Electronic Supplementary Material (ESI) for Nanoscale.

Unexpected monoatom catalytic-host synergetic OER/ORR by graphitic carbon nitride: Density functional theory

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Calculation Details

Two difference activity sites are considered and shown in Fig.1a, where the M_1 atom are labeled as site 1 and host atoms in the neighboring holes of M_1 atoms are labeled as site 2. The adsorption energies follow the approach of Nøeskov *et al*., [1]

$$\Delta E_{*H2O} = E(\text{sub}/H_2O) - E(\text{sub}) - E(H_2O) \quad \text{(S1)}$$

$$\Delta E_{*O2} = E(\text{sub}/O_2) - E(\text{sub}) - 2\times(E(H_2O) - E(H_2)) \quad \text{(S2)}$$

$$\Delta E_{*O} = E(\text{sub}/O) - E(\text{sub}) - [E(H_2O) - E(H_2)] \quad \text{(S3)}$$

$$\Delta E_{*OH} = E(\text{sub}/OH) - E(\text{sub}) - [E(H_2O) - E(H_2)/2] \quad \text{(S4)}$$

$$\Delta E_{*OOH} = E(\text{sub}/OOH) - E(\text{sub}) - [2\times E(H_2O) - 3\times E(H_2)/2] \quad \text{(S5)}$$

where $E(\text{sub}/H_2O)$, $E(\text{sub}/O_2)$, $E(\text{sub}/O)$, $E(\text{sub}/OH)$ and $E(\text{sub}/OOH)$ denote the total energies of H_2O, O_2, O, OH and OOH groups on substrate. $E(\text{sub})$, $E(H_2O)$ and $E(H_2)$ are the total energies of bare substrate, water, and hydrogen gas, respectively.

The electrochemical model of OER/ORR developed by Nøreskov[2] can be divided into four one–electron reactions:

$$H_2O + * \rightarrow *OH + (H^+ + e^-) \quad \text{(S6)}$$

$$*OH + (H^+ + e^-) \rightarrow *O + 2(H^+ + e^-) \quad \text{(S7)}$$

$$H_2O + *O + 2(H^+ + e^-) \rightarrow *OOH + 3(H^+ + e^-) \quad \text{(S8)}$$

$$*OOH + 3(H^+ + e^-) \rightarrow O_2 + * + 4(H^+ + e^-) \quad \text{(S9)}$$

The detailed Gibbs free energy changes of steps 6-9 can be calculated by:

$$\Delta G_1 = \Delta G_{*OH} - eU \quad \text{(S10)}$$

$$\Delta G_2 = \Delta G_{*O} - \Delta G_{*OH} - eU \quad \text{(S11)}$$

$$\Delta G_3 = \Delta G_{*OOH} - \Delta G_{*O} - eU \quad \text{(S12)}$$

$$\Delta G_4 = 4.92\text{eV} - \Delta G_{*OOH} - eU \quad \text{(S13)}$$

where the sum of $\Delta G_{1\text{-}4}$ is fixed to the negative of experimental Gibbs free energy of formation of two water molecules ($-2^{\Delta_{H_2O}^{exp}} = 4.92$ eV).[2] The Gibbs free energy of $(H^+ + e^-)$ in solution is estimated as the half energy of H_2 molecule at standard condition.[3] Since ORR $[O_2 + 4(H^+ + e^-) \rightarrow 2H_2O]$ is the reverse of OER, the Gibbs free energies of ORR are related to OER intermediates by the reference of +4.92 eV, *i.e.*, $\Delta_G^{OER}(int) = \Delta_G^{ORR}(int) + 4.92$ eV.[4]

The over–potential of OER is determined by following equations:

$$\eta^{OER} = U_{OER} - 1.23 \quad \text{(S14)}$$

$$U_{OER} = \text{Max}(\Delta G_{*OH}, \Delta G_{*O} - \Delta G_{*OH}, \Delta G_{*OOH} - \Delta G_{*O}, 4.92\text{ eV} - \Delta G_{*OOH})/e \quad \text{(S15)}$$

The ORR under acidic conditions follows the opposite processes from *Eq*.S10 to *Eq*. S7. The over–potential of ORR is expressed as:

$$\eta^{ORR} = 1.23 - U_{ORR} \quad \text{(S16)}$$

$$U_{ORR} = -\text{Max}\,(\Delta G_{*OOH} - 4.92\ \text{eV},\ \Delta G_{*O} - \Delta G_{*OOH},\ \Delta G_{*OH} - \Delta G_{*O},\ -\Delta G_{*OH})/e \quad \text{(S17)}$$

Figure S1. The total energy for (a) Fe_1, (b) Co_1, (c) Ni_1, (d) Cu_1, (e) $Zn_1/g–C_3N_4$ specimens during the whole dynamics simulation of 10 ps. The atomic structures at 0 ps and 10 ps of each specimen (Inset).

