Electronic Supporting Information

β-PdBi$_2$ Monolayer for Efficient Electrocatalytic NO Reduction to NH$_3$: A Computational Study

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COMPUTATIONAL DETAILS

The ΔG value can be obtained by the formula: $\Delta G = \Delta E + \Delta ZPE - T\Delta S + \Delta G_{pH} + eU$, where ΔE is the reaction energy of reactant and product species adsorbed on the catalyst directly obtained from DFT computations; ΔZPE and ΔS are the changes between the adsorbed species and the gas phase molecules in zero-point energies and entropy at 298.15 K, which can be calculated from the vibrational frequencies. In the CHE model, ΔG_{pH} is the free energy correction of pH, and can be calculated by: $\Delta G_{pH} = K_B T \times pH \times ln10$. Notably, the pH value was set to be zero in this work for simplicity; U was the applied potential.

According to the obtained free energy change of each elementary step, the limiting potential (U_L) was further computed as follows: U_L = -max (ΔG_1, ΔG_2, ΔG_3, ΔG_4......, ΔG_i)/e.

Constant-Potential Calculations In the constant-potential calculations, in order to elucidate the reaction mechanism at different electrode potentials, the excess charge per unit cell (Δn) from $-$ 2.0 e$^-$ to $+$ 2.0 e$^-$ with a step size of 0.5 e$^-$ was added. A reference value of 4.6 eV was adopted for the standard hydrogen electrode (SHE).

The potential-dependent energy can be calculated by:

$$E = E_{DFT} - \Delta n(V_{sol} + \varphi_q/e)$$

where E_{DFT} is the DFT-calculated energy, V_{sol} is the electrostatic potential of the bulk

electrolyte, and $^-\varphi_q$ is the work function of the charged system.

The relation between φ_q and the corresponding electrode potential referenced to the standard hydrogen electrode (SHE) scale is calculated by:

$$U_q(U/SHE) = -4.6V - \varphi_{q/e}$$

The E-Uq quadratic form could be written as:

$$E(U_q) = -\frac{1}{2}C(U_q - U_0)^2 + E_0$$

where U_0, C, and E_0 are the fitted values of the potential of zero charge (PZC), capacitance of the corresponding system, and the energy of the system at the PZC, respectively.

Fixed potential, the potential reference to the SHE scale changes by changing the pH value, which could be calculated by:

$$U_{RHE} = U_{SHE} + 0.0592 \times pH$$

The dissolution potentials To evaluate the stability of β-PdBi$_2$ monolayer in strong acidic media, we computed the dissolution potentials (U_{diss}, in V) of Bi in β-PdBi$_2$ monolayer at pH = 0, which was defined as:

$U_{diss} = U_{Bi}^0 + \left[E_{Bi,bulk} - \left(E_{\beta-PdBi2} - E_{d-\beta-PdBi2}\right)\right]/ne$, where U_{Bi}^0 is the standard dissolution potential of Bi in the bulk form，d−β-PdBi$_2$ is the defective β-PdBi$_2$ monolayer by dissolving (removing) one Bi to solutions and n is the coefficient for the aqueous dissolution reaction: Bi + H$^+$ ↔ Bi$^+$ + 1/2H$_2$, namely, n equals to 1.

Table S1. The computed free energy changes ($\Delta \boldsymbol{G}$, eV) of each possible elementary step for NORR to generate NH_3 product on β-$PdBi_2$ monolayer. The mared red step represent its higher selectivity.

Elementary step	Free energy change (ΔG)
$NO\ (g) + ^* \rightarrow {}^*NO$	-0.24
$^*NO + H^+ + e^- \rightarrow {}^*NHO$	0.35
$^*NO + H^+ + e^- \rightarrow {}^*NOH$	0.74
$^*NHO + H^+ + e^- \rightarrow {}^*NH_2O$	-0.54
$^*NHO + H^+ + e^- \rightarrow {}^*NHOH$	-0.04
$^*NH_2O + H^+ + e^- \rightarrow {}^*NH_3 + {}^*O$	-1.73
$^*NH_2O + H^+ + e^- \rightarrow {}^*NH_2OH$	0.13
$^*O + H^+ + e^- \rightarrow {}^*OH$	-0.62
$^*OH + H^+ + e^- \rightarrow H_2O + {}^*$	-0.64

Table S2. The quadratic relation between the energy (E) of the reaction intermediates and dependence of applied electrochemical potential U.

