Supporting information file

Density Functional Theory-Based Modeling of Half Metallic g-C_3N_4/CoN_4 Heterojunction for Photocatalytic Water Splitting Reaction

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List of contents:

Table S1. Calculated energies of different magnetic states of CoN_4 bulk

System	Nonmagnetic state	Ferromagnetic state	Anti-ferromagnetic state
Energy(eV)	0	-2.0	-1.5

Table S2. Calculated energies of the systems and surface energies (γ) of slabs.

System	g-C_3N_4 (2× 2×1)	CoN_4 bulk			CoN_4(111) slab ($\sqrt{3} \times \sqrt{3} \times 1$)	g-C_3N_4/CoN_4
Energy(Ry)	-951.88	-2987.11			-2240.15	-3192.38
Surface energy(J/m^2)		(100)	(110)	(111)		
		0.36	0.37	0.11		

Table S3. Calculated lattice mismatch (δ) of different structures

System	Lattice parameter of g-C_3N_4 system (Å)	Lattice Parameter of CoN4 system (Å)	Lattice mismatch (%)
1×1×1 g-C_3N_4 / 1×1×1 CoN4(111)	7.2	8.06	10
1×1×1 g-C_3N_4 / 2×2×1 CoN4(111)	7.2	16.12	55
2×2×1 g-C_3N_4 / 1×1×1 CoN4(111)	14.4	8.06	44
2×2×1 g-C_3N_4 / 2×2×1 CoN4(111)	14.4	16.12	10
$\sqrt{2} \times \sqrt{2} \times 1$ g-C_3N_4 / 1×1×1 CoN4(111)	10.08	8.06	20
1×1×1	7.2	11.3	36

g-C_3N_4 / $\sqrt{2} \times \sqrt{2} \times 1$ CoN4(111)			
$\sqrt{2} \times \sqrt{2} \times 1$ g-C_3N_4 / $\sqrt{2} \times \sqrt{2} \times 1$ CoN4(111)	10.08	11.3	10
$\sqrt{3} \times \sqrt{3} \times 1$ g-C_3N_4 / 1×1×1 CoN4(111)	12.45	8.06	35
1×1×1 g-C_3N_4 / $\sqrt{3} \times \sqrt{3} \times 1$CoN4(111)	7.2	13.94	48
$\sqrt{3} \times \sqrt{3} \times 1$ g-C_3N_4 /$\sqrt{2} \times \sqrt{2} \times 1$ CoN4(111)	12.45	11.3	9
$\sqrt{2} \times \sqrt{2} \times 1$ g-C_3N_4/$\sqrt{3} \times \sqrt{3} \times 1$ CoN4(111)	10.08	13.94	27
$2 \times 2 \times 1$ g-C_3N_4/$\sqrt{3} \times \sqrt{3} \times 1$ CoN4(111)	**14.4**	**13.94**	**3[#]**
$\sqrt{3} \times \sqrt{3} \times 1$ g-C_3N_4 /$2 \times 2 \times 1$ CoN4(111)	12.45	16.12	22
$\sqrt{3} \times \sqrt{3} \times 1$ g-C_3N_4/$\sqrt{3} \times \sqrt{3} \times 1$ CoN4(111)	12.45	13.94	11

[#]Lattice mismatch is least while considering $2 \times 2 \times 1$ g-C3N4/$\sqrt{3} \times \sqrt{3} \times 1$ CoN4(111). Henceforth, this particular geometry was chosen in the present investigation.

Table S4. Calculated energies of different configurations of g-C_3N_4/CoN_4 system

System	Co atoms are facing monolayer g-C_3N_4	N atoms are facing monolayer g-C_3N_4.
Energy(Ry)	-3192.38	-3192.22

Table S5. Band gaps of CoN_4 bulk and g-C_3N_4 using different exchange-correlation functionals

System		Band gap(eV)			
	PBE	PBE+U	HSE06	R2SCAN	Reported Band gap
g-C_3N_4	1.31	-----	2.9	1.80	2.65*(Experiment) 1.41(PBE)** 2.7(HSE06)***
CoN_4 bulk	2.6	3.19	4.55	4.63	2.56(PBE)****
CoN_4 (111) slab	------	2.37	------	2.99	------
g-C_3N_4/ CoN_4	------	1.81	------	2.22	------

