

Supporting Information

Combined catalyst-pathway design for efficient and green urea synthesis

Zhuohang Li, Xuezi Xing, Ruichao Zhang, Xue Zeng*, Ke Chu*
School of Materials Science and Engineering, Lanzhou Jiaotong University, Lanzhou
730070, China

*Corresponding author. E-mail: zengxue@lztu.edu.cn (X. Zeng),
chuk630@mail.lztu.cn (K. Chu)

Experimental Section

Materials

All the reagents were of analytical grade and were used as received without further purification. TiO_2 ($\geq 99.9\%$), AgNO_3 ($\geq 99.0\%$), $\text{C}_4\text{H}_6\text{N}_2$ ($\geq 99.9\%$), CH_4O ($\geq 99.9\%$), NaOH ($\geq 96.0\%$), $\text{C}_7\text{H}_6\text{O}_3$ ($\geq 99.5\%$), KOH ($\geq 99.9\%$), KHCO_3 ($\geq 99.9\%$), NH_4Cl ($\geq 99.5\%$), $\text{C}_6\text{H}_5\text{Na}_3\text{O}_7 \cdot 2\text{H}_2\text{O}$ ($\geq 99.0\%$), $\text{C}_5\text{FeN}_6\text{Na}_2\text{O} \cdot 2\text{H}_2\text{O}$ ($\geq 99.0\%$), urease, NaClO ($\geq 99.9\%$) and Nafion (5 wt%) were provided from Sigma-Aldrich Chemical Reagent Co, Ltd. H_2SO_4 (98%), $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$ ($\geq 99.9\%$) and $\text{C}_2\text{H}_5\text{OH}$ (99.0%) were purchased from Sigma-Aldrich Chemical Reagent Co, Ltd. CO_2 ($\geq 99.999\%$) and Ar ($\geq 99.999\%$) are provided from Lanzhou Xinwanke, Co, Ltd.

Synthesis of $\text{Ag}_1/\text{TiO}_{2-x}$

All the chemicals were used as received without further purification. 2 g of pure TiO_2 powder was dispersed in 40 mL of 5 M NaOH solution under stirring for 1 h. The suspension was then hydrothermally treated in a Teflon-lined autoclave at 180°C for 24 h. After cooling, the precipitates were collected, dried and further annealed in Ar atmosphere at 500°C for 2 h. The obtained TiO_{2-x} was re-dispersed in an aqueous solution containing dissolved AgNO_3 and maintained for 2 h. The resulting sediments were then collected, washed thoroughly and dried to obtain $\text{Ag}_1/\text{TiO}_{2-x}$.

Electrochemical experiments in H-type cell

Electrochemical measurements were conducted utilizing a CHI-760E electrochemical workstation. The experimental setup comprised a three-electrode cell configuration, consisting of an $\text{Ag}_1/\text{TiO}_{2-x}$ working electrode, an Ag/AgCl reference electrode, and a Pt foil counter electrode. The catalyst slurry was prepared by dissolving 25 mg of catalyst in 3 mL of isopropanol followed by the addition of 20 μL of Nafion ionomer solution (5 wt% H_2O solution). The catalyst slurry was slowly dripped onto carbon paper (Sigracet 29 BC) to obtain $\sim 0.5 \text{ mg cm}^{-2}$ of catalyst loading as electrode. All potentials were calibrated with respect to a reversible hydrogen electrode (RHE) using the formula $E (\text{V vs. RHE}) = E (\text{V vs. Ag/AgCl}) + 0.198 \text{ V} + 0.059 \times \text{pH}$. The catholyte was a solution containing gases generated through plasma

and 0.1 M KHCO_3 , while the anolyte consisted of a 1 M KOH solution within an H-type two-compartment electrochemical cell separated by a Nafion 211 membrane. Before utilizing the Nafion membrane, a pretreatment procedure was carried out. The membrane was heated in a 5% H_2O_2 aqueous solution at 80°C for 1 h, followed by rinsing with deionized water at 80°C for an additional 1 h. The catholyte was purged with CO_2 or Ar prior to the electrochemical experiments. After electrolysis for 1 h, the produced urea was quantitatively determined by the urease decomposition method.

Electrochemical experiments in flow cell

Flow cell measurements were conducted using a commercially available flow cell electrolyser (101017, Gaoss Union Technology Co, LTD). In flow cell, the anodic and cathodic chambers were separated by a Nafion 211 proton exchange membrane (PEM). For the electrochemical measurements, a gas diffusion electrode (GDE) was used as the working electrode, Ni foams served as the counter electrode, and an Ag/AgCl electrode was employed as the reference electrode. During the electrolysis, CO_2 gas was fed from the no-catalyst side of the GDE at a flow rate of 20 s.c.c.m., and both catholyte and anolyte were continuously cycled at a rate of 20 mL min^{-1} under pump drive. After electrolysis at specified potentials for 1 h, the produced urea was quantitatively determined by the urease decomposition method.

Plasma-assisted air-to- NO_x conversion

A pulsed high-voltage plasma discharge (PHPD) system was employed to activate and dissociate air molecules for NO_x generation. The system primarily comprised three key components: power regulation module, plasma reactor and gas flow control system. The power regulation module was powered by a low-voltage direct current (DC) power supply and integrated with a high-voltage module (Model: DC High-Voltage Modules-150KV, Guangao Technology (Wuhan) Co., Ltd) to amplify the voltage. The output potential was precisely measured using a high-voltage voltmeter (Model: 69C17, Wenzhou Telun Electric Co., Ltd). The plasma reactor comprised a glass tube (2 mm in inner diameter), two copper electrodes with multiple parallel microcolumns, along with a gas inlet and outlet for feeding and discharging gases, respectively. Ambient air was directly introduced into the plasma reactor at a

controlled volumetric flow rate regulated by a gas flow control system (Model: ACU10FD-XS, Beijing Precision Technology Co., Ltd). After a period of plasma discharge, the outlet NO_x gas was absorbed in an Erlenmeyer flask containing 1 M KOH solution, where NO_x was converted into NO_x ions ($\text{NO}_2^-/\text{NO}_3^-$). The resulting NO_2^- and NO_3^- concentrations were subsequently quantified with ultraviolet-visible (UV-Vis) absorption spectroscopy.

Characterizations

X-ray diffraction (XRD) pattern was collected on a Rigaku D/max 2400 diffractometer with Cu $K\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$, 40 kV). Transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) were recorded on a Tecnai G² F20 microscope. Aberration-corrected high-angle annular dark-field scanning transmission microscopy (AC-STEM) was performed on a Titan Cubed Themis G² 300 microscope. Electron paramagnetic resonance (EPR) measurements were conducted on a Bruker ESP-300 spectrometer. Operando Raman spectroscopy analysis was carried out on a confocal Raman spectrometer (Horiba HR-800) with a wavelength of 532 nm. Operando Fourier-transform infrared (FTIR) spectroscopy was performed on a Nicolet 6700 FTIR spectrometer. Online differential electrochemical mass spectrometry (DEMS, QAS 100) was performed by QAS 100 spectrometer.

Determination of urea

Urea concentration was detected via urease decomposition method¹. Typically, 0.2 mL of urease solution with concentration of 5 mg mL⁻¹ was added into 2 mL of urea electrolyte, and then reacted at 37°C in constant temperature shaker for 40 min. Urea was decomposed by urease into CO_2 and two NH_3 molecules. After the decomposition, NH_3 concentration of urea electrolyte with urease (c_{urease}) was detected via above indophenol blue method. Meanwhile, NH_3 concentration contained in urea electrolyte without urease (c_{NH_3}) was also quantified by indophenol blue

method. Urea concentration (c_{urea}) in electrolyte were calculated by the following equation:

$$c_{\text{urea}} = (c_{\text{urease}} - c_{\text{NH}_3})/2 \quad (1)$$

The urea yield rate and FE_{urea} were calculated by the following equation:

$$\text{Urea yield rate (mmol h}^{-1} \text{ g}^{-1}) = \frac{c_{\text{urea}} \times V}{60.06 \times t \times m} \quad (2)$$

$$\text{FE}_{\text{urea}} (\%) = \frac{12 \times F \times c_{\text{urea}} \times V}{60.06 \times Q} \times 100\% \quad (3)$$

where c_{urea} (mg mL^{-1}) is the measured urea concentration, V (mL) is the volume of the electrolyte, t (h) is the reduction time, m (g) is the mass loading of the catalyst on CC, F (96500 C mol^{-1}) is the Faraday constant, Q (C) is the quantity of applied electricity.

Determination of NH_3

NH_3 in electrolyte was quantitatively determined by the indophenol blue method². Typically, 2 mL of electrolyte was removed from the electrochemical reaction vessel and diluted with deionized water. Then 2 mL of diluted solution was removed into a clean vessel followed by sequentially adding NaOH solution (2 mL, 1 M) containing $\text{C}_7\text{H}_6\text{O}_3$ (5 wt.%) and $\text{C}_6\text{H}_5\text{Na}_3\text{O}_7$ (5 wt.%), NaClO (1 mL, 0.05 M), and $\text{C}_5\text{FeN}_6\text{Na}_2\text{O}$ (0.2 mL, 1wt.%) aqueous solution. After the incubation for 2 h at room temperature, the mixed solution was subjected to UV-vis measurement using the absorbance at 655 nm wavelength. The concentration-absorbance curves were calibrated by the standard NH_4Cl solution with a series of concentrations.

Determination of NO_2^-

NO_2^- in electrolyte was determined by a Griess test³. Typically, 2 mL of electrolyte was removed from the electrochemical reaction vessel and diluted with deionized water. The coloring solution was prepared by dissolving N-(1-naphthyl) ethylenediamine dihydrochloride (0.1 g), sulfonamide (1.0 g) and H_3PO_4 (2.94 mL, 85%) into 50 mL of deionized water. Add 0.1 mL of coloring solution to the diluted electrolyte. After incubation for 30 min at room temperature, the mixture was

subjected to UV-vis measurements and the absorption spectrum (range 400-700 nm) was obtained. The absorbance at 540 nm was measured to determine the concentration of generated NO_2^- with a standard curve of NaNO_2 .

Determination of NO_3^-

NO_3^- in electrolyte was quantitatively determined by a reported method⁴. The electrolyte was collected and diluted to the detection range. 2 mL of diluted electrolyte was mixed with 40 μL of 1.0 M HCl containing 4.0 μL of 0.8 wt% sulfamic acid. After the incubation for 20 min at room temperature, the mixed solution was subjected to UV-vis measurement using the absorbance at 220 nm wavelength. The concentration-absorbance curves were calibrated by the standard KNO_3 solution with a series of concentrations.