Reaction intermediates	Energy (E)	R^2
*	$E = -1.60U^2 - 4.42U - 227.96$	0.99
*NO	$E = -1.43U^2 - 3.71U - 240.64$	0.99
*NHO	$E = -1.39U^2 - 3.67U - 244.08$	0.99
*NH$_2$O	$E = -1.66U^2 - 4.48U - 248.99$	0.99
*O	$E = -1.29U^2 - 3.28U - 233.43$	0.99
*OH	$E = -1.72U^2 - 4.48U - 238.45$	0.99
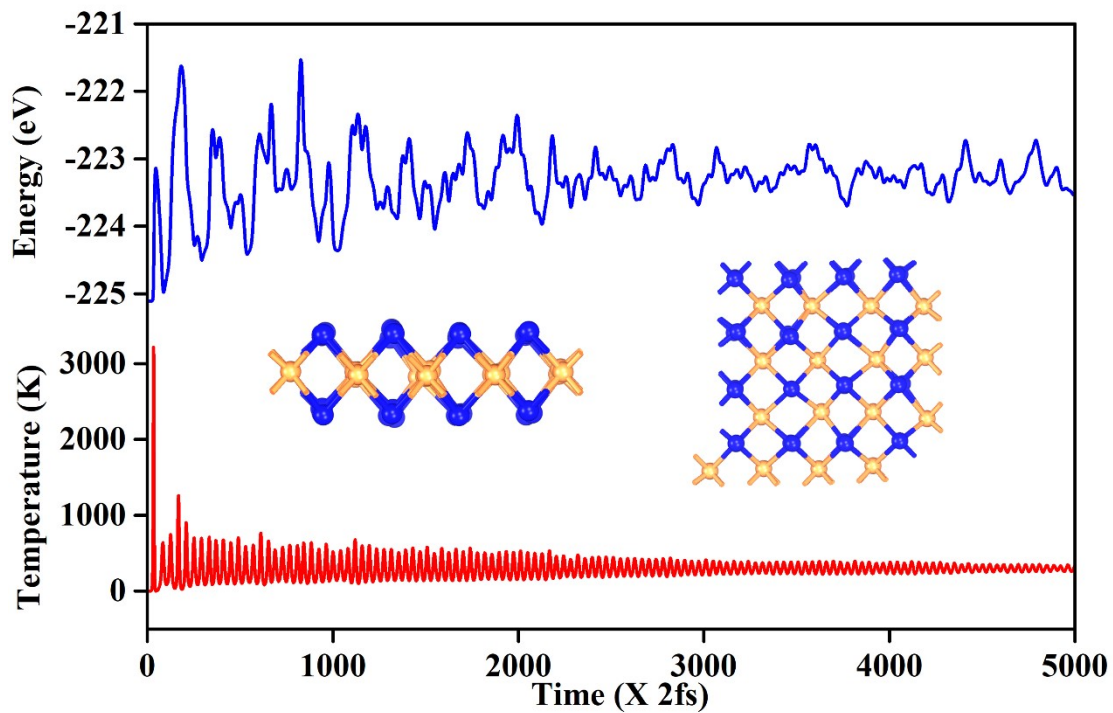
Fig. S1. Variations of temperature and energy as a function of the time for AIMD simulations of β-PdBi$_2$ monolayer; insert are top and side views of the snapshot of atomic configuration. The simulation is run under 500 K for 10 ps with a time step of 2 fs. Blue and orange spheres represent the Bi and Pd atoms, respectively.
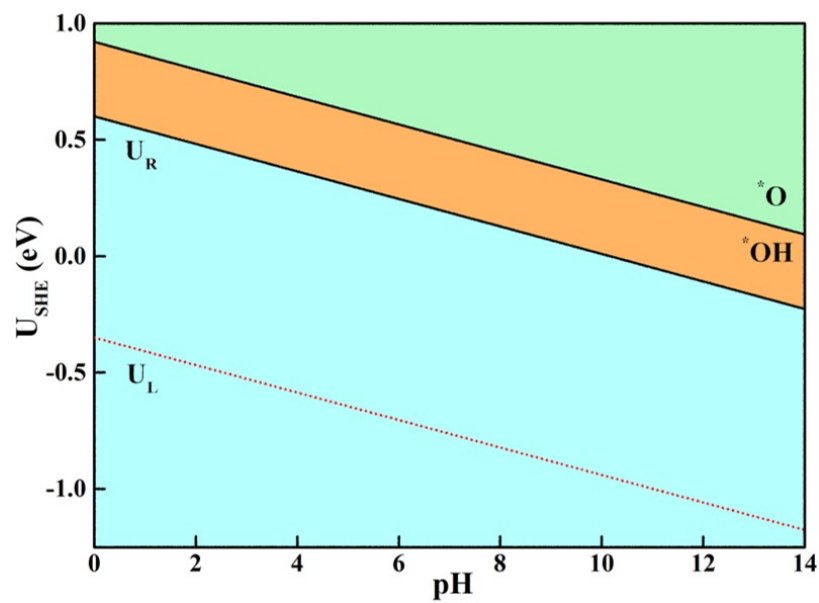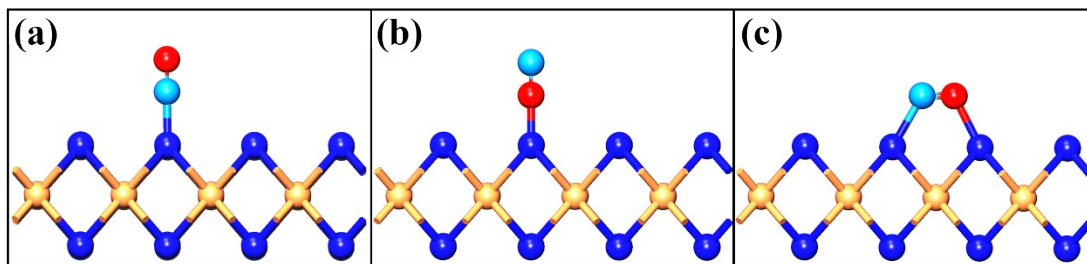
Fig. S2. The surface Pourbaix diagrams of β-PdBi$_2$ monolayer.

