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# Investigation of strain and doping on the electronic properties of single layers of $C_6N_6$ and $C_6N_8$ : a first principles study†

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In this work, by performing first-principles calculations, we explore the effects of various atom impurities on the electronic and magnetic properties of single layers of  $C_6N_6$  and  $C_6N_8$ . Our results indicate that atom doping may significantly modify the electronic properties. Surprisingly, doping Cr into a holey site of  $C_6N_6$  monolayer was found to exhibit a narrow band gap of 125 meV upon compression strain, considering the spin–orbit coupling effect. Also, a C atom doped in  $C_6N_8$  monolayer shows semi-metal nature under compression strains larger than  $-2\%$ . Our results propose that Mg or Ca doped into strained  $C_6N_6$  may exhibit small band gaps in the range of 10–30 meV. In addition, a magnetic-to-nonmagnetic phase transition can occur under large tensile strains in the Ca doped  $C_6N_8$  monolayer. Our results highlight the electronic properties and magnetism of  $C_6N_6$  and  $C_6N_8$  monolayers. Our results show that the electronic properties can be effectively modified by atom doping and mechanical strain, thereby offering new possibilities to tailor the electronic and magnetic properties of  $C_6N_6$  and  $C_6N_8$  carbon nitride monolayers.

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## 1 Introduction

Recently, two-dimensional carbon nitride (2D-CN) nanomaterials have attracted remarkable attention, not only because of astonishing experimental advances concerning their synthesis but also due to their exciting physics<sup>1–5</sup> and promising prospects for various advanced applications, like nano-electronics, energy storage and catalysis.<sup>6–16</sup> Two-dimensional carbon nitride (2D-CN) nanomaterials belong to a group of allotropes with a common chemical formula of  $C_nN_m$ , where  $n$  and  $m$  represent the number of C and N atoms in the unit cell, respectively, which can be stabilized as monolayers by taking advantage of the multifarious chemistry of C and N atoms. Depending on the composition of C and N atoms in the atomic lattice, these allotropes can show diverse electronic properties,

ranging from semiconducting to half-metallic. 2D-CN monolayers exhibit considerable structural, electronic and magnetic properties<sup>17–21</sup> with diverse electronic properties, originating from their unique and different atomic lattices, made from strong covalent bonds.<sup>22–25</sup>

The successful synthesis and fabrication of two-dimensional carbon nitride (2D-CN) nanomaterials, including  $C_2N$ ,  $C_3N$ ,  $C_6N_8$  and  $C_6N_6$  through bottom-up procedures, has motivated researchers to consider possible approaches for tuning the band gap and electronic response of these attractive nanosheets.<sup>22,26–28</sup> Some 2D-CN nanosheets have been experimentally realized using different approaches.<sup>1,3,29–33</sup>  $C_6N_6$  is a 2D-CN allotrope in which two hexagonal rings are separated by a C–C bond,<sup>1</sup> and it has already been theoretically investigated.<sup>34–36</sup> Recent theoretical work showed that  $C_6N_6$  exhibits a topologically nontrivial band gap, which can be modulated to a topological insulator by doping.<sup>1</sup> To search for a suitable spintronic material such as a diluted magnetic semiconductor, first-principles calculations of transition metal (TM) atoms doped in semiconducting 2D-CN sheets have been performed<sup>2,37,38</sup> using density functional theory (DFT) calculations.<sup>39,40</sup> The semiconducting nature and band alignment in this nanosheet are suitable for hydrogen generation *via* photo-catalytic water splitting.<sup>41–44</sup>

First-principles calculations indicated that topologically nontrivial electronic states near the Fermi level can be characterized by a ruby model.<sup>45</sup> Recently, carbon nitride materials with stoichiometry of  $C_6N_8$  have been synthesized

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experimentally.<sup>12,26,46,47</sup>  $C_6N_8$  are the prevailing building blocks that are joined together directly or by  $sp^2$ -hybridized nitrogen/carbon atoms.<sup>12</sup> The electronic and magnetic properties have subsequently been studied,<sup>48,49</sup> and theoretical studies demonstrate that  $C_6N_8$  is not a magnetic material; however, after replacing a nitrogen atom with a carbon atom in the unit cell of  $C_6N_8$ , it displays intrinsic half-metallicity.<sup>3</sup> Hydrogenation can also induce magnetism in carbon-based nonmagnetic materials.<sup>50,51</sup> It was predicted theoretically that hydrogen doping on the irradiation-induced carbon vacancy with hydrogen adsorption could induce a stronger magnetic moment than the bare vacancy.<sup>52</sup> Moreover, first-principles calculations also show that semihydrogenated graphene sheets are ferromagnetic semiconductors with a small indirect gap.<sup>53</sup> On the other hand, it is well-known that the application of mechanical strain can be an effective way to adjust the electronic structure of 2DM,<sup>54</sup> and in previous studies strain has been proven as a common way to regulate properties. In order to enhance the application of a material in electronic and optoelectronic devices, it can be very useful to regulate the electronic properties. Atom impurities can tailor the electronic properties and can be used for a wide range of applications. Despite the fact that many 2D nanosheets have been synthesized recently, their tunable electronic properties have rarely been reported.<sup>55–90,108–110</sup>

In this paper, using first-principles calculations, we systematically investigate the effect of different atom impurities in the holey sites of  $C_6N_6$  and  $C_6N_8$  monolayers. Our results confirm that the electronic properties can be modified by doping with Cr atoms. In addition, by applying strain, we found that the magnetic moment can be modulated and a transition from semiconductor to metal can be achieved. Our results reveal that the band gap and magnetism can be modified or induced by various atom impurities, thereby offering effective possibilities to tune the electronic and magnetic properties of  $C_6N_6$  and  $C_6N_8$  monolayers.

