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Introduction

Half-metallic ferromagnets (HMFs), introduced by de Groot on the basis of band structure calculations of NiMnSb in 1983,¹ are promising candidates for spin injection devices.^{2,3} The exceptional property of HMFs is that one of the spin subbands is metallic, whereas the Fermi level falls into a gap of the other one, namely, electrons at the Fermi level are 100% spin polarized.¹ Threedimensional (3D) HMFs mainly comprise Heusler compounds,¹ manganese perovskites⁴ and dilute magnetic semiconductors (DMS).^{5,6} One of the disadvantages of these HMFs is that most of them are transition-metal-contained systems and may suffer from ferromagnetic (FM) precipitate problems.

Following the discovery of graphene and other two-dimensional (2D) atomic materials,⁷ low dimensional HMFs have attracted more and more research interest due to their future applications in electric devices. As we know, to form collective magnetic ordering,

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Designing half-metallic ferromagnetism at atomic scale is always one of the hottest topics for the scientific community due to its potential in spintronics applications. Although the band alignment strategy is broadly adopted in semiconductor-based research, it has not touched the field of low-dimensional spintronics. Here, taking graphitic C_3N_4 (g- C_3N_4) as an example, we show that perfect half-metallic ferromagnetism can be realized through a band alignment strategy. According to the alignment of the valence band maximum (VBM) and the conduction band minimum (CBM) of $g-C_3N_4$, and the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of superhalogens, BF4 is predicted to be a promising building unit which induces half-metallic ferromagnetism in the $g-C_3N_4$ sheet by forming hybrid structures. Verified by density functional simulations, we found that a net magnetic moment of 1 $\mu_{\rm B}$ per BF₄ is induced in the g-C₃N₄ sheet. The magnetic moment distributes evenly on the double-coordinated nitrogen atoms with ferromagnetic coupling, and dynamics simulations confirmed that the structure of $q-C_{3}N_{4}$ is well protected. Thus, our study proposes a promising way to design half-metallic ferromagnetism at atomic scale, which will evoke further experimental interest.

> there are at least two basic necessary requirements, namely, local spin moments and an interplay among the spin moments. However, most of the intrinsic 2D materials do not have spontaneous spin moments. Consequently, magnetic ordering and half-metallicity are absent in such materials. Graphene nanoribbons (GNRs) are taken initially as an attempt to find the solutions of low-dimensional spintronics. Son et al. explored the existence of spin ordering in zigzag GNRs, and predicted that half-metallicity is realizable if in-plane homogeneous electric fields are applied across the ribbons.8 We have predicted that half-metallicity can be obtained in zigzag graphene nanoribbons through asymmetric chemical modification at two edges or formation of BN-C hybrid ribbons.⁹ Since such results open the possibility of one-dimensional spintronics applications, finding one-dimensional robust spintronics has now become an interesting topic.10-12

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For 2D atomic materials, it becomes more difficult to introduce spin moments in the flat and inert planes. Currently, there are three known schemes to induce magnetic ordering in 2D atomic materials: (1) Transition-metal (TM) contained structures. With the localized d electrons, TM elements are the natural choices to build magnetic systems. Intrinsic TM-contained 2D materials are more preferred because of their robust magnetism and stable geometric structures. Many studies have reported such materials, for example Cr2Ge2Te6 atomic layers,¹³ CrI3,¹⁴ Fe2Si,¹⁵ La(Mn, Zn)AsO alloy,¹⁶ Ni-TCNQ (tetracyanoquinodimethane),¹⁷ TiC,¹⁸