* Jiang, T.; Nan, F.; Zhou, J.; Zheng, F.; Weng, Y.; Cai, T.; Ju, S.; Xu, B.; Fang, L. *A.I.P. Adv.* **2019**, *9*, 055225.
** A.M. Silva, M.I. Rojas, Comput.Theor. Chem. **2016,** *1098*, 41–49
***Jianjun Liu, Enda Hua, J. Phys. Chem. C (2017) 121 25827-25835
****Jun Deng, Ning Liu, Jiangang Guo, Xiaolong Chen, Phys. Rev B (2019) 99 184409

6. Computational methodology for calculating the band gap in presence of solvent

The solvent related calculations were done suing VASPsol[1] computational package, which integrates solvation into VASP through a self-consistent continuum model. VASPsol is widely used due to its ease of use and low computational costs, making it a valuable tool for chemical systems.[3,4] This approach incorporates DFT energy through two parameters. (i) The electrostatic interactions between solute and solvent molecules and (ii) the cavitation energy required to create the solute within the solvent. The expressions for these two terms are as follows:

$$E_{ele} = \int dr\varepsilon(r)\frac{|\nabla\varphi(r)|^2}{8\pi}$$

$$E_{vac} = \tau \int dr\ |\nabla S(r)\,|$$

ε(r) represents the dielectric constant, which can be calculated using the equation

$$\varepsilon(r) = 1 + (\varepsilon_b - 1)S(r)$$

where ε_b is the dielectric constant for the bulk solvent.

The cavity shape function is given by

$$S(r) = \frac{1}{2}erfc\left\{\frac{\ln\left(\frac{\rho(r)}{\rho(c)}\right)}{\sigma\sqrt{2}}\right\}$$

The parameters $\rho(r)$ and $\rho(c)$ represent the electron density and cutoff electron density, respectively, while σ represents the cavity width. These parameters define the transition region

between the solute and solvent, where the dielectric constant changes smoothly from 1 to the bulk dielectric constant.

Input files

7. Input file for optimization of g-C_3N_4(Quantum ESPRESSO)

relax.in

```
&CONTROL
   calculation   = "relax"
   pseudo_dir    = "."
/
&SYSTEM
   a          =  1.4400e+01
   c          =  2.00000e+01
   degauss    =  1.00000e-02
   ecutwfc    =  10.50000e+01
   ibrav      = 4
   nat        = 56
   ntyp       = 2
   occupations = "smearing"
   smearing    = "gaussian"
   vdw_corr    ="Grimme-D2"
/
&ELECTRONS
   startingpot      = "atomic"
   startingwfc      = "atomic+random"
/

&IONS
   ion_dynamics = "bfgs"
/
K_POINTS {automatic}
 12  12  1  0 0 0

ATOMIC_SPECIES
N      14.00674  N.pbe-n-rrkjus_psl.1.0.0.UPF
C      12.01070  C.pbe-n-rrkjus_psl.1.0.0.UPF

ATOMIC_POSITIONS {angstrom}
N       4.817083   2.886329   9.140414
N       0.078283   2.886329   9.140414
C      -1.152319   3.596817   9.140414
N      -1.152317   5.017790   9.140414
N       2.539483   2.886329   9.140414
C       1.308881   3.596817   9.140414
N       1.308883   5.017790   9.140414
C       0.078281   5.728278   9.140414
N       3.678283   0.913869   9.140414
C       3.770081   3.596817   9.140414
N       3.770083   5.017790   9.140414
C       2.539481   5.728278   9.140414
```