## 2 Methods

We report the results of our spin-polarized DFT calculations for the electronic structure as implemented in the OpenMX 3.8 package.<sup>91</sup> Wave functions were expanded by the linear combination of multiple pseudoatomic orbitals (LCPAOs) created using a confinement scheme.<sup>92,93</sup> The generalized gradient approximation method proposed by Perdew–Burke–Ernzerhof (GGA-PBE)<sup>94</sup> was applied to deal with the exchange-correlation functionals, along with the norm-conserving pseudopotentials.<sup>95</sup> A quasi-Newton algorithm was employed to find the energy-minimized structures using the OpenMX package. The convergence criteria for the structural optimization were set as a force of less than  $1 \text{ meV } \text{\AA}^{-1}$  acting on each atom. After the completion of this step, we used a cutoff energy of 300 so that the total energies converge to below  $1.0 \text{ meV}$  per atom. The Brillouin zone was sampled by a  $k$ -point grid of  $23 \times 23 \times 1$  for the primitive unit cell and scaled according to the size of the supercells, on the basis of the Monkhorst–Pack scheme.<sup>96</sup> The monolayers are modelled as a periodic slab with a large vacuum region ( $20 \text{ \AA}$ ) in order to prevent interactions between adjacent

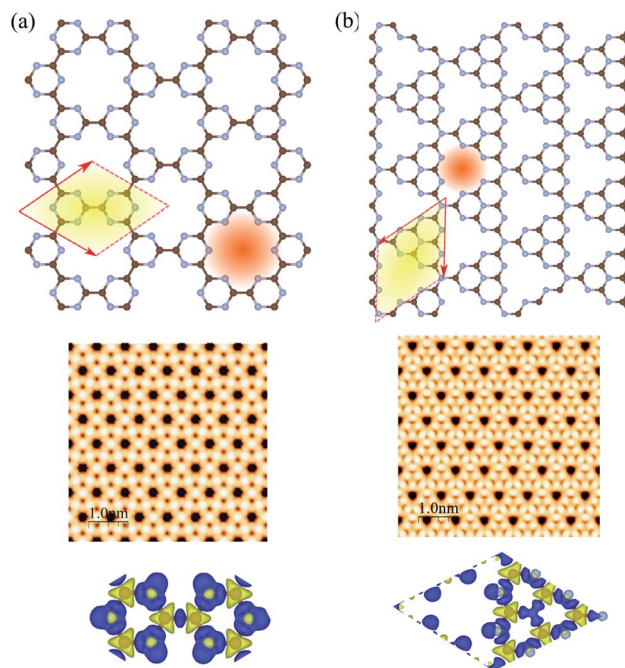


Fig. 1 Atomic structures (top), simulated STM images (middle) and charge density differences (bottom) of (a)  $C_6N_6$  and (b)  $C_6N_8$  monolayers. The primitive unit cells are indicated by red parallelograms. The brown and blue atoms represent C and N atoms, respectively. The blue and yellow regions represent the charge accumulation and depletion regimes, respectively.

layers. To describe the vdW interactions we use the empirical correction method described by Grimme (DFT-D2).<sup>97</sup> The charge transfer was calculated using Mulliken charge analysis.<sup>98</sup> Scanning tunneling microscopy (STM) images were simulated using the Tersoff–Hamann theory.<sup>99</sup> The STM simulated images were plotted using WSxM software.<sup>100</sup>

## 3 Results

### 3.1 Pristine $C_6N_6$ and $C_6N_8$ monolayers

The atomic structures, simulated STM images, and charge density differences of  $C_6N_6$  and  $C_6N_8$  monolayers are shown in Fig. 1(a) and (b), respectively. The optimized lattice constant of  $C_6N_6$  is calculated to be  $7.11 \text{ \AA}$  and the corresponding C–C and C–N bond lengths are found to be  $1.503 \text{ \AA}$  and  $1.343 \text{ \AA}$ , respectively. The nanopore diameter is found to be  $5.447 \text{ \AA}$ , which is equivalent to the distance from one N atom to the opposite N atom across the pore. These results are consistent with previous reports.<sup>36,101–103</sup> The charge density difference, in which the blue and yellow colors show the charge accumulation and depletion, respectively, reveals that the positively charged C atoms are surrounded by negatively charged N atoms. Moreover, the simulated STM image indicates that the atoms around the C atom sites show bright spots. The electronic band structure, density of states (DOS) and partial DOS (PDOS) of  $C_6N_6$  and  $C_6N_8$  monolayers are shown in Fig. 2(a) and (b), respectively. Apparently, the  $C_6N_6$  monolayer is a semiconductor with a direct band gap of  $1.5 \text{ eV}$  located at the K-point, which is also



