Transition Metal Embedded Two-Dimensional C_3N_4-graphene Nanocomposite: A Multifunctional Material

Dibyajyoti Ghosh[1], Ganga Periyasamy[1], Swapan K Pati[2,3]*

Chemistry and Physics of Materials Unit[1], Theoretical Sciences Unit[2] and New Chemistry Unit[3], Jawaharlal Nehru Centre for Advanced Scientific Research, Bangalore, 560064, India

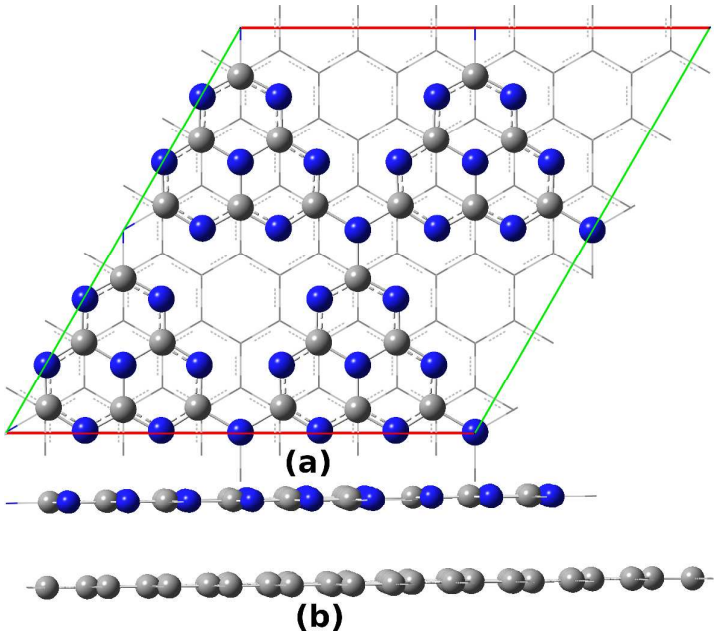


Figure S1. (a) Top and (b) side-view of optimized structure of g-C3N4@graphene. Notice that adhesion of buckled g-C_3N_4 on top of graphene makes it (i.e. g-C_3N_4) planar.

