Electronic Supplementary Material (ESI) for Nanoscale.

Electrochemically synthesized SnO_2 with tuned oxygen vacancy for efficient electrocatalytic nitrogen fixation

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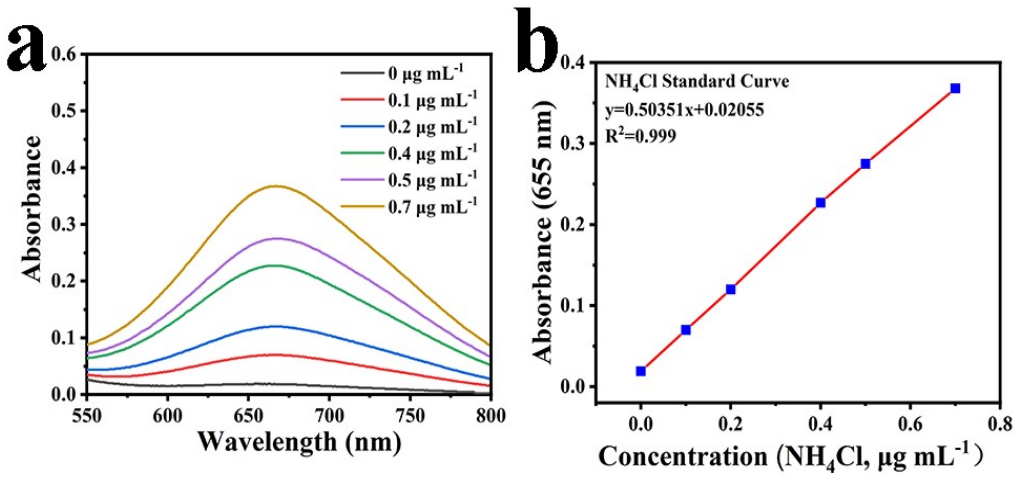

Fig. S1. (a) UV-Vis absorption spectra of indophenol assays with different NH_4Cl concentrations after incubated for 2 h in the dark. (b) Calibration curve used for calculation of NH_3 concentrations by NH_4Cl.

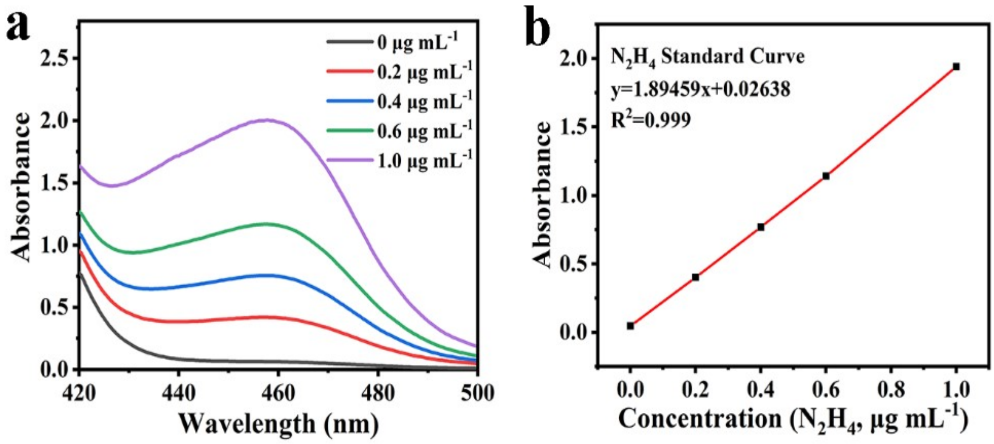

Fig. S2. (a) UV-Vis absorption spectra of various N_2H_4 concentrations after adding into chemical indicator for 20 min in the dark. (b) Calibration curve used for calculation of N_2H_4 concentrations.

