Adsorption of atoms and molecules on $s$-triazine sheet with embedded manganese atom: First-principles calculations

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The mechanical, structural, electronic and magnetic properties of $s$-triazine sheet ($C_6N_6$) with embedded Mn atom ($Mn-C_6N_6$) is investigated under the influence of external environment using density functional theory. Our results show that Mn-$C_6N_6$ system is structurally and mechanically stable. The binding energy of Mn embedded in $C_6N_6$ sheet can be modulated under the influence of symmetric deformation and perpendicular electric field respectively. The semiconducting property of pure $C_6N_6$ sheet is maintained upon embedment of Mn atom in the porous site. It is also found that small increment in bi-axial tensile strain enhances the band gap (from 0.630 eV at zero strain to 0.802 eV at 5% strain) while the magnetic moment of the embedded Mn atom is preserved. The electronic and magnetic properties of the Mn-$C_6N_6$ systems are maintained up to 10 V/nm in electric field strength. We also explore the geometries, electronic and magnetic properties of Mn-$C_6N_6$ with adsorbed atoms and molecules. The Mn-$C_6N_6$ with adsorbed O atom and O$_2$ molecule systems shows half-metallic character whereas the remaining systems preserve their semiconducting property. The total magnetic moment
per unit cell in most of the systems is found to reduce as compared to that of the Mn-C\textsubscript{6}N\textsubscript{6} sheet. The reduction in magnetic moment can be related to the strong interactions among the Mn atom and the surrounding atoms which lead to the formation of low-spin configurations. Overall, our results indicate that the Mn-C\textsubscript{6}N\textsubscript{6} systems with and without adsorbed atoms and molecules can serve as potential candidates for future spintronics and catalysis applications.
1 Introduction

Research interest in magnetic materials has gained its spectacular boost after the discovery of exotic magnetic properties [1, 2]. Additionally, continued device miniaturization has also opened up many research opportunities to reveal the magnetic properties of these nanostructures in hope for potential applications in spintronics and catalysis. At present, investigations on magnetic nanostructure are directed towards clusters of transition metals (TM). This is due to their large magnetic moments as the dimensionality and coordination (bonds per atom) of the TM cluster are reduced [3, 4]. However, their net magnetic moments can also become decreased, depending on the configuration (ferromagnetic and anti-ferromagnetic geometries) and surrounding of the clusters [5-8]. It is desirable to study the magnetic properties of a TM cluster which is evenly bound to an inert substrate such that the magnetic moment is comparable to that of a cluster in isolation. The interaction of TM atoms with certain metal surfaces is known to be very strong [8,9]. This could potentially affect their net magnetic moments. In contrast, carbon nanostructures are known to be inert, and stand as the right candidate for encapsulation of TM atoms.

Considering two-dimensional carbon nanostructures as substrates, many efforts have been devoted to study the physical and chemical properties of bound TM clusters on graphene [6,7,10] and boron nitride [11,12] sheets. However, previous works have shown that TM atoms bind weakly on graphene and boron nitride monolayers [7,12,13]. Such a weak binding may render TM atoms to diffuse easily on the surface and aggregate to form clusters. Many attempts have been made to create defects in the aforementioned surfaces to prevent the diffusion. However, not much success [12] has been achieved due to technical impracticability to realize controlled defect formation in compacted hexagonal 2D surfaces. Binding of dispersed TM atoms on the surfaces of graphene and other related 2D monolayers presents a practical challenge.

To practically produce controllable nanostructures with desired magnetic properties without altering the physical properties of the bound structures is not technically trivial. Such a challenge has led to the discovery of a new set of graphitic carbon-nitride (CN) sheets [14]. Graphitic CN sheet comes naturally with a regular array of cavities which is wide enough to accommodate any nanostructures that are evenly dispersed. CN sheet has many graphitic allotropes depending on the choice of the primitive unit cell and the C and N atomic coverage in their hexagonal rings. For example, the semiconducting heptazine (t-s-triazine) sheet comprises of 14 C and N atoms in the form of three abreast rings of triazine (consisting of 3 C and 4 N atoms in the unit cell) [15] whereas s-triazine sheet of similar electronic character consists of 12 C and N atoms having two rings of triazines linked together by C-C bond [16].
Both aforementioned allotropes are found to be structurally, energetically and mechanically stable under ambient conditions [15-17].

Having explained the motivation for the choice of graphitic CN sheet over the rest of 2D sheets with compacted hexagonal rings, the embedment of single atoms on the pure graphitic CN sheet has been the most recent interest for many theoretical [18-21] and few experimental [22-25] studies. The structural, electronic and magnetic properties of B, Al, and Cu atoms doped graphitic triazine-based $g$-$C_3N_4$ ($gt$-$C_3N_4$) systems have been theoretically investigated [26]. Their results have shown that Cu atoms are more stable when situated above the center of the triazine ring. Moreover, they have reported that doping at the interstitial sites leads to thermodynamically stable non-planar structures. It is found that Cu-doped triazine produces a total magnetic moment of 1.0 $\mu$B which is mainly localized around $p_z$ like-orbitals of the sheet. The electronic property of Cu-doped triazine systems calculated based on GGA-PBE and HSE06 method exhibits half-metallic behavior. The Cu-doped triazine system has an anti-ferromagnetic ground state. They did not estimate the Curie temperature for Cu-doped triazine system due to the fact that long-range magnetic ordering is usually favorable for the system having ferromagnetic order at zero temperature.