Fig. S3. NO were adsorbed on β-PdBi$_2$ monolayer via the (a) N-end, (b) O-end, and (c) side-on patterns.
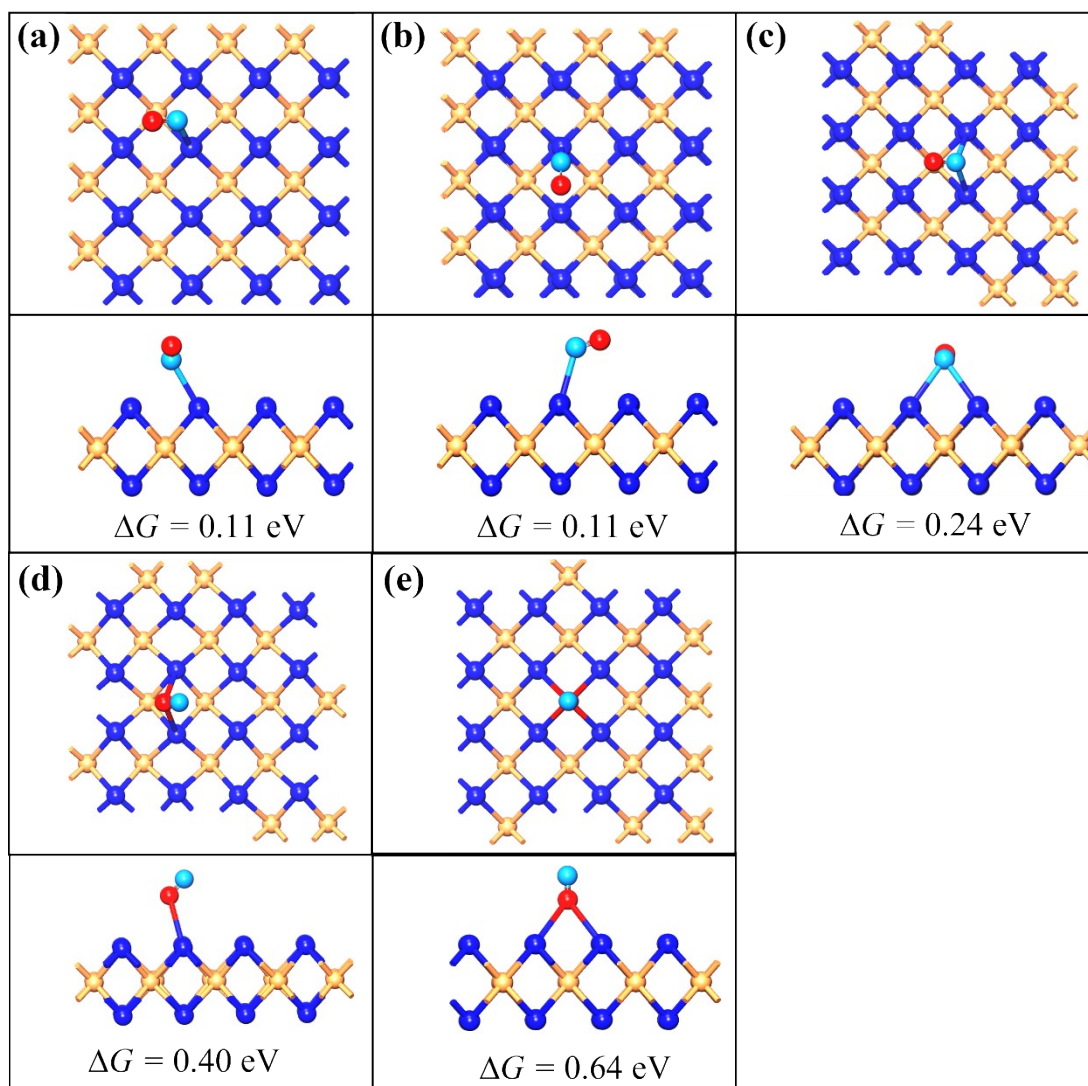
Fig. S4. The optimized configuration of (a) NO adsorbed on the Bi-top position via the N-end pattern. (b) and (c) two possible Bi-Bi