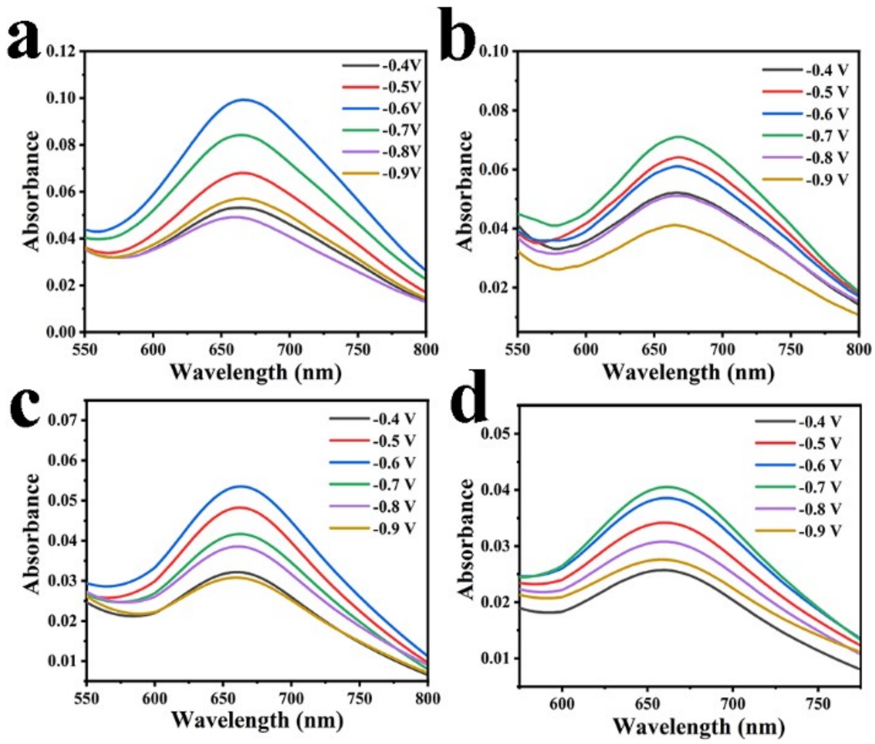

Fig. S3. UV-vis absorption spectra of the indophenol assays of the electrolyte after 2 h electrolysis of (a) SnO_2 (V_O)_12, (b) SnO_2 (V_O)_9, (c) SnO_2 (V_O)_6 and (d) commercial SnO_2 at various potentials.

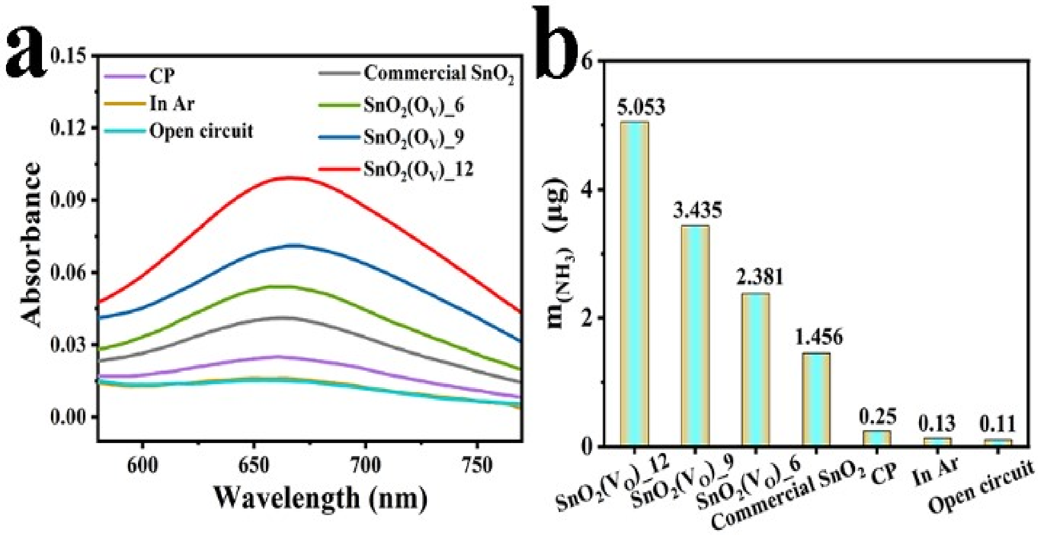

Fig.S4. (a) UV-vis absorption spectra of the indophenol assays of the electrolyte and (b) corresponding NH_3 yield after 2 h electrolysis at – 0.6 V of SnO_2 (V_O)_6 and SnO_2 (V_O)_12, at – 0.7 V of SnO_2 (V_O)_9 and commercial SnO_2, at -0.6 V of SnO_2 (V_O) _12 in Ar- saturated, at – 0.6 V of pure carbon paper, and of SnO_2 (V_O) _12 at open circuit.

