter and $S=3/2$ is magnetic quantum number of Cr atom. We just consider the nearest neighbor coupling, then $\Delta E$ can be expressed approximatively as

$$\begin{align*}
\Delta E_1 &= 2J_1 S^2 + 4J_2 S^2 \\
\Delta E_2 &= 2J_2 S^2 + 4J_3 S^2 \\
\Delta E_3 &= 2J_3 S^2 + 4J_4 S^2
\end{align*}$$

By this method, the J of pristine CrI$_3$ is calculated to be 4.66 meV. The $\Delta E_3$ results from the flipping of Cr3 atom is 63.2 meV, and it is very similar to the 62.9 meV in pristine CrI$_3$. Consequently, $J_4$ is expect to approximate the nearest neighbor exchange interaction of pristine CrI$_3$. Then we can solve $J_1$, $J_2$ and $J_3$, and the results are plotted in Fig. 4(b). We find that only $J_1$ increases greatly, such as in F@CrI$_3$, $J_1$ increases to 42.88 meV, which is about ten times as large as the $J_4$. Nevertheless, the $J_2$ and $J_3$ are very close to $J_4$. Therefore, X adatom can enhance $J_1$ markedly, while has little influence on $J_2$, $J_3$ and $J_4$.

In CrI$_3$, the EX between Cr atoms is mediated by ligand I atoms. It is realized by the virtual hopping between Cr d orbitals and intermediate I p orbitals. As the bond angle of Cr-I-Cr is about 90°, the effective EX between Cr atoms is ferromagnetic. According to the superexchange theory, the magnitude of J of CrI$_3$ is direct proportion to $t^4_{pd}$/$U_{pd}$, where $t_{pd}$ and $U_{pd}$ are the hopping matrix element and energy difference between Cr d and I p orbitals, respectively. Based on the Bloch wave functions obtained from density functional calculations, we construct the maximum localized Wannier orbitals in local coordinate. By these Wannier orbitals, the $t_{pd}$ and $U_{pd}$ in CrI$_3$ and F@CrI$_3$ are calculated, as summarized in Table II. We can find there is obvious increase in the $t_{pd}$ between Cr d orbitals and p orbitals of the I atom that bonded with F adatom. Conversely, the $\Delta_{pd}$ drops significantly. Finally, the effective exchange coupling J increases. On the contrary, the $t_{pd}$ and $U_{pd}$ in Cr-I pair that is far away from F adatom are very similar to pristine CrI$_3$, thus the J will not change obviously. This is consistent with the result derived from magnetic Hamiltonian in the above. We note that the hopping parameters between Cr d and F p orbitals are nonzero, and the magnitude can be up
charged by charge transfer, and indicates X adatoms pre-
to the Coulomb repulsive interaction, for X adatoms are
44.5 meV for F, Cl and Br, respectively. This is due
bi-X@CrI
one atom at position A, and the second one at L, M
interaction, we consider three configurations by placing
multiple adatoms may be developed. To understand the
ent from single atom adsorption, the interaction among
3
I atoms on CrI
5
ferromagnetic coupling channel, and contributes to the
3
µBE
0.9092 0.1290 0.1291 0.9103 0.1292
F@CrI (Cr1-I) 0.019112 0.025609 0.002415 0.036971 0.485436
F@CrI3 (Cr1-F) 0.059039 0.017436 0.018420 0.113458 0.043808
Energy difference |U_{pd}|

|              | d_{x^2-p_z} | d_{yz-p_z} | d_{xz-p_z} | d_{x^2-p_z} | d_{xy-p_z} |
|--------------|-------------|------------|-------------|-------------|-------------|
| CrI3         | 0.012661    | 0.048880   | 0.026073    | 0.065627    | 0.630948    |
| F@CrI3 (Cr1-I) | 0.019112    | 0.025609   | 0.002415    | 0.036971    | 0.485436    |
| F@CrI3 (Cr2-I) | 0.8877      | 0.1144     | 0.1175      | 0.8881      | 0.1162      |
| F@CrI3 (Cr1-F) | 1.5013      | 1.4699     | 2.2493      | 1.4699      | 1.4893      |

B. Bi-atom adsorption

To explore effects of multiple X adatoms on the ferro-
magnetism of CrI3, we adsorb two X atoms on 2×2 super-
cell of CrI3, and the associated coverage is 16.6%. Diff-
ferent from single atom adsorption, the interaction among
multiple adatoms may be developed. To understand the
interaction, we consider three configurations by placing
one atom at position A, and the second one at L, M
or N site, as sketched in Fig. 5. The total energies of
bi-X@CrI3 at AN are lower than AL by 19.7, 48.5 and
44.5 meV for F, Cl and Br, respectively. This is due to
the Coulomb repulsive interaction, for X adatoms are
charged by charge transfer, and indicates X adatoms pre-
fer to distribute uniformly on CrI3 surface. Note that two
I atoms on CrI3 surface will desorb as I2 molecule. The
EX energy E_{EX} and MA energy E_{MAE} of bi-X@CrI3
at most energetically favorable configuration are calcu-
ated, and depicted in Fig. 5. Compared with single atom
adsorption, bi-adatom enhance the E_{EX} and E_{MAE}
by greater extend. For instance, the E_{EX} and E_{MAE}
of bi-F@CrI3 are 499.2 meV and 11.03 meV, respectively,
which are 2.74 and 2.13 times as much as the pristine
CrI3. This is because the X adatom increases CrI3 fer-
romagnetism locally, and more adatoms result in more
increased sites, as well as the greater total EX energy.