Calculation details

DFT calculations were carried out using the Cambridge sequential total energy package (CASTEP) with ultrasoft pseudopotentials. The exchange-correlation functional is evaluated using the Perdew-Burke-Ernzerhof (PBE) in the generalized gradient approximation. DFT-D3 method was employed to calculate the van der Waals (vdW) interactions. According to the experimental characterizations, the $\text{Ag}_1/\text{TiO}_{2-x}$ (101) slab was modeled and a vacuum region of 15 Å. A vacuum region of 15 Å was used to separate adjacent slabs. The cutoff energy was set as 450 eV and the k-point meshes were set as $2 \times 2 \times 1$. The AIMD simulation was carried out to estimate the thermal stability, in which the NVT ensemble is chosen with the total simulation time of 5 ns at a time step of 1 fs.

The computational hydrogen electrode (CHE) model was adopted to calculate the Gibbs free energy change (ΔG) for each elementary step as follows:

$$\Delta G = \Delta E + \Delta E_{\text{ZPE}} - T\Delta S \quad (4)$$

where ΔE represents the electronic energy contribution directly derived from DFT calculations. ΔE_{ZPE} and $T\Delta S$ denote the contributions of zero-point energy and

entropy (at 298.15 K), respectively. These values can be obtained from the NIST database for free molecules⁵.

Molecular dynamics (MD) simulations were performed using the Forcite module. The electrolyte system was modeled by a cubic cell with placing catalyst at the center of the cell and randomly filling 1000 H₂O, 50 NO₂⁻, 50 CO₂ molecules, and 50 H atoms. The force field type was chosen as universal. After geometry optimization, the MD simulations were performed in an NVT ensemble (698 K) with the total simulation time of 5 ns at a time step of 1 fs.

The radial distribution function (RDF) is calculated by⁶:

$$g(r) = \frac{dN}{4\pi\rho r^2 dr} \quad (5)$$

where dN is the amount of molecules in the shell between the central particle r and $r+dr$, ρ is the number density of NO₂⁻, CO₂, H₂O and H.

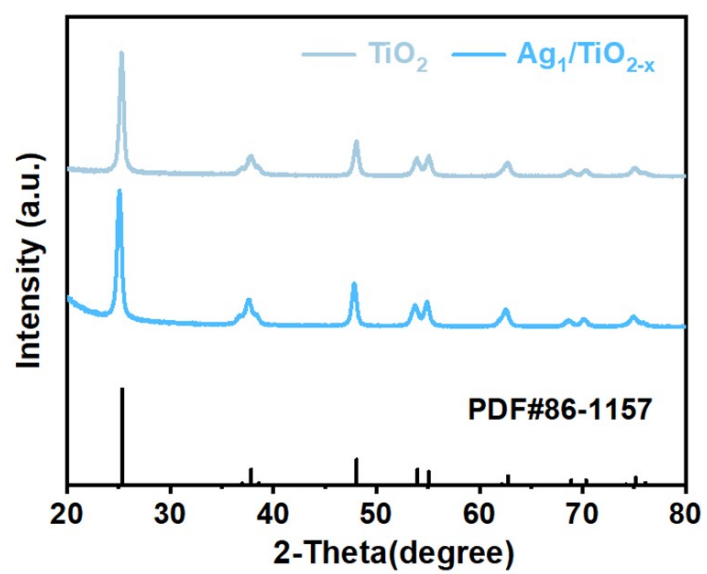


Fig. S1. XRD patterns of $\text{Ag}_1/\text{TiO}_{2-x}$ and TiO_2 .

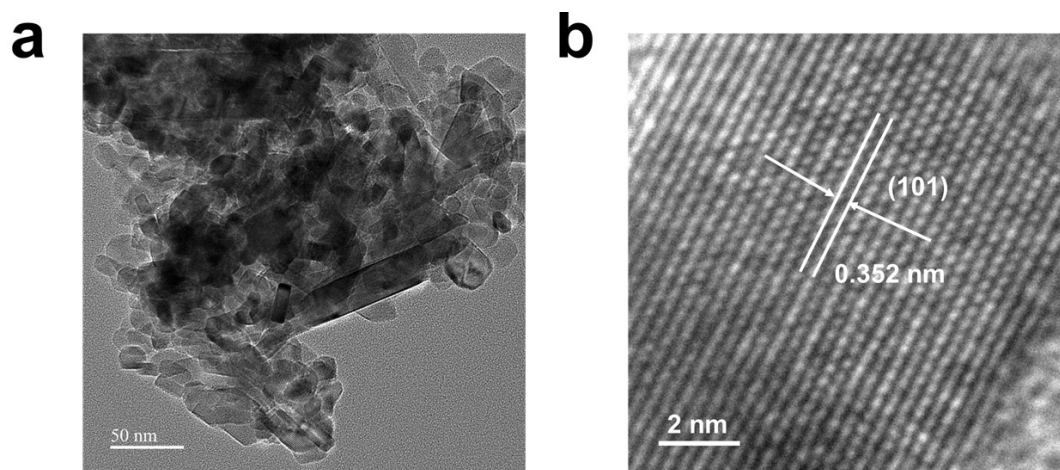


Fig. S2. (a) TEM and (b) HRTEM images of $\text{Ag}_1/\text{TiO}_{2-x}$.

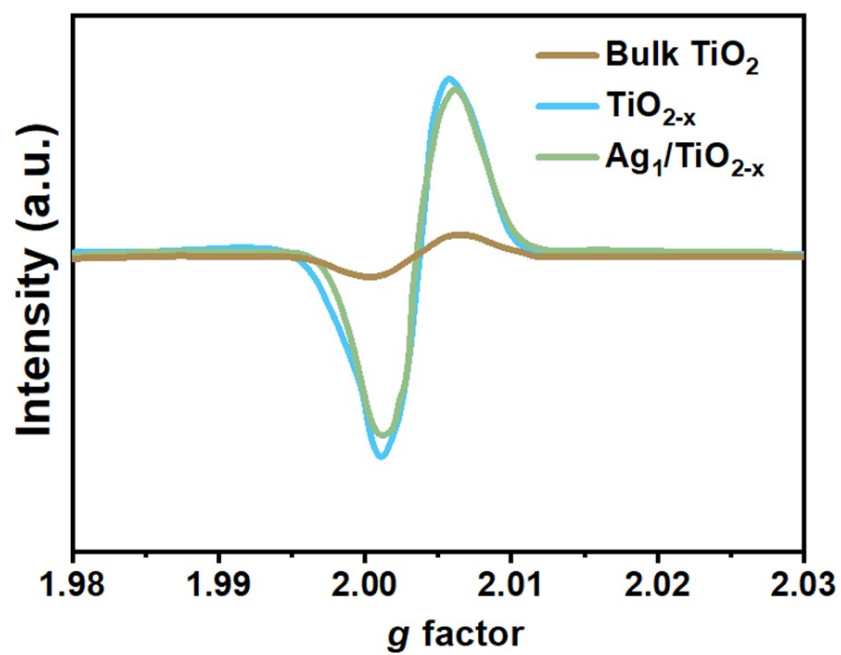


Fig. S3. EPR spectra of bulk TiO_2 , TiO_{2-x} and $\text{Ag}_1/\text{TiO}_{2-x}$.

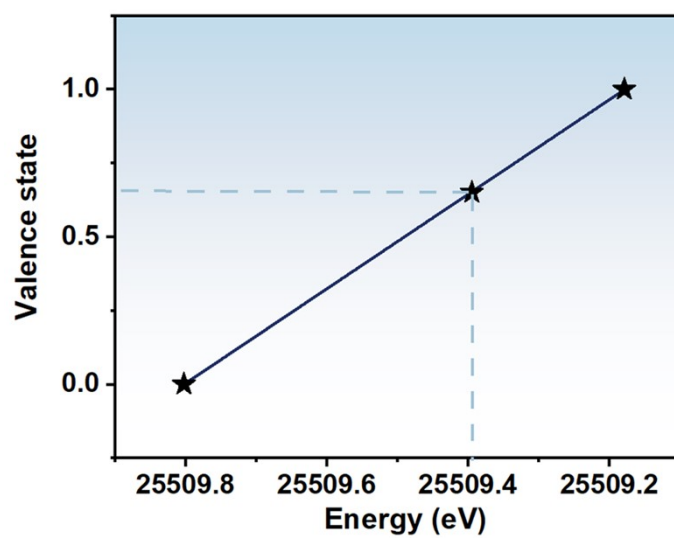


Fig. S4. XANES fitted average Ag valence state of $\text{Ag}_1/\text{TiO}_{2-x}$.

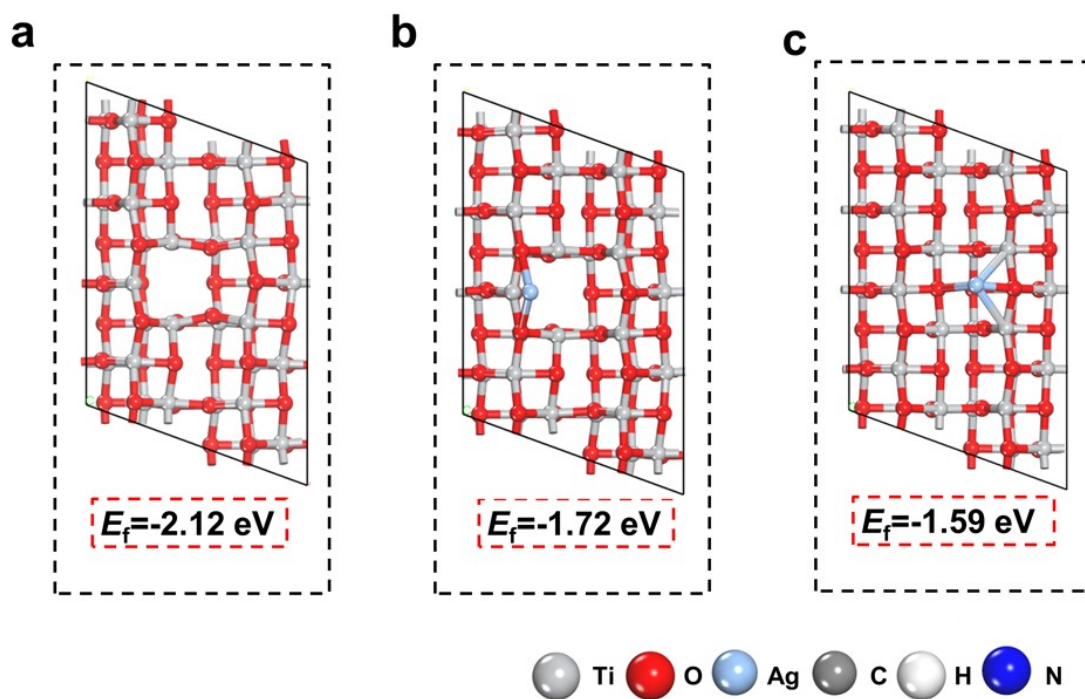


Fig. S5. Calculated formation energies (E_f) of (a) TiO_{2-x} , (b) $\text{Ag}_1/\text{TiO}_{2-x}$ and (c) Ag_1/TiO_2 .

The calculated formation energies (E_f) indicate that OV can be energetically favorable formed on TiO_2 to form TiO_{2-x} (Fig. S5a), and Ag_1 can be well anchored onto OV to generate $\text{Ag}_1/\text{TiO}_{2-x}$ catalyst (Fig. S5b).

