# Supporting Information

# Zeolitic Octahedral Niobium Oxide with Microchannels of Seven-Membered Rings for photocatalytic H₂ evolution from Saline Water

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## Computational Details

Density functional theory (DFT) calculations in this work were performed based on the Perdew-Burke-Ernzerbof (PBE) form of generalized gradient approximation functional (GGA) by employing the Vienna ab-initio simulation package (VASP).[1] To describe the interactions between valence electrons and ion cores, the Blöchl's all-electron-like projector augmented wave (PAW) method was employed.[2] A kinetic cutoff energy of 400 eV was applied for the plane wave basis set. Brillouin zone integration was approximated by a $3 \times 3 \times 1$ k-points using the Monkhorst–Pack grid.[3] Geometries were optimized until the energy was converged to $1.0 \times 10^{-6}$ eV/atom and the force was converged to 0.01 eV/Å. To avoid the periodic interactions for all the structures, a vacuum layer as large as 20 Å is used along the c direction normal to the surface.

The free energy ($G$) of hydrogen evolution reaction (HER) on the catalysts surface was calculated using the equation:[4]

$$G = E + ZPE - TS$$

where $E$, $ZPE$ and $TS$ are the total energy from DFT calculations, zero point energy and entropic contributions (T was set to be 300K), respectively. $ZPE$ values are derived after the frequency calculation by:[5]

$$ZPE = \frac{1}{2} \sum h v_i$$

$TS$ values of adsorbed species are calculated using the vibrational frequencies:[6]

$$TS_v = k_B T \left[ \sum_K \ln(\frac{1}{1 - e^{-h v_K / k_B T}}) + \sum_K \frac{h v_K}{k_B T} \frac{1}{(e^{h v_K / k_B T} - 1)} \right]$$