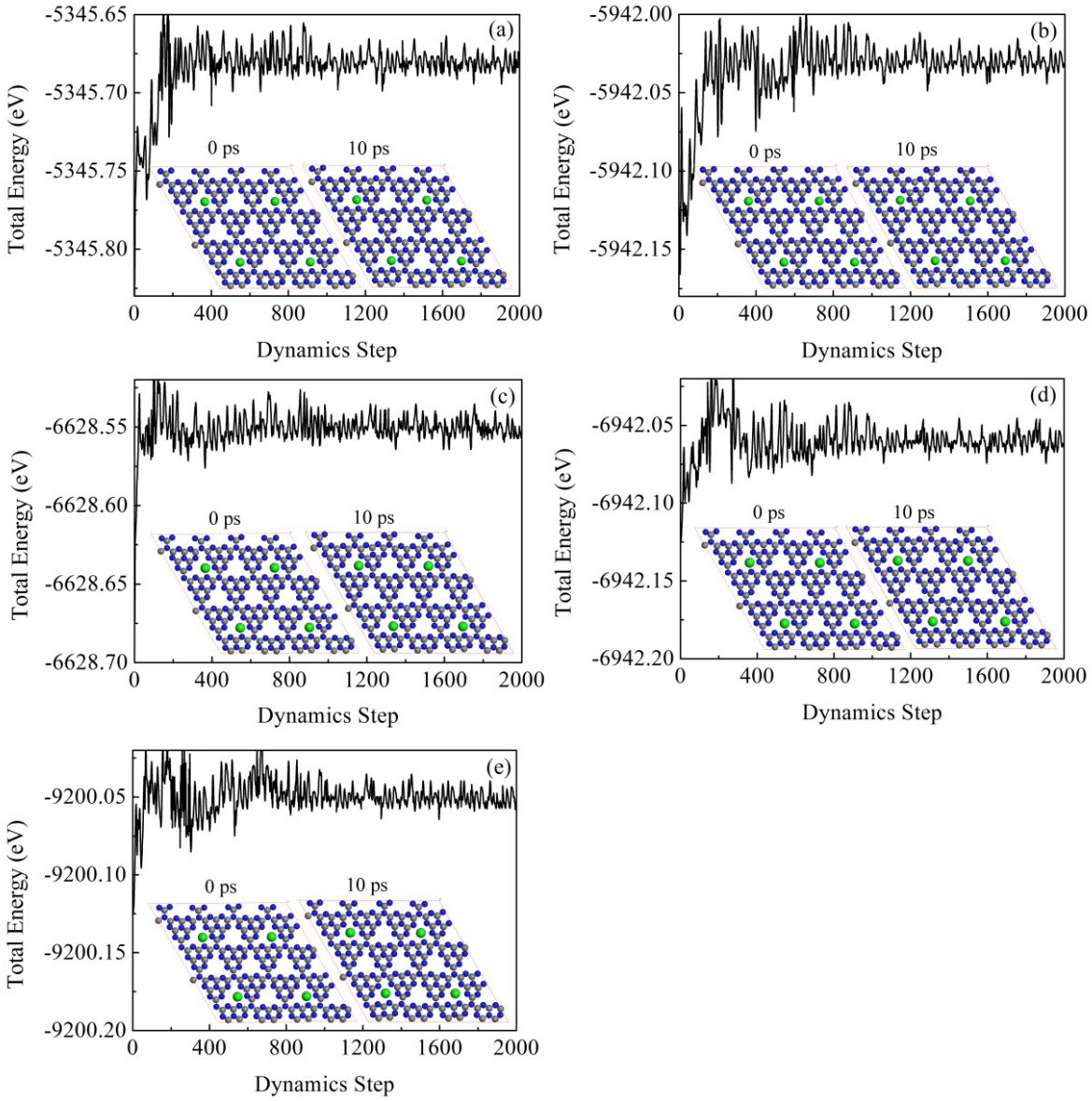


Figure S2. The electron density differences of $M_1/g–C_3N_4$ specimens (left), where the red and bule regions denote the obtained and lost electrons. The VBM (red regions) and CBM (yellow regions) of $M_1/g–C_3N_4$ specimens (right), the isosurface is taken at a value of 0.003 e/Bohr^3