The energetic, electronic, magnetic and optical properties of two-dimensional graphitic carbon nitride ($g$-$C_3N_4$) sheets upon embedment of 3d-transition metal (TM) atoms have been investigated by Ghosh et al. The $g$-$C_3N_4$ sheets with embedded TM atoms are found to be energetically stable when located in the porous sites. It was also reported that the system becomes metallic upon TM (including Cu) embedment. The d orbitals of TMs hybridize with the $\pi$-orbitals of the $g$-$C_3N_4$ framework and close the band gap in TM-embedded $g$-$C_3N_4$ (TM-$g$-$C_3N_4$). In most cases the magnetic moment of the 3d TM atoms are well preserved when compared to their isolated values. However, Mn atoms couples antiferromagnetically whereas Cu and Zn atoms are nonmagnetic in the ground state of their corresponding TM-$g$-$C_3N_4$ sheets [21]. The claims for magnetic ordering in Mn, Cu embedded $g$-$C_3N_4$ sheets and metallic behavior for Cu embedded system at relatively the same separations are in contrast to what was observed by Zhang et al. [20] and Meng et al. [26] in the same allotropes. In a similar alltrope, Du et al. [27] suggest that Mn and Cu atom embedded in $C_2$N monolayers possess ferromagnetic and paramagnetic ground state respectively when the TM atoms are close to each other, while Meng et al. [26] observed antiferromagnetic ground state with half-metallic electronic character for Cu-doped triazine system. In general, the claim for magnetic ordering of TM atoms embedded in CN remains unclear. However, it is feasible to envisage that if the embedded TM atoms were well separated, the possible interactions among themselves could be minimized. The effort to clarify the magnetic ordering issue hence could become less complicated.
More recently, Choudhuri et al. [27] investigated newly formed allotrope of the carbon-nitride monolayer (gt-C$_3$N$_3$) with embedded 3d transition metal atoms (TM@gt-C$_3$N$_3$) systems based on density functional theory. It was found that the Cr, Mn and Fe embedded gt-C$_3$N$_3$ systems are dynamical, thermally and mechanically stable. Moreover, Cr, Mn and Fe embedded in the gt-C$_3$N$_3$ systems have been found to exhibit high temperature ferromagnetism and high magnetic anisotropy energy (MAE) with a peak value per atom occurring in Cr@gt-C$_3$N$_3$. Their finding for the ferromagnetic ordering of Mn atom in similar graphitic CN sheet under ambient conditions agrees well with that reported by Du et al. [28]. Choudhuri et al. [27] further claimed a more enhanced MAE in the presence of an external electric field, an amount far larger than the value computed without electric field.

In our recent studies, it was shown that the band gap of heptazine with embedded Mn atom increases under small biaxial tensile strain whereas the magnetic moment of heptazine with embedded Mn systems remain unperturbed under both tensile strain and applied electric field [18]. It was also observed that the binding energy of heptazine with embedded Mn atom systems decreases as more tensile strain is applied. In contrast, we observed significant increase in binding energy as the strength of electric filed is increased. Modulating binding energy via an applied external field could serve as an effect way to control catalytic process.

Besides spintronics, CN with embedded TM systems can also be utilized for heterogeneous catalysis and in membrane for hydrogen purification from other gases [29-31]. Heterogeneous catalysis based on single atomic crystal (SAC) is the cheapest and easiest way of achieving efficient catalysis. To date, various 2D sheets have been theoretically and experimentally proposed for heterogeneous catalysis [32-37]. Among others, monolayers carbon and related 2D nanostructures, e.g. boron nitride [32,33], graphene [34,35], graphyne [36], silicene [37], carbon nitride sheet [35] have received enormous attentions due to their availability, thermal stability and large surface area. Density functional theory (DFT) calculations have shown that graphene with embedded Au, Fe and Pt [34,38,39] atoms yield good catalytic activity for CO oxidation and oxygen reduction. Experimentally, excellent catalytic activities have been reported for graphene with supported single Pd and Pt using monolayer deposition method [29,40]. Although favorable catalytic process has been reported for SACs of graphene and related 2D materials, the adsorption/binding energies of 3d atoms on their surfaces are relatively weak and could result in formation of cluster that renders reduction in catalytic activity.

2D porous carbon sheets embedded with TM atoms [14,16] are desirable SACs that can serve as membrane for hydrogen purification from other gases [30,31]. This is because they naturally come with regularly array of cavities. These cavities are reported to strongly bind to 3d TM while maintaining structural and electronic features of the sheets [18,21]. A recent
work along this direction has confirmed theoretically that it is possible to synthesize high quality SACs using porous 2D materials with well dispersed 3d TM atoms. More importantly, the 3d TM atoms are found to strongly bind to the C$_2$N sheet in the cavity without cluster formation, while the intrinsic properties of both porous substrate and the atoms are preserved [41].

In this paper, we are interested to theoretically study the geometries, electronic and magnetic properties of TM-embedded graphitic systems in which different types of atoms and molecules are made to adsorbed onto their surfaces. To be specific, Mn-embedded s-triazine will be studied, as well as the adsorption of C, N, O, H atoms and six molecules (CH$_4$, N$_2$, O$_2$, H$_2$, CO, CO$_2$) on its surface. s-triazine sheet is an allotrope of graphitic carbon nitride which shares some structural similarities with C$_2$N sheet. It also comes with well separated porous sites which will ensure no interactions between the embedded TM atoms. Mn is chosen instead of other 3d TM species due to its well-ordered spin configurations in the d orbital and desirable characteristics for SAC applications which was reported in previous works.