where $k_B$ is the Boltzmann constant, $T$ is Temperature, which is set as 300 K, $v$ is vibrational frequency for the intermediates and $K$ is vibrational mode, which is obtained from DFT calculations using VASP. The Gibbs free energy of ($H^+ + e^-$) is equivalent to the energy of $1/2 G_{H2}$ in the study.
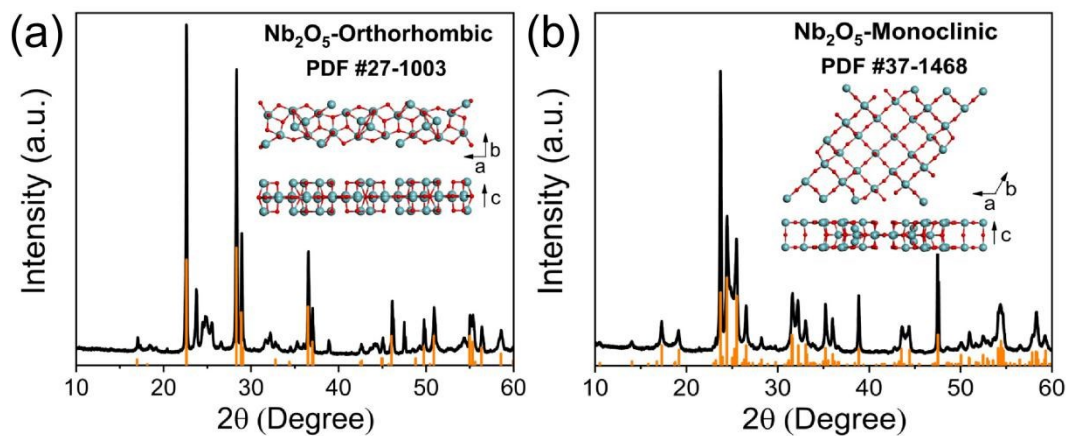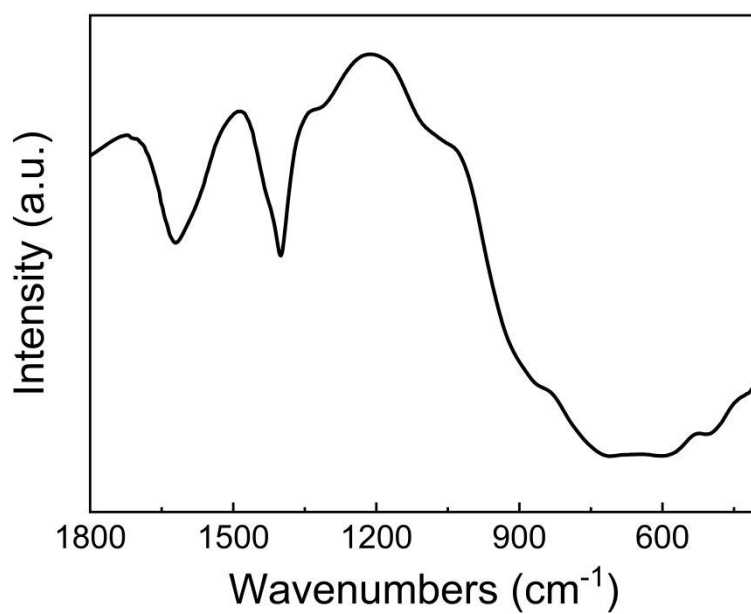
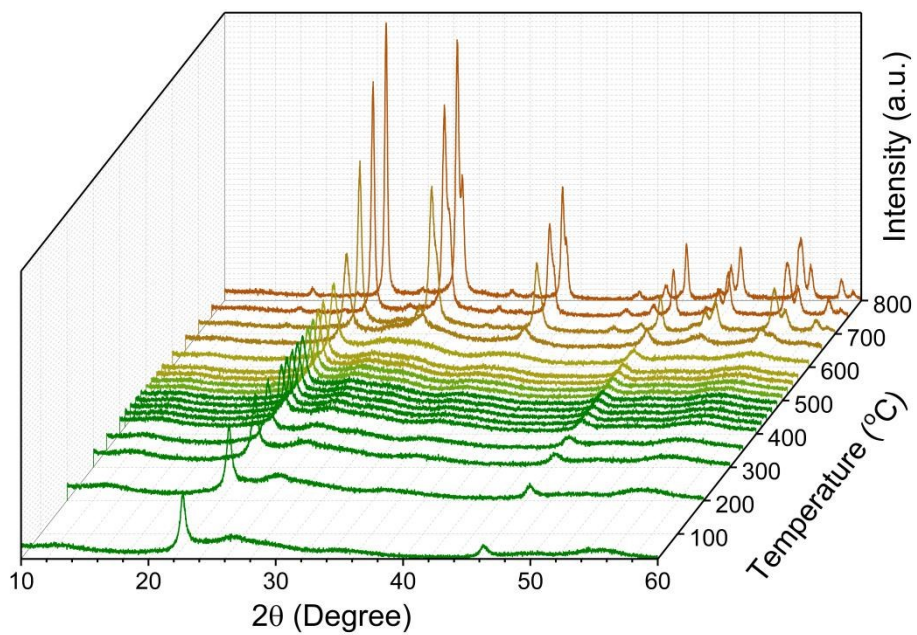**Figure S1**. XRD patterns of pristine $Nb_2O_5$ with various symmetric structures: orthorhombic (a), monoclinic (b).
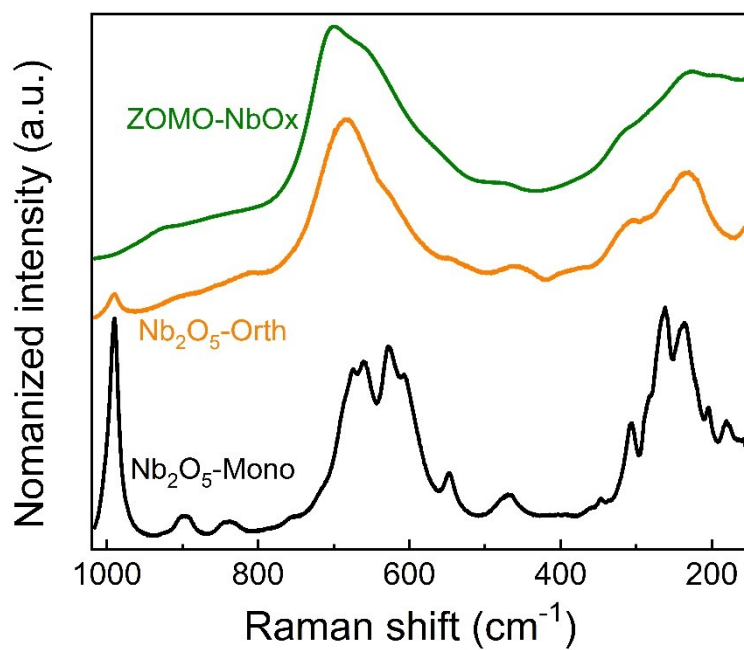