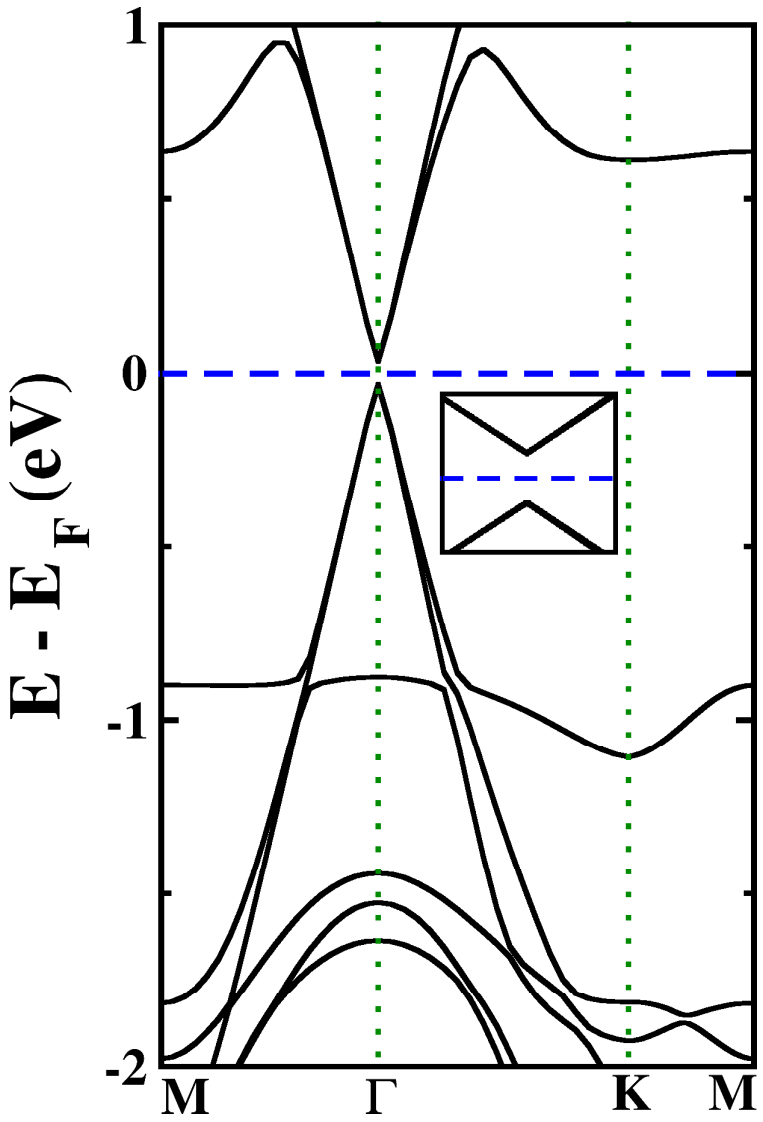


Figure S2: Band structure of g-C_3N_4@graphene are plotted considering high symmetry K-points (Γ(0,0,0), M(1/2,1/2,0), K(2/3,1/3,0). Fermi level is scaled to zero. The zoomed picture of dirac-cone at Γ-point (graphene fold K-point) clearly shows band-gap opening. Symbols: blue dashed and green dotted lines show Fermi levels and high symmetry K-points, respectively.

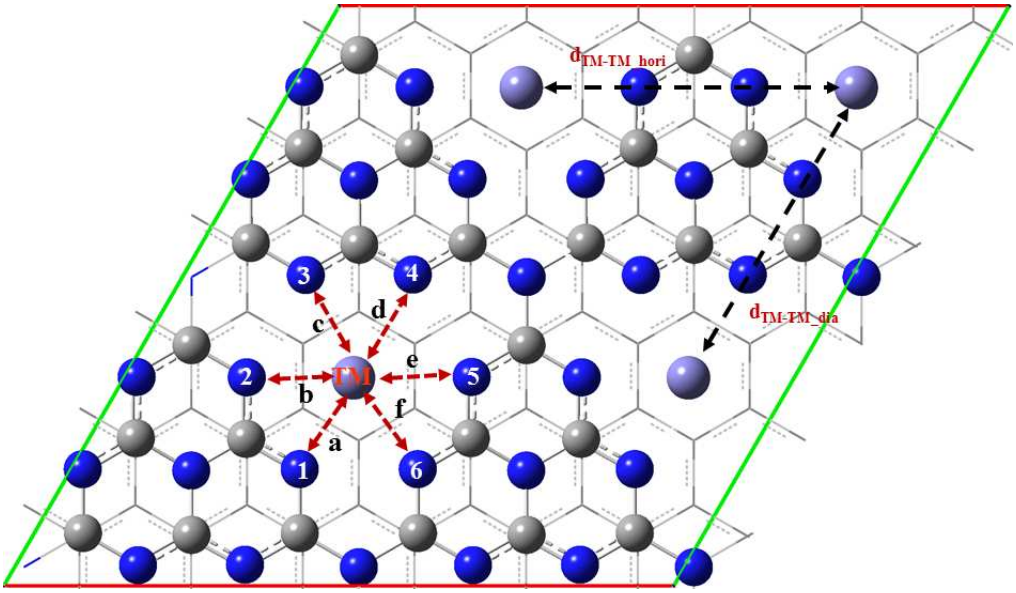


Figure S3. 2×2 supercell of TM-C_3N_4@graphene. This cell has been used to find out the magnetic ground state of these sheets. $d_{TM\_TM\_hori}$ and $d_{TM\_TM\_dia}$ are the distances between two TM atoms at horizontal and diagonal direstion, respectively. $d_{M\text{-}Nedge}$ (a-f) are the distances between N_{edge} and TM.