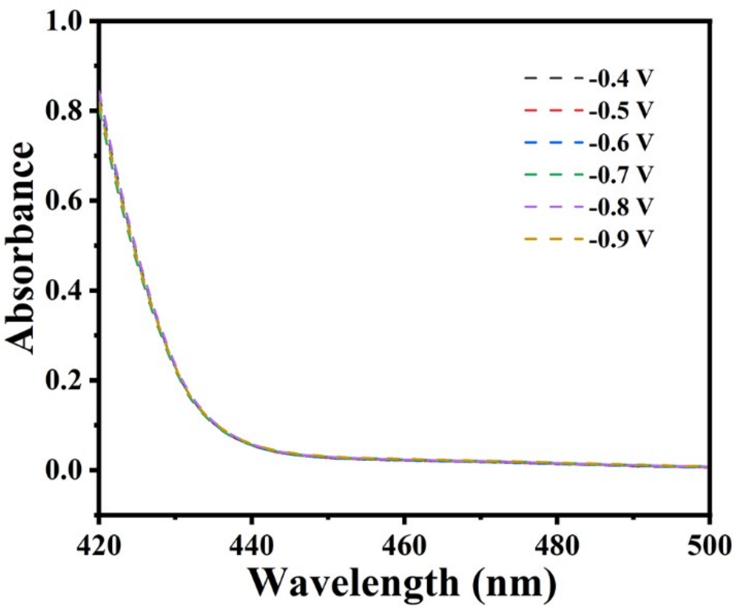

Fig.S5. UV-Vis absorption spectra of the electrolytes estimated by the method of Watt and Chrisp after electrolysis in N_2-saturated 0.1 M Na_2SO_4 at various potentials for 2 h of SnO_2 (V_O) _12 nanoparticles.

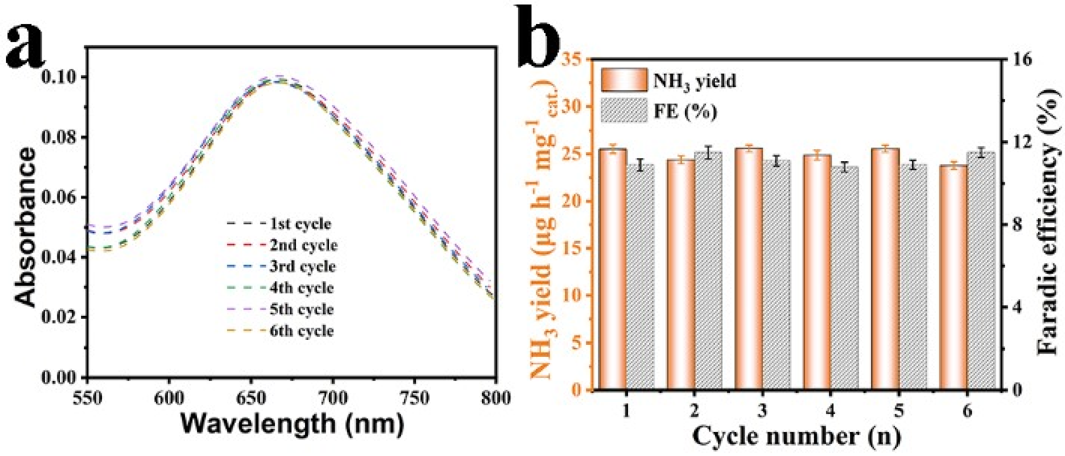

Fig.S6. (a) UV-vis absorption spectra of the indophenol assays of the electrolyte and (b) corresponding NH_3 yield rates and FEs after 2 h electrolysis at – 0.6 V of SnO_2 (V_O)_12.