**Figure S2**. Raman spectra of as-synthesized ZOMO-NbOx, and pristine $Nb_2O_5$ with orthorhombic, and monoclinic symmetric structure.
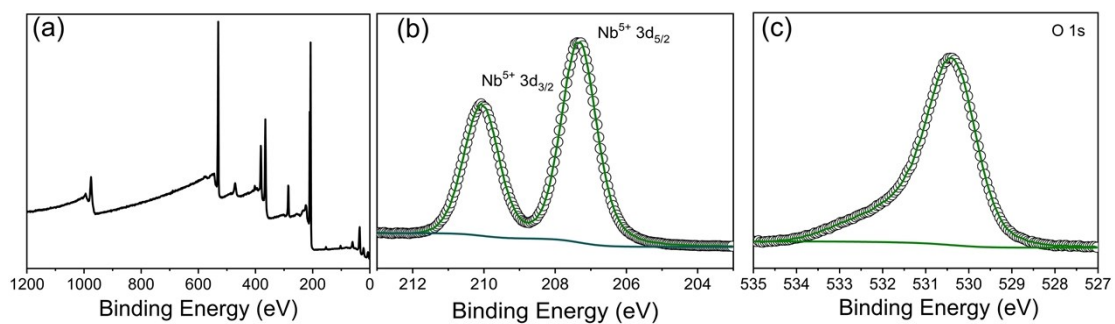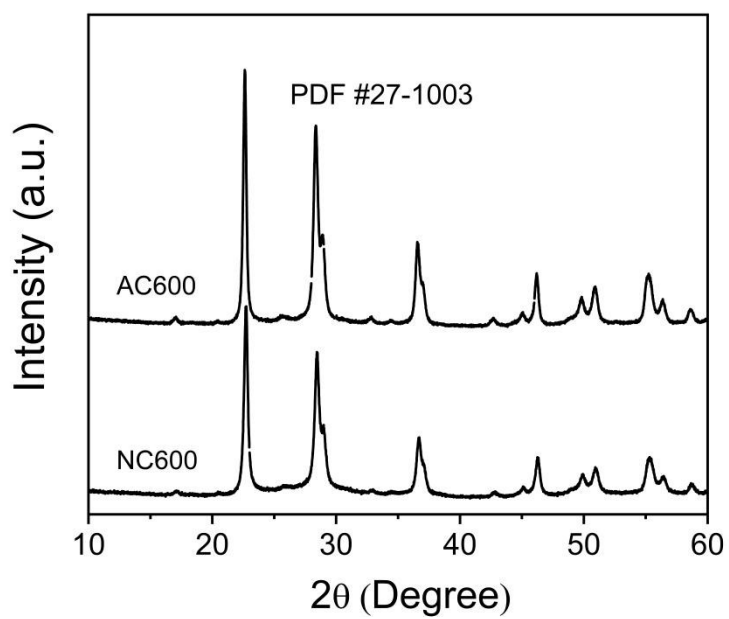
**Figure S3**. The XPS survey (a), Nb 3d (b), and O 1s spectra (c) of ZOMO-NbOx.
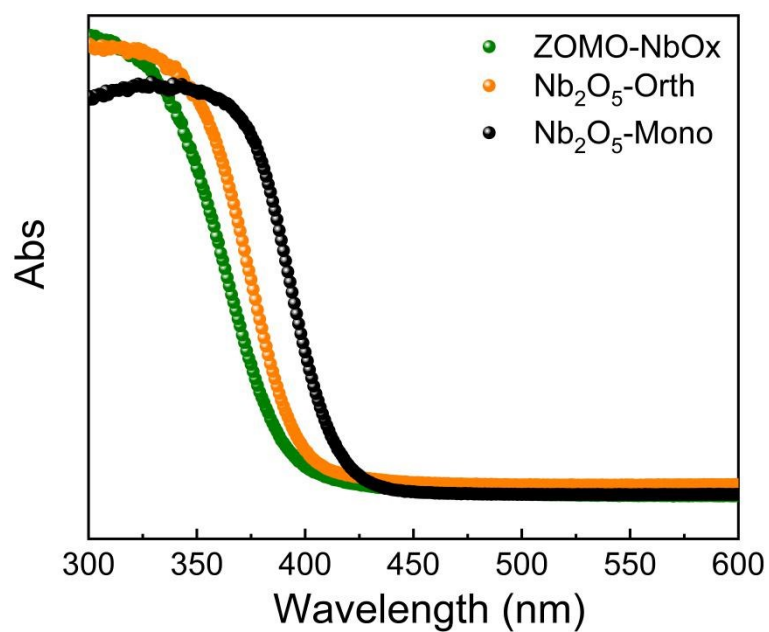