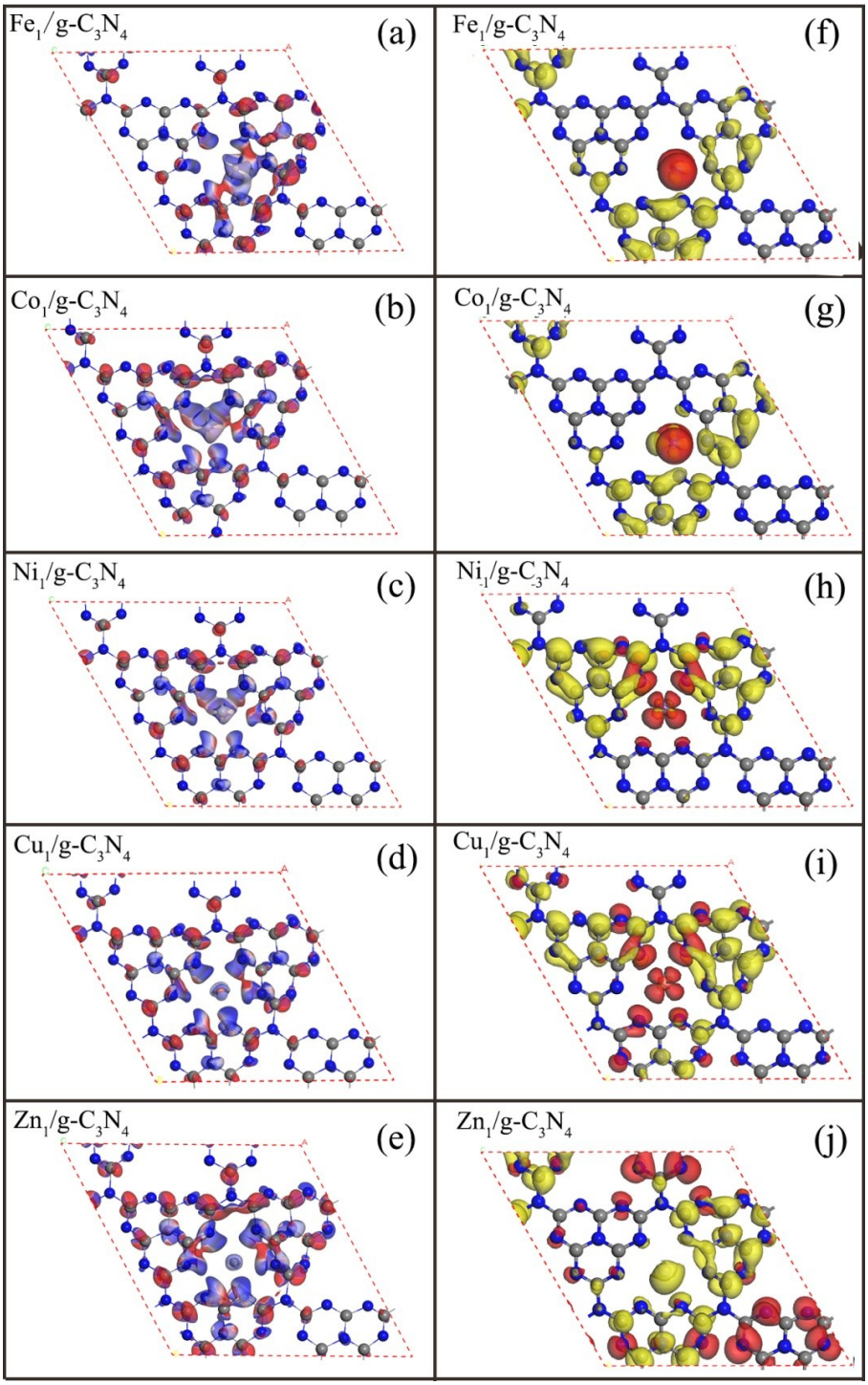


Figure S3. The atomic structures of H_2O and O_2 on both active site of $M_1/g–C_3N_4$.

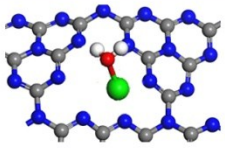
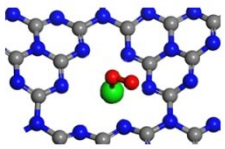
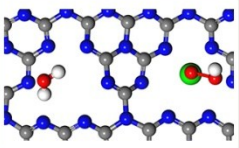
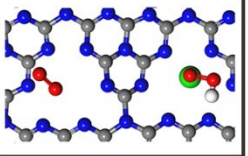
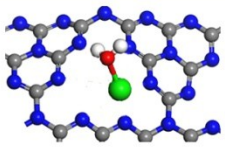
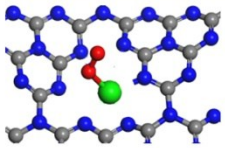
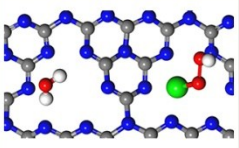
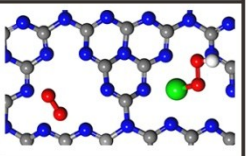
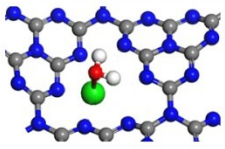
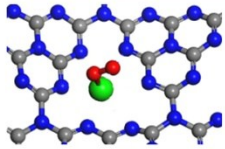
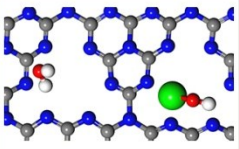
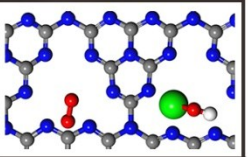
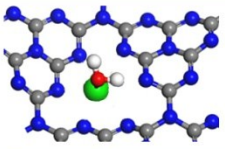
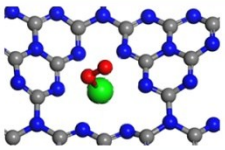
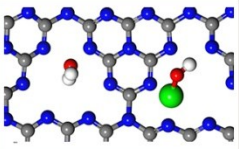
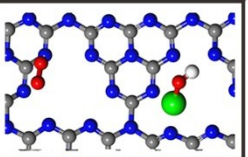
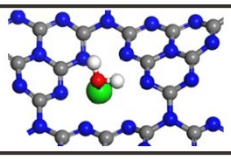
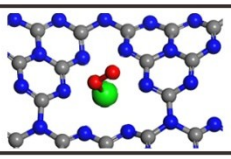
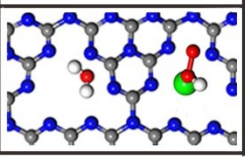
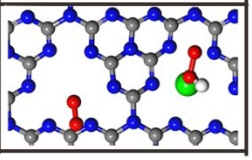
	*H_2O	*O_2	*H_2O	*O_2
$Fe_1/g\text{-}C_3N_4$				
$Co_1/g\text{-}C_3N_4$				
$Ni_1/g\text{-}C_3N_4$				
$Cu_1/g\text{-}C_3N_4$				
$Zn_1/g\text{-}C_3N_4$				

Figure S4. The atomic structures of OH, O and OOH groups on g–C_3N_4, Co_1/g–C_3N_4 and 4Co_1/g–C_3N_4, where the OOH bonding with Co_1 atom is considered as each intermediate is adsorbed on site 2.

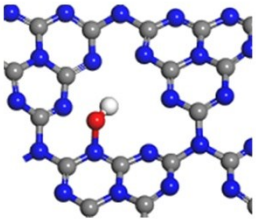
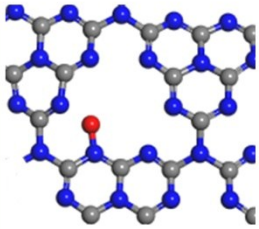
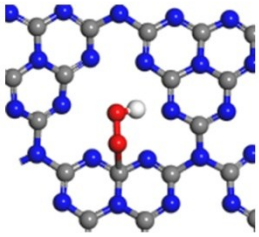
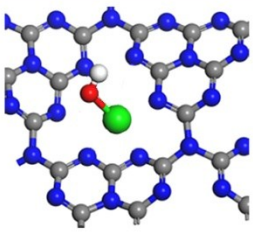
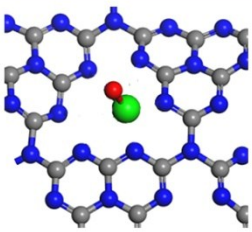
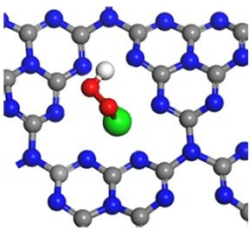
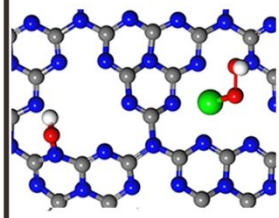
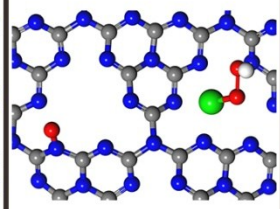
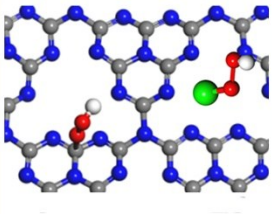
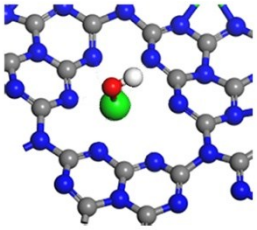
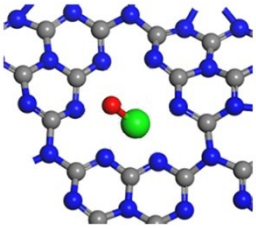
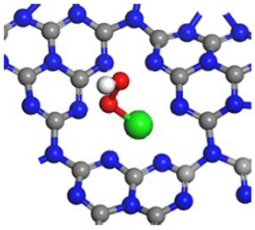
	*OH	*O	*OOH
g-C_3N_4			
Co_1/g-C_3N_4 Site 1			
Co_1/g-C_3N_4 Site 2			
4Co_1/g-C_3N_4			