2 Calculation method

We carried out density functional theory (DFT) [42] calculations using the QUANTUM ESPRESSO code [43]. Generalized gradient approximation (GGA) of Perdew-Burkew-Enzerhof (PBE) [44] and Hubbard $U$ correction [45] (GGA+$U$) is employed to describe the exchange-correlation energy of strongly localized 3d orbital of Mn atom. Ultrasoft pseudopotentials are used for C, N, and Mn (semi-core included) atoms to account for the core and valence electrons [46]. We employed plain wave basis set with kinetic energy cut-off of 550 eV to expand the wave functions. Marzari-Vanderbilt smearing method with Gaussian spreading is employed [47] to facilitate the convergences of our systems. We used $8 \times 8 \times 1$ and $15 \times 15 \times 1$ k-point meshes of Brillouin zone (BZ) sampling using the Mankhorst-Pack method for the self-consistent field and density of state calculations respectively [48].

The relaxed structure of 2$\times$2 pure graphitic C$_6$N$_6$ sheet (left figure in Fig. 2(a)) consists of 4 units of s-triazine (right figure in Fig. 1(a)) with a total of 48 C and N atoms. Each s-triazine has two rings of C$_3$N$_3$ connected via a C-C bond. The averaged optimized C-C bond length connecting adjacent s-triazine unit, C-N bond length and the lattice constant in the pure C$_6$N$_6$ are found to be 1.51 Å, 1.34 Å and 14.27 Å respectively (see the left figure in Fig. 1(a)). In the s-triazine structure, all C atoms are sp$^2$-like hybridized whereas N atoms have sp$^3$-like hybridized structure. Porous site in the graphitic C$_6$N$_6$ is encircled by solid line in the left figure in Fig. 1(a). The left figure in Fig 1. (b) shows Mn atom embedded
in the porous site. Henceforth, we shall refer the $2 \times 2$ supercell in Fig. 1(a) as $C_6N_6$, while Mn embedded in $C_6N_6$ as Mn-C$_6$N$_6$ in the left figure of Fig. 1(b). A thick vacuum space of 16 Å along the direction perpendicular to the Mn-C$_6$N$_6$ sheet is adopted to avoid the interaction between the periodic sheets. All atoms are fully relaxed until all remaining force on each atom was smaller than 0.05 eV/Å.

As suggested in our previous works [18], inclusion of Hubbard $U$ parameter yield better ground state properties for strongly correlated systems involving TM atoms. We therefore employed linear response approach formulated by Cococcioni et al. [45], which is implemented in the PWSCF package [43], to compute the $U$ parameter in this study. In the linear-response scheme calculations, we first evaluated $\chi_0$ and $\chi$ which represent the non-interacting (bare) and interacting density response functions of the system with respect to localized perturbations, as illustrated in Fig. 2(a). The parameter $U_{\text{eff}}$ is then obtained from the expression: $U_{\text{eff}} = (\chi_0^{-1} - \chi^{-1})$. The calculated $U_{\text{eff}}$ value for Mn-C$_6$N$_6$ is depicted in Fig. 2(a).

3 Results and Discussions

3.1 Structural and mechanical properties of Mn-C$_6$N$_6$ system

Fig. 1(c) displays the relaxed structure of Mn-C$_6$N$_6$. The averaged optimized C-C bond length connecting adjacent $s$-triazine unit and the lattice constant in the Mn-C$_6$N$_6$ are found to be 1.48 Å and 14.20 Å respectively. The optimized C-N bond lengths within the porous site are in the range 1.35 - ∼1.37 Å. The calculated values do not deviate much from the un-doped C$_6$N$_6$ system and is consistent with that of the previous work [16]. Using strain energy minimization procedures in steps of 0.005 for both uni- and biaxial tensile strains within the linear elastic region (see Fig. 3 and Table 1), mechanical properties are obtained. The elastic constants $k_{11}$, $k_{12}$, for uni- and bi-axial strains are 146.90 N/m and 26.20 N/m respectively, which are obtained from Eq. (1). The in-plane stiffness (Young modulus), and poison ration can be deduced from Eq. (2). These equations are expressed as:

\[
k_{11} = \frac{1}{A_0} \left[ \frac{\partial^2 U}{\partial s^2} \right]_{s=0} \quad \text{(uniaxial)}
\]

\[
2(k_{11} + k_{12}) = \frac{1}{A_0} \left[ \frac{\partial^2 U}{\partial s^2} \right]_{s=0} \quad \text{(biaxial)}
\]
In-plane stiffness and Poisson’s ratio:

\[
\begin{align*}
Y &= k_{11}(1 - \nu^2), \\
\nu &= \frac{k_{12}}{k_{11}}
\end{align*}
\]

(2)

where \( k_{11}, k_{22} \) denote elastic constants, \( A_0, U \), and \( s \) are equilibrium unit-cell area, strain energy and applied tensile strain. The computed in-plane stiffness and Poisson’s ratio are 1421.4 GPa·Å (= 142.14 N/m) and 0.18 respectively. This shows that Mn-C₆N₆ is less stiff than heptazine [15] and graphyne sheets [48]. The decreased in stiffness in comparison with heptazine can be linked to a weaker bonding of the hexagonal rings of the sheet. Moreover, the calculated Poisson’s ratio is slightly larger than the value for graphene [50]. To evaluate the bulk modulus, we use second derivative of the bi-axial strain energy as a function of area of the Mn-C₆N₆ sheet, which is expressed as

\[
G = A \times \left( \frac{\partial^2 U}{\partial A^2} \right) \bigg|_{A_m}
\]

(3)

where \( A, U \) and \( A_m \) denote the area of the Mn-C₆N₆ sheet, the bi-axial strain energy and the equilibrium area of Mn-C₆N₆ respectively. Fig.[iii] shows the bi-axial strain energy as a function of the area of Mn-C₆N₆ sheet. The computed value for the bulk modulus of Mn-C₆N₆ sheet is 86.49 N/m which is also lower than the value for Mn embedded in heptazine sheet [18]. The lowering of the value for bulk modulus can also be related to the compact hexagonal rings within the heptazine sheet as compared to separated rings in s-triazine sheet. All the computed results of elastic constants confirm that Mn-C₆N₆ is mechanically stable.