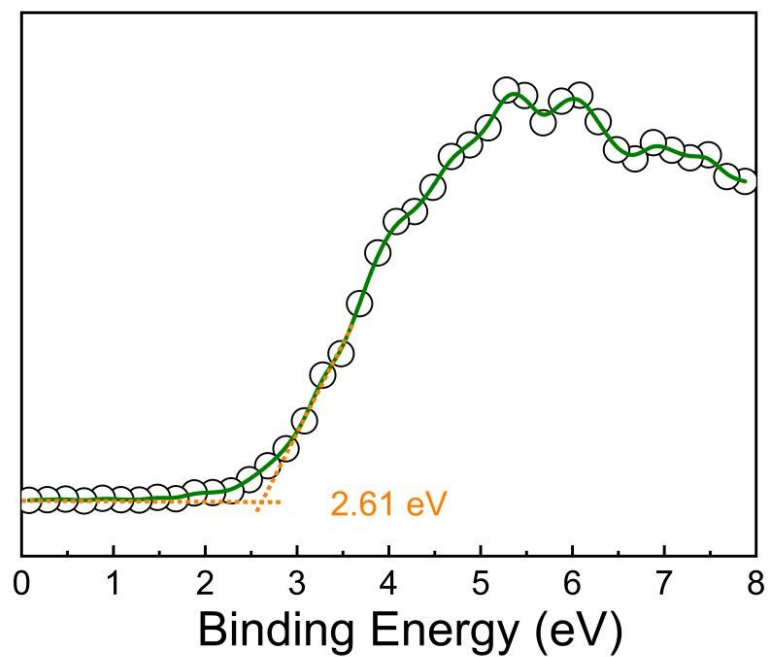**Figure S4**. FTIR spectra of ZOMO-NbOx.

**Figure S5**. *In situ* temperature programming XRD patterns of ZOMO-NbOx under Ar atmosphere.



**Figure S6**. XRD patterns of ZOMO-NbOx calcined at 600°C in air (AC600) and $N_2$ (NC600) for 2h.

**Figure S7.** UV-vis DRS spectra comparison of as-synthesized ZOMO-NbOx, and pristine $Nb_2O_5$ with orthorhombic, and monoclinic symmetric structure.



**Figure S8**. XPS valence band (VB) spectrum determined the band structure of as-synthesized ZOMO-NbOx.
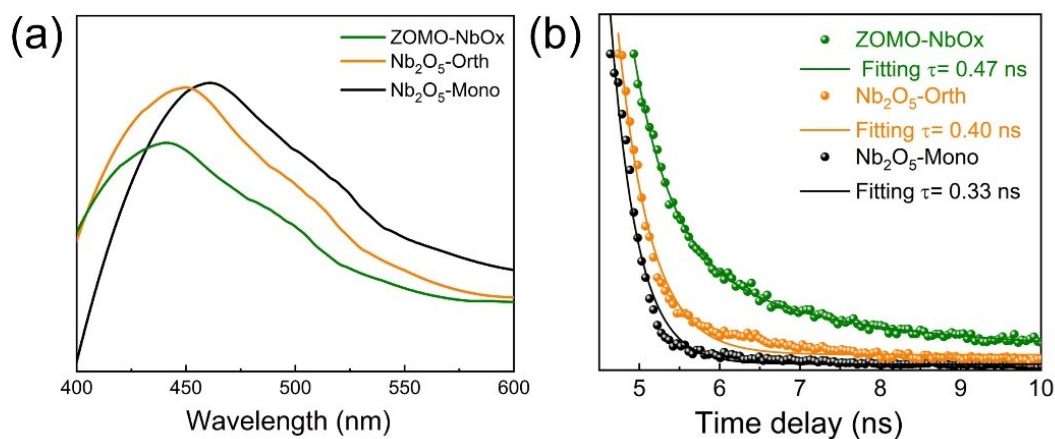
**Figure S9**. PL (a) and time-resolved fluorescence decay spectra (b) of as-synthesized ZOMO-NbOx, and pristine $Nb_2O_5$ with orthorhombic, and monoclinic symmetric structure.
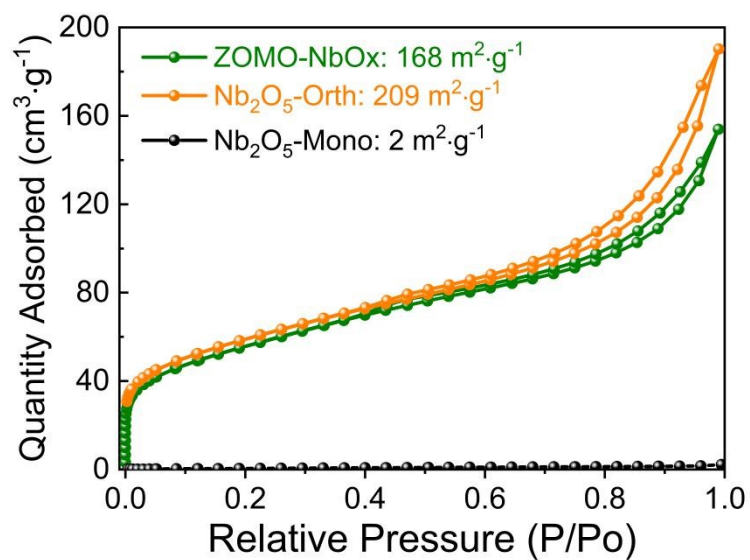