Figure S5. (a) The transition states of OH, O and OOH groups form site 2 to site 1 of all $M_1/g–C_3N_4$. (b) The adsorption energies of OH, O and OOH groups on site 1 and site 2 of all $M_1/g–C_3N_4$.

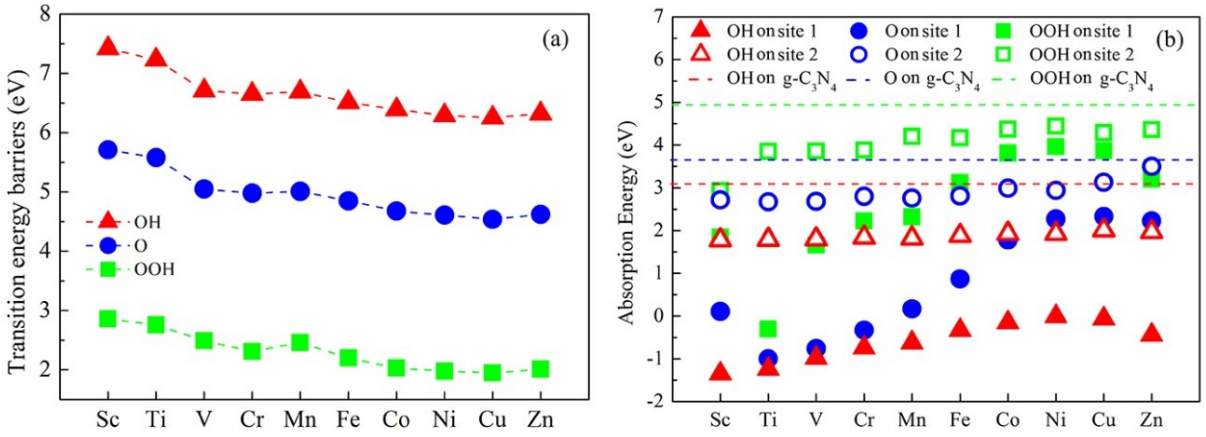


Figure S6. The atomic structures of OH, O and OOH groups on site 1 of $M_1/g–C_3N_4$.

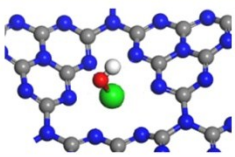
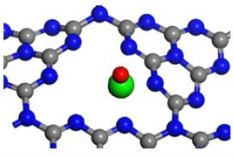
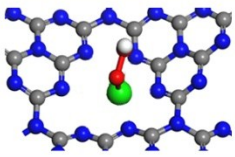
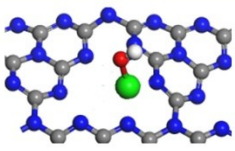
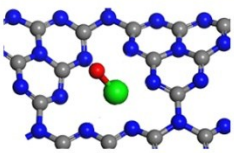
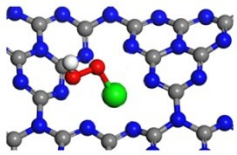
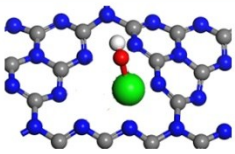
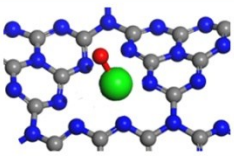
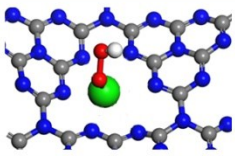
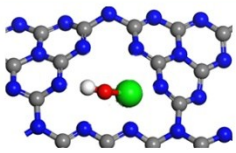
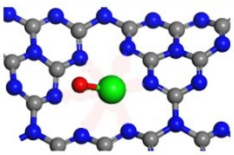
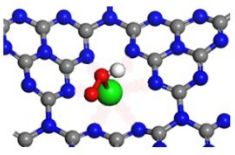
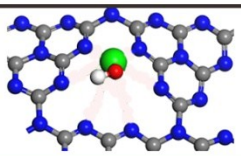
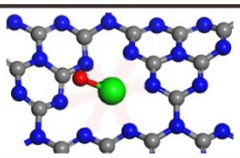
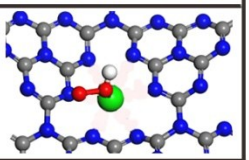
	*OH	*O	*OOH
$Fe_1/g\text{-}C_3N_4$			
$Co_1/g\text{-}C_3N_4$			
$Ni_1/g\text{-}C_3N_4$			
$Cu_1/g\text{-}C_3N_4$			
$Zn_1/g\text{-}C_3N_4$			

Figure S7. The atomic structures of OH, O and OOH groups on site 2 of $M_1/g–C_3N_4$, where the OOH or OH bonding with M_1 atom is considered to calculate the adsorption energies of intermediate on site 2 on account of the determining steps of reaction on site 1.