N	6.139483	0.913869	9.140414
C	4.908881	1.624357	9.140414
N	1.217083	9.121712	9.140414
N	-3.521717	9.121712	9.140414
C	-4.752319	9.832200	9.140414
N	-4.752317	11.253173	9.140414
N	-1.060517	9.121712	9.140414
C	-2.291119	9.832200	9.140414
N	-2.291117	11.253173	9.140414
C	-3.521719	11.963661	9.140414
N	0.078283	7.149252	9.140414
C	0.170081	9.832200	9.140414
N	0.170083	11.253173	9.140414
C	-1.060519	11.963661	9.140414
N	2.539483	7.149252	9.140414
C	1.308881	7.859740	9.140414
N	12.017083	2.886329	9.140414
N	7.278283	2.886329	9.140414
C	6.047681	3.596817	9.140414
N	6.047683	5.017790	9.140414
N	9.739483	2.886329	9.140414
C	8.508881	3.596817	9.140414
N	8.508883	5.017790	9.140414
C	7.278281	5.728278	9.140414
N	10.878283	0.913869	9.140414
C	10.970081	3.596817	9.140414
N	10.970083	5.017790	9.140414
C	9.739481	5.728278	9.140414
N	13.339483	0.913869	9.140414
C	12.108881	1.624357	9.140414
N	8.417083	9.121712	9.140414
N	3.678283	9.121712	9.140414
C	2.447681	9.832200	9.140414
N	2.447683	11.253173	9.140414
N	6.139483	9.121712	9.140414
C	4.908881	9.832200	9.140414
N	4.908883	11.253173	9.140414
C	3.678281	11.963661	9.140414
N	7.278283	7.149252	9.140414
C	7.370081	9.832200	9.140414
N	7.370083	11.253173	9.140414
C	6.139481	11.963661	9.140414
N	9.739483	7.149252	9.140414
C	8.508881	7.859740	9.140414

8. Input files for the band structure calculation of g-C_3N_4 using VASP involves 4 files (a) INCAR, (b) POSCAR, (c) KPOINTS and (d) POTCAR. All of these input files are pasted below:

a) INCAR

Global Parameters

```
 ISTART =  1          (Read existing wavefunction; if there)
 # ICHARG =  11       (Non-self-consistent: GGA/LDA band structures)
 LREAL  = Auto        (Projection operators: automatic)
 ENCUT  =  540        (Cut-off energy for plane wave basis set, in eV)
 PREC   =  Normal     (Precision level)
 LWAVE  = .TRUE.      (Write WAVECAR or not)
 LCHARG = .TRUE.      (Write CHGCAR or not)
 ADDGRID= .TRUE.      (Increase grid; helps GGA convergence)
```

Static Calculation

```
 ISMEAR =  0          (tetrahedron method for DOS)
 LORBIT =  11         (PAW radii for projected DOS)
 NELM   =  60         (Max electronic SCF steps)
 EDIFF  =  1E-05      (SCF energy convergence; in eV)

 METAGGA = R2SCAN
 LASPH=.TRUE.
 LMAXMIX=4
```

b) POSCAR

```
CIF
1.0
     14.3999996185       0.0000000000       0.0000000000
     -7.1999998093      12.4707654841       0.0000000000
      0.0000000000       0.0000000000      20.0000000000
  N   C
 32  24
Cartesian
    4.901860441        2.935269099        9.140400290
    0.130579158        2.969962609        9.140400290
   -1.053712865        5.021216564        9.140400290
    2.473372799        2.970386671        9.140400290
    1.302415217        5.014108237        9.140440226
    3.718000576        0.814602853        9.140400290
    3.658716033        5.022114489        9.140400290
    6.087549358        0.815276296        9.140400290
    1.301853670        9.170639205        9.140400290
   -3.469435123        9.205395154        9.140400290
   -4.653726931       11.256598934        9.140400290
   -1.126598567        9.205819587        9.140400290
   -2.297577606       11.249428912        9.140440226
    0.118065688        7.049973330        9.140400290
    0.058701752       11.257496859        9.140400290
    2.487513619        7.050646774        9.140400290
   12.101860250        2.935269099        9.140400290
    7.330593773        2.969912807        9.140400290
    6.146229653        5.021266366        9.140400290
    9.673358232        2.970411572        9.140400290
    8.502450861        5.014120502        9.140440226
   10.918022165        0.814590402        9.140400290
```