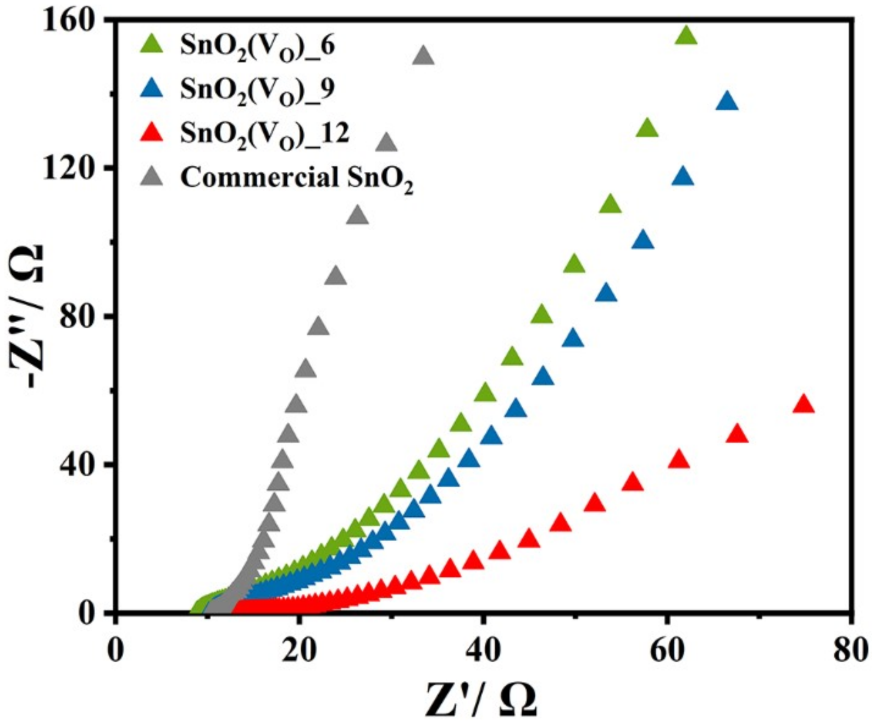

Fig.S7. The EIS plots for SnO_2 (V_O)_6, SnO_2 (V_O)_9, SnO_2 (V_O)_12, and commercial SnO_2 in N_2-saturated electrolyte. For comparison, the R_Ω was omitted in the Nyquist plots.

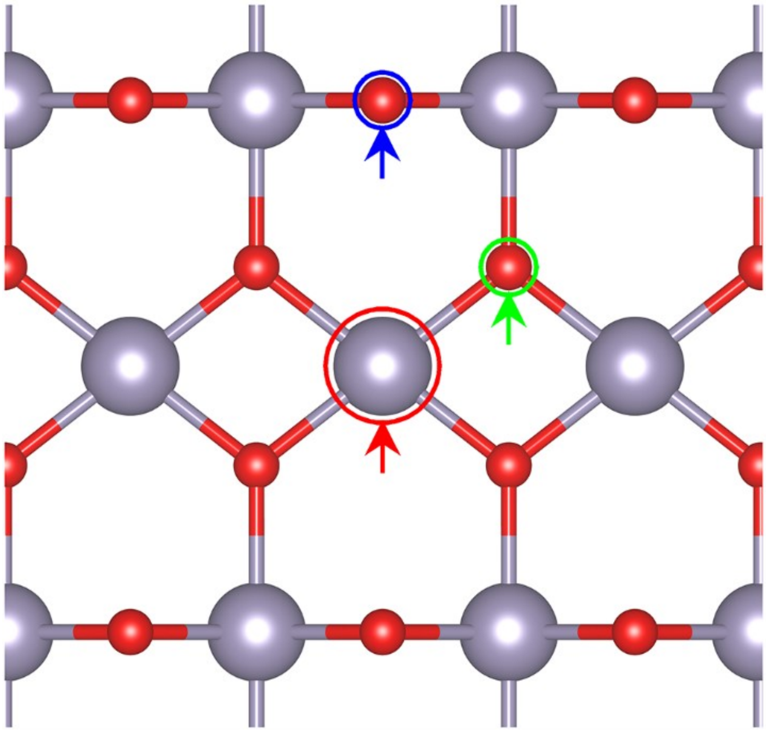

Fig. S8. Top view of $SnO_2(110)$. The active site, O_{side} and O_{top} are marked in red, green and blue circles.