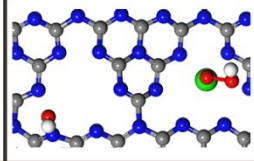
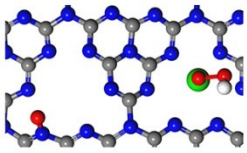
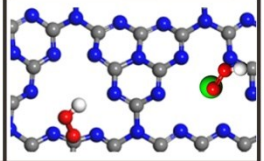
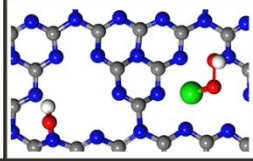
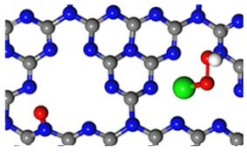
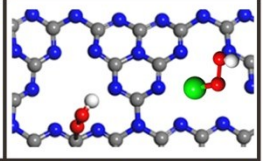
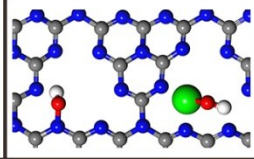
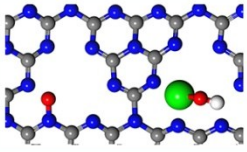
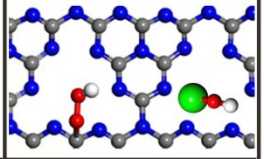
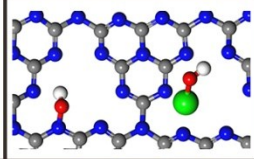
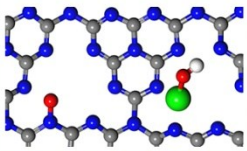
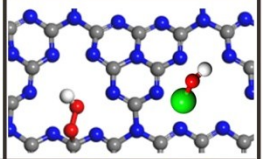
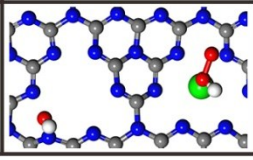
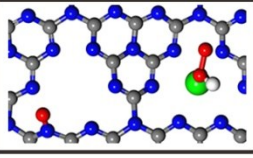
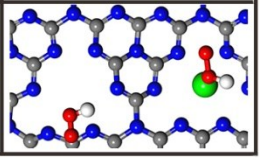
	*OH	*O	*OOH
$Fe_1/g\text{-}C_3N_4$			
$Co_1/g\text{-}C_3N_4$			
$Ni_1/g\text{-}C_3N_4$			
$Cu_1/g\text{-}C_3N_4$			
$Zn_1/g\text{-}C_3N_4$			

Figure S8. The Gibbs free energy changes during OER on site 1 (left) and site 2 (right) of all $M_1/g–C_3N_4$.

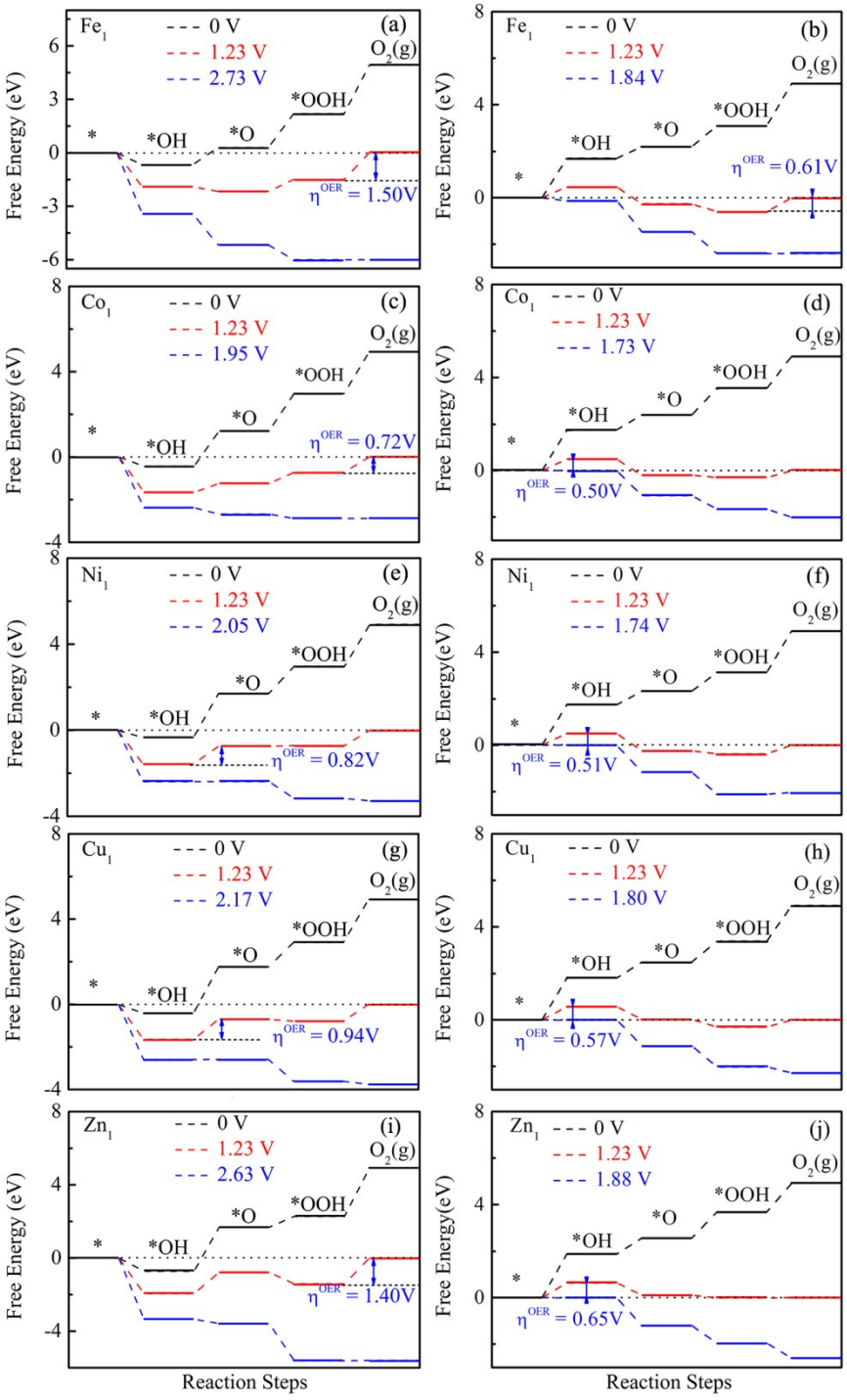


Figure S9. The Gibbs free energy changes during ORR on site 1 (left) and site 2 (right) of all $M_1/g–C_3N_4$.