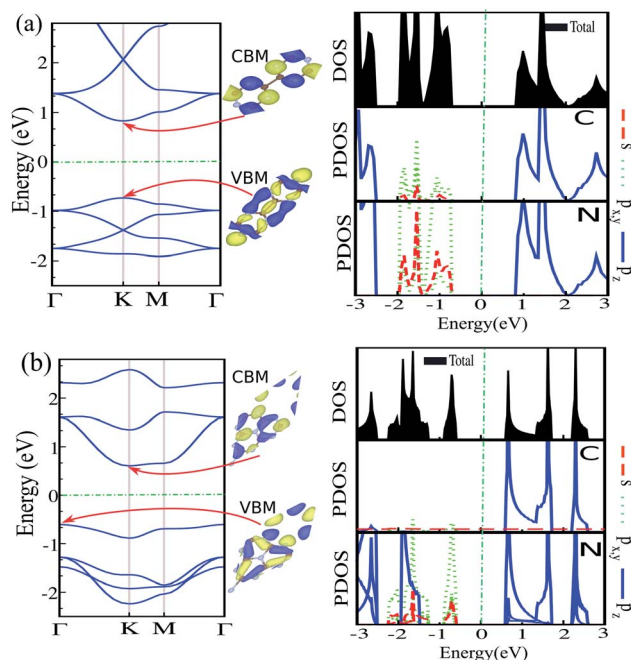


Fig. 2 Electronic band structure (left), density of states and partial density of states (right) of (a)  $C_6N_6$  and (b)  $C_6N_8$  monolayers. The insets represent the charge densities of the VBM and CBM. Zero energy is set at the Fermi level.

supported by a previous report.<sup>36</sup> From the PDOS, we found Fermi-level sharp peaks +2 eV below the Fermi level, suggesting that there are localized wave functions in  $C_6N_6$  and indicating that sharp double peaks (flat shallow bands) are formed from the N s and  $p_{x,y}$  orbitals. In the VBM, the N atoms are in the  $sp^2$  configuration and their lone pairs are further exhibited in the rising band structure from the  $\Gamma$  to the K point near the Fermi-level. The lone pairs of N s and  $p_{x,y}$  lie in in-plane orbitals, suggesting the donor nature of the nanopore, although the N/C

$p_z$  antibonding delocalized orbitals form the CBM above the Fermi-level, showing the acceptor nature of  $C_6N_6$ . The filling of all the in-plane bonding orbitals implies high stability of the  $C_6N_6$  structure.

The optimized lattice constant of monolayer  $C_6N_8$  is found to be 7.14 Å, with two inequivalent C–N bonds (1.414 and 1.455 Å). In addition, the ring is not a regular hexagon since the C–N–C angle is equal to  $120^\circ$ , while the N–C–N angles are  $118^\circ$  and  $122^\circ$ , respectively. It is clear that every six C–N hexagon rings enclose a nanopore, while the edges are surrounded by six N atoms, with a nanopore diameter of 4.773 Å (see Fig. 2(b)), which is in agreement with previous reports.<sup>39,101,104,105</sup> The electronic structure of  $C_6N_8$  exhibits an indirect semiconductor with a 1.22 eV band gap, which is in agreement with the previous result.<sup>106</sup> In addition, from the PDOS of  $C_6N_8$  it can be clearly seen that the VBM is determined by the N s and  $p_{x,y}$  orbitals; however, the CBM originates from the N/C  $p_z$  orbitals.

### 3.2 Doping of atom into holey site

Here, we discuss the effect of atom doping on the structural and electronic properties of  $C_6N_6$  and  $C_6N_8$  monolayers. A  $2 \times 2 \times 1$  supercell of  $C_6N_6$  and  $C_6N_8$  contains 49 and 57 atoms, respectively. A schematic view of the doped atom in the holey site of the  $C_6N_6$  and  $C_6N_8$  monolayers is shown in the ESI, Fig. S1.† For the different atoms considered in our present study, the stable binding sites are uniformly at the nanopore. Through the rest of the study, the atom-doped  $C_6N_6$  structure is labeled as atom@ $C_6N_6$ . For instance, Mg doped  $C_6N_6$  is labeled Mg@ $C_6N_6$ .

The optimized structures of Mg@, Ca@ and Cr@ $C_6N_6$  are shown in Fig. 3(a–c), respectively. The Mg and Ca atoms interact through  $sp^2$ -hybridization and form two and six  $\sigma$  bonds with the neighboring N atoms, respectively. Our results show that the bond lengths of the Mg and Ca atoms with the nearest N atoms are 2.62 and 2.37 Å, respectively (see Table 1). The Cr atom binds to the two nearest N atoms facing the nanopore of the  $C_6N_6$  monolayer with a bond length of 1.94 Å. Notably, upon