To further examine the structural stability of Mn-C₆N₆, the averaged bond lengths \( d_{\text{Mn-N}} \) between the embedded Mn and six nearest neighbor N atoms in the porous site, the averaged bond lengths \( d \) connecting adjacent s-triazine, and \( h \) the height of the Mn atom with respect to the Mn-C₆N₆ plane for strained and unstrained systems are listed in Table 2. We have also checked the binding energy of Mn in the Mn-C₆N₆ sheet as a function of bi-axial tensile strain for the range of 0-6%. The binding energy of the Mn-C₆N₆ is calculated as

\[
E_b = (E_{\text{C₆N₆}} + E_{\text{Mn}}) - E_T
\]

(4)

where \( E_T \) is the total energy of Mn-C₆N₆ sheet, \( E_{\text{C₆N₆}} \) represents the energy of pristine C₆N₆ sheet, and \( E_{\text{Mn}} \) is the total energy of an isolated Mn atom. Positive binding energy is an indication of a stable structure. According to Eq. (4), the unstrained Mn-C₆N₆ has a binding energy of 4.14 eV, which is roughly the same as that obtained in the recent works [41,51]. As can be seen in Table 2 there is little difference in the predictions of structural and magnetic
properties of unstrained Mn-C$_6$N$_6$ calculated in this work as compared to previous results. Here we state clearly the differences in terms of methodology and the choice of the unit cell between our calculations and the previous works. While we consider DFT+$U$ calculations in our Mn-C$_6$N$_6$ system, the work in Ref. [51] employed only DFT without Hubbard $U$ in the presumably same system. We opine that accurate computation of geometries and electronic properties in a system involving strongly correlated atoms can only be achieved if Hubbard $U$ is included [45]. The main difference between the present work and that of Ref. [41] lies within the choice of the unit cell. We use allotrope of graphitic carbon nitride (CN) sheet with equal number of C and N in all the hexagonal rings, with two rings connected via C-C bond in the unit cell with no dangling bond, whereas Ref. [41] used different allotrope of graphitic CN sheet. We anticipate that our results should agree with theirs since the environment where Mn atom is placed is probably the same.

We have further investigated the energetic, structural, electronic and magnetic properties under uniform tensile strain from 0% to 6%. For increasing tensile strain, the calculated value of the Mn height $h$ in the optimized Mn-C$_6$N$_6$ plane confirms the planarity of the sheet, where only slight movement of the Mn within the plane was found. We also observed that as the applied tensile strain increases the binding energy of Mn in the porous site becomes less pronounced. The decrease of the binding energy can be understood as follows. In general, elastic energy, $U$, for small deformations is positive. It is proportional to the product of square of the strain and the elastic module(s) related to biaxial tensile strain, which is (are) supposed to be positive as well. So for positive elastic moduli, the total energy (which is negative in value) of the Mn-C$_6$N$_6$ system should increase under small strain. Consequently, the binding energy (which is positive in value), according to the definition of Eq. [4], would become lower. We observe a uniform increase in the average C-C bond lengths connecting the heptazine units. Additionally, it was found that the average bond lengths between the embedded Mn and six nearest neighbor N atoms in the porous site increase accordingly as well. Overall, the decrease in the binding energy is due to structural distortion. At a 6% tensile strain, metastable structure is formed in which the binding energy, $E_b$, becomes negative (see Table 2).

3.2 Electronic and magnetic properties Mn-C$_6$N$_6$

Our calculations show that Mn embedded in C$_6$N$_6$ maintains its isolated magnetic moment for both strained and unstrained systems. This indicates that the magnetic moment is less sensitive to the applied bi-axial tensile strain. The corresponding magnetic moments for various systems are listed in Table 2, and the magnetic moment for unstrained Mn-C$_6$N$_6$ system agrees well with the previous literatures [41,51]. We can as well observe from the
magnetic moments per atom in Table 2 that the magnetism of Mn-C₆N₆ systems is mainly contributed by the Mn atom. Lowdin’s charge analysis shows that electron redistribution of Mn orbitals are mainly from s, p orbitals of Mn whereas d orbital relatively retain its unpaired electrons (high-spin configuration is maintained in each deformation. It is found that charge transfer into the C₆N₆ sheet, Q, which is calculated from Lowdin’s charge analysis, is relatively maintained in all deformations.

The coupling (i.e., ionic interaction between the Mn atom and C₆N₆ sheet) does not decrease the number of spin-polarized d orbital electrons of Mn atom. We also show the top view plot of the charge-density difference between the Mn atom and the surrounding C and N atoms of strain-free system in the right figure of Fig. 1(b). The figure indicates charge localization around the most electronegative N edge (dotted black color) atoms in the porous site. The charge depletion between the atoms confirms the covalent property of the bonds.

The total density of state (TDOS) of pure C₆N₆ is illustrated in Fig. 2(b). The pure C₆N₆ is a direct band gap semiconductor with a band gap of approximately 1.53 eV. The calculated bang gap tallies well with the previous work [16]. The embedment of Mn atom into the C₆N₆ induces magnetism for Mn-C₆N₆ system while maintaining the intrinsic electronic property of the C₆N₆ sheet. This is evident by comparing Fig. 2(c) (which shows the TDOS of the pure C₆N₆ sheet) and Figs. 4(a)-(c) (which shows the spin-polarized TDOS for the strain-free Mn-C₆N₆ system). The asymmetric TDOS of Mn-C₆N₆ system confirms the presence of magnetic moment in the system.

