Supporting Information

Transition-Metal Doped Planar Carbon Nitride Systems: High-Temperature

Ferromagnetism and Half-Metallicity

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Figure S1: (a) Optimized structure of $gt-C_3N_4$ (top view). Unitcell represented by a red dashed hexagonal box. (b) Charge density plot of $gt-C_3N_4$ (top view).



Figure S2: Spin polarized (a) TDOS/PDOS and (b) band structure of $gt-C_3N_4$. Fermi level is set to zero and indicated by a black dashed line.

Compound	Bond length (Å)		Net Effective Charge		
			С	Ν	ТМ
gt-C ₃ N ₄	$C-N_{link} = 1.46$		+1.45	$N_{link} = -0.96$	
	$C-N_{in} = C-N_{in} = C-N_{in} = 1.33$			$N_{in} = -1.19$	
	C-N = 1.39 (avg)			$N_{in} = -1.19$	
		-		$N_{in} = -1.01$	
Cr@gt-C ₃ N ₄	Cr-N1= 2.06	C-N1 = 1.40, 1.37	+1.11	N1 = -1.26	Cr = +1.49
	Cr-N2 = 2.08	C-N2 = 1.40, 1.37		N2 = -1.19	
	Cr-N3= 1.85	C-N3 = 1.29, 1.30		N3 = -1.18	
	Cr-N4 = 2.00	C-N4 = 1.33, 1.34		N4 = -1.19	
Mn@gt-C ₃ N ₄	Mn-N1= 2.96	C-N1 = 1.32, 1.33	+1.14	N1 = -1.45	Mn =+1.54
	Mn-N2= 2.07	C-N2 = 1.29, 1.30		N2 = -1.18	
	Mn-N3= 1.97	C- N3 = 1.36, 1.44		N3 = -1.18	
	Mn-N4= 1.80	C-N4 = 1.49, 1.42		N4 = -1.17	
Fe@gt-C ₃ N ₄	Fe-N1= 3.16	C-N1 = 1.33, 1.32	+1.20	N1 = -1.37	Fe = +1.32
	Fe-N2= 2.03	C-N2 = 1.28, 1.30		N2 = -1.19	
	Fe-N3= 1.95	C- N3 = 1.36, 1.43		N3 = -1.19	
	Fe-N4= 1.75	C-N4 = 1.37, 1.41		N4 = -1.18	

Table S1: Bond lengths and net effective charges calculated from Bader Charge analysis of $gt-C_3N_4$ and $TM@gt-C_3N_4$

Text S1. Formation Energy (E_f) , Binding Energy (E_B) and Cohesive Energy (E_{coh}) Calculations:

The formation energy (E_f) is calculated for each TM embedding in the pore of gt-C₃N₄ (Figure 1) using the following equation:

$$E_{f} = [E_{TM@gt-C3N4} - (E_{gt-C3N4} + \mu_{TM})]$$
(1)

where $E_{TM@gt-C3N4}$ is the total energy of TM@gt-C₃N₄, $E_{gt-C3N4}$ is the total energy of gt-C₃N₄ sheet, and μ_{TM} represents the chemical potential of TM in their respective bulk structure. The chemical potentials of Cr (μ_{Cr}), Mn (μ_{Mn}), and Fe (μ_{Fe}) are calculated from their most stable crystals such as Cr in bcc,¹ Mn in cubic,³ and Fe in bcc,³ respectively.

We have also calculated the binding energy (E_B) of TM in the pore of gt-C₃N₄ using the following equation:

$$E_{\rm B} = E_{\rm gt-C3N4+TM} - (E_{\rm gt-C3N4} + E_{\rm TM})$$
(2)

where, E_{TM} represents the total energy of the isolated atom.

The cohesive energy of a solid is the energy required to dissociate the solid into their isolated atomic species. It is calculated by using the following equation:

$$E_{\rm coh} = E_{\rm Solid} - \sum_{\rm A} E_{\rm A}^{\rm isolated}$$
(3)

Table S2: Comparison between our calculated metal-metal distances (d_H = Horizontal and d_D = Diagonal distances), binding energy, magnetic moments with previous report by Ghosh et al.⁴