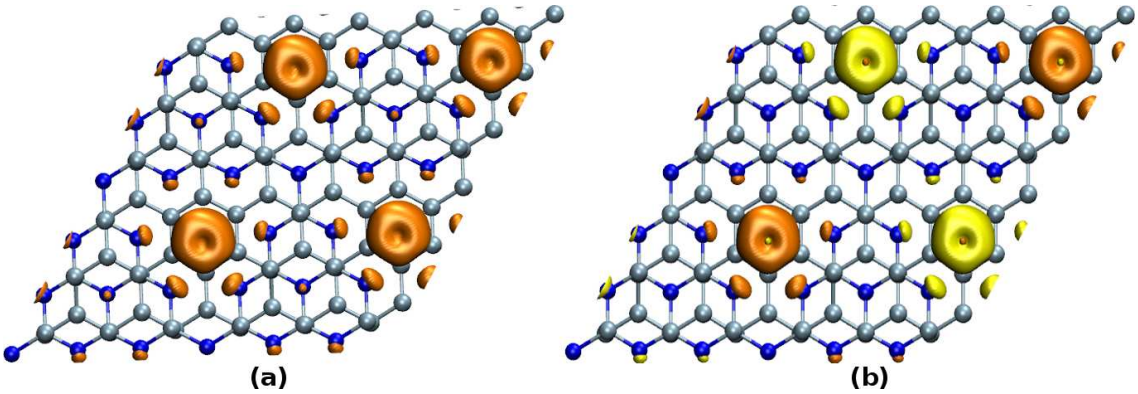


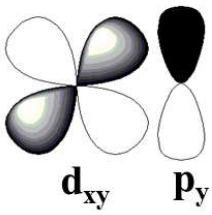
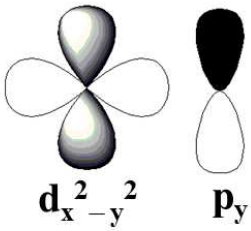
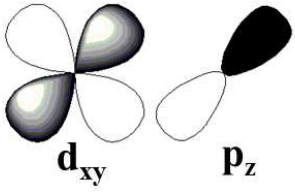
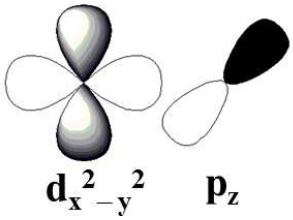
Figure S4. Demonstrations of (a) ferromagnetic and (b) antiferromagnetic coupling between Fe atoms of Fe-C_3N_4.@graphene. Isosurface at a value of 0.1 e/Å^3 is taken. Up and down spin densities are represented as orange and yellow coloured surfaces, respectively.

Detail of d-p exchange in TM-g-C_3N_4@graphene:

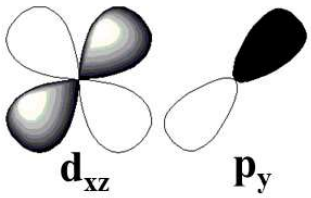
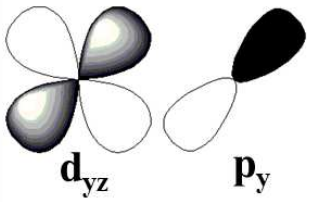
According to Goodenough-Kanamori-Anderson rules, when the interacting magnetic d-orbitals of TM couple with p orbitals of ligand, depending upon their symmetry, ferromagnetic or antiferromagnetic ground state appear. When the orbitals of interest interact but total overlap is zero due to symmetry of lobes, ferromagnetism appears Among various such type of situations, one common scenario is when the interacting spin-polarized d-orbitals and p_π (i.e. p_z/p_y) orbitals remain perpendicular to each other, they produce a zero overlap and consequently a ferromagnetic coupling.