10.858687089	5.022064687	9.140400290
13.287520414	0.815276296	9.140400290
8.501853050	9.170639205	9.140400290
3.730565115	9.205345351	9.140400290
2.546244125	11.256624207	9.140400290
6.073393947	9.205806950	9.140400290
4.902436794	11.249453442	9.140440226
7.318044039	7.049960694	9.140400290
7.258701132	11.257472330	9.140400290
9.687470084	7.050646774	9.140400290
-1.001044688	3.684138328	9.140400290
1.302040781	3.614514191	9.140419960
0.090179942	5.713518736	9.140440226
3.605162191	3.684624828	9.140419960
2.514959912	5.714154643	9.140440226
4.902465601	1.437604880	9.140419960
-4.601044593	9.919496169	9.140419960
-2.297951828	9.849909198	9.140419960
-3.509834340	11.948901478	9.140440226
0.005191469	9.919982298	9.140419960
-1.085011024	11.949512484	9.140440226
1.302458347	7.673024881	9.140419960
6.198983767	3.684138328	9.140400290
8.502054967	3.614514191	9.140419960
7.290172455	5.713531001	9.140419960
10.805190968	3.684599927	9.140419960
9.714952855	5.714142006	9.140440226
12.102457954	1.437642325	9.140419960
2.598955324	9.919496169	9.140400290
4.902040256	9.849897305	9.140419960
3.690165040	11.948901478	9.140440226
7.205212736	9.919970405	9.140419960
6.114974623	11.949512484	9.140440226
8.502450861	7.673037518	9.140419960

c) KPOINTS

K-Path Generated by VASPKIT.
20
Line-Mode
Reciprocal

0.0000000000	0.0000000000	0.0000000000	GAMMA
0.5000000000	0.0000000000	0.0000000000	M
0.5000000000	0.0000000000	0.0000000000	M
0.3333333333	0.3333333333	0.0000000000	K
0.3333333333	0.3333333333	0.0000000000	K
0.0000000000	0.0000000000	0.0000000000	GAMMA

d) POTCAR contains pseudopotentials of Carbon and Nitrogen

9. Input files for the PDOS calculation of g-C_3N_4 using VASP requires 4 files (a) INCAR, (b) POSCAR (c) KPOINTS and (d) POTCAR

a) INCAR

```
Global Parameters
 ISTART =  1          (Read existing wavefunction; if there)
 LREAL  = Auto        (Projection operators: automatic)
 ENCUT  =  540
 NELM = 1000
 EDIFF = 1E-5
 PREC   =  Normal
 ALGO = A
 ISPIN =2
 LORBIT =  11
 LWAVE  = .TRUE.       (Write WAVECAR or not)
 LCHARG = .TRUE.       (Write CHGCAR or not)
 SIGMA  =  0.05
 METAGGA = R2SCAN
 LASPH=.TRUE.
 LMAXMIX=4
```

b) POSCAR (same as band structure calculation)

c) KPOINTS

```
k-points
0
Monkhorst-pack
 12 12 1
 0 0 0
```

d) POTCAR contains pseudopotentials of Carbon and Nitrogen

10. Input files for the work function calculation of g-C_3N_4 needs 3 files, (a) scf.in, (b) pp.in and (c) avg.in all of them are given below.

a) scf.in

```
&CONTROL
   calculation   = "scf"
   pseudo_dir  = "."
   outdir      = "data"
   verbosity   = "high"
/
&SYSTEM
   a          =  1.4400e+01
   c          =  2.00000e+01
   degauss     =  1.00000e-02
   ecutwfc     =  10.50000e+01
   ibrav       = 4
   nat         = 56
   ntyp        = 2
   occupations = "smearing"
   smearing    = "gaussian"
```

```
   vdw_corr    ="Grimme-D2"
/
&ELECTRONS
   startingpot      = "atomic"
   startingwfc      = "atomic+random"
/

K_POINTS {automatic}
 12  12  1  0 0 0

ATOMIC_SPECIES
N      14.00674  N.pbe-n-rrkjus_psl.1.0.0.UPF
C      12.01070  C.pbe-n-rrkjus_psl.1.0.0.UPF

ATOMIC_POSITIONS (angstrom)
N            4.9018571031       2.9352663273       9.1404028751
N            0.1305810907       2.9699658975       9.1404000433
C           -1.0010478436       3.6841346545       9.1404095881
N           -1.0537186275       5.0212188802       9.1404030826
N            2.4733704285       2.9703894290       9.1404053092
C            1.3020471198       3.6145094129       9.1404261983
N            1.3024107533       5.0141056835       9.1404329964
C            0.0901823662       5.7135200753       9.1404317644
N            3.7180044075       0.8146032337       9.1404045642
C            3.6051630824       3.6846205373       9.1404210857
N            3.6587135913       5.0221093963       9.1404061216
C            2.5149669892       5.7141506483       9.1404305338
N            6.0875518926       0.8152825109       9.1404062546
C            4.9024634453       1.4376066175       9.1404174105
N            1.3018511808       9.1706402490       9.1404048993
N           -3.4694306709       9.2053894499       9.1403995761
C           -4.6010511019       9.9194951841       9.1404101286
N           -4.6537265009      11.2566050821       9.1404015047
N           -1.1265983403       9.2058203287       9.1404024292
C           -2.2979470827       9.8499086432       9.1404253225
N           -2.2975729614      11.2494253930       9.1404344347
C           -3.5098406160      11.9489059014       9.1404309198
N            0.1180631452       7.0499710001       9.1404074318
C            0.0051983754       9.9199816570       9.1404211315
N            0.0587009543      11.2574951118       9.1404074851
C           -1.0850118024      11.9495171142       9.1404317900
N            2.4875129849       7.0506428370       9.1404050870
C            1.3024565521       7.6730288717       9.1404184829
N           12.1018572516       2.9352691252       9.1404022407
N            7.3305891061       2.9699157822       9.1403983350
C            6.1989779477       3.6841428138       9.1404082020
N            6.1462325349       5.0212604007       9.1404001535
N            9.6733637277       2.9704126825       9.1404044066
C            8.5020579612       3.6145140636       9.1404254317
N            8.5024603119       5.0141159922       9.1404333567
C            7.2901793429       5.7135282307       9.1404299690
N           10.9180180274       0.8145964000       9.1404045674
```