The spin-polarized projected density of state (PDOS) in Figs. 4(d)i - (f)i, illustrate the atomic orbital contributions of Mn-C₆N₆ system to valence and conduction bands around Fermi level. The 6 edge N atoms in the porous site formed bonds with the embedded Mn atom. In the plane of C₆N₆, the lone pairs of N atoms face the dₓᵧ and dₓ²−y² orbitals of Mn atom. Due to repulsive effect between the pₓ, pᵧ orbitals of N atom and the dₓᵧ, dₓ²−y² orbitals of Mn atom, the pₓ orbital will be at higher energy. Additional evidence can be referred to Fig. 4(d) which shows that the bottom of the conduction band is dominated by pₓ-like orbitals of the six edge N atoms in both spin states, whereas the other orbitals (e.g., s, pₓ, pᵧ) are located in the valence band (which is at a lower energy). This is supported by the measured EC values as shown in Table 2, where these values increase with increasing tensile strain. Moreover, the top of valence band displays dominance by lone pairs of N atoms. The remnant d-like orbitals would be forced to the lower energies. At approximately -6.5 eV and -8.0 eV the bonding orbitals are mainly due to sp-like orbitals of the edge N atoms, and s-, pₓ- and d-like orbitals of the Mn atom. Around -4.5 eV there is a hybridization which is occupied by s-, dₓz- and dₓz²-like orbitals of the Mn atom, as well as sp-like orbitals.
of the edge N atoms in the minority spin state. The sp-like orbitals of the Mn atom in both spin up and spin down channels portray intra-orbitals electron transfer.

We also observe band gap modulation of Mn-C$_6$N$_6$ under uniform deformation. Small increment in the band gap when bi-axial tensile strain is applied can be explained as follows. From the PDOS Figs. 4 (d)ii-(f)ii of strained Mn-C$_6$N$_6$ sheet (3% bi-axial tensile strain), we observe a uniform shift of $p_z$-like states towards higher energy and backward shift of lone pairs of N edge atoms as larger bi-axial tensile strain is applied. This results in band gap increase. We note that the symmetric deformation causes the lone pairs to become misaligned, thereby causing $p_z$-like orbital to shift towards higher energy so as to reduce the steric repulsions between the $p_x$, $p_y$ orbitals of N atom and the $d_{xy}$, $d_{x^2-y^2}$ orbitals of Mn atom.

### 3.3 Electric field effect

To study more effects of external environment on the Mn-C$_6$N$_6$ sheet, we have perturbed the Mn-C$_6$N$_6$ system with an applied perpendicular electric field ranging from 0.0 to 10 V/nm. Under each applied electric field strength, the Mn-C$_6$N$_6$ system was fully-optimized. The Mn-C$_6$N$_6$ system slightly buckles after optimization. The buckling becomes more prominent at the maximum value of 10 V/nm (bottom figure in Fig. 1(b)). Related to the buckling, the binding energy calculated at each applied electric field strength shows an increasing pattern (see Fig. 2(b)). This indicates that the larger the applied electric field is, the stronger the binding of Mn atom in the porous site becomes. It is expected that the semiconducting property of Mn-C$_6$N$_6$ system would change under the application of electric fields, as reported for some related 2D materials [53]. However, despite the small wrinkles, the electronic and magnetic properties of Mn-C$_6$N$_6$ are retained up to a peak value of 10 V/nm. To show that the semiconducting property remains unchanged, we have plotted the TDOS of Mn-C$_6$N$_6$ at a maximum of 10 V/nm (see Fig. 2(d)). This can be obviously seen by comparing Fig. 2(d) and Fig. 2(c). Specifically, the semiconducting property remains unchanged.

The appearance of wrinkles in the Mn- C$_6$N$_6$ under applied electric field is due to distortion caused by $d_{xy}$, $d_{x^2-y^2}$ orbitals of Mn in trying to lower the system’s energy. As a result, the hexagonal structure is distorted. We refer to the projected density of states plots (see Figs. 4 (d)-(f)) where we show the orbital hybridizations between $p_x, p_y$ orbitals of N and $d_{xy}$, $d_{x^2-y^2}$ of Mn. This clearly indicates that both the orbitals are on the same plane. Due to repulsion between the orbitals, the system energy becomes lower. These conditions of having preserved electronic and magnetic properties under applied electric field of Mn-C$_6$N$_6$ sheet could be used in future nano-devices.
3.4 Adsorption of atoms on Mn $C_6N_6$ sheet

We first relaxed the Mn-$C_6N_6$ with each type of atoms (C, N, O, H) adsorbed at a height of 2 Å above Mn atom in the sheet. We do not impose any geometry constraint during structural relaxation. After relaxation, the Mn-$C_6N_6$ sheets remain planar with no sign of wrinkles in the structures (see Figs. 5 (i)-(iv). The optimized structural properties and corresponding adsorption energies are listed in Table 3. We find that the calculated optimized bond length between the embedded Mn atom and the adsorbed atoms, $d_{\text{Mn-X}}$ ($X$ stands for atoms or molecules), varies only slightly in the range 1.70-1.92 Å. This range of value confirms the expected covalent bond length between the Mn and the adatoms (adsorbed atoms). To quantify the extent of chemisorption of the adsorbates on Mn-$C_6N_6$ sheet, we compute their adsorption energies defined in the Eq. (5) below,

$$E_{\text{ads}} = (E_{\text{Mn-C6N6}} + E_X) - E_T$$

where $E_T$ is the total energy of Mn-$C_6N_6$ with adsorbates, $E_{\text{Mn-C6N6}}$ represents the energy of Mn-$C_6N_6$ system, and $E_X$ is the total energy of an isolated atom or molecules. Positive adsorption energy shows a stable structure. As illustrated in Table 3, N atom has the lowest adsorption energy and the weakest covalent bond length. This can be related to the nature of interaction between the Mn and N atom, in which nitrogen is the most electronegative among the adatoms. In general, the adsorption energies and their corresponding bond lengths show that the structures are stable and all atoms are chemically bonded to the embedded Mn atom in the $C_6N_6$ sheet.