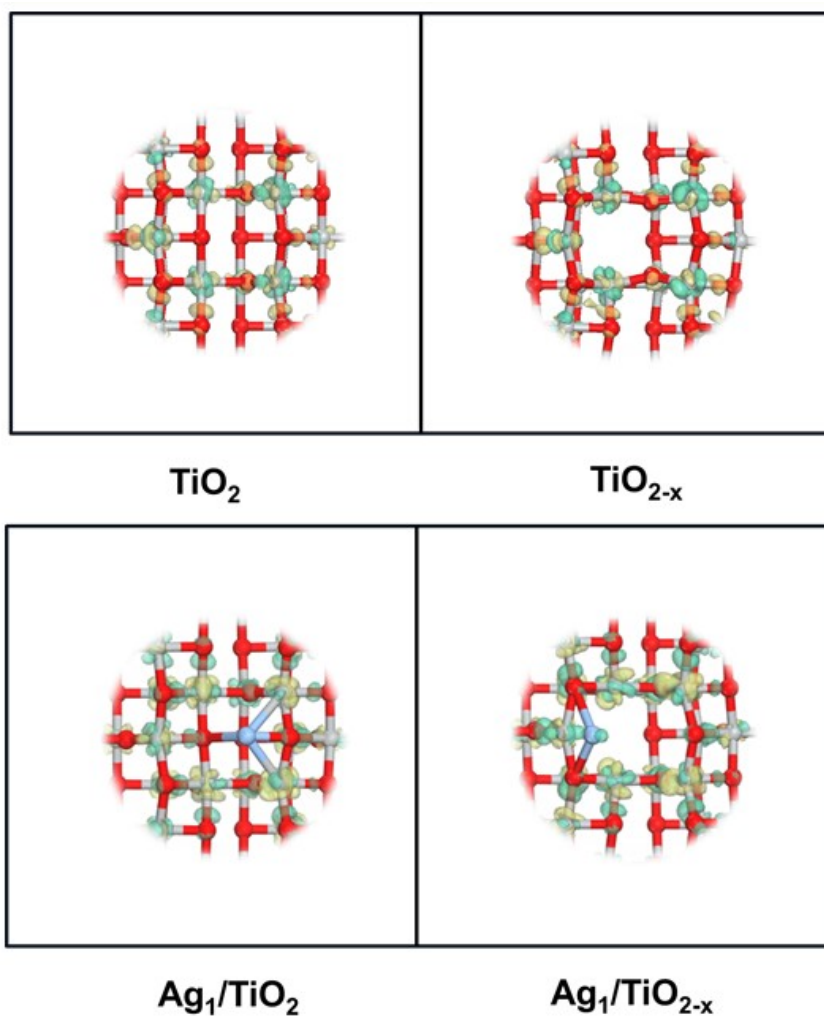


Fig. S6. Differential charge density maps of TiO₂, TiO_{2-x}, Ag₁/TiO₂ and Ag₁/TiO_{2-x} (Yellow: accumulation and cyan: depletion).

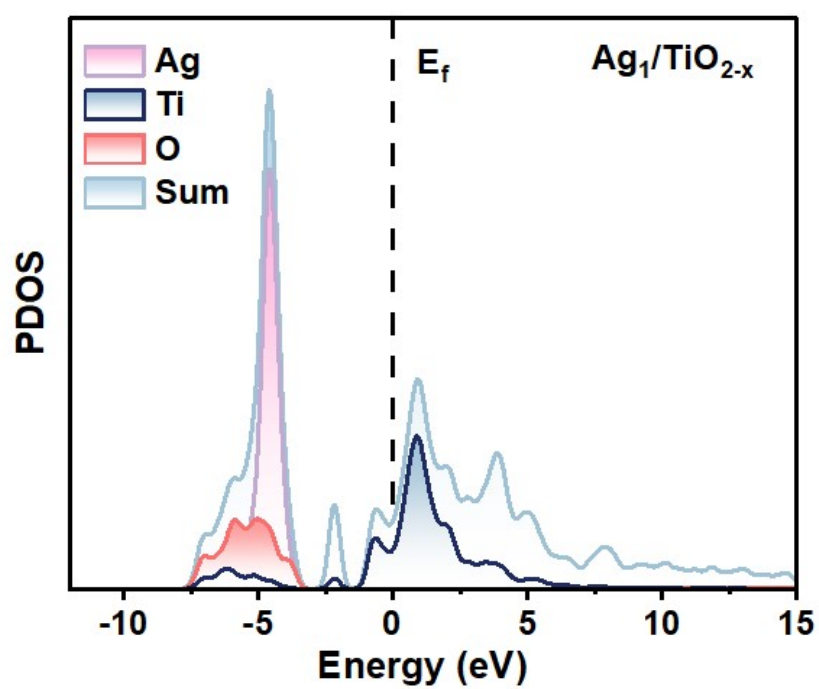


Fig. S7. PDOS profile of $\text{Ag}_1/\text{TiO}_{2-x}$.

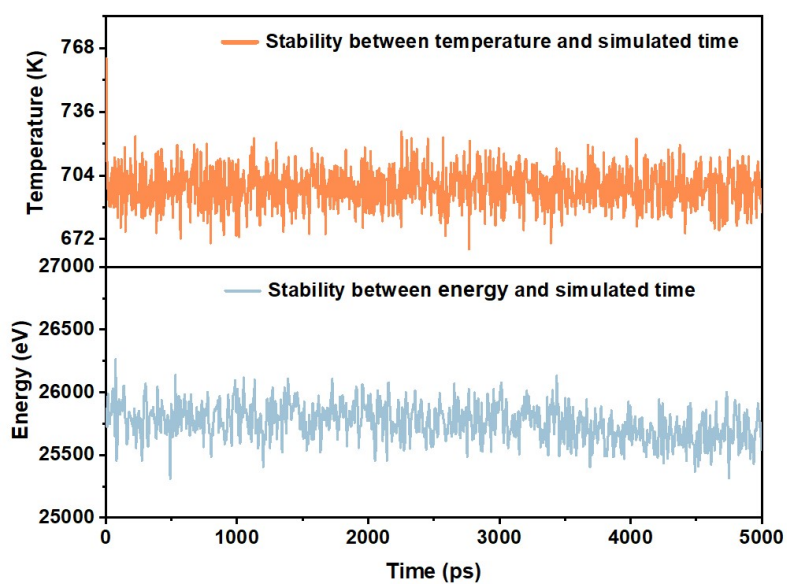


Fig. S8. AIMD simulation of the $\text{Ag}_1/\text{TiO}_{2-x}$ atomic structure. The AIMD simulation was carried out to estimate the thermal stability, in which the NVT ensemble is chosen with the total simulation time of 5 ns at a time step of 1 fs.

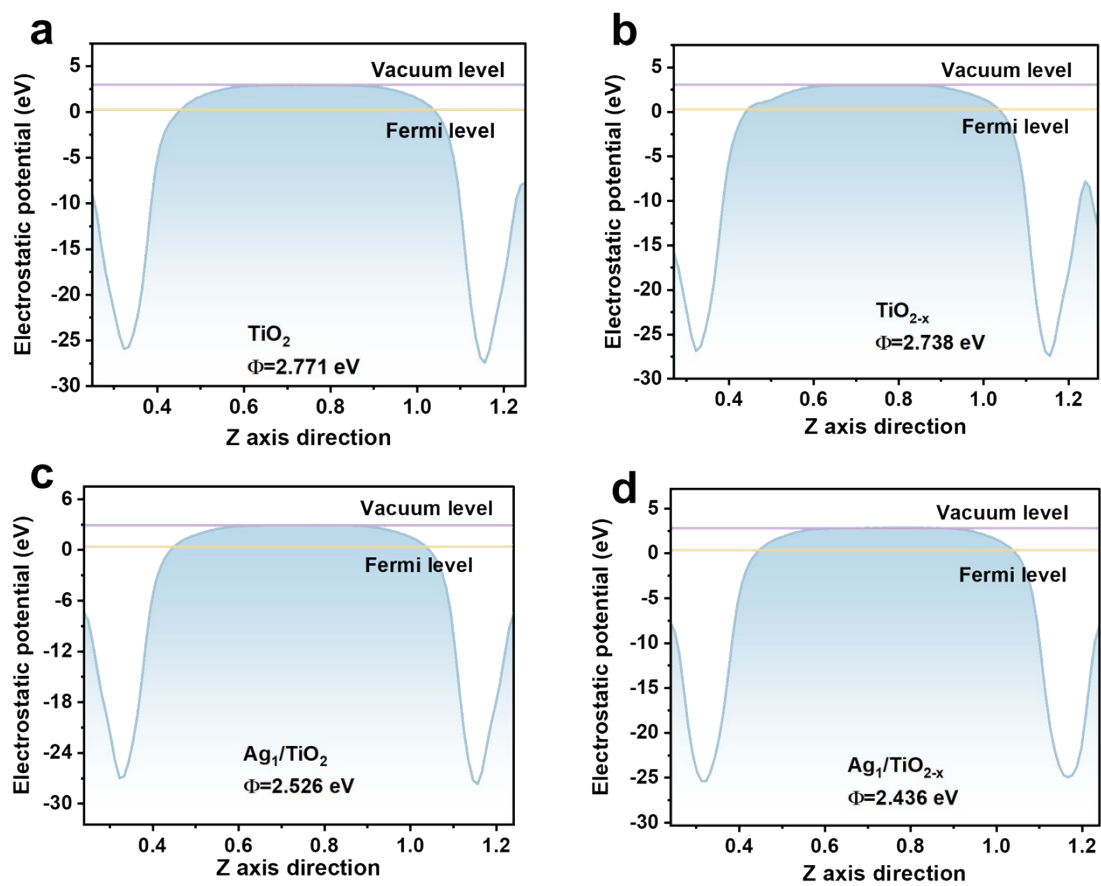


Fig. S9. Average potential profiles along c-axis direction for calculating the work functions of (a) TiO_2 , (b) TiO_{2-x} , (c) Ag_1/TiO_2 and (d) $\text{Ag}_1/\text{TiO}_{2-x}$.

