Supporting Information File

Photocatalytic and Piezocatalytic Properties of Visible Light Active BiN Monolayer as an Efficient Hydrogen and Oxygen Evolution Catalyst

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Computational Methodology

Optical Property

The material optical characteristics were determined by analyzing their frequency-dependent complex-dielectric function, which can be expressed as $\varepsilon(\omega) = \varepsilon_1(\omega) + \iota\varepsilon_2(\omega)$, where $\varepsilon_1(\omega)$, and $\varepsilon_2(\omega)$ correspond to the real and imaginary components of the dielectric constants. By examining the dielectric functions, which are comprised of the $\varepsilon_1(\omega)$ and $\varepsilon_2(\omega)$ values, the absorption coefficient can $\alpha(\omega)$ be calculated using the following relation:[1]

$$\alpha(\omega) = \frac{\sqrt{2\omega}}{c}[(\varepsilon_1(\omega)^2 + \varepsilon_2(\omega)^2)^{\frac{1}{2}} - \varepsilon_1(\omega)]^{\frac{1}{2}} \tag{1}$$

The dielectric tensor of a polar material is the sum of an electronic and ionic part:[2]

$$\varepsilon_{r,ij} = \varepsilon_{r,ij}^{elec}(\omega) + \varepsilon_{r,ij}^{ionic}(\omega) \tag{2}$$

Where ε_r stands for relative permittivity and i, j is cartesian directions. The electronic part can be calculated from the optical spectrum while the ionic part is related to the Born effective charge and phonon modes. At low frequencies, the ions can also respond to an optical field. The ionic part is calculated as:

$$\varepsilon_{r,ij}^{ionic}(\omega) = \frac{1}{\varepsilon_0 \Omega_0} \sum_\lambda \frac{S_{ij}^\lambda}{\omega_\lambda^2 - \omega^2 - \iota\Gamma\omega} \tag{3}$$

Where ε_0, and Ω_0 is vacuum permittivity and unit cell volume respectively. And $S_{ij}^\lambda = p_i^{*\lambda} p_j^\lambda$ is the mode oscillator strength which is related to born effective charge and phonon mode (λ) via following relation:

$$p_i^\lambda = \sum_{(k,j)} Z_{ij}(k) \frac{e_j^\lambda}{\sqrt{m_k}} \tag{4}$$

Here m_k and e_j^λ is mass and eigen displacement of phonon mode λ with frequency ω_λ for k-th atom.

Elastic Constant Calculation

The elastic constants connect how the stress tensor (sigma) responds linearly to an external strain applied to the system. These constants characterize how materials resist deformation in particular directions. Both stress and strain tensors are 3×3 symmetric matrices, and they can be represented more concisely as 6-vectors in what is known as Voigt notation.[3,4]

$$\sigma = (\sigma_{xx}, \sigma_{yy}, \sigma_{zz}, \sigma_{yz}, \sigma_{xz}, \sigma_{xy}) \tag{5}$$

And

$$\varepsilon = (\varepsilon_{xx}, \varepsilon_{yy}, \varepsilon_{zz}, \varepsilon_{yz}, \varepsilon_{xz}, \varepsilon_{xy}) \tag{6}$$

The stress vector's linear response to a given strain vector can be expressed as follows:

$$\sigma = C\varepsilon \tag{7}$$

The symmetric 6×6 matrix contains elastic constants, with the number of independent entries reduced based on crystal symmetry. Different deformations are applied to the simulation cell along specific strain vectors to find these constants, and resulting stress vectors are computed. Linear stress contributions are obtained by fitting strain-stress curves for each Voigt stress component and strain vector. Independent elastic constants are then calculated using a least-squares approach, considering crystal symmetry. QuantumATK uses Lagrangian strain and stress tensors and minimizes stress calculations by employing Universal Linearly-Independent Coupling Strain (ULICS) vectors. For each strain vector, three deformations are typically applied $(-\eta, 0, +\eta)$, centered at the reference configuration ($\eta = 0$). Atomic positions are optimized before stress calculation to obtain an elastic relaxed-ion configuration closer to experimental results.[5,6]