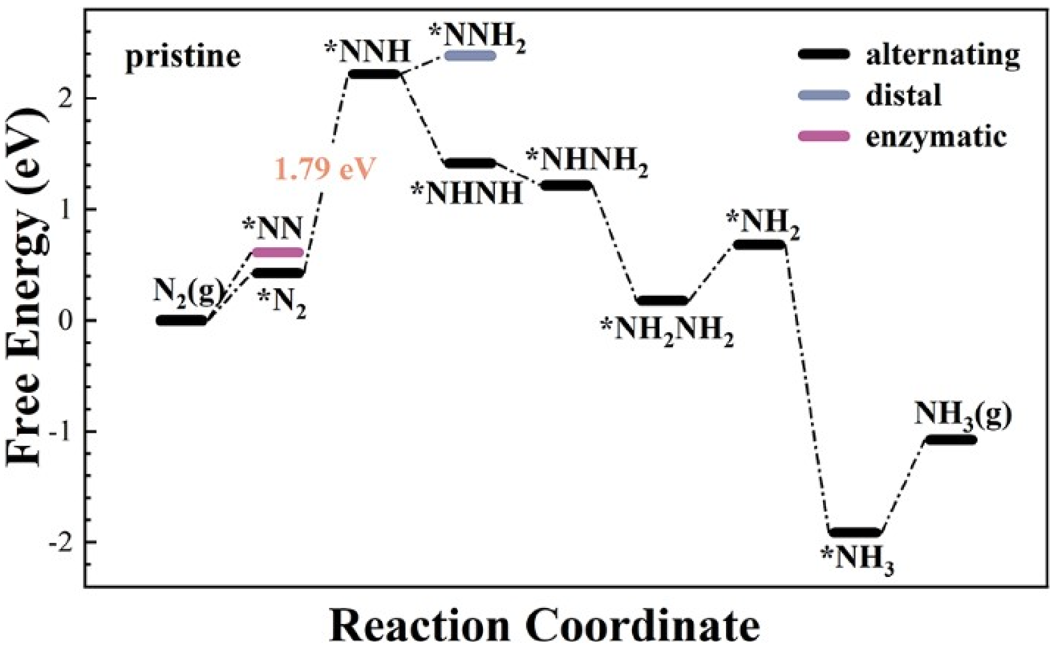

Fig. S9. Calculated free energy changes of NRR on pristine $SnO_2(110)$ surface.