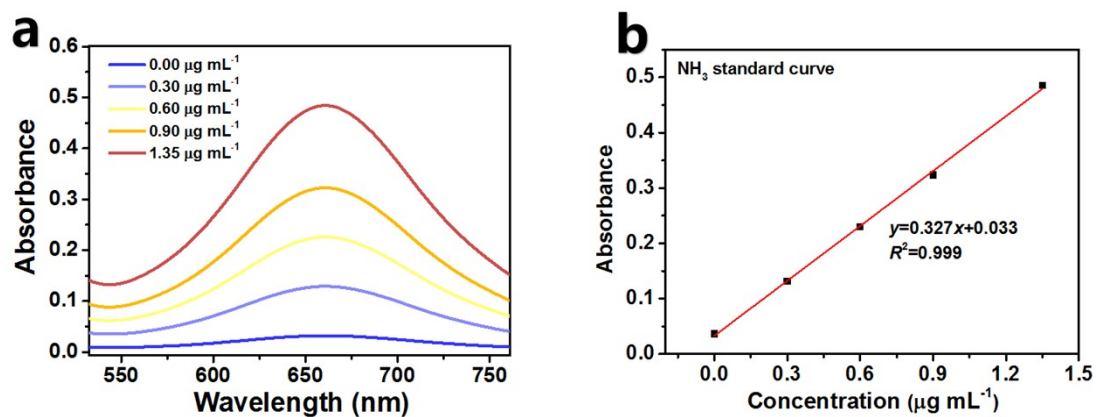


Fig S10. (a) UV-vis absorption spectra of NH_4Cl assays after incubated for 2 h at ambient conditions. (b) Calibration curve used for the calculation of NH_3 concentrations.

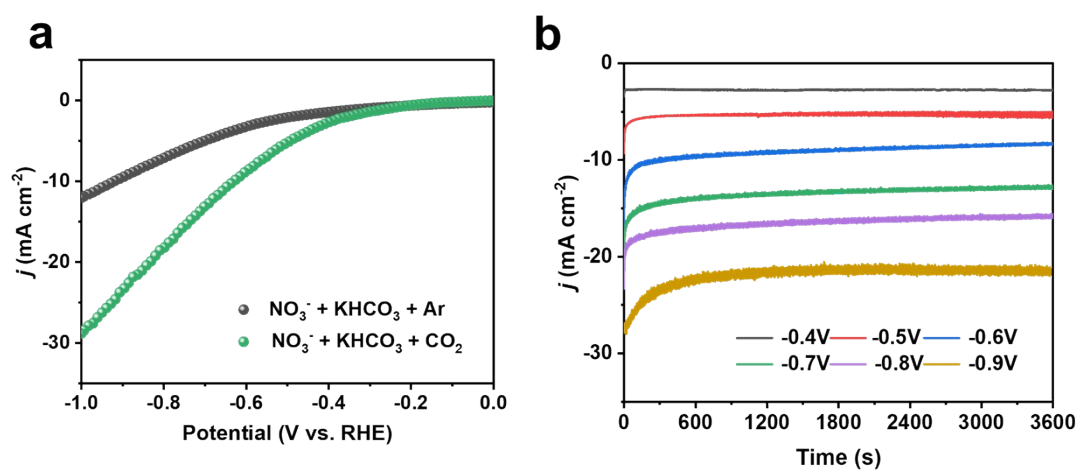


Fig S11. (a) LSV curves of $\text{Ag}_1/\text{TiO}_{2-x}$ during the UECN electrolysis in H-cell. (b) Chronoamperometry curves at different potentials of $\text{Ag}_1/\text{TiO}_{2-x}$ in H-cell.

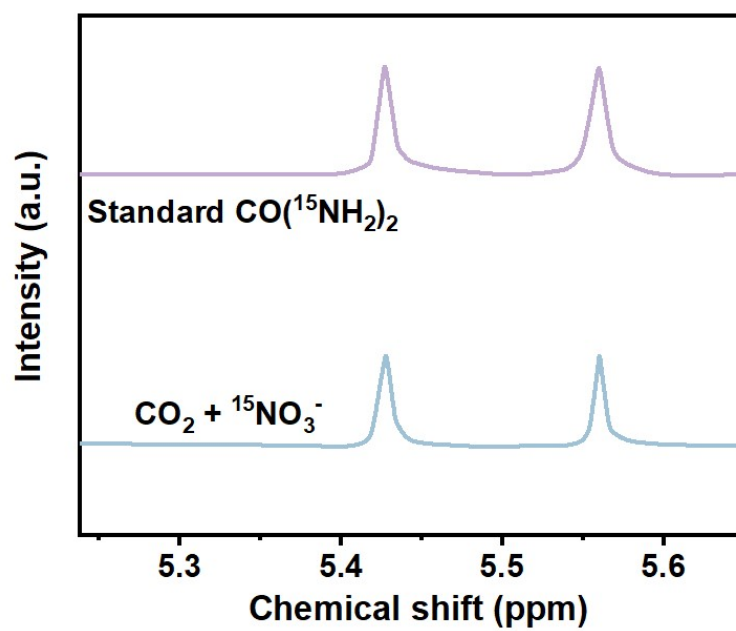


Fig. S12. ^1H NMR spectra of $\text{CO}(^{15}\text{NH}_2)_2$ standard sample and those electrolyzed in $^{15}\text{NO}_3^-$ electrolyte at -0.7 V.

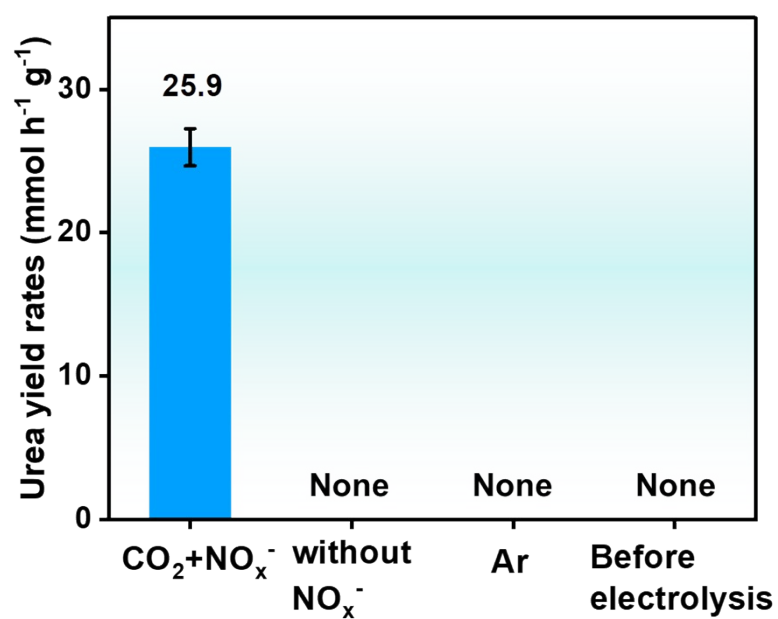


Fig. S13. Amounts of produced urea on Ag₁/TiO_{2-x} under different conditions: (1) electrolysis in NO_x⁻ +CO₂⁻ solution, (2) without NO_x⁻, (3) without CO₂, (4) before electrolysis.

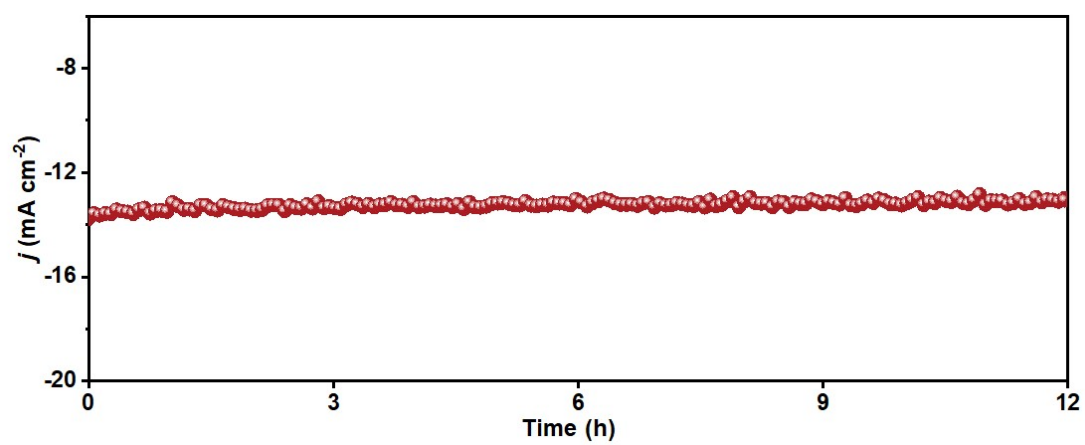


Fig. S14. Long-term test of AgI/TiO_{2-x} in H-cell at -0.7 V.

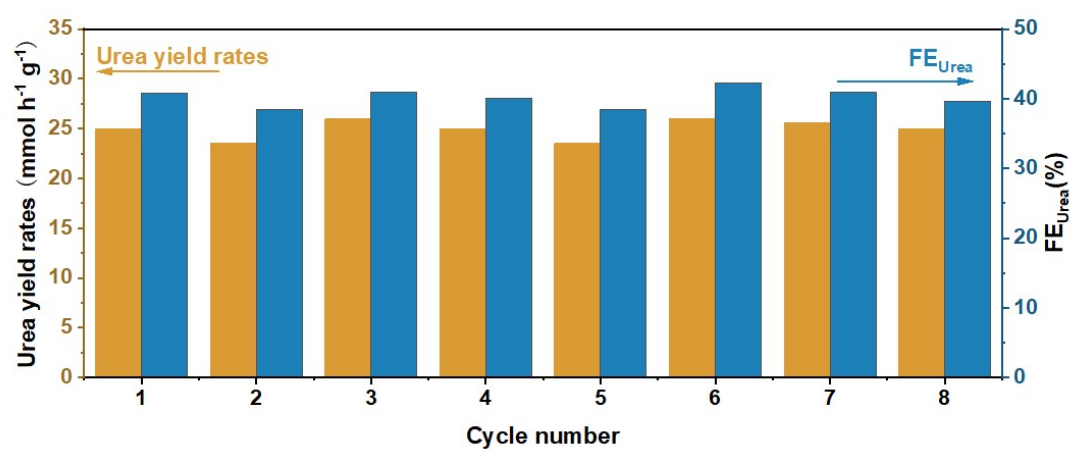


Fig. S15. Cycling test of Ag₁/TiO_{2-x} in H-cell at -0.7 V.

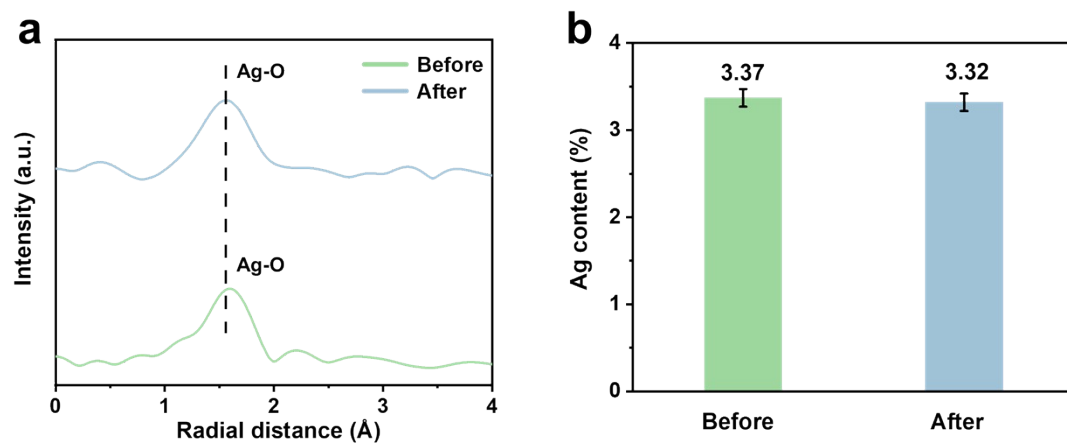


Fig. S16. (a) EXAFS spectra and (b) ICP analyses of $\text{Ag}_1/\text{TiO}_{2-x}$ before and after long-term electrolysis test.

