ELECTRONIC SUPPLEMENTARY INFORMATION (ESI)

Unravelling the electrochemical mechanisms for nitrogen fixation on single transition metal atom embedded in defective graphitic carbon nitride

Xingzhu Chen,[a] Xiujian Zhao,[a] Zhouzhou Kong,[a] Wee-Jun Ong*[b] and Neng Li*[a]

a State Key Laboratory of Silicate Materials for Architectures, Wuhan University of Technology, Hubei, 430070, China

b Department of Chemical Engineering, Xiamen University Malaysia, Jalan Sunsuria, Bandar Sunsuria, 43900 Sepang, Malaysia

* Corresponding authors:

E-mail: lineng@whut.edu.cn (N. Li), Tel.: +86-027-87652553

E-mail: weejun.ong@xmu.edu.my; ongweejun@gmail.com (W.-J. Ong), Tel.: (+603) 8705 5149

Contents	Pages

ADDITIONAL COMPUTATIONAL DETAILS

Settings for DFT-D3 geometry optimisation

```
ISTART = 0
ISYM = 0
ENCUT = 520
PREC = Medium
EDIFF = 1E-4
EDIFFG = -0.05
NSW = 200
ISIF = 2
ISPIN = 2
ISMEAR = -5
IBRION = 2
POTIM = 0.5
LCHARG = .FALSE.
LWAVE = .FALSE.
LREAL = AUTO
# DFTD3
IVDW = 11
```

Pseudo-potentials applied:

C: PAW_PBE C 08Apr2002

N: PAW_PBE N 08Apr2002

H: PAW_PBE H 15Jun2001

Ti: PAW_PBE Ti_sv 07Sep2000

V: PAW_PBE V_sv 07Sep2000

Fe: PAW_PBE Fe_sv 23Jul2007

Co: PAW_PBE Co_sv 23Jul2007

Ni: PAW_PBE Ni 02Aug2007

Cu: PAW_PBE Cu 22Jun2005

Zr: PAW_PBE Zr_sv 07Sep2000

Mo: PAW_PBE Mo_sv 02Feb2006

Ru: PAW_GGA Ru_sv 28Jan2005

Pd: PAW_PBE Pd_pv 28Jan2005
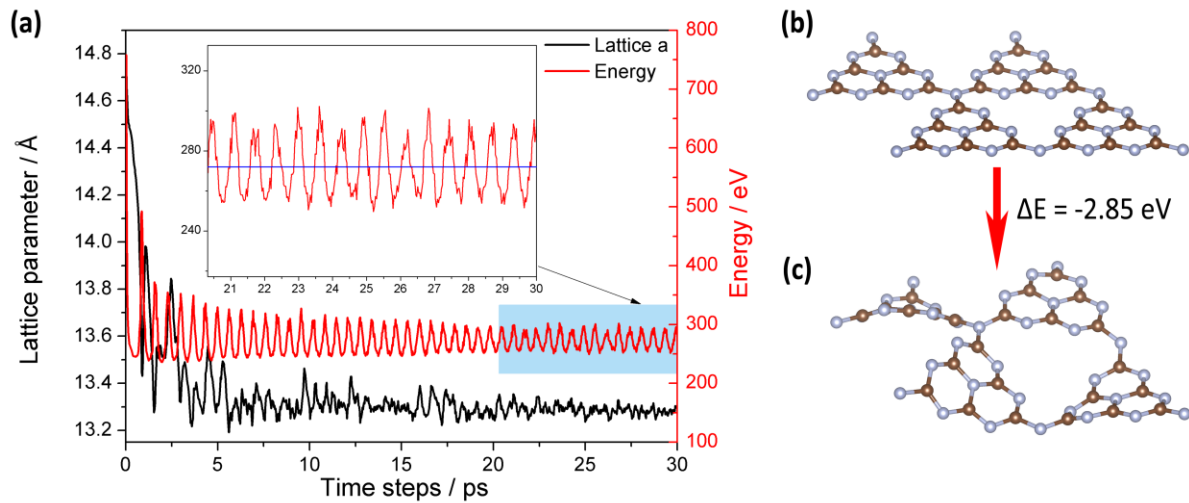
Pt: PAW_PBE Pt 04Feb2005

Fig. S1 (a) Total energy and lattice parameter of g-C$_3$N$_4$ in 2 × 2 supercell during 30 ps at 300 K, the molecular dynamics simulation was carried out with a universal force field as implemented in Forcite code. (b) The planar and (c) corrugated structures of g-C$_3$N$_4$.