For Cr-C_3N_4@graphene, d_{xy} and $d_{x^2-y^2}$ of Cr and p_z and p_y of N_{edge} atoms get involved in magnetic coupling interaction. The pictorial representations of orbital overlaps as well as resulting magnetic coupling natures are tabulated below. Among four type of overlap, only one kind results antiferromagnetic coupling whereas other three gives ferromagnetic interaction. As a result, the Cr atoms at Cr-C_3N_4@graphene show a ferromagnetic ground state.

As can be seen in Figure S5, the interacting Fe and ligand orbitals in Fe-C_3N_4@graphene are d_{xz}/d_{yz} and p_y, respectively. It is evident from orbital overlap pictures that the effective d-p overlap is zero here and consequently the exchange becomes ferromagnetic in nature.

Interacting Orbital	Magnetic Coupling Nature	Interacting Orbital	Magnetic Coupling Nature
	AFM		FM
	FM		FM

Orbital pictures for d-p overlaps in Cr-C_3N_4@graphene

Interacting Orbital	Magnetic Coupling Nature	Interacting Orbital	Magnetic Coupling Nature
	FM		FM

Orbital pictures for d-p overlaps in Fe-C_3N_4@graphene

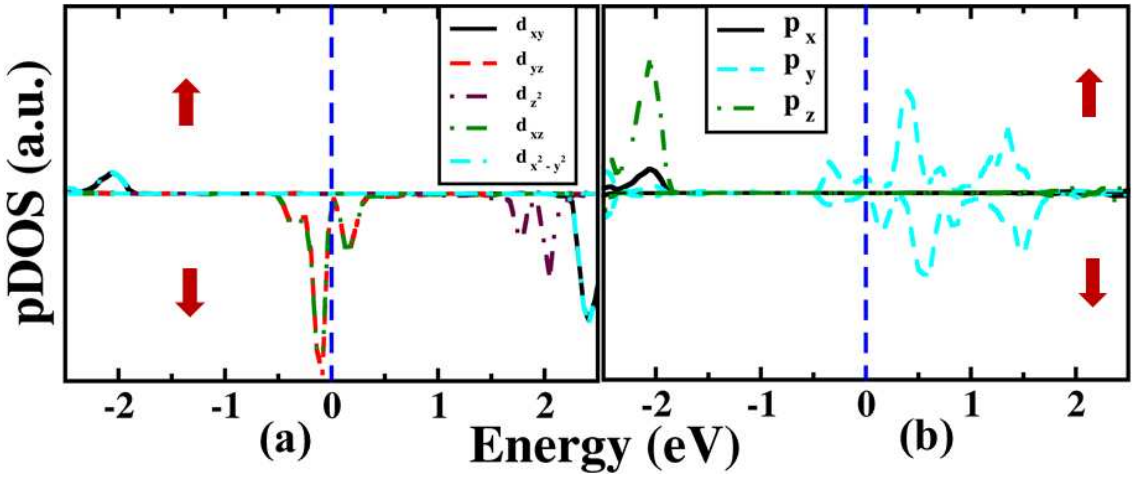


Figure S5. (a) pDOS of d-orbitals on the Fe atom of Fe-C_3N_4@graphene (symbols: solid black, dashed red, dashed doted maroon, dashed double doted deep green and double dashed doted cyan represent d_{xy}, d_{yz}, d_z^2, d_{xz} and $d_{x^2-y^2}$ orbitals, respectively). (b) pDOS of p-orbitals on the N_{edge} of same structure has been plotted. Note, up and down red coloured arrows represent majority and minority spins, respectively.