bridge sites was obtained. (d) and (e) the bridge and hollow sites for the O-end pattern.
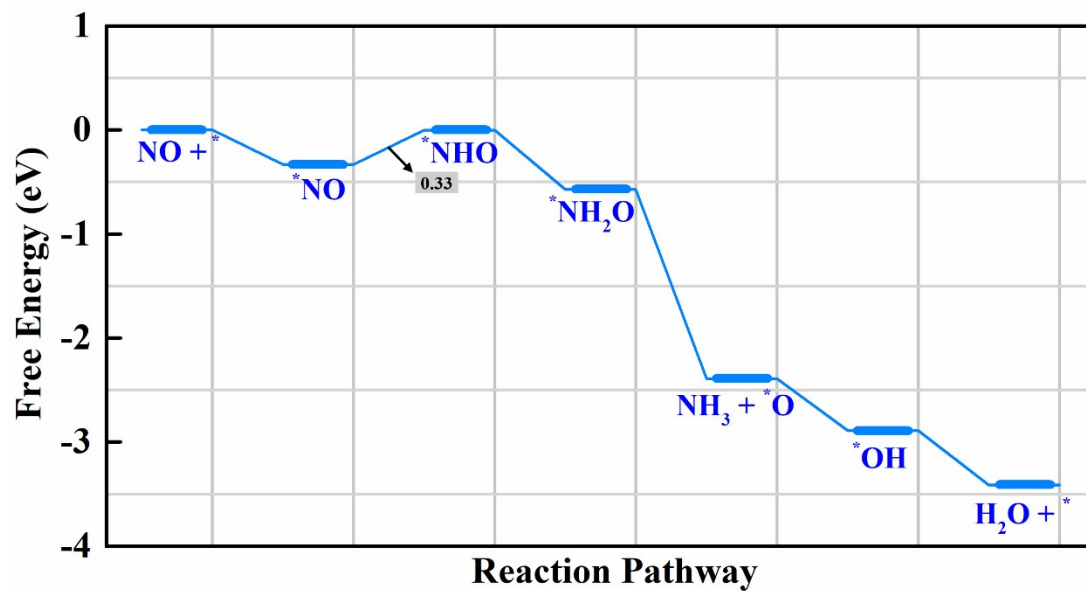
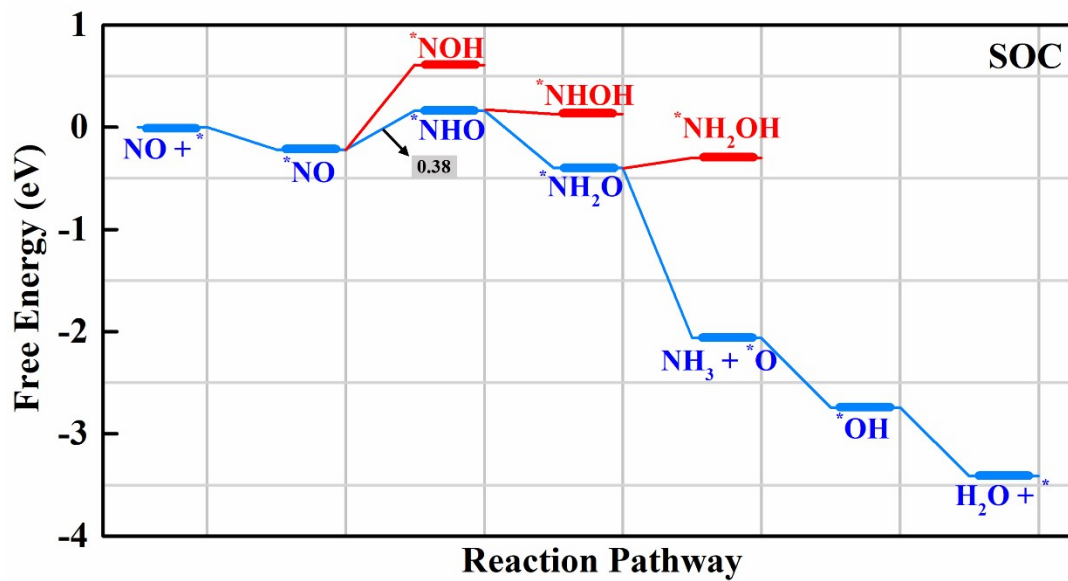**Fig. S5.** The effect of aqueous solution on the catalytic activity of β-PdBi$_2$ for NO-to-NH$_3$ conversion.

