Supporting Information for

Computational Studies on Magnetism and Optical Properties of Transition Metal Embedded Graphitic Carbon Nitride Sheet

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Figure S1.Isosurface of charge density with 1.7 e Å⁻³ of g-C₃N₄. The N_{edge} and N_{bridge} atoms are electron rich in nature. Ochre coloured surface denotes the electron density.



Figure S2. Partial density of states (pDOS) for $g-C_3N_4$. From the plot it is clear that valance bands are majorly contributed from N whereas valance bands are coming from C.



Figure S3. 2×2 supercell of TM-g-C₃N₄. This cell has been used to find out the magnetic ground state of these sheets. $d_{TM_TM_hori}$ and $d_{TM_TM_dia}$ are the distances between two TM atoms at horizontal and diagonal direction, respectively. $d_{M-Nedge}$ (a-f) are the distances between N_{edge} and TM. We have numbered the N_{edge} atoms to show the dihedral angles among them and TM.

Table S1. Structural details of fully optimized geometry of TM-g-C₃N₄. Distances between two TMs, TM and N_{edge} (M-N; denoted as a, b, c as can be seen in Figure S2) and dihedral angles N_{edge} - N_{edge} - N_{edge} -TM (notation is according to Figure S2) are given.

Metal		V	Cr	Mn	Fe	Со	Ni	Cu	Zn
d _{TM_TM_hori} (Å)		7.03	7.05	7.02	7.04	6.98	6.84	6.84	6.98
d _{TM_TM_dia} (Å)		7.03	6.97	7.01	7.04	6.78	6.85	6.81	6.87
d _{M-Nedge}	a(1-TM)	2.35	2.28	2.35	2.36	2.39	2.52	2.40	2.34
	b(2-TM)	2.35	2.43	2.37	2.35	2.54	2.53	2.46	2.48
	c(3-TM)	2.35	2.46	2.40	2.35	2.77	2.72	2.76	2.85
	d(4-TM)	2.35	2.35	2.34	2.35	2.10	2.03	2.12	2.23
	e(5-TM)	2.35	2.43	2.40	2.36	2.10	2.02	2.11	2.29
	f(6-TM)	2.35	2.37	2.39	2.36	2.65	2.71	2.70	2.17
Dihedral	1-2-3-TM	4.81	0.42	5.82	6.49	21.36	28.65	30.44	21.46
Angles	2-3-4-TM	3.76	2.07	0.86	4.48	5.31	7.24	7.18	8.03
	3-4-5-TM	3.58	-18.3	-16.9	3.57	-14.29	-8.87	-13.41	-20.09
	4-5-6-TM	4.69	-0.4	2.65	6.17	2.89	5.46	8.34	3.61
	5-6-1-TM	3.78	3.07	0.67	4.36	5.14	6.04	5.31	0.18
	6-1-2-TM	3.48	-17.4	-18.43	3.47	-30.5	-30.6	-33.63	-23.33

Ions(+2)	Crystal ionic radii
V	0.93
Cr	0.94
Mn	0.97
Fe	0.92
Со	0.88
Ni	0.83
*Cu	0.90
Zn	0.88

Table S2. The crystal ionic radius of 3d-transition metal atoms is tabulated. These are taken from Shannon *R., Acta Crystallographica Section A* **1976**, 32, 751-767.

* For Cu oxidation state is (+1).



Figure S4. Top view and side view of V-g-C₃N₄ (a) at initial i.e. DFT optimized, (b) after 1 picosecond (ps) and (c) after 2 ps run. Top view and side view of Cu-g-C₃N₄ at (d) initial and (e) after 2ps run. Orange and grey coloured balls are V and Cu, respectively.



Figure S5. Top view and side view of V-g-C₃N₄ (a) after 1 ps and (b) 2 ps run at 500K and (c) after 1 ps and (d) 2 ps at 1000K.



Figure S6. Demonstrations of (a) ferromagnetic and (b) antiferromagnetic coupling between TM atoms of TM-g-C₃N₄. Isosurface at a value of 0.025 e/Å³ is taken. Up and down spin densities are represented as ochre and yellow coloured surfaces, respectively.