Piezoelectric Tensor Calculation

Total polarization P of a solid is the sum of the spontaneous polarization (P_s) (strain independent) of the equilibrium structure, and of the strained indued polarization $i.e$ piezoelectric polarization (P_p) such as:[7,8]

$$P = P_s + P_p \tag{8}$$

Now piezoelectric tensor can be expressed as:

$$e_{ij} = \frac{\Delta P_i}{\Delta \varepsilon_j} \tag{9}$$

In QuantumATK e_{ij} is calculated using a finite-difference approach and P using a Berry-phase approach. A relatively high 31 k-points is used for the convergence of piezoelectric coefficients calculation. As reported in the literature the relaxed-ion piezoelectric coefficients are closer to the experimental observed one. Therefore, atomic positions are relaxed at each strain before piezoelectric tensor calculation.

Gibbs Free Energy Calculation

The hydrogen electrode model proposed by Norskov $et.al$. is used to calculate the Gibbs free energy change in water redox reactions given as:[9]

$$\Delta G = \Delta E + \Delta E_{\text{ZPE}} - T\Delta S + \Delta G_U + \Delta G_{\text{pH}} \tag{10}$$

Where T is the temperature (298 K), ΔE is the adsorption energy, ΔE_{ZPE} and ΔS are the difference in the zero point energy and entropy. $\Delta G_U = -eU$, U is electrode potential relative to standard hydrogen electrode (SHE) and stands for extra potential of photogenerated charge carriers (electrons and hole) as depicted in Fi. S4. $\Delta G_{pH} = k_B T \ln_{10} \text{pH}$ the contribution of Gibbs free energy at different pH concentrations. In the calculation of the adsorption energy of different intermediate species, counter-poise correction is also included to provide a better understanding of the interactions The Gibbs free energy of oxidation evolution reaction (OER) and hydrogen evolution reaction (HER) were calculated as follows[10] The HER process includes a fast photon/electron transfer step and a fast hydrogen release step:

$$* + H^+ + e^- \rightarrow {}^*H \tag{11}$$
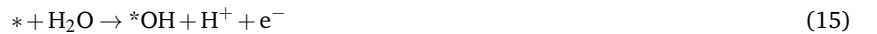
$$^*H + H^+ + e^- \rightarrow * + H_2 \tag{12}$$

Here, * denotes the adsorbed species. The Gibbs free energy change for each intermediate step of HER is determined by:

$$\Delta G_{11} = G_{*H} - \frac{1}{2}G_{H_2} - G_* + \Delta G_U + \Delta G_{\text{pH}} \tag{13}$$

$$\Delta G_{12} = G_* + \frac{1}{2}G_{H_2} - G_{*H} + \Delta G_U + \Delta G_{\text{pH}} \tag{14}$$

The OER process involves four electron oxidation steps:

$$* + H_2O \rightarrow {}^*OH + H^+ + e^- \tag{15}$$

$$*OH \rightarrow {}^*O + H^+ + e^- \tag{16}$$

$$^*O + H_2O \rightarrow {}^*OOH + H^+ + e^- \tag{17}$$

$$^*OOH \rightarrow * + O_2 + H^+ + e^- \tag{18}$$

The Gibbs free energy change for each intermediate OER step is determined by:

$$\Delta G_{12} = G_{*OH} - \frac{1}{2}G_{H_2} - G_* - G_{H_2O} + \Delta G_U - \Delta G_{\text{pH}} \tag{19}$$

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Table S 1 Zero point energy correction (E_{ZPE}, entropy contribution (S), total energy (E) and Gibbs free energy (G) of molecules and adsorbents on pristine BiN and +5% (in bracket) monolayer.

Adsorbent	$E_{ZPE}(eV)$	$TS(eV)$	$E(eV)$	$G(eV)$
H_2	0.31	0.41	-31.65	-31.76
H_2O	0.61	0.67	-482.85	-482.91
Photocatalyst	0	0	-20106.09 (-20104.20)	-20106.09 (-20104.20)
*O	0.06	0	-20544.32 (-20552.70)	-20554.26 (-20552.64)
*OH	0.32	0	-20571.58 (-20570.17)	-20571.26 (-20569.85)
*OOH	0.42	0.21	-21019.76 (-20118.41)	-21019.55 (-21017.82)
*H	0.09	0	-20119.99 (-20118.41)	-20119.90 (-20118.32

$$\Delta G_{13} = G_{*O} + \frac{1}{2}G_{H_2} - G_{*OH} + \Delta G_U - \Delta G_{pH} \tag{20}$$

$$\Delta G_{14} = G_{*OOH} + \frac{1}{2}G_{H_2} - G_{*O} - G_{H_2O} + \Delta G_U - \Delta G_{pH} \tag{21}$$

$$\Delta G_{15} = G_{*} + \frac{1}{2}G_{H_2} - G_{*OOH} + G_{O_2} + \Delta G_U - \Delta G_{pH} \tag{22}$$