The total magnetic moment per unit cell and per atom are also shown in Table 3. Unlike the Mn-$C_6N_6$ system, the magnetic moment per unit cell are found to be reduced when atoms are adsorbed on the Mn-$C_6N_6$ sheet. The order of magnetic moment of Mn-$C_6N_6$ with adatoms is C>N>O>H. As can be seen in Table 3, magnetism is mainly contributed by the Mn atom, and the adatoms couple antiferromagnetically with the embedded Mn atom. To clarify the reason for reduction in total magnetic moment per unit cell, we have evaluated the charge transfer into the $C_6N_6$ sheet and adatoms in the structure. It can be clearly seen that the reduction is a consequence of electron injection into the $C_6N_6$ sheet from the adatoms and Mn. Such an electron redistribution between the orbitals of Mn and the surrounding atoms induces strong interaction. The interaction reduces the number of spin-polarized electrons of Mn atom. Consequently, these low-spin configurations lead to the reduction of the system’s total magnetic moment. The TDOS of Mn-$C_6N_6$ with adsorbed atoms are depicted in Fig. 5. In spite of hybridization between the adatoms and the embedded Mn atom, the electronic structures of the majority of the systems remain semiconducting.
with their respective band gaps listed in Table 3. The TDOS for Mn-C$_6$N$_6$ with adsorbed O atom shows half metallic electronic character.

### 3.5 Adsorption of molecules on Mn-C$_6$N$_6$ sheet

Six molecules (CH$_4$, N$_2$, O$_2$, H$_2$, CO, CO$_2$) adsorbed at a height of 2 Å above the porous sites in the Mn-C$_6$N$_6$ sheet are considered. We do not impose any geometry constraint during structural relaxation. As depicted in Fig. 6(i) – (vi), the Mn-C$_6$N$_6$ sheet remains planar with no sign of buckling in the structure after relaxation. The optimized bond length between the embedded Mn atom and the nearest atom in the adsorbed molecules $d_{\text{Mn-X}}$ are in the range 2.1-2.6 Å and the adsorption energies are in the range of 0.11 - ~ 0.76 eV. The optimized bond lengths for isolated molecules in all cases, except oxygen, are maintained after adsorption. Based on the previous report [41], the interaction between embedded 3d TM and O$_2$ is usually strong; we have confirmed this assertion for the embedded Mn atom with adsorbed O$_2$. We note that Mn-C$_6$N$_6$ with adsorbed O$_2$ has the highest adsorption energy and lowest optimized bond length, $d_{\text{Mn-O}_2}$, due to strong chemisorption. The bond length of the isolated O$_2$ is slightly lower than the bond length of the adsorbed O$_2$. This finding is consistent with the previous work [41].

Interestingly, $d_{\text{Mn-CO}}$ is the largest among all $d_{\text{Mn-X}}$, showing that CO is the weakest of all molecules that bind to the surface., Correspondingly, its adsorption energy is also low. The weak chemisorption energy for CO confirms the previously reported assertion that O$_2$ would preferentially cover the Mn-C$_6$N$_6$ as compared to CO when the two gases are simultaneously released at constant pressure on the surface [41]. Their conclusion was reached based on the calculation that assumes O$_2$ has larger adsorption energy as compared to that of CO molecule. Here we would like to contribute to the understanding of adsorption of O$_2$ and CO based on our previous computations of binding energies of Mn-C$_6$N$_6$ systems under bi-axial tensile strain and applied perpendicular electric field. The binding energy is found to reduce under symmetric deformation induced by bi-axial tensile strain, and increase as larger electric field strength is applied. Therefore, these external environments can be used to modulate the adsorption energy. For example, the adsorption energy for O$_2$ shows decreasing pattern from 0.789 eV @ 0.5% to 0.658 @ 1% as larger symmetric deformations (biaxial tensile strain) are applied. Correspondingly, adsorption energy of CO on Mn-C$_6$N$_6$ becomes larger from 0.189 eV @ 1 V/nm to 0.243 @ 2 V/nm as larger electric field strengths are applied. We hope that the two methods of modulating the adsorption energy could be useful in the single crystal field (SAC) application.

The adsorption energies for CH$_4$, N$_2$, H$_2$ molecules on Mn-C$_6$N$_6$ are in agreement with recent adsorption energies reported for the same molecules adsorbed on pure C$_6$N$_6$ [54].
However, due to interactions between the embedded Mn atom and the molecules, the corresponding $d_{\text{Mn}-X}$ are found to be lower. Our calculated adsorption energy for CO$_2$ is within the value suggested by Deng et al. [55], and the molecule is slightly physisorbed on Mn-C$_6$N$_6$ sheet.

The total magnetic moments per unit cell for molecular adsorption on Mn-C$_6$N$_6$ are comparable to Mn-C$_6$N$_6$ except for the O$_2$ molecule. As for previous cases, this observation can be explained in terms of electron redistribution between the orbitals in Mn atom and the surrounding atoms (O adatoms included) induced by strong interaction among themselves. This causes the number of spin-polarized electrons of Mn atom to become reduced. The consequent low-spin configurations resulted from reduction in number of unpaired electron renders the total magnetic moment to reduce. We have also calculated the charge transfer into the C$_6$N$_6$ sheet and adatoms in the structure. It is evident that the reduced unpaired electrons are resulted from the electron injection into the C$_6$N$_6$ sheet and the adatoms from Mn atom. The TDOS of Mn-C$_6$N$_6$ with adsorbed molecules are shown in Fig. 6 (i) – (vi). Except Mn-C$_6$N$_6$ with adsorbed O$_2$ molecule showing half metallic character, all the remaining systems have their semiconducting electronic structure maintained. The band gaps are listed in Table 3.