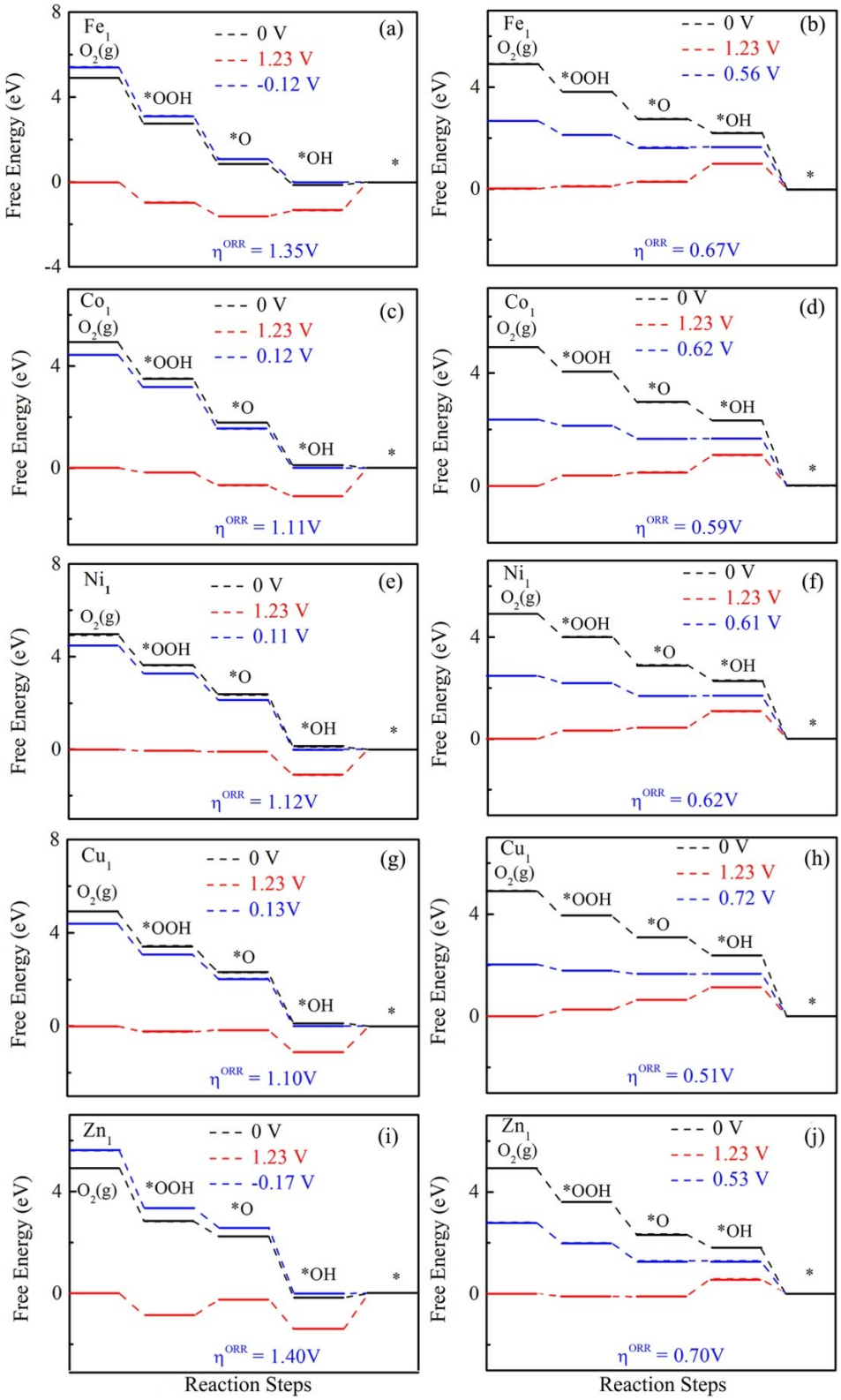


Figure S10. The structure schematic diagrams of 3×3 supercell samples.