The terms G_{O_2} and $G_{H^+ + e^-}$ mentioned in above equations are calculated as; $G_{O_2} = 2G_{H_2O} - 2G_{H_2} + 4.92$ and $\frac{1}{2}G_{H_2}$, respectively. The change in zero-point energy (δE_{ZPE}) is determined by the summation of the vibrational modes of adsorbed intermediates while monolayer was fixed using the following relation: [11]

$$E_{ZPE} = \sum_i \frac{\hbar w_i}{2} \tag{23}$$

And potential provided by the photogenerated electron and hole is obtained using the follwoing relation:

$$U_e = E_{CBM} - (-4.44 + 0.059 \times pH) \tag{24}$$

$$U_h = (-4.44 + 0.059 \times pH) - E_{VBM} \tag{25}$$

Where E_{CBM} and E_{VBM} corresponds to conduction band minima and valence band maxima energy levels respectively (see Fig. S4).

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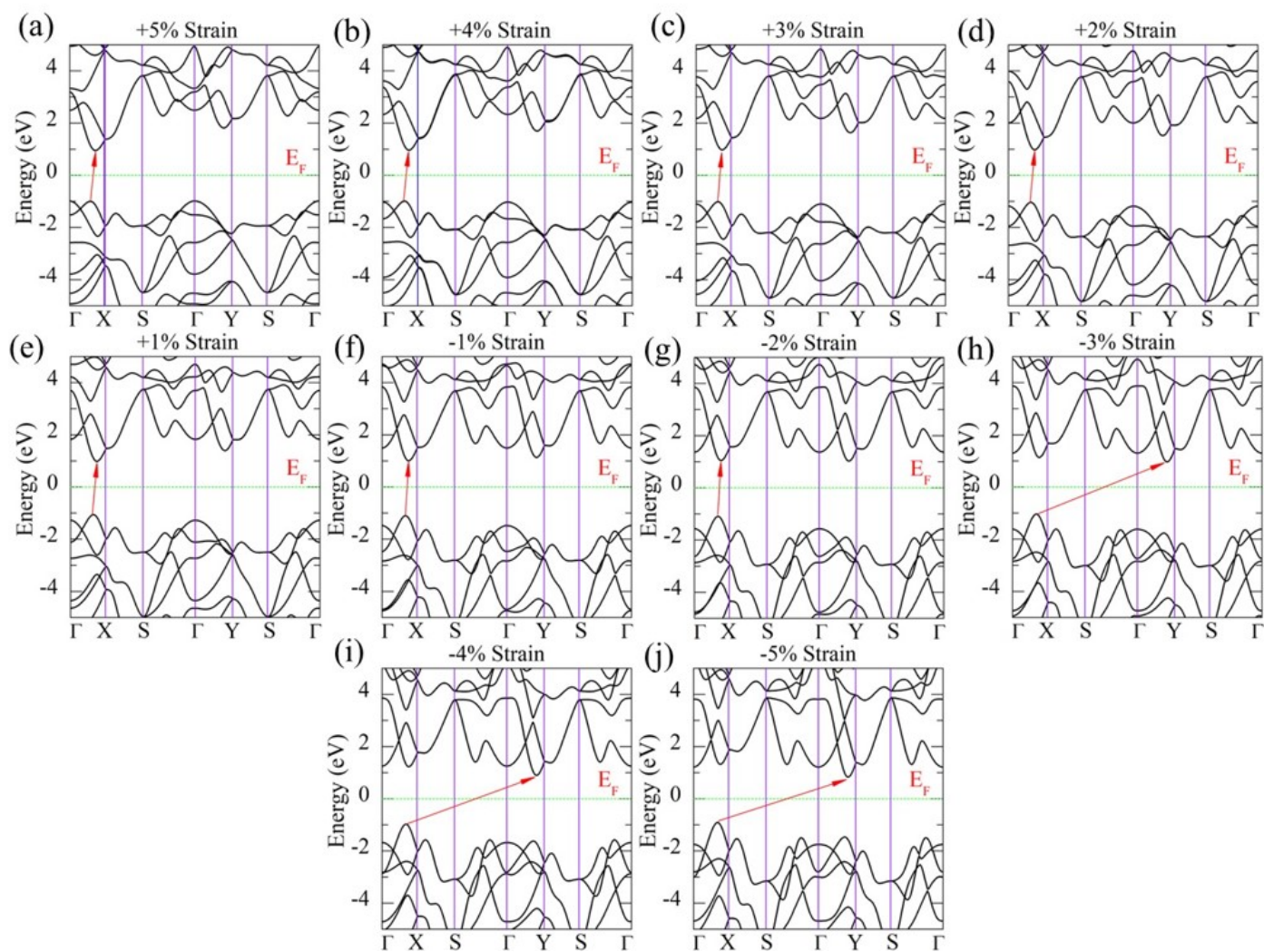
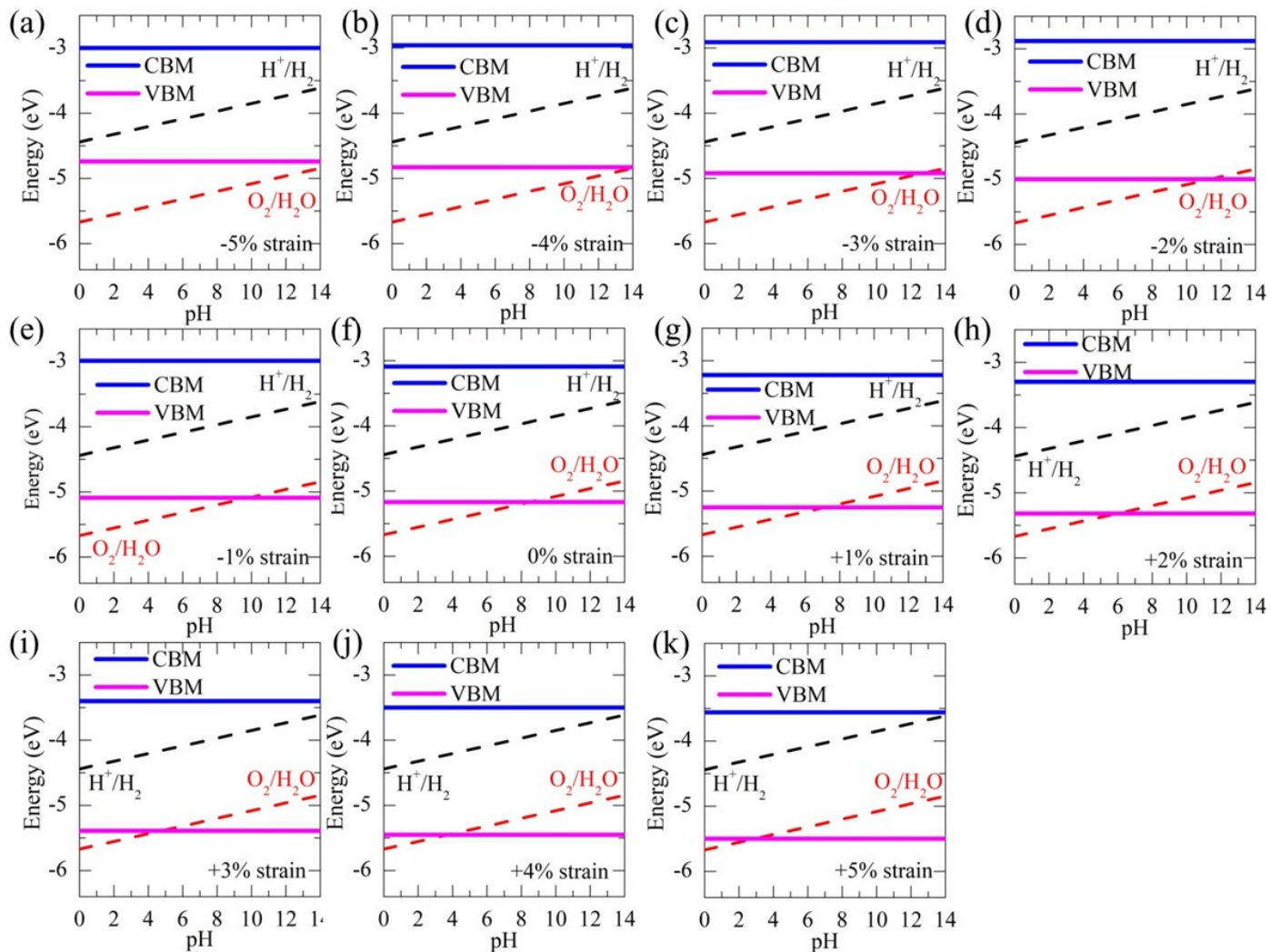Fig. S 1 HSE06 computed electronic band structure of biaxially strained BiN monolayer.