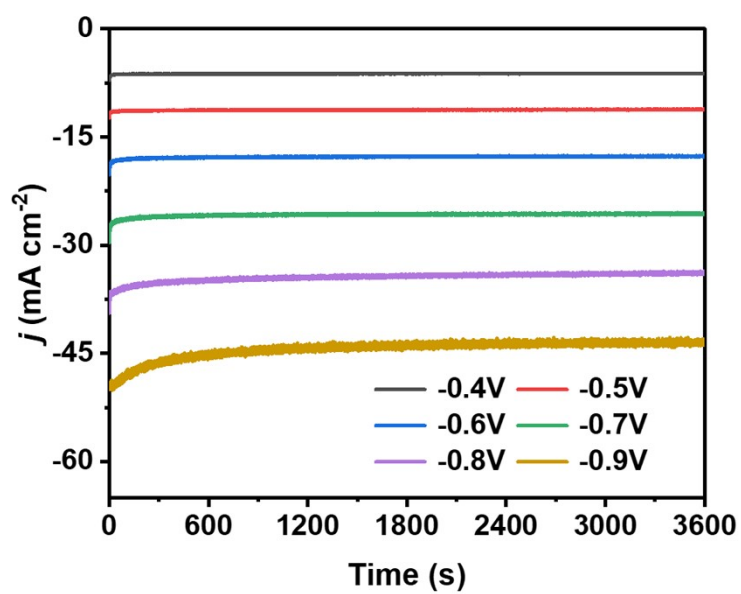


Fig. S17. Potential-dependent chronoamperometry curves of $\text{Ag}_1/\text{TiO}_{2-x}$ after 1 h electrolysis in flow cell.

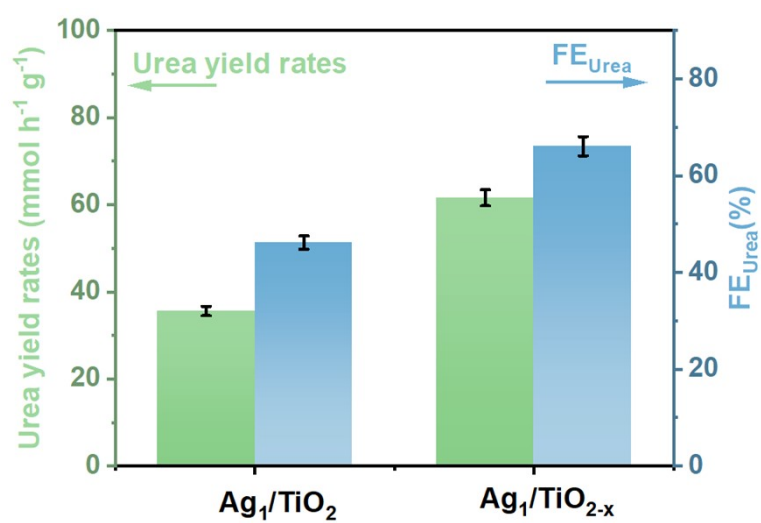


Fig. S18. UECN performance comparison between Ag₁/TiO₂ and Ag₁/TiO_{2-x} after electrolysis for 1 h in flow cell.

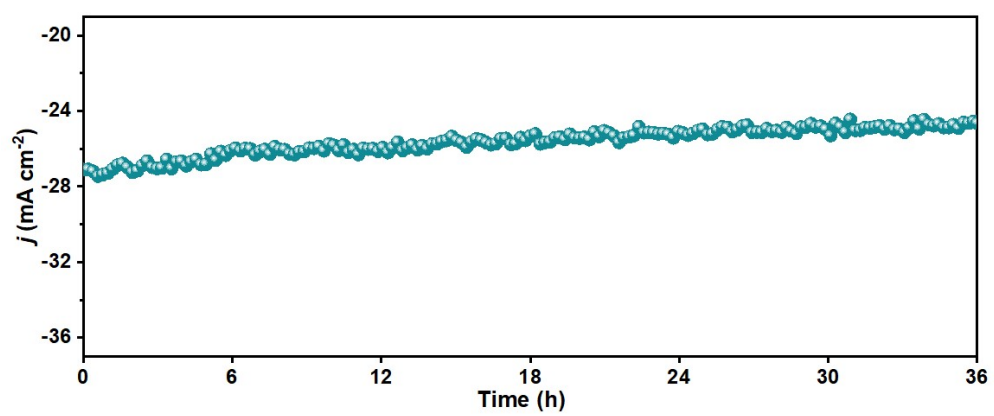


Fig. S19. Long-term test of AgI/TiO_{2-x} in flow-cell at -0.7 V.

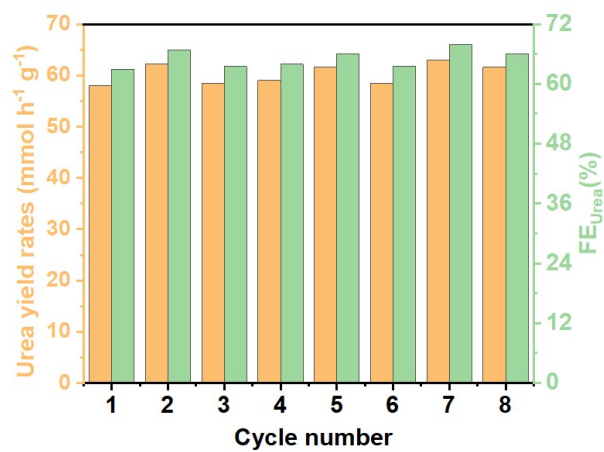


Fig. S20. Cycling test of Ag₁/TiO_{2-x} in flow cell at -0.7 V.

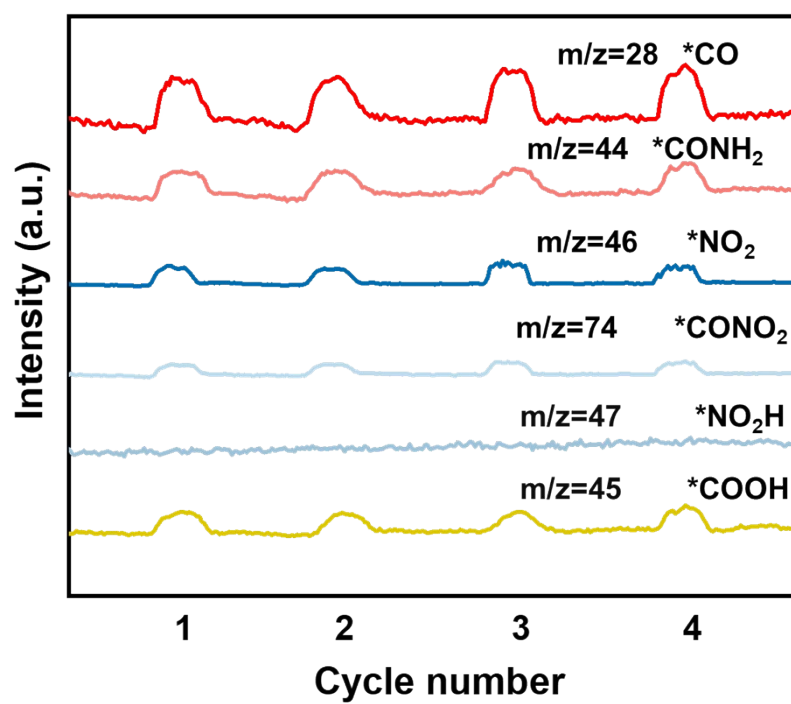


Fig. S21. Online DEMS spectra of Ag₁/TiO_{2-x} during the UECN electrolysis at -0.7 V.

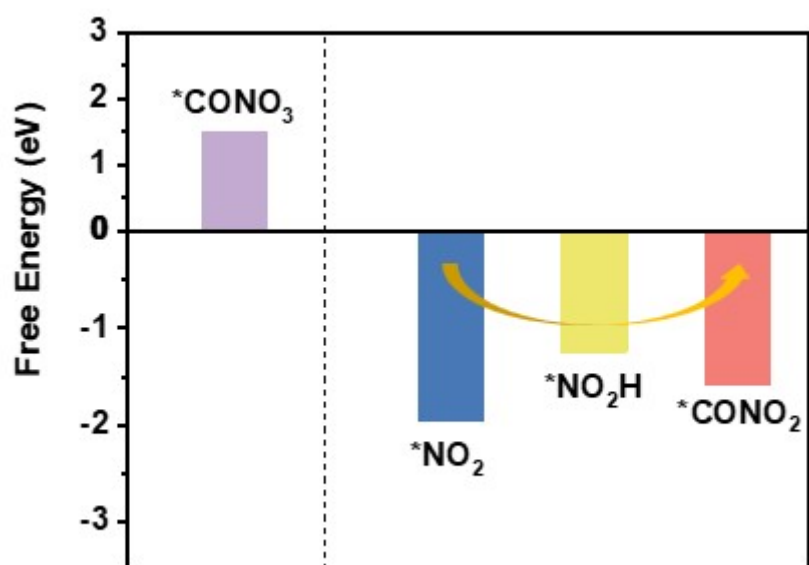


Fig. S22. Free energy diagrams of various potential N-intermediates.

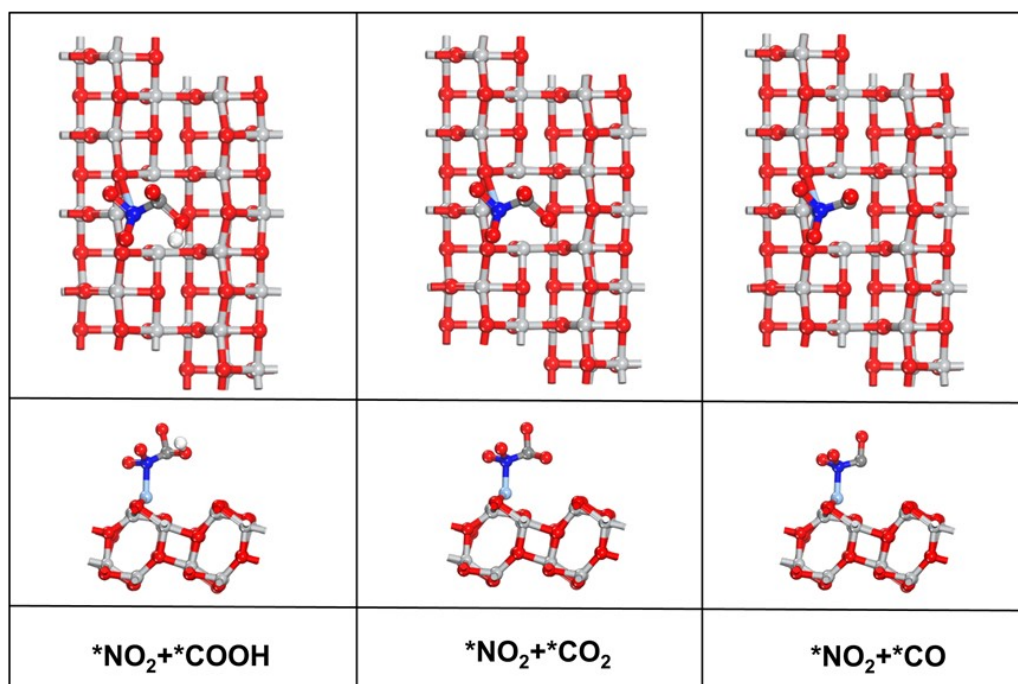


Fig. S23. Optimized structures of the coupling of *NO₂ with various C-intermediates.