Table S1 Computed total energies per unit cell of corrugated g-C_3N_4 using different supercell sizes.

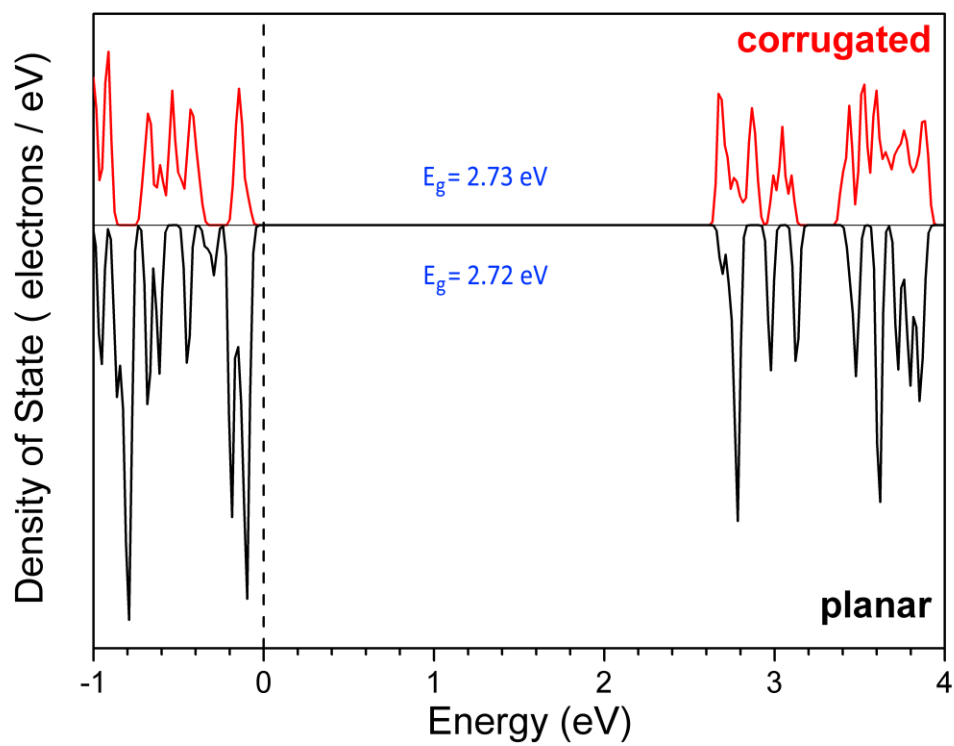| Supercell	Total energy per unit cell (eV)
2×2	-118.91
3×3	-119.01
4×4	-119.09
5×5	-119.11

Fig. S2 The calculated density of state for planar and corrugated g-C$_3$N$_4$ with the hybrid HSE06 functional.

Table S2 Computed formation energies ($E_{\text{formation}}$) for three types of N vacancy in g-C$_3$N$_4$ with the following equation: $E_{\text{formation}} = E \, (\text{NV-g-C}_3\text{N}_4) - [E \, (\text{g-C}_3\text{N}_4) - \frac{1}{2} E \, (\text{N}_2)]$.

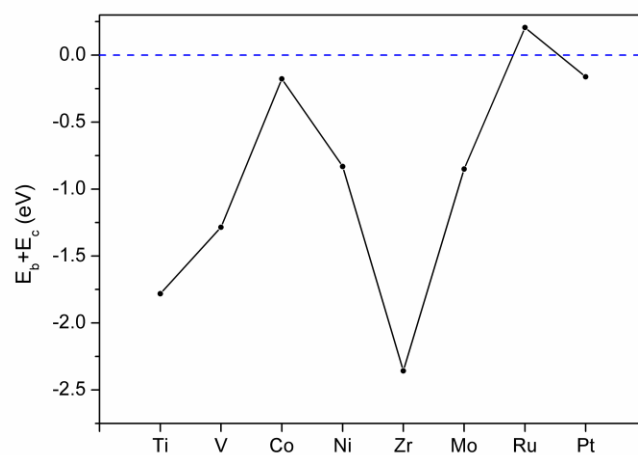| N vacancy type	Formation energy (eV)
Type I	3.92
Type II	1.35
Type III	2.03

Fig. S3 The sum of binding energy and cohesive energy (per atom) for various TM. Cohesive energy per atom is calculated using the equation of $E_c = 1/n\ [E(\text{Metal}) - nE(\text{TM})]$, where n represents the number of atoms in an unit metal crystal.