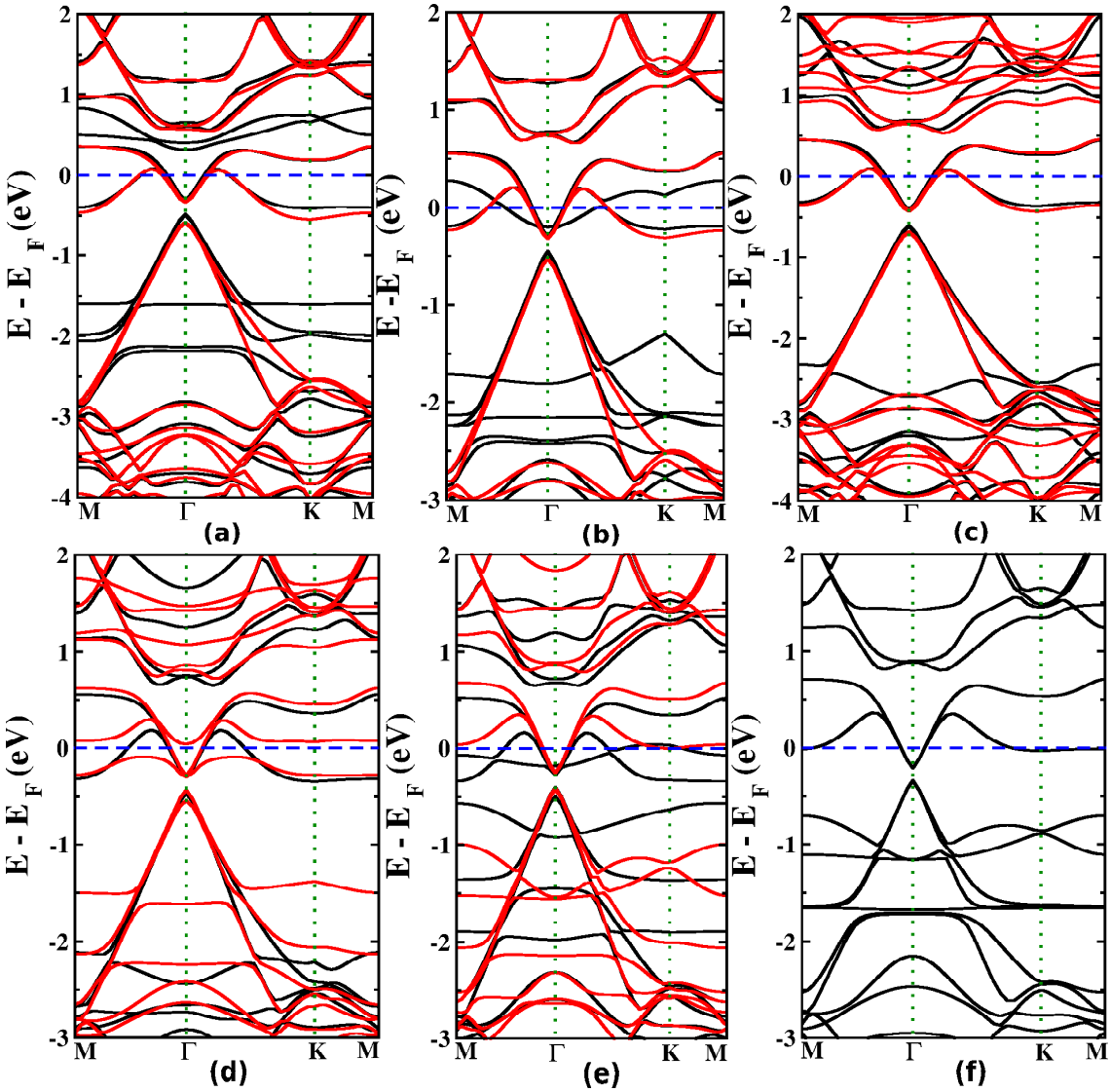


Figure S6. Calculated band structures for TM-g-C_3N_4 where TM is (a) V, (b) Cr, (c) Mn, (d) Co, (e) Ni and (f) Cu.