System	TM-TM distances (Å)		Formation Energy		Magnetic Moment	
	Calculated	Previous Report	Calculated	Previous Report	Calculated	Previous Report
Cr@gh-C ₃ N ₄	$d_{\rm H} = 7.04$	$d_{\rm H} = 7.05$	-3.63	-3.65	4	4
	$d_{\rm D} = 6.99$	$d_{\rm D} = 6.97$				
Mn@gh-C ₃ N ₄	$d_{\rm H} = 7.02$	$d_{\rm H} = 7.02$	-4.45	-4.48	5	5
	$d_{\rm D} = 7.02$	$d_{\rm D} = 7.01$				
Fe@gh-C ₃ N ₄	$d_{\rm H} = 7.04$	$d_{\rm H} = 7.04$	-0.67	-0.68	4	4
	$d_{\rm D} = 7.04$	$d_{\rm D} = 7.04$				



Figure S3: Phonon band structures and PhDOS of (a) Cr@gt-C₃N₄, (b) Mn@gt-C₃N₄ (c) Fe@gt-C₃N₄. High-symmetric q-point paths: Γ (0, 0) \rightarrow M (1/2, 1/2) \rightarrow K (2/3, 1/3) \rightarrow Γ (0, 0).



Figure S4: Phonon band structures and PhDOS including dielectric effect for (a) Cr@gt-C₃N₄, (b) Mn@gt-C₃N₄ (c) Fe@gt-C₃N₄. High-symmetric q-point paths: Γ (0, 0) \rightarrow M (1/2, 1/2) \rightarrow K (2/3, 1/3) \rightarrow Γ (0, 0).



Figure S5: Structure of (a) $Cr@gt-C_3N_4$, (b) $Mn@gt-C_3N_4$ and (c) $Fe@gt-C_3N_4$ supercell (2×2) after molecular dynamics simulation after 5 ps at room temperature (300 K).



Figure S6: Molecular dynamics simulations of (a) $Cr@gt-C_3N_4$, (b) $Mn@gt-C_3N_4$ and (c) $Fe@gt-C_3N_4$ supercell (2×2) with 5 ps (5000 fs) at different temperature (300 K, 500 K and 1000 K).



Figure S7: Structure of (a) $Cr@gt-C_3N_4$, (b) $Mn@gt-C_3N_4$ and (c) $Fe@gt-C_3N_4$ supercell (3×3) after molecular dynamics simulation after 5 ps at room temperature (300 K).



Figure S8: (a) Molecular dynamics simulation and (b) root mean square displacement (RMSD)

of $Cr@gt-C_3N_4$ supercell (3×3) with 5 ps (5000 fs) at different temperature (300 K, 500 K and 1000 K).



Figure S9: (a) Molecular dynamics simulation and (b) root mean square displacement (RMSD) of Mn@gt-C₃N₄ supercell (3×3) with 5 ps (5000 fs) at different temperature (300 K, 500 K and 1000 K).



Figure S10: (a) Molecular dynamics simulation and (b) root mean square displacement (RMSD) of Fe@gt-C₃N₄ supercell (3×3) with 5 ps (5000 fs) at different temperature (300 K, 500 K and 1000 K).



Figure S11: Total electron density plots of (a) $Cr@gt-C_3N_4$, (b) $Mn@gt-C_3N_4$, and (c) $Fe@gt-C_3N_4$ (Isosurface value: 0.18 e.Å⁻³). Electrostatic potentials (ESP) plots of (d) $Cr@gt-C_3N_4$, (e) $Mn@gt-C_3N_4$, and (f) $Fe@gt-C_3N_4$ (Isosurface value: 0.03 e.Å⁻³). The blue and red colours denote less and more electron dense area in the electrostatic potential surface.



Figure S12: Strain energy of Cr@gt-C₃N₄ under in-plane uniaxial and equi-biaxial strains.

Table S3: Calculated Young's Modulus and Poisson's ratio of $TM@gt-C_3N_4$ by applyinguniaxial and equi-biaxial strain.

Compound	Young's Modulus (GPa)	Poisson's Ratio
Cr@gt-C ₃ N ₄	200.10	0.18
Mn@gt-C ₃ N ₄	49.96	0.08
$Fe@gt-C_3N_4$	140.99	0.04



Figure S13: Energy diagram of d-orbital splitting of different TM@C₃N₄ systems.