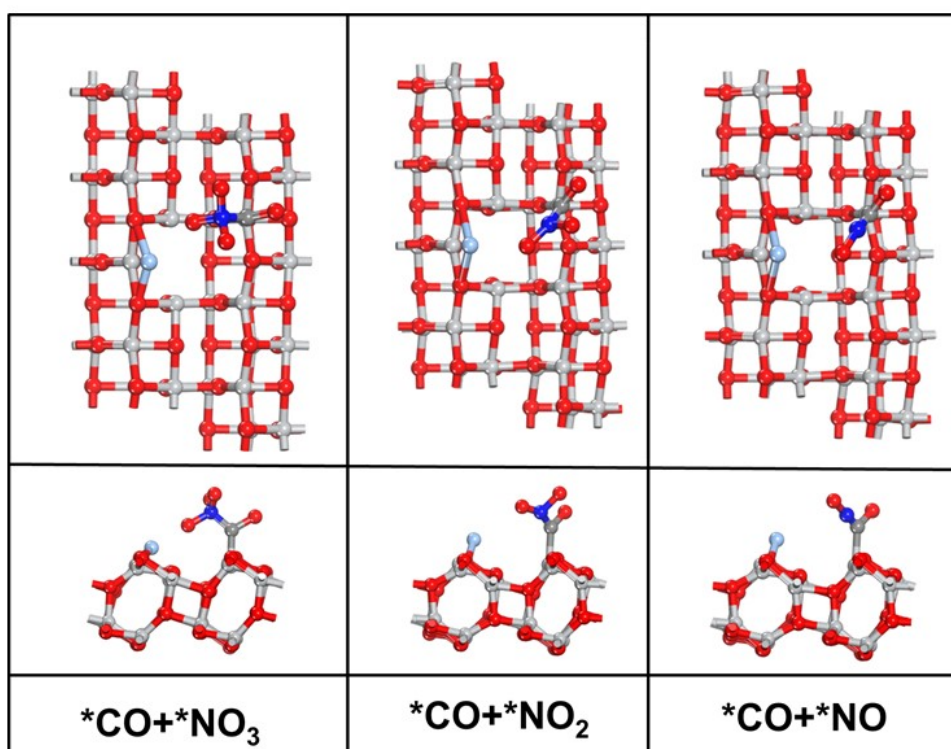


Fig. S24. Optimized structures of the coupling of *CO with various N-intermediates.

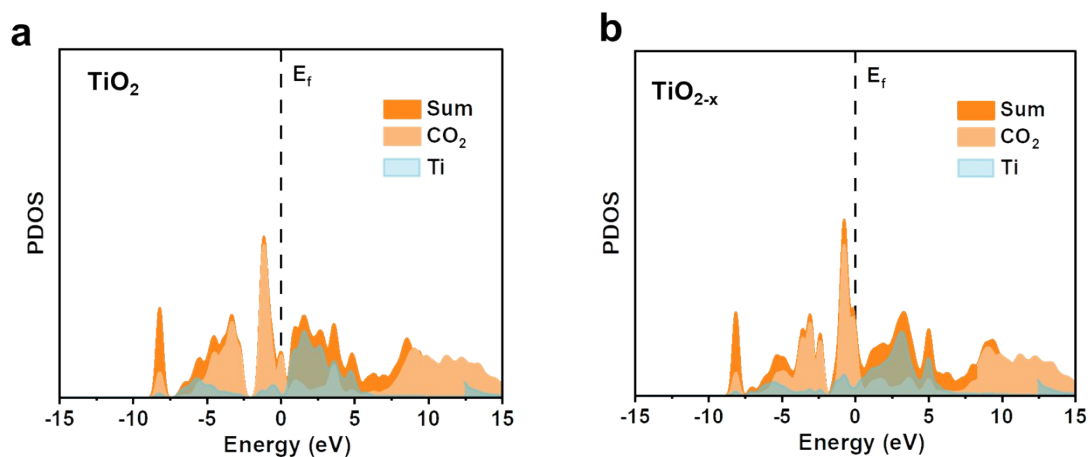


Fig. S25. PDOS profiles of adsorbed CO_2 on (a) TiO_2 and (b) TiO_{2-x} .

PDOS map shows pronounced $\text{Ti}_{\text{OV}}/^*\text{CO}_2$ electronic interaction where Ti_{OV} can effectively donate electrons into the unoccupied orbitals of $^*\text{CO}_2$, facilitating its activation and C=O bond cleavage.

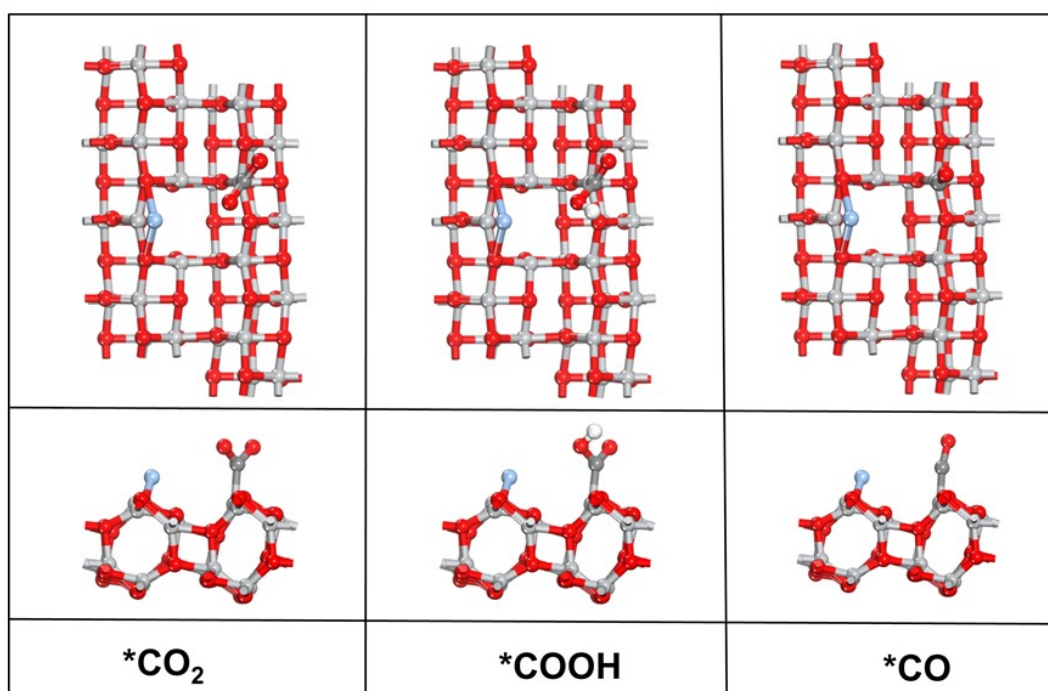


Fig. S26. Optimized structures of the reaction intermediates on Ag₁/TiO_{2-x} along CO₂→*CO pathway.

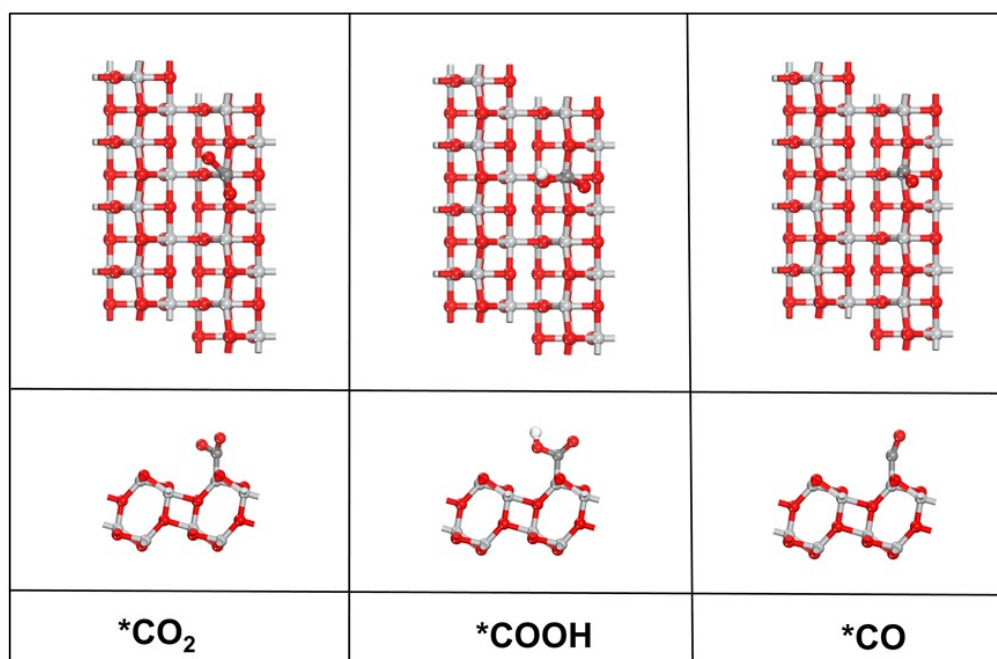


Fig. S27. Optimized structures of the reaction intermediates on TiO₂ along
CO₂→*CO pathway.