Adhesion Energy

To know the strength of interaction between TM@g-C_3N_4 and graphene, we have calculated interface adhesion energy using following formula,

$$E_{adhesion} = E_{composite} - (E_{g\text{-}C3N4\text{-}TM} + E_{graphene})$$

where $E_{composite}$, $E_{g\text{-}C3N4\text{-}TM}$ and $E_{graphene}$ are the energies of the TM-g-C_3N_4@graphene, TM@g-C_3N_4 and graphene, respectively. Calculated values are tabulated in Table S1.

Table S1. Structural details of fully optimized geometry of TM-C_3N_4@graphene. Distances between two layers, two TMs, TM and N_{edge} (M-N; denoted as a-f as can be seen in Figure S3) at g-C_3N_4 layer are given. The Fermi level shift due to charge transfer and adhesion energies/unit cell are also tabulated for all systems.

Metal		**V**	**Cr**	**Mn**	**Fe**	**Co**	**Ni**	**Cu**	**Zn**
Interlayer distance (Å)		2.98	2.97	2.98	2.97	2.95	2.97	2.96	2.95
$d_{TM\_TM\_hori}$ (Å)		7.28	7.28	7.29	7.29	7.28	7.32	7.29	7.29
$d_{TM\_TM\_dia}$ (Å)		7.28	7.28	7.29	7.29	7.27	7.30	7.29	7.29
$d_{M\text{-}Nedge}$	a(1-TM)	2.44	2.72	2.46	2.19	2.71	1.95	2.47	2.47
	b(2-TM)	2.44	2.57	2.46	2.43	2.75	2.51	2.48	2.48
	c(3-TM)	2.44	2.53	2.45	2.70	2.65	3.00	2.47	2.48
	d(4-TM)	2.44	2.18	2.45	2.72	2.18	3.00	2.46	2.47
	e(5-TM)	2.44	2.16	2.45	2.49	2.16	2.58	2.46	2.46
	f(6-TM)	2.44	2.63	2.46	2.21	2.44	1.95	2.46	2.46
Transferred electrons to graphene (e^-)		0.18	0.15	0.23	0.16	0.15	0.12	0.10	0.14
Fermi level shift (eV)		0.41	0.38	0.51	0.43	0.37	0.33	0.27	0.36
Adhesion Energy (eV)		-0.22	-0.24	-0.29	-0.23	-0.31	-0.28	-0.29	-0.25

Calculation of Magnetic Coupling Constants:

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

$$H = \sum_{<ij>} J_{ij}(S_i.S_j)$$

considering rhombic (2×2) supercell and imposing periodic boundary condition.

The H turns out to be

$H = J\,(s_1s_2 + s_2s_3 + s_3s_4 + s_4s_1 + s_2s_4 + s_3s_4)$

Now, we can write total spin as,

$$S^2_T = (s_1+s_2+s_3+s_4)^2 = s_1^2 + s_2^2 + s_3^2 + s_4^2 + 2(s_1s_2 + s_2s_3 + s_3s_4 + s_4s_1 + s_2s_4 + s_3s_4)$$

For spin state S, S^2 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 Cr-g-C_3N_4, where $s_1 = s_2 = s_3 = s_4 = 2$ (as Cr^{+2} has 4 unpaired electrons);

E comes out to,

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

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

$$E_{AFM} = -12J$$

For ferromagnetic configuration, $S_T = 8$,

Thus, $E_{FM} = 24J$

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

$= 36J$

From DFT calculation, ΔE_{ex} for this system appears as – 179 meV.

Thus, ***J* = - 4.97 meV**

Next, **for Fe-g-C_3N_4,** where $s_1 = s_2 = s_3 = s_4 = 2$ (as Fe^{+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, $\Delta E_{ex} = 36\,J$
From DFT calculation, $\Delta E_{ex} = -201$ meV

Therefore, $\boldsymbol{J = -5.58}$ **meV**