Table S3 Gibbs free energies at 298.15 K in eV, corresponding to the isolated N_2, H_2, and NH_3, and the different adsorbed states along the N_2 reduction pathway catalyzed by Ti and V@NVs-g-C_3N_4.

Species	G (PBE) / eV
N_2	-17.09
H_2	-6.90
NH_3	-19.18

Catalyst	Ti@g-C_3N_4	V@g-C_3N_4
Clean	-473.58	-474.31
*N_2	-491.24	-491.42
*NNH	-494.41	-494.33
*NHNH	-497.97	-497.86
*NNH_2	-497.65	-497.91
*$NHNH_2$	-502.27	-501.92
*NH_2NH_2	-504.99	-505.00
NH+NH_3	-506.44	-506.75
*NH_2	-491.14	-490.81
*NH_3	-494.08	-494.32

Table S4 Gibbs free energies calculated by revPBE (G (revPBE)) at 298.15 K in eV, corresponding to the isolated N_2, H_2, and NH_3, and the different adsorbed states along the N_2 reduction pathway catalyzed by Ti@NVs-g-C_3N_4.

Species	G (revPBE) / eV
N_2	-17.64
H_2	-7.16
NH_3	-19.73

Catalyst	Ti@g-C_3N_4
Clean	-479.44
*N_2	-497.44
*NNH	-500.62
*NHNH	-504.21
*NNH_2	-503.98
*$NHNH_2$	-508.59
*NH_2NH_2	-511.39
NH+NH_3	-513.03
*NH_2	-497.26
*NH_3	-500.25

Note: Computation of activation barriers

We employed a method developed by Janik et al. to determine the potential-dependent activation barriers along an electrocatalytic reaction pathway.[1] The activation barriers for the non-electrochemical reactions are extrapolated to the potential-dependent system using the following equation:

$$G_{act}(U) = G^0_{act} + F\beta(U - U_0)$$

Where G^0_{act} is the activation barrier for the non-electrochemical hydrogenation reaction; U is the applied electrode potential, which is set to 0; β is symmetry coefficient, approximately equals to 0.5 for all steps; U_0 is the equilibrium potential for the reductive adsorption of a proton, which equals to the energy of the (*Adsorbate + *H•) reactants to (*Adsorbate + H^+ + e^-).

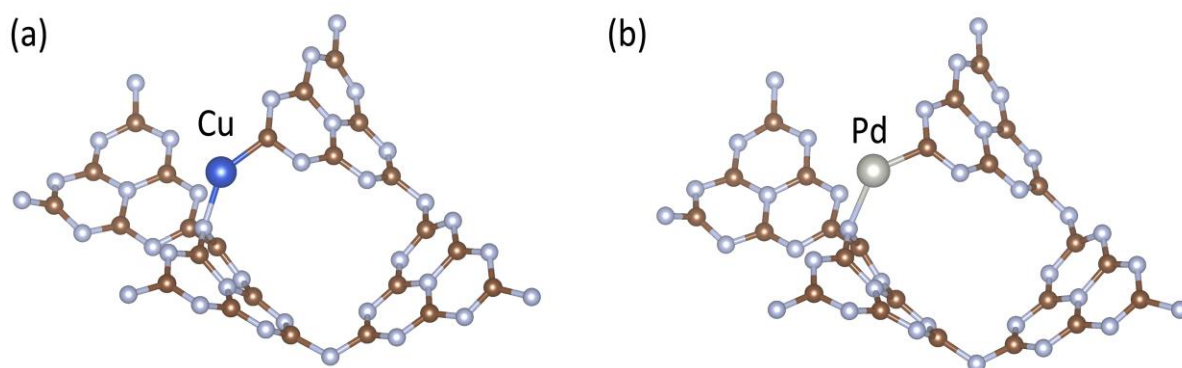| Transition State	G_{act}
TS1	0.57
TS2	0.27
TS3	-
TS4	0.49
TS5	0.23

Fig. S4 Optimized geometry structures of (a) Cu and (b) Pd supported by NVs-g-C_3N_4 after 4-ps *ab*-initio molecular dynamics simulations.

Table S5 The adsorption free energy and the N-N bond length of N_2 on Cu and Pd@NVs-g-C_3N_4 (the horizontal-configuration N_2 adsorption cannot exist in the Cu and Pd embedded NVs-g-C_3N_4).