Calculation of Magnetic Coupling Constants:

We have calculated magnetic coupling constant J by using following Heisenberg Hamiltonian,

$$H = \sum_{\langle ij \rangle} J_{ij}(S_i S_j)$$

by considering rhombic (2×2) supercell and imposing periodic boundary condition. The H turns out to be

$$H = J (s_1 s_2 + s_2 s_3 + s_3 s_4 + s_4 s_1 + s_2 s_4 + s_3 s_4)$$

Now, we can write total spin as,

$$S^{2}_{T} = (s_{1} + s_{2} + s_{3} + s_{4})^{2} = s_{1}^{2} + s_{2}^{2} + s_{3}^{2} + s_{4}^{2} + 2(s_{1}s_{2} + s_{2}s_{3} + s_{3}s_{4} + s_{4}s_{1} + s_{2}s_{4} + s_{3}s_{4})$$

For spin state S, S² has eigen value of $S(S+1)\hbar^2$. We have considered $\hbar = 1$ here after. Thus, in terms of eigen values of above mentioned Hamiltonian we can write,

$$E = J/2 [S_T(S_T+1) - s_1(s_1+1) - s_2(s_2+1) - s_3(s_3+1) - s_4(s_4+1)]$$

This energy equation is quite general and now depending upon TM, we will consider different s_1 , s_2 , s_3 and s_4 values and derive the exchange coupling constant.

For V-g-C₃N₄, where $s_1 = s_2 = s_3 = s_4 = 3/2$ (as V⁺² has 3 unpaired electrons);

E comes out to,

 $E = J/2 [S_T(S_T + 1) - 15]$

Therefore we can write, energy for antiferromagnetic configuration taking $S_T = 0$;

$$E_{AFM} = -15J/2$$

For ferromagnetic configuration, $S_T = 6$ and so

$$E_{FM} = 27J/2$$

So, $\Delta E_{ex} = E_{FM} - E_{AFM}$

= 21J

From DFT calculation, ΔE_{ex} for this system appears as – 90 meV.

Thus, *J* = - 4.3 meV

Next, for Cr-g-C₃N₄, where $s_1 = s_2 = s_3 = s_4 = 2$ (as Cr⁺² has 4 unpaired electrons);

$$E = J/2 [S_T(S_T + 1) - 24]$$

For antiferromagnetic configuration, $S_T = 0$

 $E_{AFM} = 12J$

For ferromagnetic configuration, $S_T = 8$

 $E_{FM} = 24J$

So, $\Delta E_{ex} = 36 \text{ J}$ From DFT calculation, $\Delta E_{ex} = -80 \text{ meV}$

Therefore, J = -2.22 meV

Now for Fe-g-C₃N₄, also $s_1 = s_2 = s_3 = s_4 = 2$ (as Fe⁺² has 4 unpaired electrons),

So, $\Delta E_{ex} = 36 \text{ J}$

From DFT calculation, $\Delta E_{ex} = -53 \text{ meV}$

Thus, *J* = - 1.5 meV



Figure S7. Calculated band structures for TM-g-C₃N₄ where TM is (a) Cr, (b) Mn, (c) Fe, (d) Co, (e) Ni and (f) Cu.

Table S3. Structural details of fully optimized geometry of Fe-g-C₃N₄ under different U_{eff} values. Distances between two TMs, TM and N_{edge} (M-N; denoted as a, b, c as can be seen in Figure S2) and dihedral angles N_{edge} - N_{edge} - N_{edge} -TM (notation is according to Figure S2) are given.

U _{eff}		2	2.5	3.5	4	4.5	5
d _{TM_TM_hori} (Å)		7.03	7.03	7.04	7.04	7.00	7.01
d _{TM_TM_dia} (Å)		7.04	7.04	7.04	7.04	7.04	7.04
d _{M-Nedge}	a(1-TM)	2.39	2.39	2.37	2.36	2.35	2.35
_	b(2-TM)	2.34	2.37	2.36	2.36	2.33	2.33
	c(3-TM)	2.34	2.34	2.35	2.35	2.35	2.35
	d(4-TM)	2.34	2.34	2.34	2.34	2.36	2.36
	e(5-TM)	2.35	2.34	2.34	2.35	2.37	2.37
	f(6-TM)	2.38	2.38	2.37	2.36	2.36	2.36
Dihedral	1-2-3-TM	6.2	6.2	6.00	5.93	5.91	6.00
Angles	2-3-4-TM	4.0	3.99	3.82	3.76	3.93	3.70
	3-4-5-TM	3.81	3.80	3.66	3.56	3.63	3.80
	4-5-6-TM	6.01	6.01	5.68	5.80	5.80	6.02
	5-6-1-TM	3.85	3.71	3.72	3.66	3.58	3.55
	6-1-2-TM	3.66	3.71	3.48	3.55	3.65	3.95



Figure S8. The energy of supercell with respect to various U_{eff} parameter for 2×1 supercell of Fe-g-C₃N₄ considering FM and AFM coupling between Fe atoms.



Figure S9. Values of average of S_z per unit cell of Fe-g-C₃N₄ with respect to the temperature. The transition from ferromagnetic to paramagnetic state occurs (i.e. Curie temperature) at 115K.