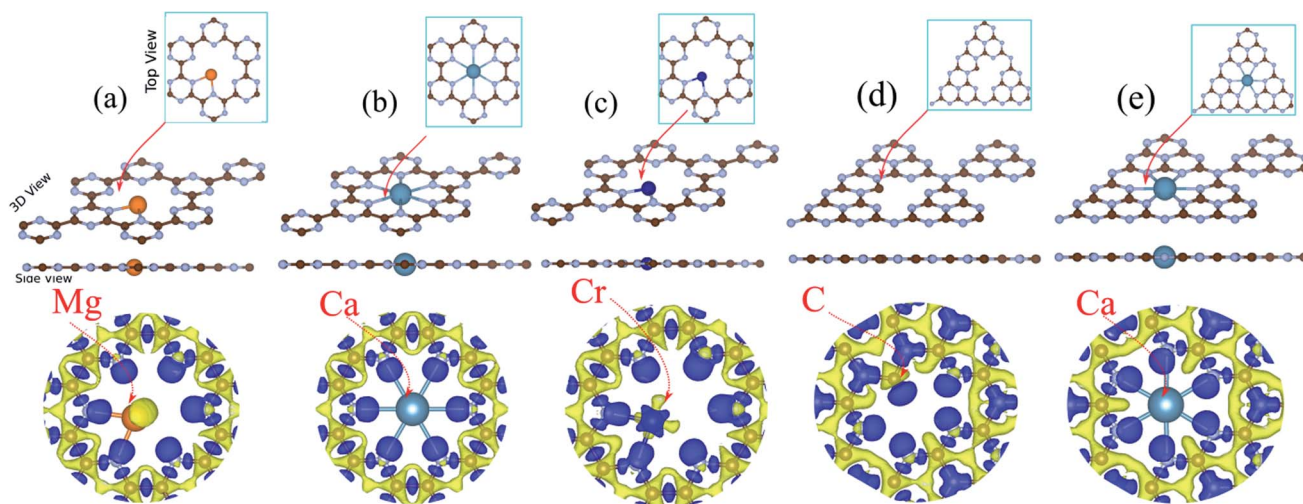


Fig. 3 Optimized structures of (a) Mg, (b) Ca, and (c) Cr atom doped  $C_6N_6$ . (d) and (e) Optimized structures of C and Ca doped  $C_6N_8$ . Charge density differences are shown in the bottom panel. Blue and yellow regions represent charge accumulation and depletion, respectively.





**Table 1** Structural, electronic and magnetic parameters of atom doped  $C_6N_6$  and  $C_6N_8$  monolayers. Bond length between doped atom and its nearest atom ( $d_{AN}$ ); bond length between N–C atoms ( $d_{NC}$ ); bond length between C–C atoms ( $d_{CC}$ ); charge transfer ( $\Delta Q$ ); magnetic moment per supercell  $M_{tot}$  ( $\mu_B$ ). Electronic state (ES), specified as metal (M), half-metal (HM), ferromagnetic metal (FM), semiconductor (SC). The values outside (inside) parentheses are for  $C_6N_6$  ( $C_6N_8$ ) monolayers

Atom	$d_{AN}$ (Å)	$d_{NC}$ (Å)	$d_{CC}$ (Å)	$\Delta Q$ (e)	$M_{tot}$ ( $\mu_B$ )	ES
C	1.46 (1.39)	1.40 (1.44)	1.42 (1.42)	0.99 (1.38)	0 (0)	SC (SC)
Mg	2.16 (2.30)	1.39 (1.41)	1.44 (1.44)	0.99 (1.38)	0 (0)	SC (M)
Ca	2.66 (2.37)	1.38 (1.38)	1.43 (1.44)	1.17 (1.32)	0 (1)	M (FM)
Cr	1.94 (2.16)	1.41 (1.40)	1.42 (1.42)	0.56 (0.63)	2.4 (2.1)	FM (HM)

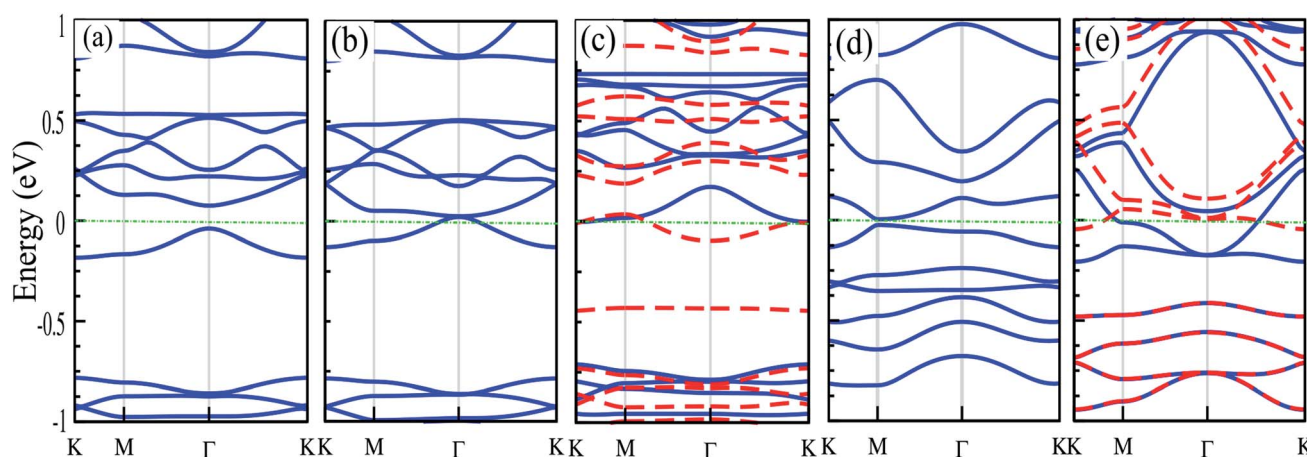
atom doping, the planar structure of monolayer  $C_6N_6$  is preserved. The charge density differences are presented in Fig. 3, where the bond formation, charge accumulation, and depletion regions can clearly be seen. The blue and yellow regions represent charge accumulation and depletion, respectively. For the stability of the structures, we calculate the binding energy ( $E_b$ ) between the doped atoms and the  $C_6N_6/C_6N_8$  sheets by the following formula:

$$E_b = E_{tot} - E_{sheet} - E_{atom} \quad (1)$$

Here,  $E_{tot}$  is the total energy of the doped  $C_6N_6/C_6N_8$  sheet, and  $E_{sheet}$  and  $E_{atom}$  are the energies of the pristine  $C_6N_6/C_6N_8$  sheet and isolated spin-polarized atom, respectively. According to this definition, a more negative value of  $E_b$  indicates that the system has stronger binding between the atom and the  $C_6N_6/C_6N_8$  sheet. Our results show that the binding energies for C, Mg, Ca and Cr atom doping in  $C_6N_6$  ( $C_6N_8$ ) sheets are  $-3.46$  eV ( $-3.38$ ),  $-3.70$  eV ( $-3.43$ ),  $-3.95$  eV ( $-3.87$ ) and  $-4.65$  eV ( $-3.65$ ).