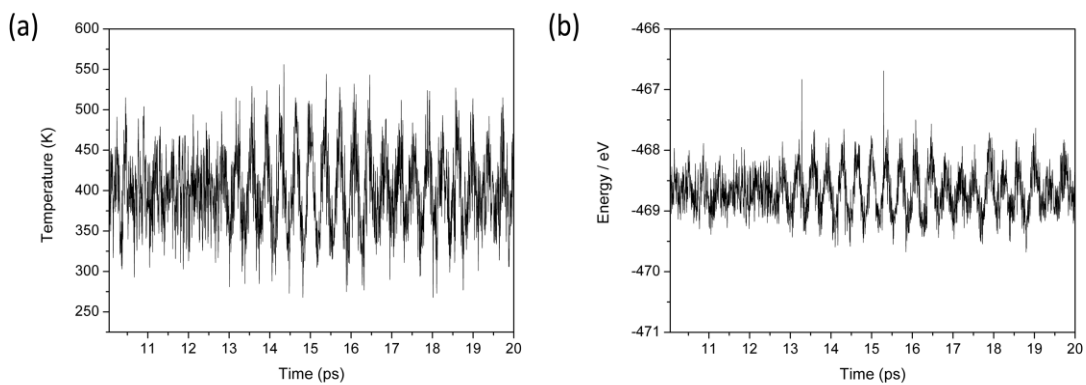|	Cu@NVs-g-C_3N_4	Pd@NVs-g-C_3N_4
Adsorption free energy	-0.06 eV	-0.11 eV
N-N bond length	1.123 Å	1.123 Å

Fig. S5 Variation of (a) temperature and (b) total energy for single Ti atom supported by NVs-g-C_3N_4 during ab-initio molecular dynamics simulation from 10 to 20 ps at 400 K.
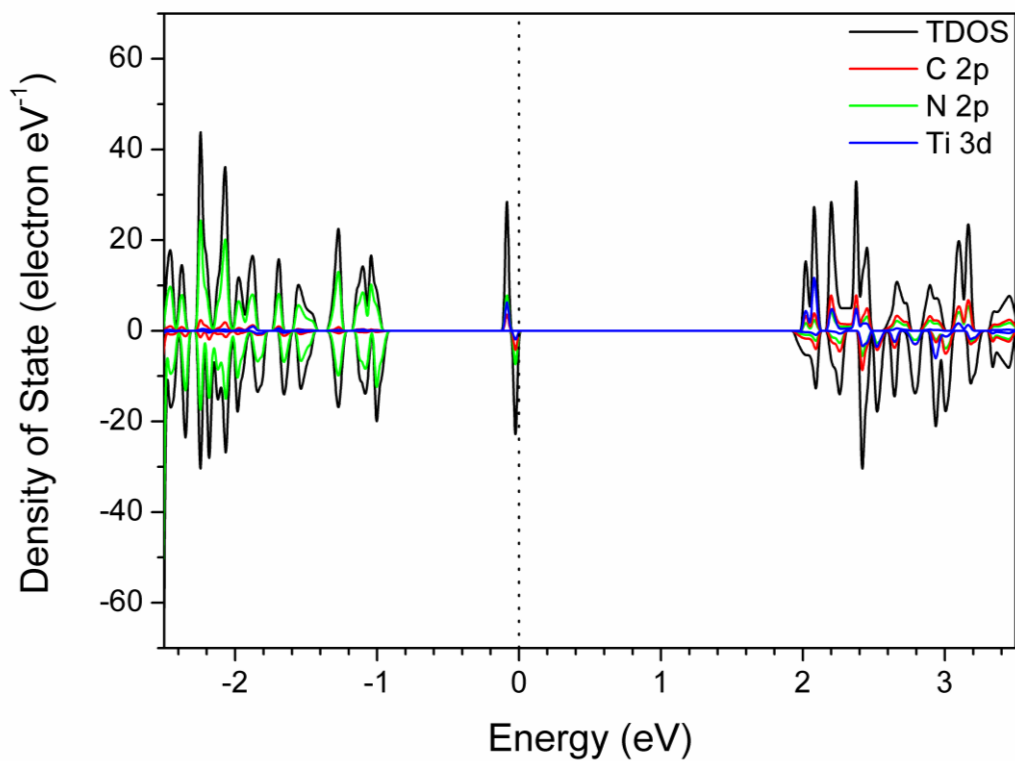
Fig. S6 Calculated total and partial density of state for Ti@ NVs-g-C$_3$N$_4$.

Reference

1. X. Nie, M. R. Esopi, M. J. Janik and A. Asthagiri, *Angew. Chem. Int. Ed.*, 2013, **52**, 2459-2462.