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Paper

TiN,¹⁹ Co₉Se₈,²⁰ MoN₂,^{21,22} MnPSe₃,²³ and organometallic single sheets;^{24,25} (2) Selective-bonding structures. Creating local unsaturated states is the key to inducing ordering magnetism in this method. Through half-hydrogenation, Zhou et al. found that a semihydrogenated graphene sheet becomes a ferromagnetic semiconductor,²⁶ and predicted the possible way to fabricate it.27 In our previous studies, we have predicted that half-fluorinated BN and ZnO monolavers will show roomtemperature ferromagnetism.²⁸ Since fluorine atoms have similar electronegativity to nitrogen and oxygen atoms, it is expected that only B (Zn) atoms can chemically interact with F atoms, producing local spin moments and collective magnetic ordering. The following experimental studies perfectly confirmed our predictions, and explored the existence of room-temperature ferromagnetism in such materials;^{29,30} (3) Metal-free porous sheets. Metal-free half-metallic materials are more important and practical because of the spinscattering problem in electron transmission. However, the magnetic and electronic properties of such materials are determined by the local states in the sheets. Du et al. have demonstrated that graphitic C_4N_3 (g- C_4N_3) exhibits a ferromagnetic ground state and intrinsic half-metallicity via density functional theory.³¹ Zhao et al. have also reported some other interesting ferromagnetic carbon nitrides with remarkably high Curie temperature (T_c) .^{32,33} Experimentally, ultrathin metal-free carbon nitrides and boron nitride nanosheets with intrinsic room temperature ferromagnetism were synthesized by Xue and Gao et al.^{34,35} Our groups have predicted that the recently synthesized dimethylmethylene-bridged triphenylamine (DTPA) porous sheet is a ferromagnetic half metal, and the size of the band gap in the semiconducting channel is roughly 1 eV.36,37 The explored novel phenomena have evoked experimental interest, which has achieved enormous progress in this direction.38-40

Since 2D atomic spintronics are always a long-sought goal, it is highly desired to develop new ideas/methods to obtain ferromagnetism or half-metallicity. Previously, the band alignment approach has been broadly adopted in semiconductor-based research, such as designing p–n junction,⁴¹ photocatalysis,⁴² metal–semiconductor junction,⁴³ *etc.* However, it has not been adopted in the design of 2D spintronics. Here, we introduce this strategy to design 2D half-metallic materials, which is totally different from the well-known methods reported in other 2D spintronics. Taking an intrinsic g-C₃N₄ monolayer as an example, we show that half-metallic ferromagnetism can be realized through the band alignment approach and the following spontaneous charge transfer. Considering the abundant analogues of adopted examples in our research, our results provide an enormous stage for further investigations.

Computational methods

Our first-principles calculations are performed based on the Perdew-Wang 91 (PW91) functional for the generalized gradient approximation (GGA), implemented in the Vienna *ab initio* simulation package (VASP).^{44,45} Two theoretical models are used in our calculations, which are marked as $g-C_3N_4$ (BF₄)_x. For x = 1, one $g-C_3N_4$ unit cell is combined with one BF₄, while

for x = 0.25, four g-C₃N₄ units (*i.e.* a $2 \times 2 \times 1$ supercell is used) are combined with one BF₄. Structures are relaxed without any symmetry constraint with a cutoff energy of 500 eV. A vacuum space about 15 Å is used to avoid the interaction between periodical images. Convergence criteria of energy and force are set to 1×10^{-5} eV and 0.01 eV Å⁻¹, respectively. DFT-D2 correction of Grimme⁴⁶ is used to account for the van der Waals interactions between the matrix and dopants. For the spinpolarized calculations, the Vosko-Wilk-Nusair modification⁴⁷ scheme was applied to interpolate the correlation energy. Reciprocal spaces are represented by the Monkhorst-Pack special *k*-point scheme.⁴⁸ For $x = 1, 13 \times 13 \times 1, 15 \times 15 \times 1$, and $15 \times 15 \times 1$ grid meshes are used for the sampling of the Brillouin zone in structure optimization, the self-consistent field (SCF) and the density of states (DOS) calculations, respectively. While for x = 0.25, $7 \times 7 \times 1$ grid meshes are used for optimization, SCF and DOS calculations. Due to the wellknown underestimation of the band gap calculated by standard density functional theory, hybrid functional calculations based on the Heyd-Scuseria-Ernzerhof (HSE06) functional⁴⁹ have also been carried out to examine the band dispersion and halfmetallic ferromagnetism in primitive g-C₃N₄ and g-C₃N₄BF₄ (computationally accessible).

Ab initio molecular dynamics (AIMD) simulations of g-C₃N₄BF₄ are performed within the *NVT* ensemble at T = 300 K embedded in the VASP. A 5 × 5 × 1 supercell containing 300 atoms is used for simulation over 5000 steps with one time step of 1 femtosecond (fs).