The electronic structures of Mg@, Ca@ and Cr@ $C_6N_6$  are shown in Fig. 4(a–c), where the solid blue and dashed red lines represent  $\uparrow$  and  $\downarrow$  spin channels, respectively. Our results show that in comparison with pristine  $C_6N_6$ , the band structures are modified and give rise to localized mid-gap states arising from the atomic doping. Note that the doping of Mg and Cr atoms gives rise to some localized states in the band structure, which modify the electronic properties. Our results show that

Mg@ $C_6N_6$  exhibits direct band gap semiconducting behavior, with a small band gap of 100 meV where the VBM and CBM are located at the  $\Gamma$  point. Interestingly, we can see that the Ca@ $C_6N_6$  monolayer exhibits metallic character. In contrast, Cr@ $C_6N_6$  is a ferromagnetic metal with a net magnetic moment of  $2.4 \mu_B$ . Note that the energy bands of the  $\uparrow$  and  $\downarrow$  spin channels near the Fermi-level cross together near to the Dirac-point. On the other hand, monolayer C@ $C_6N_8$  becomes a direct band gap semiconductor with a narrow band gap of 25 meV, with the VBM and CBM located at the M point. With Ca atom doping in  $C_6N_8$ , we see a spin-polarized ferromagnetic metal with impurity levels crossing the Fermi-level and inducing a net magnetic moment of  $1 \mu_B$  per formula unit. The atomic contributions to the electronic states can be further seen by the PDOS, which are presented in Fig. 5. It is clear that the Mg and Ca states in  $C_6N_6$  mostly contribute to the deep valence and conduction states. On the other hand, Cr in  $C_6N_6$  and C in  $C_6N_8$  also contribute to the states around the Fermi-level. The optimized structures and electronic structures of C@ $C_6N_6$ , Mg@ $C_6N_8$  and Cr@ $C_6N_8$  are shown in Fig. S2(a–c),† respectively. We found that the C atoms interact through  $sp^2$ -hybridization and form two  $\sigma$  bonds with the neighboring N atoms of  $C_6N_6$ . The C@ $C_6N_6$  structure shows semiconductor behavior with an indirect band gap of 1 eV, where the VBM and CBM are located at the K and M points, respectively (see Fig. S2(a)†). Our results show that the Cr atom bonds to the N host atoms of  $C_6N_8$



**Fig. 4** Electronic structures of (a) Mg@ $C_6N_6$ , (b) Ca@ $C_6N_6$ , (c) Cr@ $C_6N_6$ , (d) C@ $C_6N_8$  and (e) Ca@ $C_6N_8$ . The energy bands of  $\uparrow$  and  $\downarrow$  spin channels are indicated by blue lines and red dashed lines, respectively. Zero energy is set at the Fermi-level.



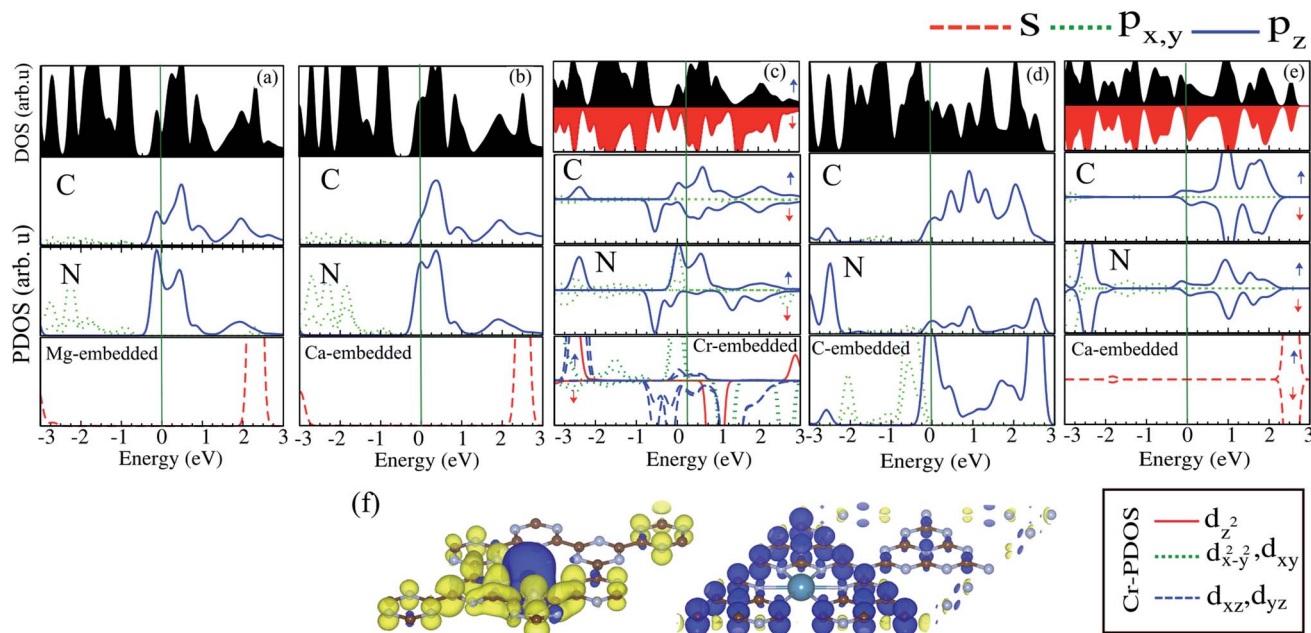


Fig. 5 DOS and PDOS of (a) Mg@C<sub>6</sub>N<sub>6</sub>, (b) Ca@C<sub>6</sub>N<sub>6</sub>, (c) Cr@C<sub>6</sub>N<sub>6</sub>, (d) C@C<sub>6</sub>N<sub>8</sub> and (e) Ca@C<sub>6</sub>N<sub>8</sub>. (f) Spin density difference. The blue and yellow regions represent the  $\uparrow$  and  $\downarrow$  spin states, respectively.