4 Conclusions

In this work, mechanical, structural, electronic and magnetic properties of C$_6$N$_6$ with embedded Mn atom is studied systematically under the influence of external environment using density functional theory calculation. The Mn-C$_6$N$_6$ is found to be structurally and mechanically stable. Our results show that the binding energy of Mn embedded in C$_6$N$_6$ decrease as larger tensile strain is applied. The decrease in binding energy can be related to the structural distortion of the C$_6$N$_6$ sheet. We find that the semiconducting property of the pure sheet is preserved after the embedment of Mn atom in porous site. We have shown a linear relation in the increment of band gap and applied bi-axial tensile strain imposed on the Mn-C$_6$N$_6$ systems. Magnetic moment of the embedded Mn atom is preserved in all cases. Additionally, Mn-C$_6$N$_6$ sheet slightly buckles after structural relaxation under the influence of applied perpendicular electric field. Despite the obvious wrinkles in the Mn-C$_6$N$_6$ structure, the electronic and magnetic properties of the Mn-C$_6$N$_6$ systems are maintained up to a peak value of 10 V/nm in electric field strength. We also investigate the geometries, electronic and magnetic properties of Mn-C$_6$N$_6$ with adsorbed atoms and molecules. Except for Mn-C$_6$N$_6$ with adsorbed oxygen atom and molecule which show half metallic character, the remaining systems maintained the semiconducting property of the Mn-C$_6$N$_6$ sheet. The
total magnetic moment per unit cell in most of the systems is found to reduce as compared to that for Mn-C$_6$N$_6$ sheet. The reduction in magnetic moment can be related to the strong interactions among the Mn atom and the surrounding atoms which lead to the formation of low-spin configurations. In general, these results indicate that Mn-C$_6$N$_6$ systems with and without adsorbed atoms and molecules can serve as potential candidates for future spintronics and catalysis applications.

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Table 1  Optimized lattice parameters and total strain energy of Mn-C₆N₆ system for mechanical properties computation.

| Strain (%) | Area (Å²) | Total energy Biaxial (Ry) | Total energy Uniaxial (Ry) | Lattice parameter Biaxial (Å) |
|------------|-----------|----------------------------|---------------------------|-------------------------------|
| -0.02      | 167.61    | -959.07561                 | -959.10937                | 13.12/24.10                   |
| -0.015     | 169.32    | -959.10183                 | -959.12084                | 13.98/24.22                   |
| -0.01      | 171.05    | -959.12023                 | -959.12875                | 14.05/24.34                   |
| -0.005     | 172.78    | -959.13109                 | -959.13287                | 14.13/24.47                   |
| 0          | 174.52    | -959.13465                 | -959.13465                | 14.20/24.59                   |
| 0.005      | 176.27    | -959.13151                 | -959.13342                | 14.27/24.71                   |
| 0.01       | 178.03    | -959.12150                 | -959.12937                | 14.34/24.83                   |
| 0.015      | 179.79    | -959.10532                 | -959.12240                | 14.41/24.96                   |
| 0.02       | 181.57    | -959.08281                 | -959.11258                | 14.48/25.08                   |
Table 2  Geometry and electronic structure for strained/unstrained Mn-C\(_6\)N\(_6\). The binding energies \(E_b\), the average bond length between Mn atom and N\(_{\text{edge}}\) atoms, average bond length connecting the \(s\)-triazine, and Mn height are respectively named as \(d_{\text{Fe-N}}\), \(d_1/d_2\), and \(h\) (is the difference in the \(z\)-coordinate of the Mn atom and the average of the \(z\)-coordinate of all the C and N atoms in the C\(_6\)N\(_6\) sheet). Charge transfer, magnetic moment per unit cell and per Mn atom, electronic character of the Mn-C\(_6\)N\(_6\) system are denoted by \(Q\), \(M_{\text{cell}}\), \(M_{\text{Fe}}\), EC respectively. All the systems are semiconducting, Values in the EC column denotes that of the semiconducting band gap.

| Strain | \(E_b\) (eV) | \(d_{\text{Mn-N}}\) (Å) | \(d\) (Å) | \(H\) (Å) | \(Q\) (electrons) | \(M_{\text{Mn}}\) (\(\mu_B\)) | \(M_{\text{cell}}\) (\(\mu_B\)) | EC  |
|--------|---------------|----------------|--------|--------|----------------|----------------|----------------|-----|
| 0%     | 4.14          | 2.70           | 1.48   | -0.011 | 0.75           | 5.00           | 5.02           | 0.630 |
| 1%     | 3.97          | 2.75           | 1.50   | -0.007 | 0.75           | 5.01           | 5.02           | 0.660 |
| 2%     | 3.44          | 2.79           | 1.52   | 0.003  | 0.76           | 5.02           | 5.02           | 0.675 |
| 3%     | 2.60          | 2.84           | 1.55   | 0.010  | 0.76           | 5.00           | 5.03           | 0.764 |
| 4%     | 1.48          | 2.89           | 1.58   | 0.014  | 0.77           | 5.04           | 5.04           | 0.807 |
| 5%     | 0.10          | 2.93           | 1.60   | 0.000  | 0.77           | 5.06           | 5.05           | 0.802 |
| 6%     | -1.49         | 2.99           | 1.63   | 0.003  | 0.77           | 5.09           | 5.07           | 0.952 |
Table 3  Geometry and electronic structure for Mn-C₆N₆ with adsorbed atoms/molecules. X refers to an adsorbate species. $E_{ads}$ refers to adsorption energy, $d_{Mn-X}$ refers to averaged bond length between Mn atom and the adsorbates. $d_{avg-X}$ refers to bond length of molecules. The values without parenthesis are that for absorbed molecules while that in parenthesis are for isolated molecules. Q refers to net charge transfer among the adsorbates and the Mn-C₆N₆ sheet. The values without parenthesis are charge transfer from Mn atom into the sheet or adsorbates. These values are all positive as electron from Mn atom always get transferred into the surrounding. The Q values in parenthesis are charge transfer into the Mn-C₆N₆ sheet from adsorbates. Positive values mean electron is transferred into the surroundings (Mn-C₆N₆ sheet) from adsorbates, and vice versa. $M_{cell}$ refers to magnetic moment per unit cell. $M_{atom}$ refers to magnetic moment of Mn atom or adsorbates. The values without parenthesis are that for Mn atom, while that in parenthesis are that for the adsorbates. EC refers to the electronic character of the Mn-C₆N₆ with adsorbates. In the present case, EC can be either half metallic (HM) or semiconducting (SC). The values in the SC case are that of its corresponding band gap.