Results and discussion

Originally, the g-C₃N₄ monolayer was explored as a promising candidate for solar energy conversion or as a photocatalyst.⁵⁰ Although its band gap is a little large, many methods have been proposed to enhance the photocatalytic properties within the visible-light absorption region.⁵¹ For the g-C₃N₄ monolayer, all carbon atoms have three nearest-neighbor nitrogen atoms, while nitrogen atoms are separated into two kinds according to different chemical environments. As shown in Fig. 1(a) and (c), pure $g-C_3N_4$ is a non-magnetic semiconductor with direct bandgaps of 1.59 eV and 3.20 eV calculated using PBE and HSE06 functionals, respectively. The relatively large band gap of the g- C_3N_4 monolayer makes the chemical doping in the sheet difficult. On the other hand, partial density of states (PDOS) (Fig. 1(b)) and band decomposed charge density (Fig. 1(d) and (e)) indicate that the CBM are contributed by the anti-bonding σ^* orbital of nitrogen and carbon atoms, while the VBM of g-C₃N₄ are contributed by the p orbital of nitrogen atoms.

To induce ferromagnetic ordering into the $g-C_3N_4$ monolayer, it is necessary to produce spontaneous spin moments in this sheet. From the calculated results, it is reasonable to speculate that hole-doping may create local magnetic moments since the competition between exchange splitting energy and Coulomb interaction energy would determine the electronic



Fig. 1 (a) Band structure and (b) partial density of states of $g-C_3N_4$ calculated using GGA-PBE. (c) Band structure calculated using HSE06. $\Gamma = (0, 0, 0), K = (-1/3, 2/3, 0), and M = (0, 0.5, 0)$. Partial charge density of (d) CBM and (e) VBM for $g-C_3N_4$. Gray and blue balls denote carbon and nitrogen atoms, respectively.

structures. To make this physical picture clear, we employ p-doping calculations with the number of holes varying from 0.1 to 1.0 per g-C₃N₄ without any spin restriction. At the level of 0.1 holes per unit cell, the ground state of g-C₃N₄ prefers a nonmagnetic solution. Starting from the level of 0.2 holes per unit cell, g-C₃N₄ possesses the FM ground state (Fig. 2(c)). By increasing the doping concentration, the Fermi level keeps on moving downward and the exchange splitting is significantly increased. Also, the minority spin subbands cross the Fermi level while majority spin subbands still stay under the Fermi level, making g-C₃N₄ half-metallic (Fig. 2(a), (b) and Fig. S1, ESI†). A physical mechanism of the induced ferromagnetism is Stoner instability.⁵² Hole-doping moves the Fermi level of g-C₃N₄ downward, electron states will cross the Fermi level. When the exchange interaction energy or density of states at the Fermi level is large enough, these states will split to decrease the total energy, thus making the system magnetic. Interestingly, magnetic moment is equal to the number of holes accurately. This simple congruent relationship makes the magnetic moment of g-C₃N₄ controllable and predictable.

Although we have demonstrated the relationship of magnetic ordering and hole-doping in the $g-C_3N_4$ monolayer, it is not easy to fabricate such materials in real experiments. Doping is frequently adopted to tune the electronic and magnetic properties in many materials. However, for real applications and uniform samples, it is quite difficult to control the cluster of doping elements, leading to many realistic problems as shown in diluted magnetic semiconductors.⁵³

Recently, You *et al.* successfully prepared trimethylchloromethyl ammonium trichloromanganese(II) [Me₃NCH₂ClMnCl₃, TMCM-MnCl₃],⁵⁴ which opens a door for hybrid materials combining with large organic molecules and layered structures. In principle, the combined large organic molecules can avoid the problems of cluster, because of the strong Coulomb interactions. Consequently, the hybrid structures are long-range ordered. To induce a uniform ferromagnetic ordering in the g-C₃N₄ monolayer, the next question is how to choose suitable organic/inorganic molecules as building units.