and forms six  $\sigma$  bonds, while the neighboring N atoms of C<sub>6</sub>N<sub>8</sub> form four  $\sigma$  bonds with the Mg atom (see Fig. S2(a) and (b)†). From the electronic band structure, we can see that Mg@C<sub>6</sub>N<sub>8</sub> turns into a metal, whereas the Cr@C<sub>6</sub>N<sub>8</sub> structure becomes a half-metal and a magnetic moment of about  $2.1 \mu_B$  is induced.

## 4 Effect of strain

Strain engineering is a robust method to tune the electronic properties and topological nature. In the following, we investigate the effects of uniaxial tensile and compressive strains on the electronic properties of atom doped C<sub>6</sub>N<sub>6</sub> and C<sub>6</sub>N<sub>8</sub> monolayers. The strain is defined as:  $\varepsilon = (a \pm a_0)/a_0 \times 100$ , where  $a$  and  $a_0$  are the strained and non-strained lattice constants, respectively, and the positive (negative) sign denotes tensile (compressive) strain. The band structures of Cr@, Mg@ and Ca@C<sub>6</sub>N<sub>6</sub>, and C@ and Ca@C<sub>6</sub>N<sub>8</sub> as a function of the applied strain are shown in Fig. 6(a–e). Cr@C<sub>6</sub>N<sub>6</sub> displays dilute magnetic semiconductor behavior under +2% tensile strain and it is preserved up to +8% strain. In addition, the magnetic moment increases from 2.8 (at –2%) to  $3 \mu_B$  (at –8%) with increasing compressive strain, while it is almost constant under tensile strain. Interestingly, when the compression strain reaches –2%, Cr@C<sub>6</sub>N<sub>6</sub> exhibits spin-polarized semi-metal characteristics.

Our results show that Mg@C<sub>6</sub>N<sub>6</sub> in the range of –2% to –6% exhibits a decreasing band gap from 90 meV to 70 meV, respectively, while in the strain-free case the band gap is 110 meV. This situation differs under tensile strain, such that the band gap changes in the range of 130 meV to 115 meV. Interestingly, at a tensile strain larger than +8%, the band structure of Mg@C<sub>6</sub>N<sub>6</sub> in both  $\uparrow$  and  $\downarrow$  spin channels becomes spin-

polarized, leading to the transition from nonmagnetic to magnetic states (see Fig. 6(b)). Ca@C<sub>6</sub>N<sub>6</sub> is naturally a metal; surprisingly, with strains of –2% and –4% the band gaps reach 25 meV and 23 meV, respectively (see Fig. 6(c)), whereas under strain larger than –6% it transforms into a metal and we see a nontrivial band gap of 30 meV in the vicinity of the Fermi-energy. On the other hand, for monolayer Ca@C<sub>6</sub>N<sub>6</sub> under +6 and +8% strain, the VBM (CBM) of the  $\downarrow$  ( $\uparrow$ ) spin channel continuously shifts upward (downward) to the Fermi level, resulting in ferromagnetic metallic behavior with magnetic moments of  $0.8 \mu_B$  (+6%) and  $1.8 \mu_B$  (+8%). The electronic band structure of C@C<sub>6</sub>N<sub>8</sub> under strain is shown in Fig. 6(d). C@C<sub>6</sub>N<sub>8</sub> is initially a direct semiconductor with a narrow band gap of 30 meV; however, under  $0\% \leq$  tensile strain  $\leq +8\%$ , the band gap increases monotonically from 70 meV (at +2%) to 200 meV (at +8%), while the VBM and CBM of the direct band gap are located at the M point. Our results show that the semi-conducting characteristics are preserved in the range of +2% to +8%. Interestingly, C@C<sub>6</sub>N<sub>8</sub> under compression strains of –2, –4 and –8% exhibits semi-metal behavior. When it reaches –6%, it transforms to a metal due to the CBM decrease and VBM increase to the Fermi-level. The electronic band structure of Ca@C<sub>6</sub>N<sub>8</sub> under uniaxial strain in the  $\uparrow$  and  $\downarrow$  spin channels is shown in Fig. 6(e). We can see that variations in the magnetic moment occur when it is subjected to tensile and compressive strain. Ca@C<sub>6</sub>N<sub>8</sub> is initially a ferromagnetic metal with a magnetic moment of  $1 \mu_B$  in the ground state. Interestingly, when a strain larger than +2% to +8% is applied, the ferromagnetic metal state is lost and both the  $\uparrow$  and  $\downarrow$  spin channels become non-spin-polarized, leading to a transition from a ferromagnetic metal to a nonmagnetic-metal state. Note that by increasing strain up to +2%, its magnetic moment vanishes.