Fig. S6. The effect of SOC on the catalytic activity of β-PdBi$_2$ for NO-to-NH$_3$ conversion.
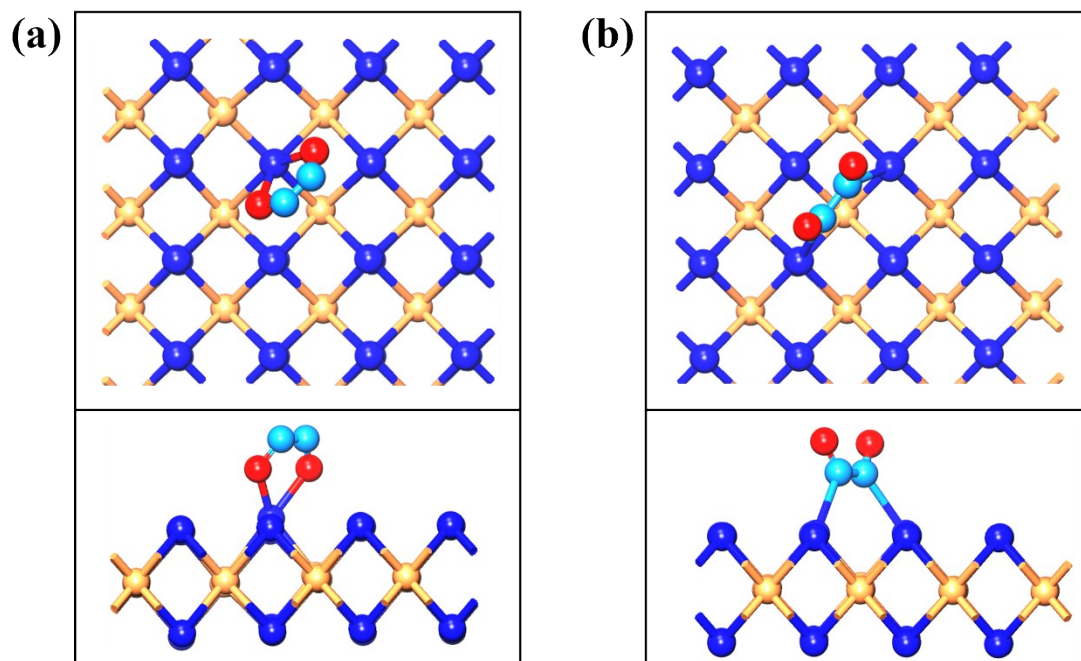
Fig. S7. The obtained $^{*}N_2O_2$ stable configurations on β-PdBi$_2$ monolayer via (a) O-end and (b) N-end patterns.
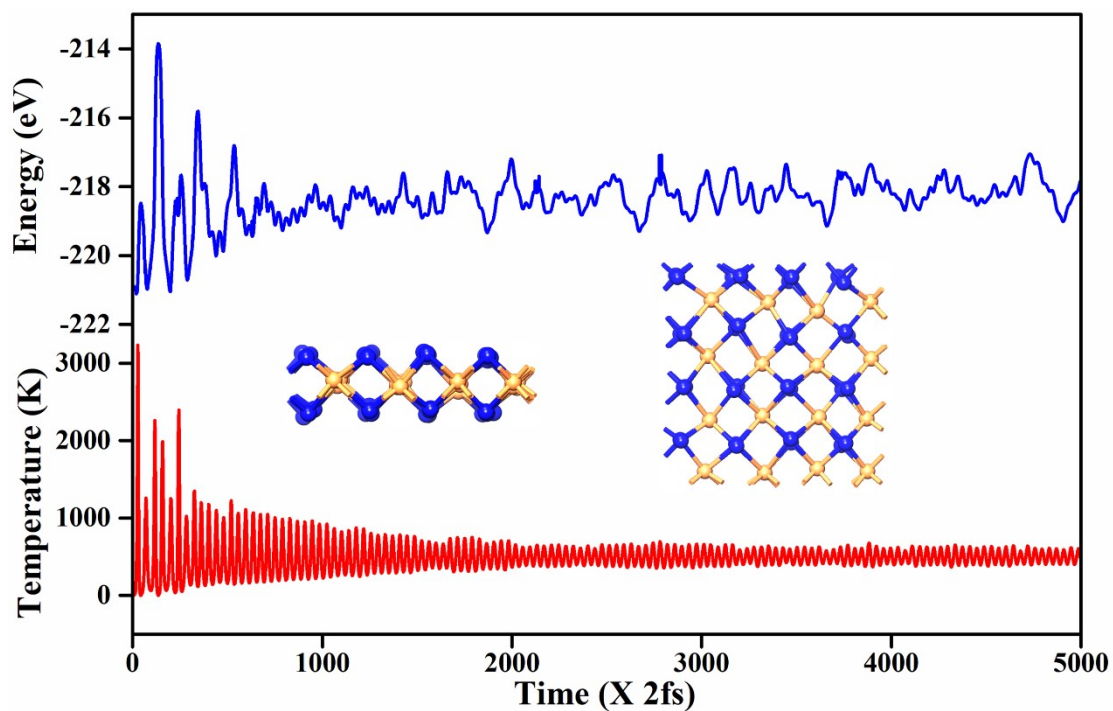