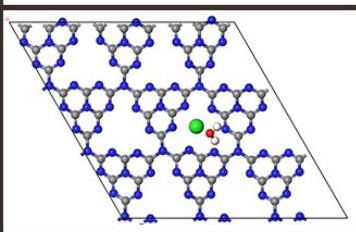
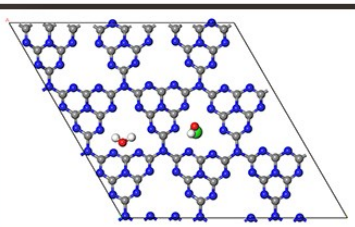
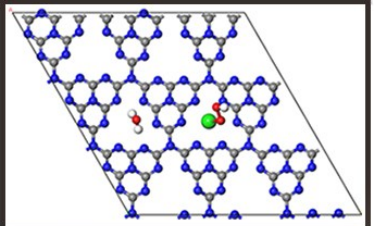
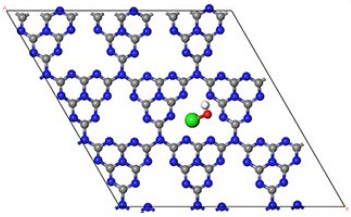
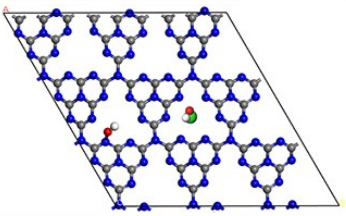
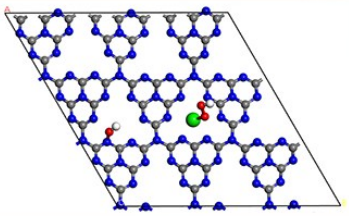
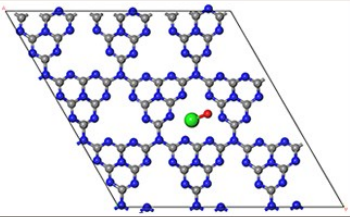
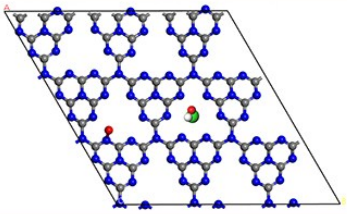
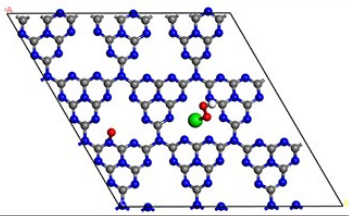
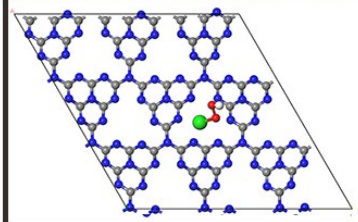
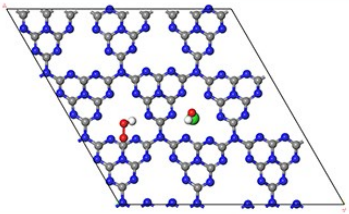
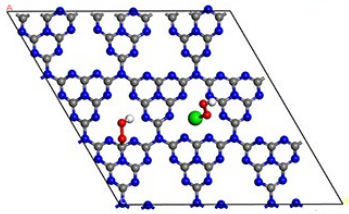
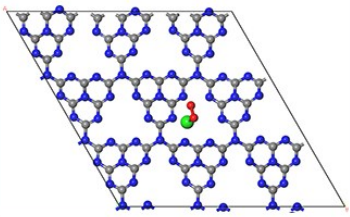
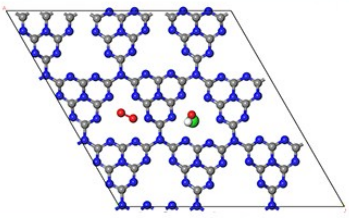
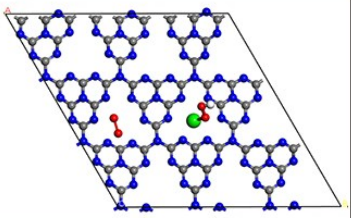
	groups adsorbed at site 1	groups adsorbed at site 2 when OH adsorbed at site 1	groups adsorbed at site 2 when OOH adsorbed at site 1
*H_2O			
*OH			
*O			
*OOH			
*O_2			

Figure S11. The Gibbs free energy changes of OER/ORR on sites 1 and 2 of 2×2 (red lines) and 3×3 (blue lines) supercells. The Gibbs free energy of site 1 for the left column and the Gibbs free energy of site 2 for the right column.