Figure S14: (a) TDOS and pDOS plot of (a) $Cr@gt-C_3N_4$, (b) $Mn@gt-C_3N_4$ and (c) $Fe@gt-C_3N_4$ (Fermi level is shifted to zero and indicated by black dashed line)

Text S2. Calculation of Magnetic Anisotropy Energy (MAE)

The magnetic anisotropy energy (MAE) is calculated by applying the torque approach.⁵ Noncollinear self-consistent calculations (including spin orbit coupling) are performed in the z, y and x axis magnetization directions, respectively. MAE originates from the perpendicular and in plane contribution of spin orbit coupling (SOC), which can be expressed in terms of angular momentum operators L_x , L_y or L_z . So the contribution of different spins (up ' \uparrow †' and down ' $\downarrow\downarrow$ ') can be expressed by the second order perturbation equation.⁶

$$MAE = \xi^{2} \sum_{o,u} \frac{| < o | L_{Z} | u > |^{2} - | < o | L_{X} | u > |^{2}}{E_{u} - E_{o}}$$

Here, o and u represent the occupied and unoccupied electronic states, respectively. The E_o and E_u in the denominator are their respective band energies. L_Z and L_X are the angular momentum operators along Z and X axis, and ξ denotes the strength of the SOC. So, a

potential with good MAE for practical application should hold a high value of ξ . Then, the MAE is calculated using the following equation:

$$MAE = E_{S0} - E_{S1} \tag{5}$$

where E_{S0} is the energy of the materials without employing any magnetic axis and E_{S1} is the energy in presence of an easy axis. Total energies are converged to a precision of 10^{-6} eV in MAE calculations.

Text S3. Details of Mean Field Theory and Monte Carlo Simulations for Curie Tempareture calculations

3.1 Mean Field Theory (MFT):

We have taken the MFT approach to calculate the Curie tempareture for the two dimentional $TM@gt-C_3N_4$ systems. This method has been previously used by Li et al.⁷ for the Curie tempareture calculation for Mn-phthalocyanine (MnPc) system. The main idea behind MFT method is to replace all interactions to any one body with an average or effective interaction.⁸ It reduces any multi-body problem into an effective one-body problem. The detailed partition function can be written as follows,

$$Z = \sum_{m = -M, -M+2, \dots, M-2, M} e^{\gamma J' m < M > /k_B T}$$
(4)

Here, 'J' is the exchange parameter, ' γ ' is the coordination number, 'm' is the ensembleaverage magnetic moment, and 'M' is the calculated magnetic moment of TM.

Thus, the average spin of each magnet becomes,

$$= \frac{1}{Z} \sum_{m=-M,-M+2,\dots,M-2,M} m \times e^{\gamma J'm < M > /k_B T}$$
 (5)

Now, if we assume that, $P = \frac{\gamma J'}{k_B T}$, then the equation 5 becomes,

The above equation can be easily deducible when the parameter 'P' varies along with the static solution <m>. At the critical point,

$$\mathbf{P} = \mathbf{P}_{c} = \frac{\gamma J'}{k_{B} T_{c}} \tag{6}$$

At this critical point, the phase transition of the system between ferromagnetic to paramagnetic occurs. This critical point is known as Curie temperature.

3.2 Monte Carlo Simulations:

Monte Carlo simulations involve generating a subset of configurations or samples, chosen using a random algorithm from a configuration space, according to a probability distribution or weight function. Observables are then computed as averages over the samples.⁹

One sample or configuration of the magnet is a particular assignment of spin values, say

$$s_1 = +1; s_2 = -1; s_3 = +1; \dots, s_{Ns} = +1$$
 (7)

in which each spin is set "up" or "down". According to statistical mechanics, the average value of an observable is got by weighting each configuration with the Boltzmann factor. For example, the average magnetization at some fixed temperature T is given by,

$$<\mathbf{M}> = \frac{\sum_{Config} M e^{-E/k_B T}}{\sum_{Config} e^{-E/k_B T}}$$
(8)

At the Curie temperature (T_c) we expect a marked fluctuation in the magnetic moment (M).

	Magnetic	Exchange energy	Energy Difference	Curie	MAE in (µeV)/TM
Compound	Moment/TM	(meV)/TM	(meV)/TM	Temperature	(Magnetic
	(µ _B)	$[\mathbf{E}_{ex} = \mathbf{E}_{FM} - \mathbf{E}_{AFM}]$	$(\mathbf{E}_{diff} = \mathbf{E}_{FM} - \mathbf{E}_{NSP})$	(T _C) in (K)	Anisotropy
					Energy)
Cr@gt-C ₃ N ₄	4	-480.87	53.79	452	137.26
Mn@gt-C ₃ N ₄	5	-344.69	46.13	324	119.83
Fe@gt-C ₃ N ₄	4	-330.87	75.21	311	116.39

Table S4: Exchange energy (E_{ex}) and Curie temperature value of TM@gt-C₃N₄ system.

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