C. Fully F-functionalized CrI3

Inspired by the EX and MA increase with cover-
age, finally we fully functionalize one side of CrI3 by F
atoms. However, only the system functionalized by F
atoms (noted as FF@CrI3) is found to be dynamic sta-
able, as there is no imaginary frequency in whole Brillouin
zone. Fig. 6(a) shows the top and side views of relaxed
FF@CrI3. The length of F-I bond is 2.17 Å, which is
shorter than the 2.20Å in the adsorption of single F atom.
On the other hand, the adsorption energy per F adatom
is 2.585 eV, and it is larger than the 2.216 eV for single F
adatom. Besides, the length of upper Cr-I bond is 2.683
Å, while the bottom one is 2.767 Å. The two values are
smaller or larger than the 2.747 Å in pristine CrI3. Con-
sequently, the lattice parameter of FF@CrI3 is shrunk by
2% relative to pristine CrI3.

Fig. 6(c) and (d) shows the band structure and DOS of
FF@CrI3. The conduction band minimum and valence
band maximum locate at K and Γ point, respectively,
leading to an indirect gap of 0.5 eV. By comparing with
the band of CrI3 adsorbed with single F adatom, we
conclude the valence band is formed by the localized
states. Nevertheless, the valence band is delocalized by
the interactions among localized states. We note that
the valence band is spin-down, in contrast to the spin-up
of conduction band. This is distinct from CrI3, in which
both conduction and valance bands are spin-up.

Now we would like to understand the magnetic prop-
erties of FF@CrI3. Fig. 6(e) and (f) depict the magnetic
moment distribution of FF@CrI3. The Cr atom has 3 \( \mu_B \)
upward moment, which is the same as CrI3. F adatom
and the bonded I atom have 1 \( \mu_B \) downward moment
totally. As a result, the total moment of unit FF@CrI3

| hopping matrix element | CrI3 | F@CrI3 (Cr1-I) | F@CrI3 (Cr2-I) | F@CrI3 (Cr1-F) |
|-----------------------|------|----------------|----------------|----------------|
| \( d_{x^2-p_z} \)    | 0.019260 | 0.012661       | 0.019112       | 0.059039       |
| \( d_{yz-p_z} \)    | 0.027227 | 0.048880       | 0.025609       | 0.017436       |
| \( d_{xz-p_z} \)    | 0.002542 | 0.026073       | 0.002415       | 0.018420       |
| \( d_{x^2-p_z} \)    | 0.034491 | 0.065627       | 0.036971       | 0.113458       |
| \( d_{xy-p_z} \)    | 0.485550 | 0.630948       | 0.485436       | 0.043808       |

TABLE II. The calculated hopping matrix element |t_{pd}| and energy difference |U_{pd}| between I p and Cr d orbitals in pristine
CrI3 and F@CrI3. The Cr1, Cr2, I1 and I2 atoms are marked in Fig. 5. The unit is eV.
Fig. 6. (a) The atomic structure, (b) phonon spectrum, (c)(d) DOS and band structure, (e)(f) top and side view of spin charge density of FF@CrI$_3$. The isosurface is set to 0.012 e/Å$^3$.

reduces to 3 $\mu_B$. By taking account of the Heisenberg exchange coupling and single ion anisotropy, the magnetism of FF@CrI$_3$ can be described as

$$\hat{H} = - \sum_{ij} J \vec{S}_i \cdot \vec{S}_j - \sum_i D S_i^z$$ \hspace{2cm} (4)

Where J is the EX parameter, D is the single-ion magnetic anisotropy parameter, $S_i^z$ represents projection of $\vec{S}$ along z direction, and the off-plane direction is chosen as z axis. By this definition, $J>0$ favors ferromagnetic interactions and $D>0$ favors off-plane easy axis. Because the occupation of Cr orbitals in FF@CrI$_3$ is very similar to CrI$_3$, the S is still equal to 3/2. We calculate the total energies at four different magnetic configurations, namely z-(anti)ferromagnetism and x-(anti)ferromagnetism. For CrI$_3$, the J and D are calculated to be 2.69 meV and 0.34 meV, respectively. By Metropolis Monte Carlo (MC) method, the $T_C$ is evaluated to be about 40 K, which is very similar to the experimental value and verifies the reliability of our calculation. For FF@CrI$_3$, the J and D are 55.05 meV and 0.55 meV, respectively, and the simulated $T_C$ is about 650 K. Therefore, FF@CrI$_3$ is a room temperature 2D ferromagnetic semiconductor.

D. Functionalization by other atoms

In addition to halogen, we also study the adsorption of other nonmetal atoms on CrI$_3$, such as H, B, C, N, O, Si, P, S, As, and Se atoms. However, the Cr-I bond of CrI$_3$ is broken by the adsorption, and the left Cr or I atom will pair with the adatom. For example, H adatom bonds with I atom, and O adatom bonds with Cr atom. As a result, the structure of CrI$_3$ will be destroyed by these adatoms. Therefore, only halogen can enhance the ferromagnetism of CrI$_3$, as well as maintain its structure.

IV. CONCLUSION

In summary, based on first-principle calculations, a systematical investigation about the properties of CrI$_3$ adsorbed by X atom (X=F, Cl, Br and I) was carried out. We find both magnetic coupling and magnetic anisotropy of CrI$_3$ can be enhanced by X (X=F, Cl and Br) adatom, and further increase with the coverage of adatom. One side fully F-functionalized CrI$_3$ is a ferromagnetic semiconductor with $T_C=650$ K. Our study demonstrates that surface functionalization is a promising way to improve the ferromagnetism of 2D magnetic material, and finds a room temperature 2D ferromagnetic material.

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