C	10.8051857981	3.6846006530	9.1404204881
N	10.8586812840	5.0220665705	9.1404053746
C	9.7149577188	5.7141380628	9.1404302798
N	13.2875199628	0.8152783623	9.1404040116
C	12.1024578335	1.4376374982	9.1404162147
N	8.5018585724	9.1706418905	9.1404058239
N	3.7305711886	9.2053466440	9.1403992092
C	2.5989479541	9.9195007761	9.1404096802
N	2.5462476268	11.2566184157	9.1404022993
N	6.0733910975	9.2058028800	9.1404067976
C	4.9020476238	9.8498956732	9.1404261043
N	4.9024373508	11.2494497001	9.1404323361
C	3.6901581224	11.9489061263	9.1404301736
N	7.3180456839	7.0499594169	9.1404047912
C	7.2052042812	9.9199751994	9.1404234997
N	7.2586990475	11.2574746546	9.1404085843
C	6.1149761874	11.9495177645	9.1404308248
N	9.6874727202	7.0506485032	9.1404046869
C	8.5024538198	7.6730355903	9.1404177064

b) pp.in

```
&inputPP
  outdir='.',
  plot_num=11
  filplot = 'gc3n4l100.pot'
/
&plot
  iflag=3,
  output_format=5,
/
```

c) avg.in

```
1
gc3n4l100.pot
1.D0
1440
3
3.835000000
```

11. Input file for the optical property calculation of g-C_3N_4 using CASTEP

task : ElectronicSpectroscopy

spectral_task : Optics
continuation : default
xc_functional : PBE
sedc_apply : true
sedc_scheme : G06
spin_polarized : false
opt_strategy : Default
page_wvfns : 0
cut_off_energy : 500.000000000000000
grid_scale : 1.500000000000000
fine_grid_scale : 1.500000000000000
finite_basis_corr : 0
elec_energy_tol : 2.000000000000000e-06
max_scf_cycles : 1000
fix_occupancy : false
metals_method : EDFT
num_occ_cycles : 6
nextra_bands : 7
smearing_width : 0.100000000000000
num_dump_cycles : 0
spectral_nbands : 120
spectral_eigenvalue_tol : 1.000000000000000e-05
calculate_stress : false
calculate_ELF : false
popn_calculate : false
calculate_hirshfeld : false
calculate_densdiff : false
pdos_calculate_weights : false
spectral_write_eigenvalues : true

References

[1] K. Mathew, R. Sundararaman, K. Letchworth-Weaver, T.A. Arias, R.G. Hennig, J. Chem. Phys. (2014) 140.

[2] J. Han, Y. Kim, H.W. Kim, D.H.K. Jackson, D. Lee, H. Chang, H.J. Chae, K.Y. Lee, H.J. Kim, Electrochem. Commun. 83 (2017) 46–50.

[3] M.C. Groenenboom, R.M. Anderson, D.J. Horton, Y. Basdogan, D.F. Roeper, S.A. Policastro, J.A. Keith, J. Phys. Chem. C 121 (2017) 16825–16830.