Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

SUPPORTING INFORMATION

Vacancy Engineering of WO_{3-x} Nanosheets for Electrocatalytic NRR Process - a First-principles Study

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Calculations

The adsorption energy of each intermediate is adopted as the indicator of every step for nitrogen reduction, taking *NNH as an example, following equation (1)

$$E_{ad}^{NNH} = E_{NNH/sur} - E_{sur} - E_{N_2} - 1/2E_{H_2} \quad (1)$$

Here the chemical potential of $(H^+ + e^-)$ is related to that of a half gaseous H_2, as $\mu(H^+ + e^-) = 1/2\mu(H_2) + \mu(e^-)$, where $\mu(e^-) = eU$, U is an applied bias against the standard hydrogen electrode (SHE).[1] Given that experiments usually proceed along with a set pH value at room temperature, which spawn vibration entropy, so that corrections should be added in the formula. Gibbs free energy at zero potential therefore follows

$$\Delta G = \Delta E + \Delta E_{ZPE} - T\Delta S \quad (2)$$

Where E_{ZPE} represents the zero-point energy of intermediate obtained by using standard vibrational corrections in the harmonic approximation to the enthalpy and entropy. Because the experiment is presumed to keep ambient throughout the process, ΔT approximates to null.

Decision of oxygen vacancy

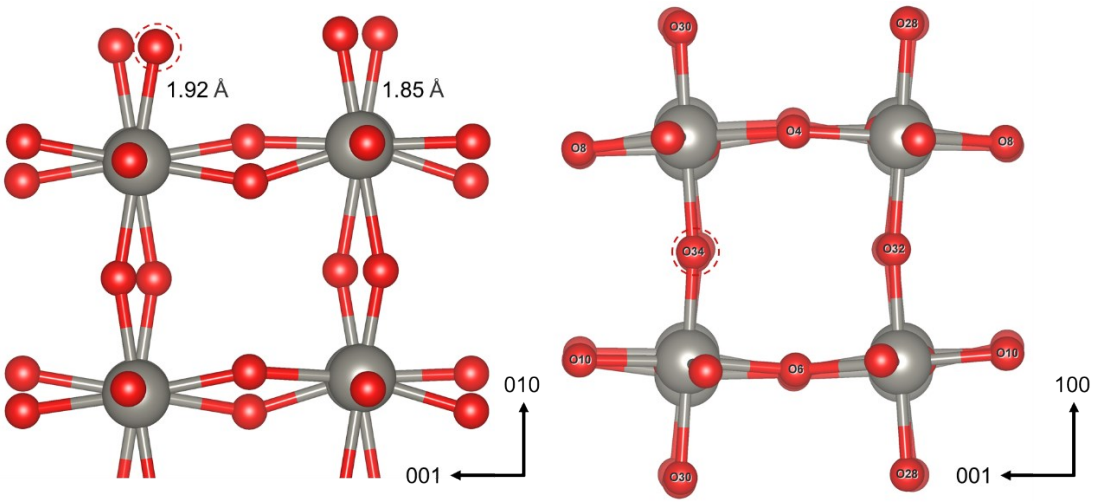

Figure S1. Schematic diagram of the WO_3 microstructure. The side view (left) and the top view (right) of WO_3 slab model with marked non-equivalent sites in the same plane are shown. Dotted circles mark the O ions to be removed. The W ions and O ions are represented in gray and red respectively.

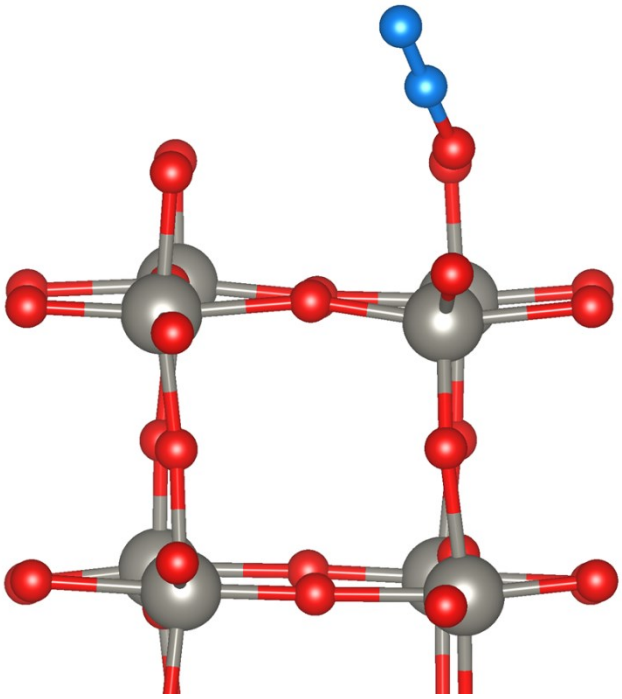

Figure S2. Optimized atomic configuration of N_2 on the fully oxidized WO_3. The W, O, and N atoms were represented in gray, red, blue, respectively. The W-O bond broke and N_2O left 2.42 Å apart from the substrate.