Fig. S8. Variations of temperature and energy as a function of the time for AIMD simulations of β-PdBi$_2$ monolayer under 7% tensile strain and the snapshots of atomic configuration. The simulation was run under 500 K for 10 ps with a time step of 2 fs. Blue and orange spheres represent the Bi and Pd atoms, respectively.
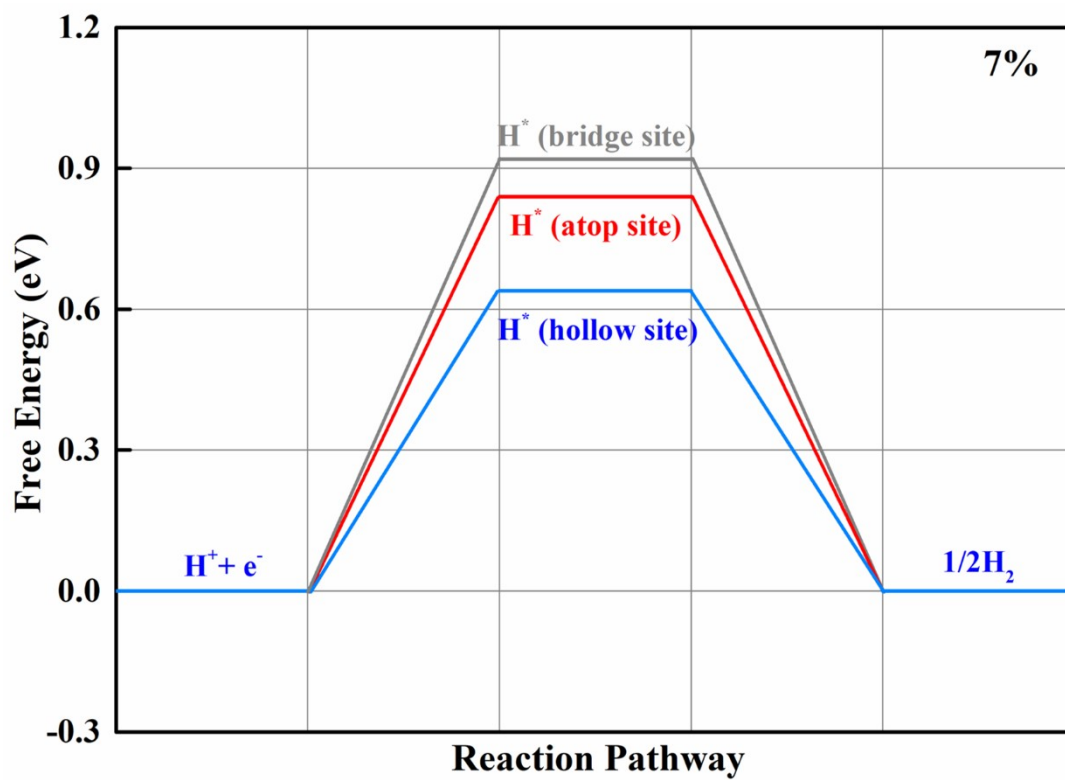
Fig. S9. The calculated Gibbs free profile of HER on β-PdBi₂ monolayer when a tensile strain of 7% was applied.
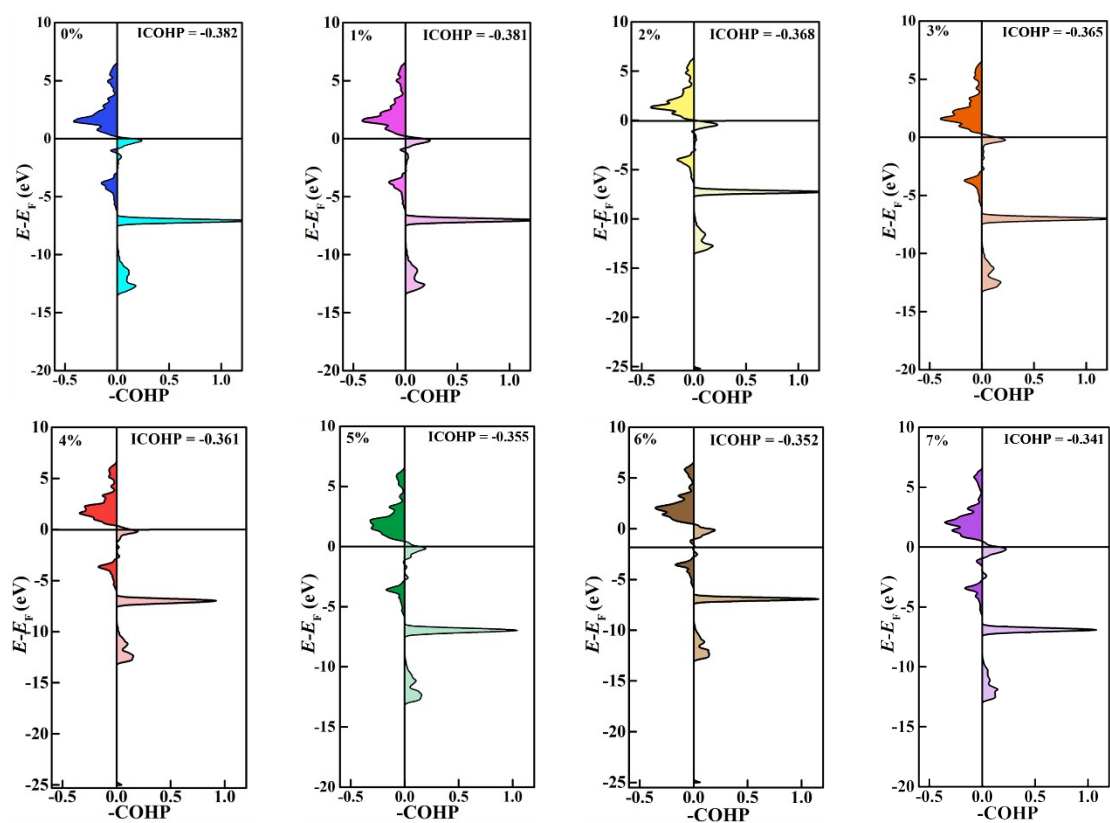
Fig. S10. The computed crystal orbital Hamilton population (COHP) between NO molecule and β-PdBi$_2$ monolayer under different tensile strain.