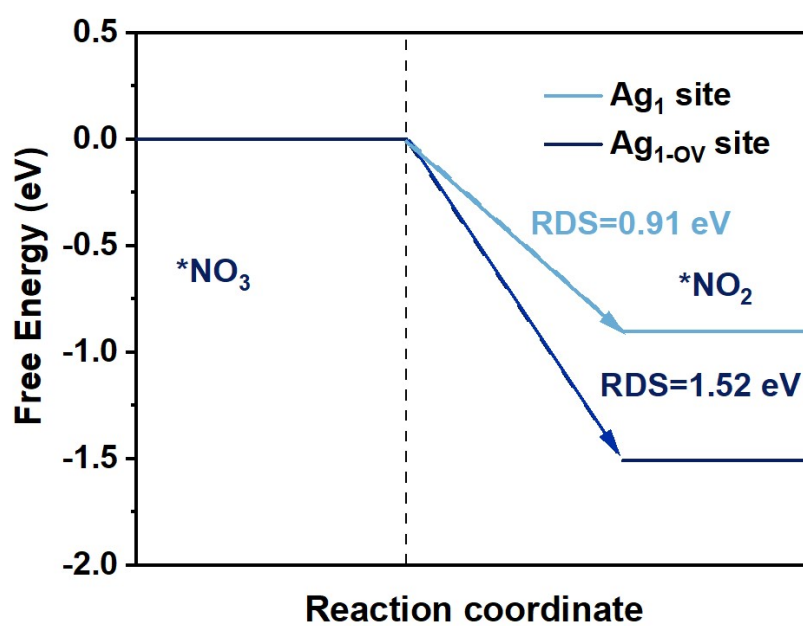


Fig. S28. Free energy diagrams of $*NO_3 \rightarrow *NO_2$ pathways.

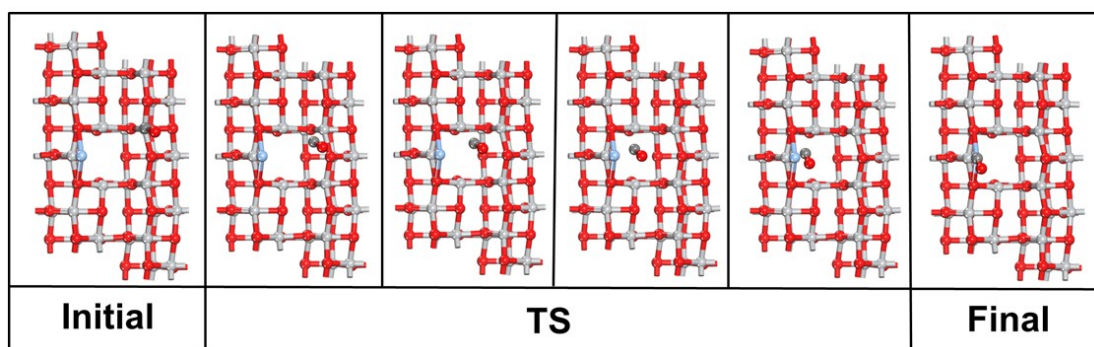


Fig. S29. Optimized structures for the TS calculation of the migration of *CO from Ti_{OV} site to Ag_{I-OV} site on Ag_I/TiO_{2-x}.

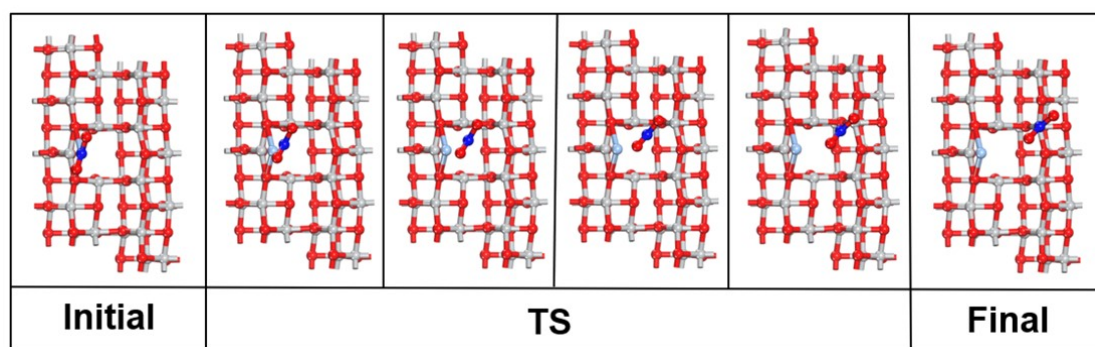


Fig. S30. Optimized structures for the TS calculation of the migration of *NO_2 from AgI-OV site to TiOV site on AgI/TiO_{2-x} .

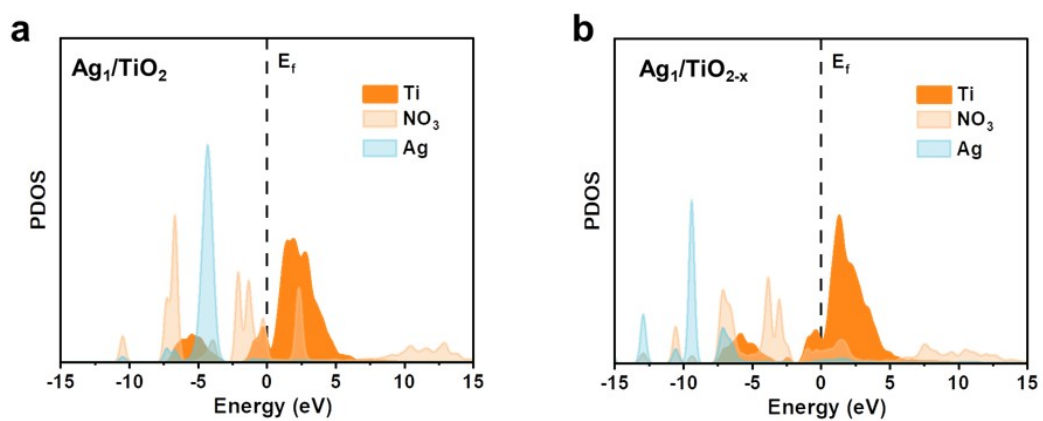


Fig. S31. PDOS profiles of adsorbed NO_3^- on (a) Ag_1/TiO_2 and (b) $\text{Ag}_1/\text{TiO}_{2-x}$.

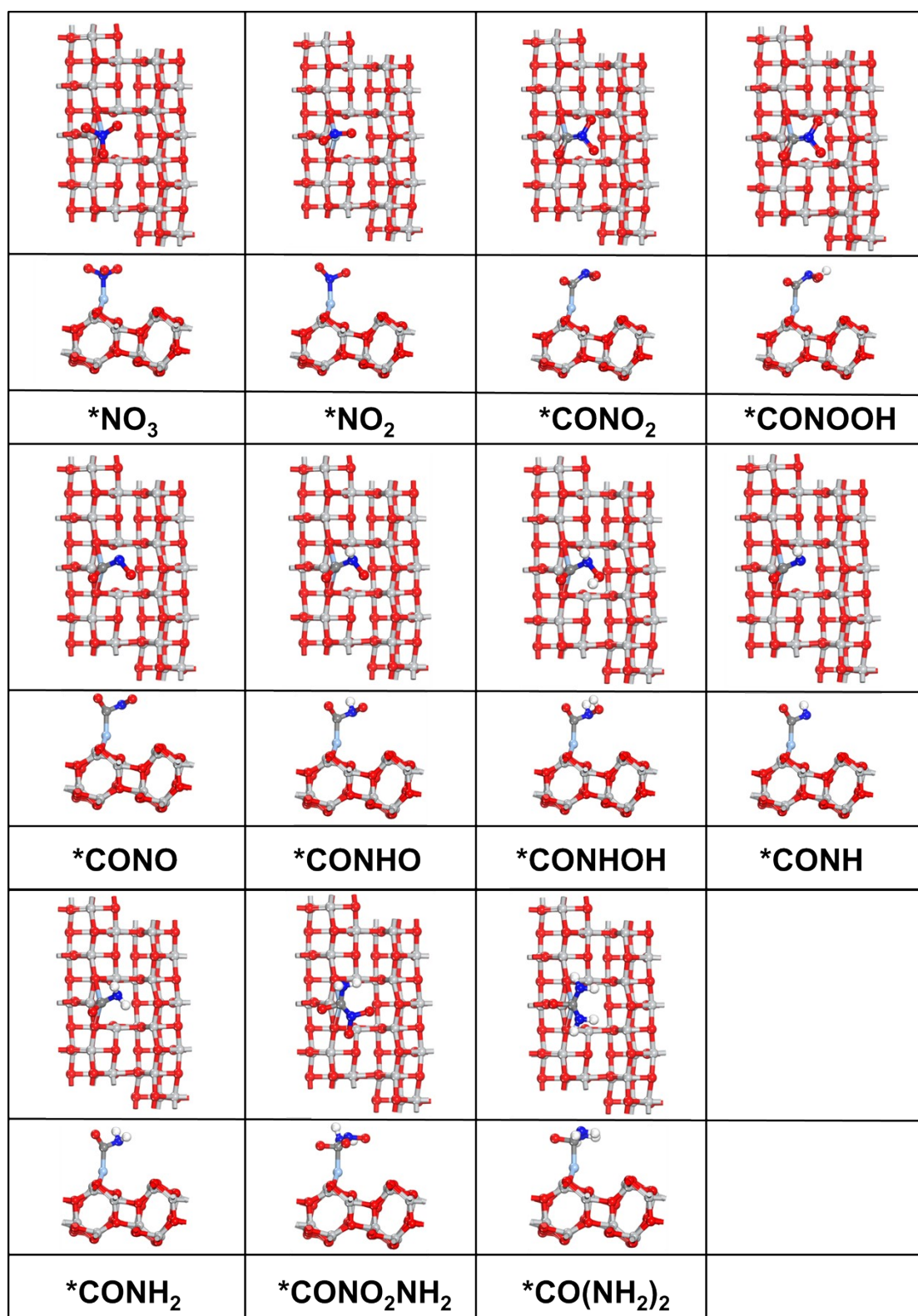


Fig. S32. Optimized structures of the reaction intermediates on Ag₁/TiO_{2-x} along

$*\text{NO}_3 \rightarrow *\text{CO}(\text{NH}_2)_2$ pathway.