Fig. S 2 Effect of biaxial tensile and compressive strain on CBM and VBM relative to redox potential of water at pH=7.
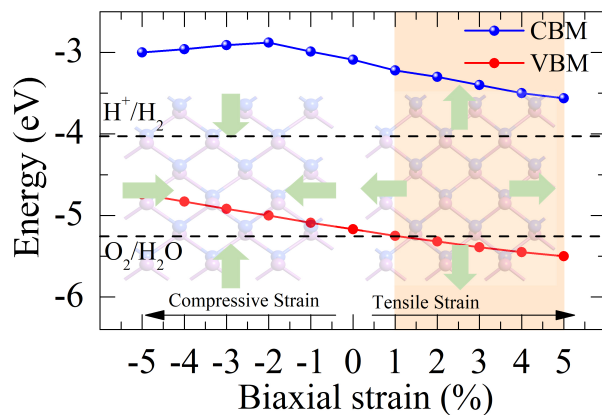

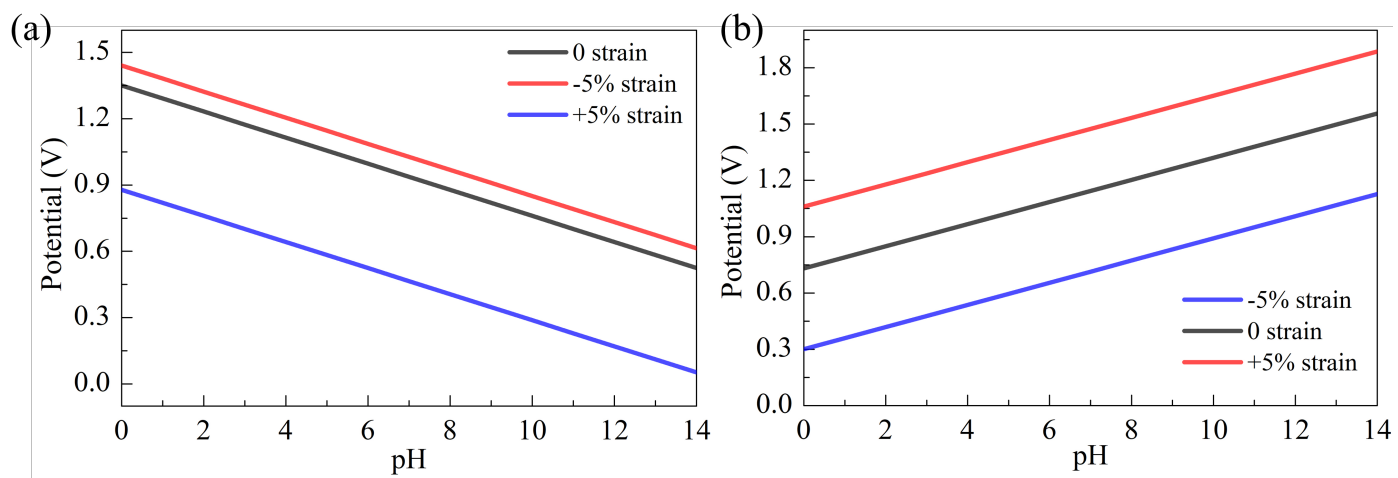Fig. S 3 CBM and VBM relative to redox potential of water with varying pH.

Fig. S 4 External potential generated by the photogenerated electron (a), and (b) hole.