Electronic analysis of N_2H/P-V_O-WO_3

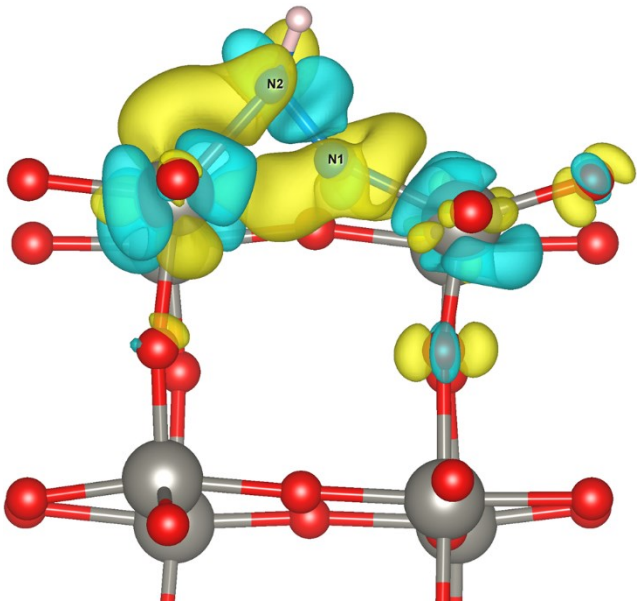

Figure S3. Charge difference density of N_2H on P-V_O site (cyan stands for electron depletion and yellow for electron accumulation). The W, O, N and H atoms were represented in gray, red, blue (with label), and pink. The isosurface illustrates the configuration with level of 0.005 eÅ^{-3}.

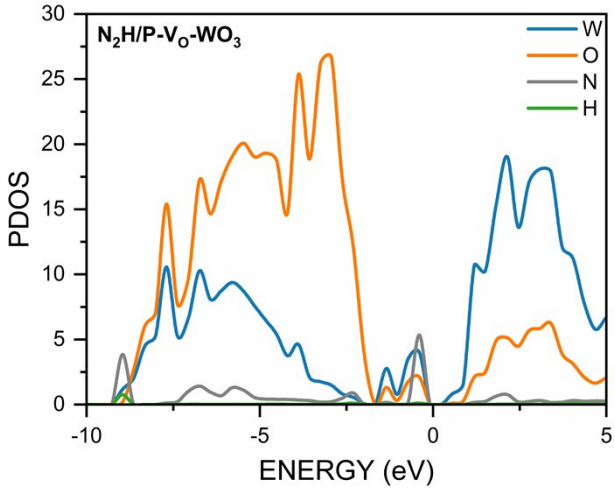

Figure S4. Projected electronic densities (PDOS) of states of tungsten (blue), oxygen (orange), nitrogen (gray), and hydrogen (green) within N_2H/P-V_O-WO_3.

TABLE S1. Bader charges of dinitrogen at initial adsorption step of the catalytic cycle with different oxygen-defective WO_{3-x}.

Steps	Elements	Charge Difference$^{\triangle}$
N_2/DV_O-WO_{3-x}	N1	+0.23|e|
	N2	-0.25|e|
N_2/PV_O-WO_{3-x}	N1	+0.50|e|
	N2	+0.24|e|

△The charge difference is defined as the charge of adsorbed nitrogen minus that of molecular nitrogen.

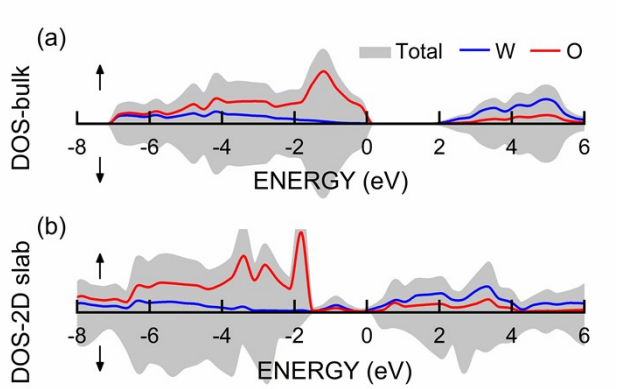

Figure S5. DOS of (a) bulk WO_3 and (b) 2D WO_3 with PDOS of tungsten (blue) and oxygen (red). For all DOS, zero at the energy scale corresponds to the Fermi level. The bulk WO_3 shows a prominent semiconductor characteristic as the calculated band gap is around 2.3 eV, which is consistent with other calculation results[2]. The "surface state" appears in the 2D WO_3 and the Fermi level traverses amidst the conduction band and the "surface state".

References

1 Nørskov, J. K. *et al.* Origin of the Overpotential for Oxygen Reduction at a Fuel-Cell Cathode. *The Journal of Physical Chemistry B* **108**, 17886-17892, (2004).

2 Migas, D. B., Shaposhnikov, V. L., Rodin, V. N. & Borisenko, V. E. Tungsten oxides. I. Effects of oxygen vacancies and doping on electronic and optical properties of different phases of WO3. *Journal of Applied Physics* **108**, 093713, (2010).