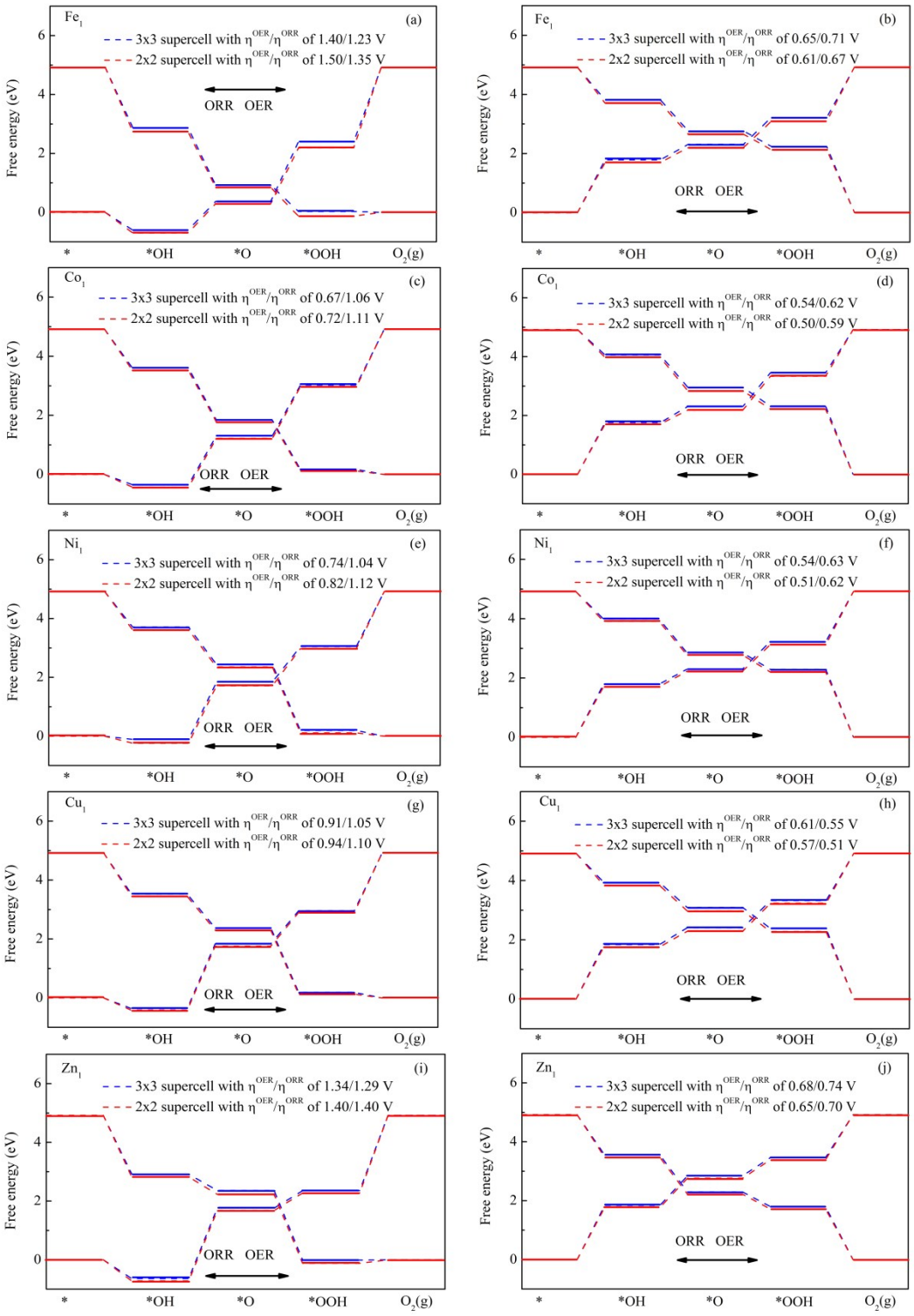


Figure S12. (a–e) The *d*–band PDOS of M_1 atoms and *p*–band PDOS of C plus N atoms at site 2 of M_1/g–C_3N_4. (f) The proportional relationships between the *d*–band centre of M_1 atoms at site 1 and the *p*–band centre of C plus N atoms at site 2.

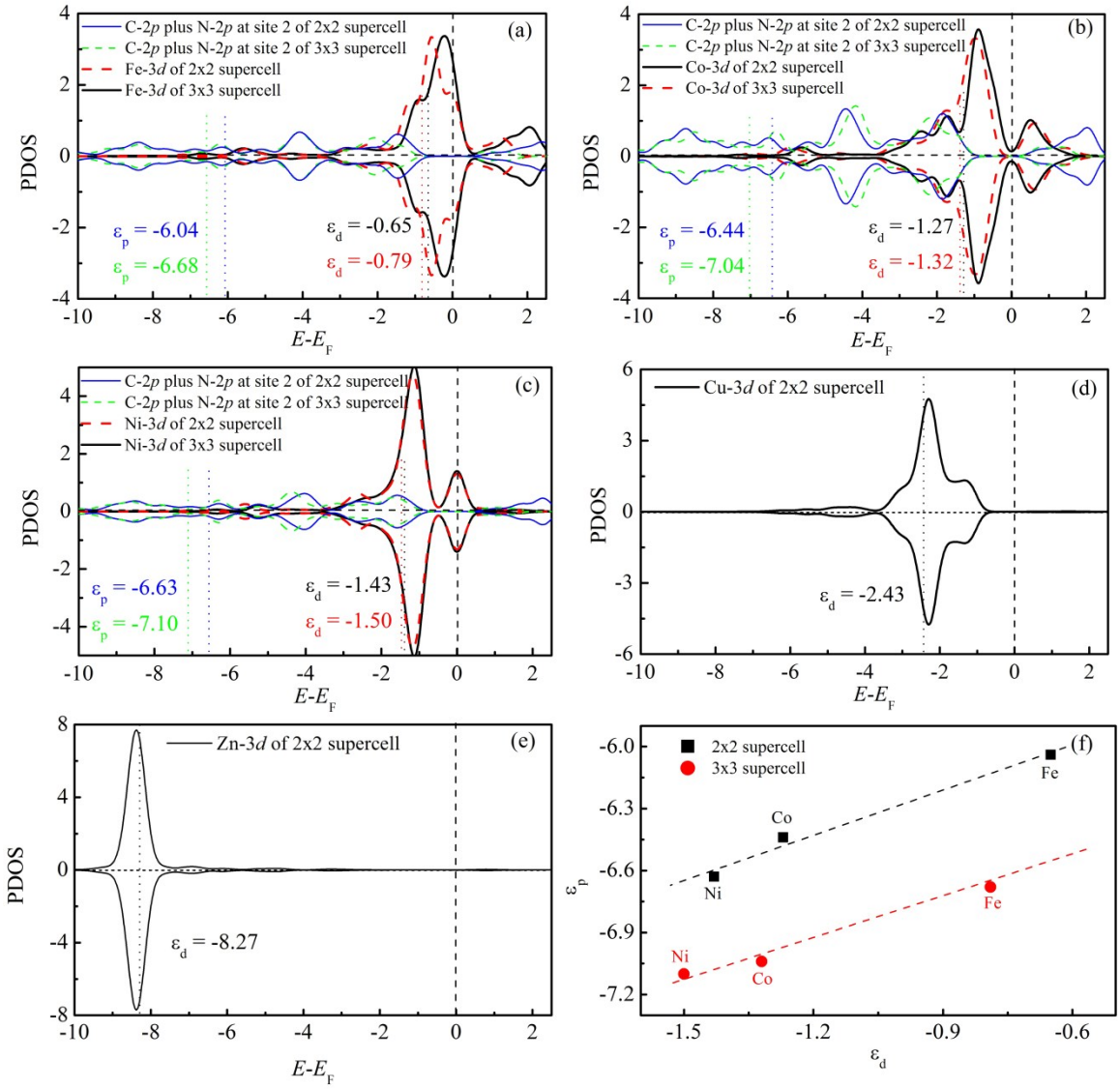


Table S1. The calcuated Mulliken charges of M_1 and the neighbouring N atoms of 2×2 supercell specimens.

	M_1	N
g–C_3N_4	/	-0.39
Fe_1/g–C_3N_4	0.79	-0.45
Co_1/g–C_3N_4	0.85	-0.46
Ni_1/g–C_3N_4	0.88	-0.47
Cu_1/g–C_3N_4	0.90	-0.48
Zn_1/g–C_3N_4	1.17	-0.50

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4. J. Rossmeisl, Z. W. Qu, H. Zhu, G. J. Kroes and J. K. Nørskov, *J. Electroanal. Chem.*, 2007, **607**, 83-89.