BH₄ and BF₄ are known as superhalogens according to the literature reports.⁵⁵ They are molecular units that mimic the chemistry of halogens.⁵⁵ Electron affinities (EA) of superhalogens are larger than those of halogens and can be tuned by controlling their composition. Superhalogens have been used as building blocks for many kinds of functional materials, such as electrolytes of lithium-ion batteries,⁵⁶ hybrid perovskite solar cells⁵⁷ and light-emitting diodes.⁵⁸ Due to large EA, superhalogens are good candidates for electron acceptor dopants. Most superhalogens are nontoxic and free from clustering tendency making them superior to halogens. Thus, BH₄ and BF₄ are the potential building blocks for the g-C₃N₄ monolayer.



Fig. 2 Spin-resolved band structures of $g-C_3N_4$ doped with (a) 0.2 and (b) 1.0 holes, respectively. (c) Magnetic moment and energy difference between FM and NM configurations as functions of doped hole concentration.



As explored by the p-doping model calculations, the ideal organic molecules should only dope holes into the sheet, and interact with the layer through ionic bonding. To find the potential candidates, we align the energy levels of the $g-C_3N_4$ monolayer and superhalogens as shown in Fig. 3. Both the lowest unoccupied molecular orbitals (LUMO) of BH4 and BF4 are lower in energy than that of the valence band maximum (VBM) of the g- C_3N_4 monolayer. It seems that both BH₄ and BF₄ molecules can be used as building blocks to form hybrid structures with the g-C₃N₄ monolayer, and produce the necessary magnetic ordering. However, the small energy difference between the LUMO of BH4 and the VBM of the g-C3N4 monolayer (only 0.07 eV), and the matched wavefunctions may lead to the strong chemical bonding, which inevitably breaks the original geometric structures. Therefore, the BH₄ molecule is not supposed to be suitable as a building block.

To confirm such pictures, we investigated the hybrid structures of $g-C_3N_4$ and BH_4 (BF₄) molecules. As shown in Fig. 4(a) and (b) of the optimized structures for $g-C_3N_4(BF_4)_{0.25}$ and $g-C_3N_4(BH_4)_{0.25}$,



Fig. 4 Optimized structures of $g-C_3N_4$ modified by (a) BF₄ and (b) BH₄. Dotted red circle denotes the hydrogen atoms combined with the nitrogen atom. Gray, blue, orange, purple and white balls denote carbon, nitrogen, boron, fluorine and hydrogen atoms, respectively.

 BF_4 stays at the hollow site of g-C₃N₄, the distance between the nearest nitrogen and fluorine is 2.8 Å. Adsorption of BF_4 makes the whole system release energy about 5.25 eV per BF_4 unit, which means that the combination between g-C₃N₄ and BF_4 is robust. While for g-C₃N₄(BH_4)_{0.25}, one hydrogen atom decomposes from BH_4 and combines with the nitrogen atom of g-C₃N₄. Since the geometric structure of the matrix g-C₃N₄ cannot be well protected upon modification of BH_4 , it is not easy to form long-range ordering structures in the hybrid structures constructed by BH_4 and the g-C₃N₄ sheet.

According to our band alignment predictions and firstprinciples simulations, BF_4 is selected as the promising unit to form hybrid structures with $g-C_3N_4$. To study the magnetic properties, we start with $g-C_3N_4(BF_4)_{0.25}$ as a representative model (see Fig. 4(a)). The energy for the spin-polarized solution (FM state) is 0.01 eV lower than that in a non-spin-polarized calculation. Moreover, the antiferromagnetic (AFM) configuration automatically converges to the FM state. The magnetic moment is found to be 1 μ_B per BF₄, and it is evenly distributed on the 12 double-coordinated nitrogen atoms as shown in a magnetic charge density plot (see Fig. 5(c)). This merit makes g-C₃N₄(BF₄)_{0.25} free from FM precipitate problems. The PDOS plot (Fig. 5(b)) indicates that magnetic moment comes from the p orbital of nitrogen atoms, which agrees well with the magnetic charge density plot (Fig. 5(c)). Importantly, a spin-resolved band