| System | $E_{ads}$ (eV) | $d_{Mn-X}$ (Å) | $d_{avg-X}$ (Å) | Q (electrons) | $M_{cell}$ ($\mu_B$) | $M_{atom}$ ($\mu_B$) | EC |
|--------|----------------|----------------|----------------|---------------|---------------------|--------------------|----|
| C      | 1.98           | 1.91           | -              | 0.40          | 2.25 (0.13) 4.56    | (-2.25) (0.843) SC |
| N      | 1.37           | 2.54           | -              | 0.58 (0.18)  2.68 | 4.76 (0.440) SC     |
| O      | 2.53           | 1.89           | -              | 0.65 (0.41)  3.89 | (-2.11) (0.98) HM   |
| H      | 1.51           | 1.70           | -              | 0.69 (0.16)  4.78 | (-0.20) (0.900) SC  |
| CO     | 0.16           | 2.66           | 1.14           | 0.67 (1.15)  5.00 | (0.00) (0.793) SC   |
| CO₂    | 0.35           | 2.40           | 1.18           | (C: -0.30, O: 0.07) | 5.00 (0.00) (0.822) |
| O₂     | 0.76           | 2.12           | 1.23           | (C: -0.79, O: -0.43) | 4.90 (0.00)  SC     |
| N₂     | 0.11           | 2.54           | 1.12           | (0.20) (0.62) | 3.48 (-1.43) HM    |
| H₂     | 0.11           | 2.38           | 0.75           | (-0.28) (0.69) | 4.99 (0.00) (0.680) |
| CH₄    | 0.13           | 2.54           | 1.10           | (0.76) (-0.16) | 4.99 (0.00) (0.062) | 5.00 (0.00) (0.708) SC |
**Figure 1**  
(a) **Left**: Top view of the optimized $2 \times 2$ geometry of $C_6N_6$. The atomic symbols and the calculated bond lengths are shown in the figure. Atoms in dotted red circles are the edge nitrogen atoms ($N_{\text{edge}}$). There are $N_{\text{edge}} = 6$ of them around the cavity. **Right**: unit cell of $s$-triazine which is made of $2 C_3N_3$ rings. (b). Left: Top view of a supercell comprised of $2 \times 2$ $s$-triazine unit cell, with an embedded Mn atom ($\text{Mn-C}_6\text{N}_6$). This $\text{Mn-C}_6\text{N}_6$ is the one that was used as the input in our calculation. **Right**: Top view plot of the charge-density difference of the Mn atom and the surrounding C and N atoms. The color scale shows ranges of charge accumulation and depletion in a.u. Carbon atoms are in black. Atoms dotted with 4-point starts are the $N_{\text{edge}}$ atoms (nitrogen atoms in dark ash color). **Down**: Side view of the optimized buckled Mn-$C_6N_6$ under applied perpendicular electric field.
Figure 2  (a) **Left**: Linear response of d orbital occupations as a function of potential shift $\alpha$. The curves depicted by the dotted red and black lines are labeled bare and interacting. The inverse response functions are deduced numerically by calculating the slope of the curves. $\chi_0$ follows from the slope of curve bare, whereas $\chi$ from the slope of curve interacting. **Right**: The magnetic moment per unit cell and binding energy depicted by the dotted red and black lines respectively as a function of an applied electric field for Mn-C$_6$N$_6$ system. **Down**: The spin-polarized total density of state (TDOS) for Mn-C$_6$N$_6$ under applied electric field.
Figure 3  Dependence of strain energy (Ry) on (i) bi-axial (ii) uni-axial and (iii) area of the Mn-C₆N₆ system for elastic constant calculation.
(a) and (b) show the band structures of materials. (c) and (d) depict the total density of states (TDOS) for different concentrations, with majority and minority spin states distinguished. The energy levels are shown relative to the Fermi level ($E_f$).
Figure 4  Spin-polarized electronic band structure (a) majority (b) minority spin states for unstrained ($s = 0$) Mn-C$_6$N$_6$ system. Spin-polarized TDOS and projected density of state (PDOS) for strain-free (b)i-(f)i and strained (b)ii-(f)ii systems respectively.
Figure 5  Spin-polarized TDOS and side view for Mn-C₆N₆ with an adsorbed (i) C (ii) N (iii) O and (iv) H atoms.
Figure 6  Spin-polarized TDOS and side view for Mn-C$_6$N$_6$ with an adsorbed (i) N$_2$ (ii) H$_2$ (iii) CO (iv) CO$_2$ (v) O$_2$ and (vi) CH$_4$ molecules.