**Figure S10**. $N_2$ adsorption-desorption isotherm of as-synthesized ZOMO-NbOx, and pristine $Nb_2O_5$ with orthorhombic, and monoclinic symmetric structure.
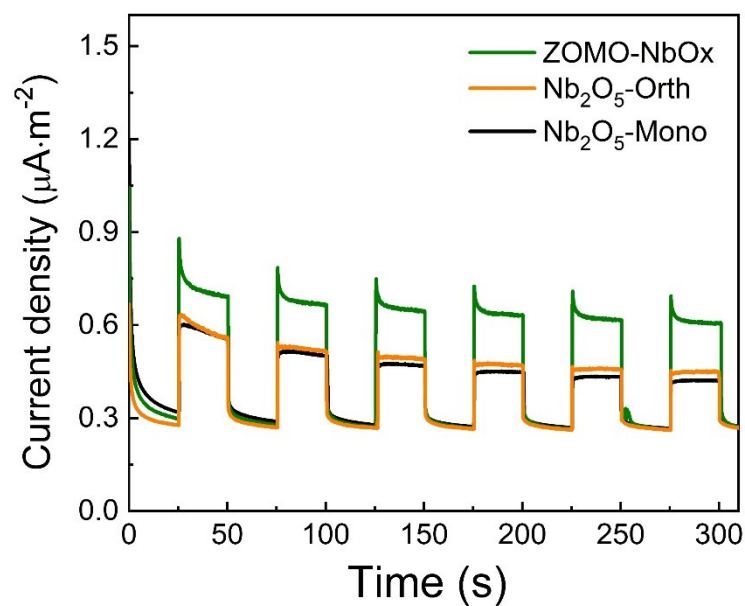
**Figure S11.** Photocurrent transient responses of as-synthesized ZOMO-NbOx, and pristine $Nb_2O_5$ with orthorhombic, and monoclinic symmetric structure.



**$H_{ad}$-$Nb_2O_5$-Orth**
$\Delta G_H (001)= -0.54$ eV

**$H_{ad}$-$Nb_2O_5$-Mono**
$\Delta G_H (110)= -1.95$ eV
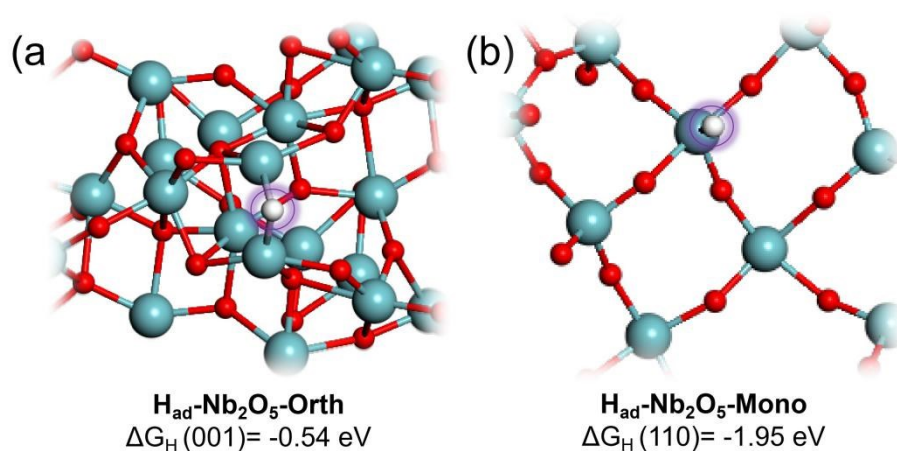
**Figure S12**. DFT calculations of hydrogen adsorption free energy on: (001) plane of pristine $Nb_2O_5$ with orthorhombic symmetric structure (a); and on (110) plane of $Nb_2O_5$ with monoclinic symmetric structure (b).

# References

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