Fig. 5 Spin-resolved (a) band structures and (b) partial density of states of $g-C_3N_4(BF_4)_{0.25}$. (c) Top and side views of 3D isosurface plots of spin charge density for $g-C_3N_4(BF_4)_{0.25}$. (d) Fluctuations of temperature and energy as a function of molecular dynamic simulation steps at 300 K. Inset plots show the structure after 5 ps.

structure and PDOS indicate that g-C₃N₄(BF₄)_{0.25} is half metal. The majority spin channel possesses a bandgap of about 2.2 eV, while the minority spin channel is metallic. Additionally, to evaluate the thermal stability of the ferromagnetism, we employed Monte Carlo (MC) simulations on the basis of the Ising model to study the variation of the average magnetic moment as a function of temperature.^{24,32} As shown in Fig. S3 (ESI[†]), the magnetic moment per (C₃N₄)₄BF₄ formula unit decreases to 0.6 $\mu_{\rm B}$ at ~100 K. The paramagnetic state is achieved at a temperature of ~240 K. Based on the study above, we come to the conclusion that BF₄ is a promising building unit to induce half-metallic ferromagnetism in g-C₃N₄.

To investigate the effect of dopant concentration on electronic properties, we take g-C₃N₄BF₄ as another representative model. Adsorption of BF4 is exothermic, releasing energy about 2.33 eV per BF4 unit. Again, half-metallic FM configuration is the ground state, and the energy difference between the FM state and the non-spin-polarized state is about 0.03 eV per unit, and the AFM state converges to the FM state automatically. Compared with g-C₃N₄(BF₄)_{0.25}, the stability of ferromagnetism is greatly enhanced. Every BF₄ can induce 1 $\mu_{\rm B}$ magnetic moment. However, apart from nitrogen atoms, fluorine atoms contribute to the magnetic moment in g-C₃N₄BF₄ (see Fig. S2, ESI^{\dagger}). The reason is that when x increases from 0.25 to 1, BF₄ cannot be seen as impurities, the flat bands (feature of impurity bands) contributed from the p orbital of F atoms around -1 to -0.8 eV (see Fig. 5(a) and (b)) go up to the Fermi level (see Fig. S2(a) and (b), ESI⁺), then split to make the structure stable. The doped electrons prefer the spin-polarized solution in BF4 units. Furthermore, Fig. S3 (ESI⁺) shows that the magnetic moment per $C_3N_4BF_4$ formula unit decreases to 0.6 μ_B at ~240 K, much higher than the $(C_3N_4)_4BF_4$ situation.

Now, we discuss the stability of hybrid structures. We investigate the thermal dynamic stability of g-C₄N₃BF₄. Fig. 5(d) shows the fluctuations in temperature and energy as a function of the simulation time at 300 K. After 5 picoseconds (ps), we find no structure destruction (insets in Fig. 5(d)) of g-C₄N₃BF₄. These results confirm that the hybrid structures of g-C₄N₃BF₄. These results confirm that the hybrid structures of g-C₄N₃BF₄ are quite stable under room temperature. Furthermore, Fig. S4 (ESI[†]) indicates that the ground state remains magnetic with an average magnetic moment of around 24 $\mu_{\rm B}$ at 300 K, which means that the FM state is robust against the structural distortion during molecular dynamics simulations. However, it should be mentioned that such a temperature does not correspond to a magnetic critical temperature, as our molecular dynamics does not include spin-dynamics.

Conclusions

In summary, we demonstrated the successful design of halfmetallic ferromagnetism through the band alignment strategy. Taking metal-free graphitic C_3N_4 (g- C_3N_4) as an example, we show that the conduction band minimum (CBM) of g- C_3N_4 is much higher in energy than the lowest unoccupied molecular orbital (LUMO) of superhalogen (BF₄) molecules. By the strong ionic bonding, the hybrid structures constructed by g- C_3N_4 and BF_4 molecules display interesting half-metallic ferromagnetism. The stability of both magnetism and geometric structures is carefully studied. The intrinsic mechanism and the idea have been well explored, which can be used in similar research with other abundant analogues. To our knowledge, our work presents the first successful result to design half-metallic ferromagnetism in such layered structures using this easy strategy. Therefore, our results provide an enormous stage to perform further studies with similar systems, and invoke experimental interest.

Conflicts of interest

There are no conflicts of interest to declare.

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