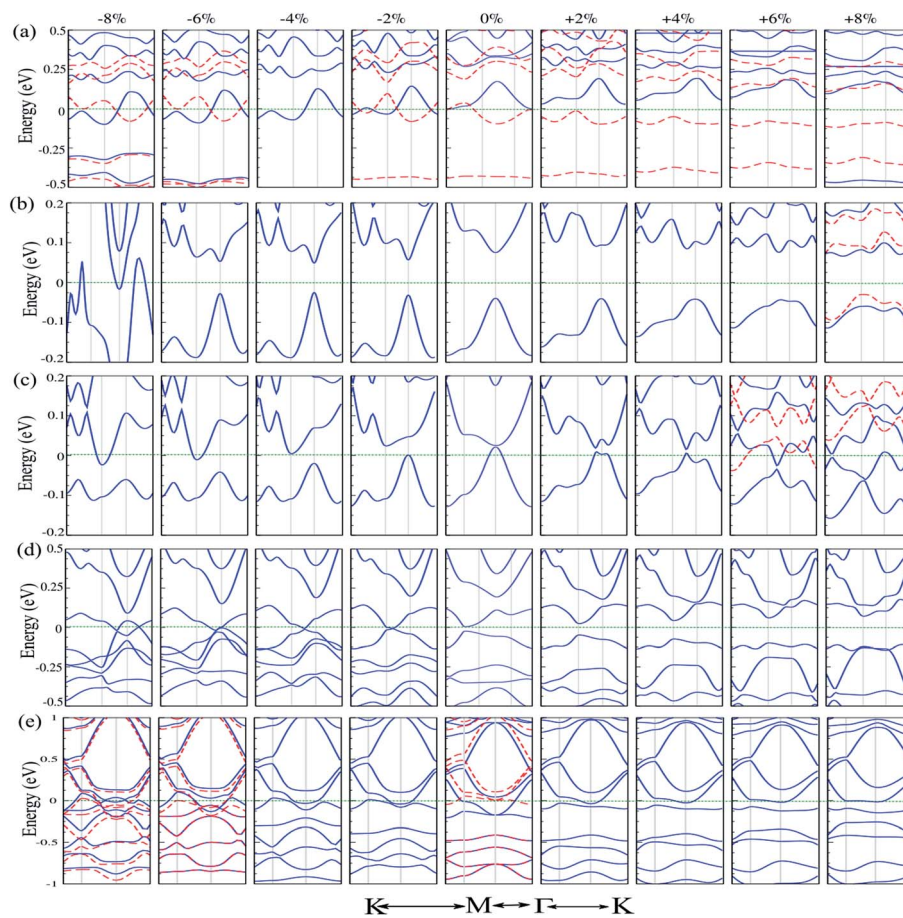


Fig. 6 Electronic band structure of (a) Cr@C<sub>6</sub>N<sub>6</sub>, (b) Mg@C<sub>6</sub>N<sub>6</sub>, (c) Ca@C<sub>6</sub>N<sub>6</sub>, (d) C@C<sub>6</sub>N<sub>8</sub> and (e) Ca@C<sub>6</sub>N<sub>8</sub> as a function of strain. The energy bands of ↑ and ↓ spin channels are indicated by blue lines and red dashed lines, respectively. Zero energy is set at the Fermi-level.

Also, for strains of 2–4%, Ca@C<sub>6</sub>N<sub>8</sub> transforms into a nonmagnetic metal, while for larger strains (>–6%) the structure transforms into a ferromagnetic metal with magnetic moments of 0.47  $\mu_B$  (–6%) and 0.53  $\mu_B$  (–8%).

The electronic structures of Cr@C<sub>6</sub>N<sub>6</sub> without strain and with –2% strain, considering spin–orbital coupling (SOC) and without SOC, are shown in Fig. 7(a) and (b). For Cr@C<sub>6</sub>N<sub>6</sub> upon –2% compression strain, without considering SOC, we can see that the ↑ and ↓ spin bands cross each other at the Fermi-level, which implies a magnetic semi-metallic nature. Our results show that when the SOC effect is considered, we see a touching point along the  $\Gamma$  and K paths at the Fermi level, and a narrow band gap of 125 meV forms in the proximity of the Fermi level, which implies a semi-metallic character. The effect of SOC correction on the evolution of electronic structure was found to be remarkable, such that degeneracies at the VBM are removed. Due to weak screening of the Coulomb interaction in the doping of transition metal atoms, the Hubbard U energy band structure may be expected to be weak. Since the accurate value of U has not been determined, we investigate the correlation effects by the value of the Hubbard U. To confirm that semi-metallicity is not an artificial result from the GGA+U method, we perform calculations for the doping of Cr atoms. The electronic band structures of Cr@C<sub>6</sub>N<sub>6</sub> without strain and with –2% strain,

without (left) and with consideration of the Hubbard U effect (right) are shown in Fig. S3(a) and (b),† respectively. The correlation effects on the electronic and magnetic properties of Cr@C<sub>6</sub>N<sub>6</sub> without and with strain are significant and cause changes in the spin polarization. In the Cr-doped C<sub>6</sub>N<sub>6</sub> without strain and upon –2% compression strain, we can see that the ↑ and ↓ spin bands cross each other at the Fermi-level, which implies a spin-polarized semi-metallic nature, without considering Hubbard U. We can see that a nodal-line forms around the K and M points when  $U = 2$  eV is considered. Our results show that the magnetic moment of Cr@C<sub>6</sub>N<sub>6</sub> in  $U = 2$  eV are 3.53  $\mu_B$  (without strain) and 3.63  $\mu_B$  (with –2% strain).