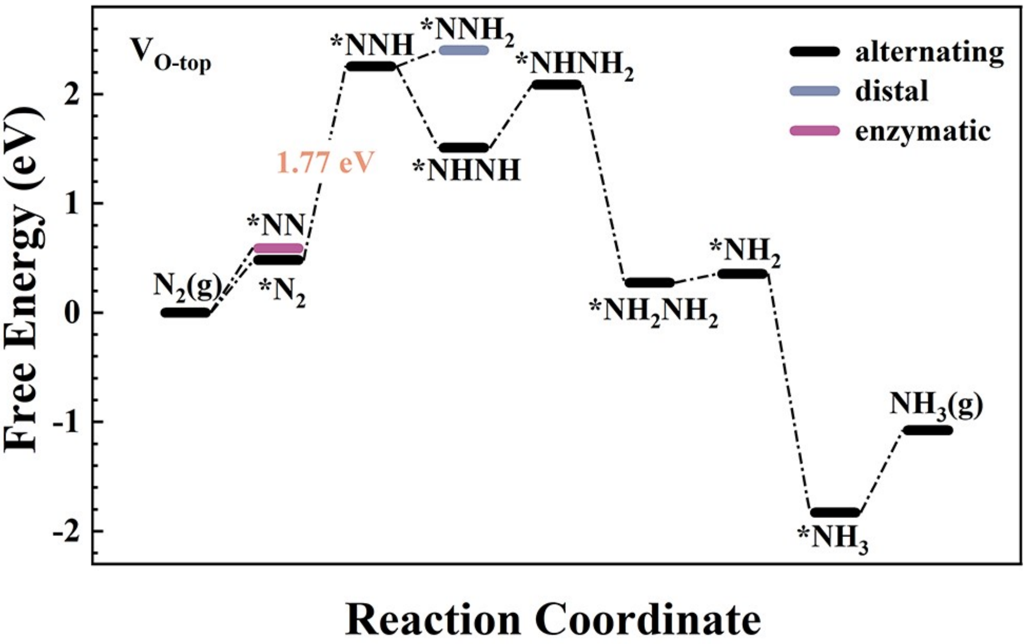

Fig. S10. Calculated free energy changes of NRR process on $V_{O\text{-}top}$ $SnO_2(110)$ surface.

Table S1. the comparative electrocatalytic NRR performance among the SnO_2 (V_O) _12 sample and other metal oxide catalysts under ambient conditions.

Catalyst	**Electrolyte**	**NH_3 yield rate**	**FE %**	**Ref.**
SnO2 (V_O) _12	0.1 M Na_2SO_4	25.27 μg h^{-1} mg^{-1}_{cat}.	11.48	This work
R-WO_3 NSs	0.1 M HCl	17.28 μg h^{-1} mg^{-1}_{cat}.	7.0	1
hollow Cr_2O_3 microspheres	0.1 M Na_2SO_4	25.3 μg h^{-1} mg^{-1}_{cat}.	6.78	2
Bi_4O_{11}/CeO_2	0.1 M Na_2SO_4	23.21 μg h^{-1} mg^{-1}_{cat}.	10.16	3
MoO_3 nanosheets	0.1 M HCl	29.43 μg h^{-1} mg^{-1}_{cat}.	1.9	4
Co_3O_4@NCs	0.05 M H_2SO_4	42.58 μg h^{-1} mg^{-1}_{cat}.	8.5	5
Activated TiO_2 with tuned vacancy	0.1M HCl	3.0 μg h^{-1} mg^{-1}_{cat}.	6.5	6
Nb_2O_5 nanofiber	0.1M HCl	43.6 μg h^{-1} mg^{-1}_{cat}.	9.26	7
β-Bi_3O_4	0.01 M Na_2SO_4	19.93 μg h^{-1} mg^{-1}_{cat}.	4.3	8
Au/TiO_2	0.1 M HCl	21.4 μg h^{-1} mg^{-1}_{cat}.	8.1	9
Au@SnO_2	0.1 M HCl	21.9 μg h^{-1} mg^{-1}_{cat}.	15.2	10
Fe_2O_3 nanorod	0.1 M Na_2SO_4	15.9 μg h^{-1} mg^{-1}_{cat}.	0.94	11
Fe-SnO_2	0.1 M HCl	82.7 μg h^{-1} mg^{-1}_{cat}.	20.4	12
Al-Doped Co_3O_4	0.1 M KOH	6.48×10^{-11} mol s^{-1} cm^{-2}	6.25	13
Mn_3O_4@rGO	0.1 m Na_2SO_4	17.4 μg h^{-1} mg^{-1}_{cat}.	3.52	14
Spinel Fe_3O_4 nanorod	0.1 M Na_2SO_4	5.6×10^{-11} mol s^{-1} cm^{-2}	2.6	15
Mn_3O_4 nanocube	0.1 m Na_2SO_4	11.6μg h^{-1} mg^{-1}_{cat}.	3.0	16

Table S2. Calculated zero-point energies and entropy of different adsorption species, where the * denotes the adsorption site. T was set as 300K.

Adsorption Species	E_{ZPE} **(eV)**	$T\Delta S$ **(eV)**
$*N_2$	0.21	0.12
$*NNH$	0.45	0.13
$*NHNH$	0.79	0.10
$*NHNH_2$	1.17	0.11
$*NH_2NH_2$	1.52	0.13
$*NH_2$	0.73	0.06
$*NH_3$	1.01	0.12
$*NN$	0.21	0.13
$*NNH_2$	0.85	0.10

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