Here, we discuss the magnetic coupling between Cr–Cr doped in C<sub>6</sub>N<sub>6</sub> monolayers. We consider two Cr atoms doped in one and two neighboring cavities for comparison. The spin density differences of Cr doped in one and two neighboring cavities of C<sub>6</sub>N<sub>6</sub> are shown in Fig. S4.† The electronic band structures are indicated in the right panels. All of the possible relative positions of two Cr atoms doped in one and two cavities of C<sub>6</sub>N<sub>6</sub> are considered, and only the most stable configurations are exhibited. The exchange energy  $E_{ex}$ , defined as  $E_{ex} = E_{FM} - E_{AFM}$ , is calculated to determine the most stable phase. Negative and positive  $E_{ex}$  indicate the FM and AFM ground states, respectively. For the case of one neighboring cavity, it is found





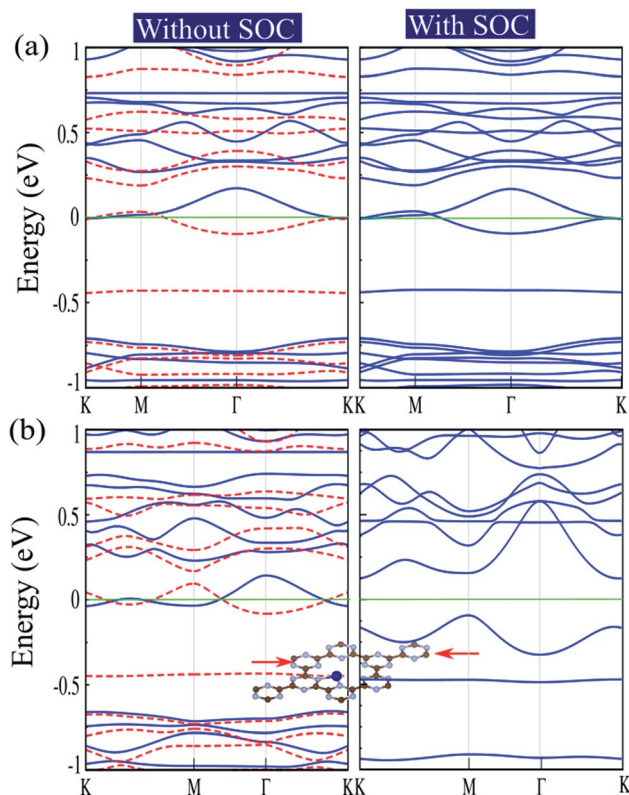


Fig. 7 Electronic structures of (a) Cr@C<sub>6</sub>N<sub>6</sub>, without and with consideration of spin–orbital coupling (SOC) effect; (b) Cr@C<sub>6</sub>N<sub>6</sub> upon –2% strain, without and with SOC effect. Optimized structures under the applied strain are shown in the insets. The energy bands of ↑ and ↓ spin channels are indicated by blue lines and red dashed lines, respectively. Zero energy is set at the Fermi-level.

that the Cr atoms exhibit FM coupling (with  $E_{\text{ex}} = 140$  meV) in their most stable phases, and the corresponding spin density differences are shown in Fig. S4(a).† Because the distance between the two Cr atoms is small ( $\sim 1.82$  Å), one may think that the two Cr atoms should show direct coupling through C/N atoms. For the case of two cavities, it is clearly seen that the case of the Cr atoms is quite different from the above findings and they show AFM coupling ( $E_{\text{ex}} = 30$  meV) with corresponding spin density differences.

## 5 Conclusion

In summary, using first-principles calculations, we have explored the effects of atom doping on the structural, electronic, and magnetic properties of C<sub>6</sub>N<sub>6</sub> and C<sub>6</sub>N<sub>8</sub> monolayers. Our theoretical results indicated that with atom doping, C<sub>6</sub>N<sub>6</sub> becomes a semiconductor with a narrow band gap (Mg-doped), semi-metal (Ca-doped) or ferromagnetic metal (Cr-doped). Additionally, we applied mechanical strain to both monolayers with atoms doped in their lattices. Our first-principles results revealed that the band gap and magnetism can be finely tuned by strain as well. Surprisingly, when the compressive strain reaches 2%, Cr-doped C<sub>6</sub>N<sub>6</sub> displays a phase transition to a spin-polarized semi-metal without SOC; when SOC is

considered, a narrow band gap of 125 meV is opened. Notably, in the case of Cr atom doped C<sub>6</sub>N<sub>6</sub> upon compressive strain, considering SOC, an unusual semi-metallic character can be observed. In the C-doped C<sub>6</sub>N<sub>8</sub> between applied tensile strains of 0–8%, the band gap was found to increase monotonically from 70 meV (at 2%) to 200 meV (at 8%), while it exhibits semi-metallic behavior under compressive strain larger than 2%. Our results show that a magnetic-to-nonmagnetic phase transition can occur under large tensile strain in the Ca doped C<sub>6</sub>N<sub>8</sub> monolayer. In addition, Mg and Ca atom doped C<sub>6</sub>N<sub>6</sub> can show topological insulator states under strain. The results provided by our extensive theoretical analysis highlight very promising electronic properties of C<sub>6</sub>N<sub>6</sub> and C<sub>6</sub>N<sub>8</sub> monolayers doped with various atoms and under mechanical strain, and will hopefully serve as a guide for future experimental and theoretical studies.

## Conflicts of interest

The authors declare that there are no conflicts of interest regarding the publication of this paper.

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