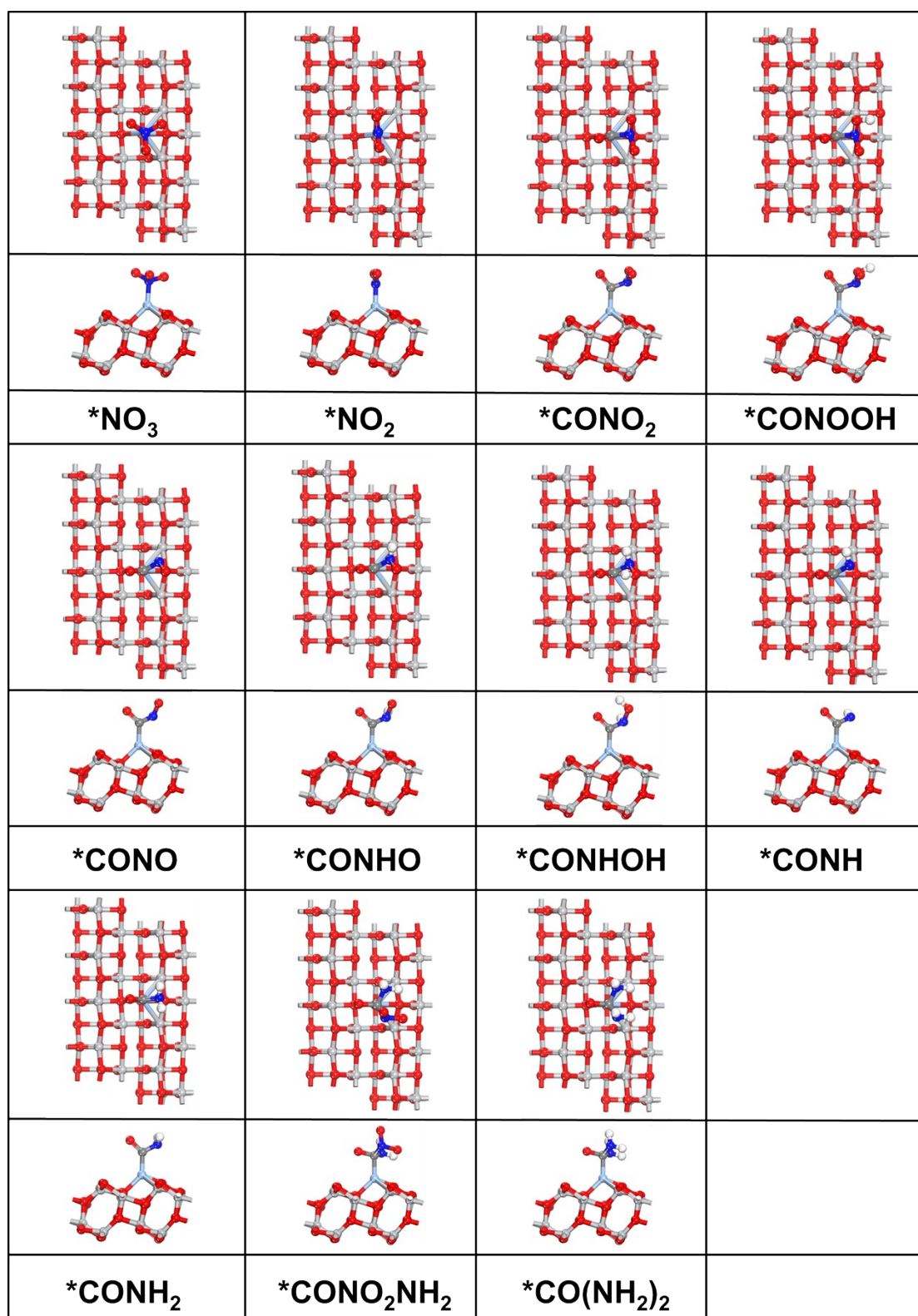


Fig. S33. Optimized structures of the reaction intermediates on Ag₁/TiO₂ along

$\text{*NO}_3 \rightarrow \text{*CO(NH}_2)_2$ pathway.

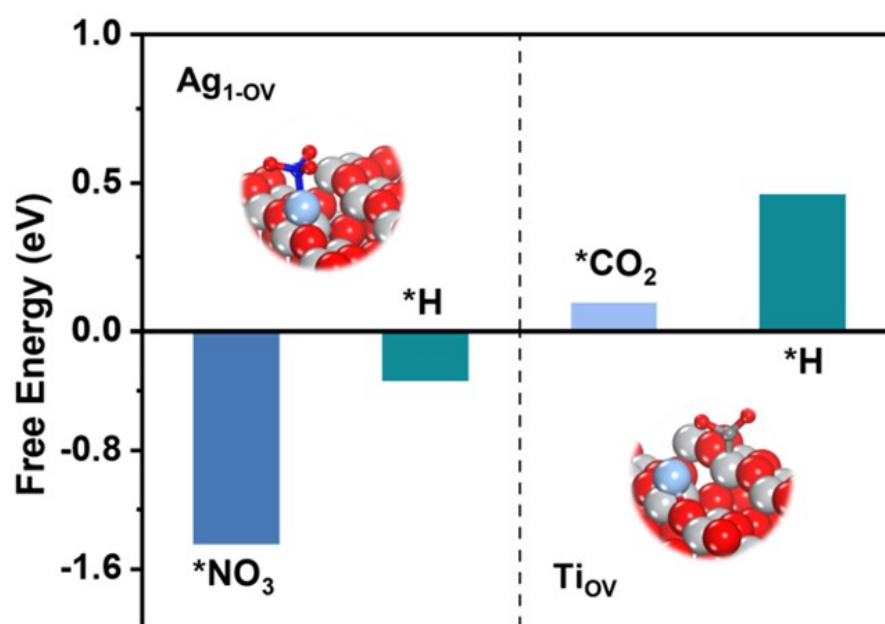


Fig. S34. Binding free energies of *NO₃ and *H on Ag_{1-ov} as well as *CO₂ and *H on TiOV of Ag₁/TiO_{2-x}.

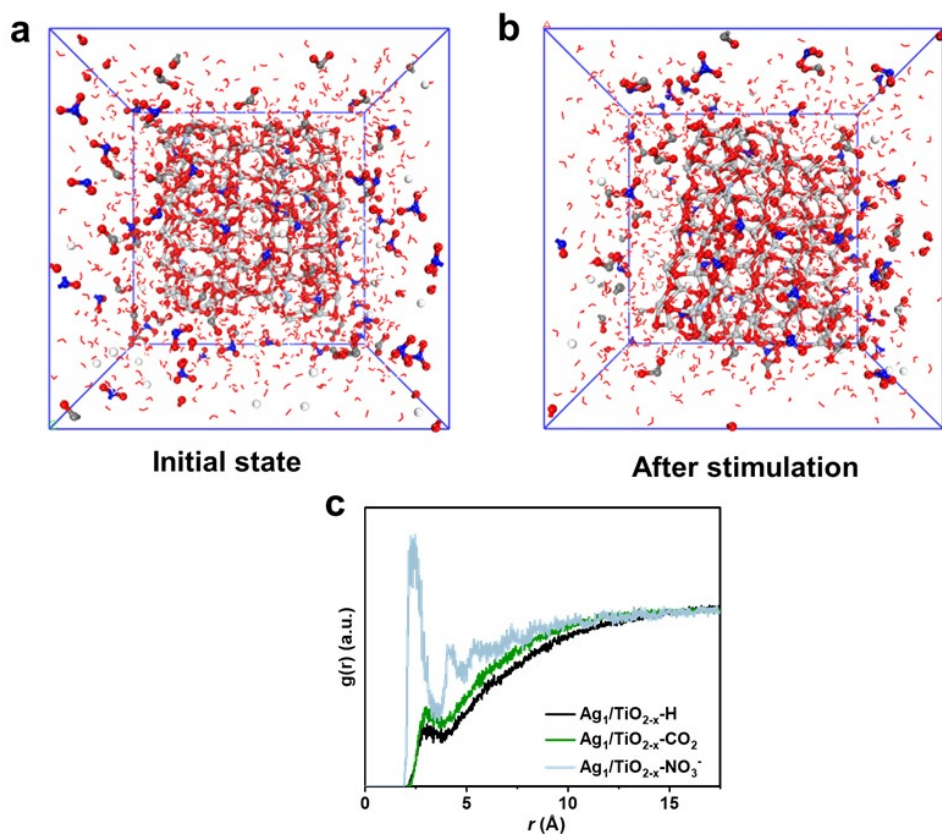


Fig. S35. (a) Initial, (b) final snapshots of the MD simulations of NO_3^- , CO_2 , H_2O and H on $\text{Ag}_1/\text{TiO}_{2-x}$ and corresponding (c) RDF curves of the interactions between $\text{Ag}_1/\text{TiO}_{2-x}$ and $\text{NO}_3^-/\text{CO}_2/\text{H}$.

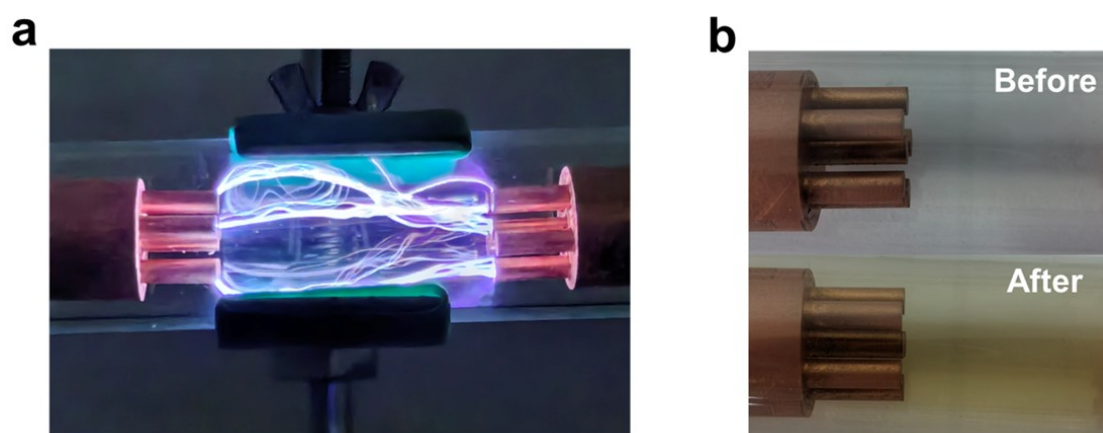


Fig. S36. (a) Photographs for the spark plasma discharge, and (b) corresponding color change in the reaction tube before and after plasma discharge for 10 min.

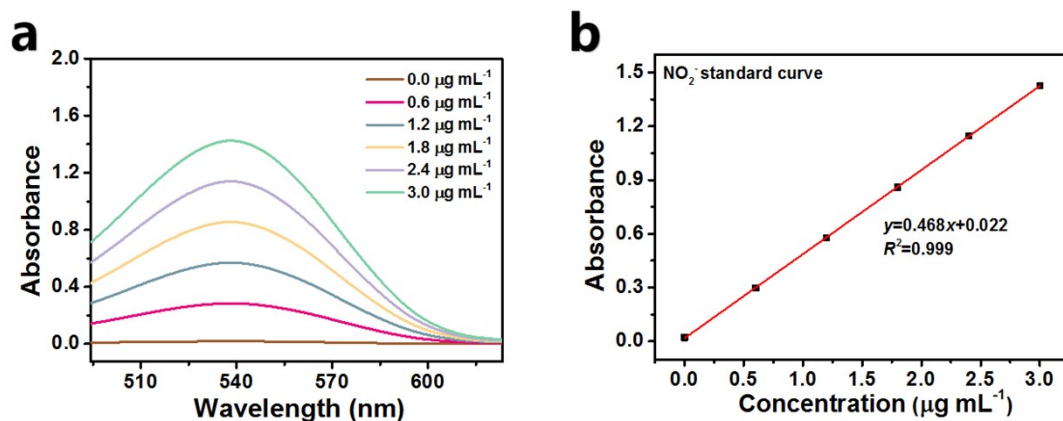


Fig S37. (a) UV-vis absorption spectra of NO_2^- assays after incubated for 20 min at ambient conditions. (b) Calibration curve used for calculation of NO_2^- concentrations.

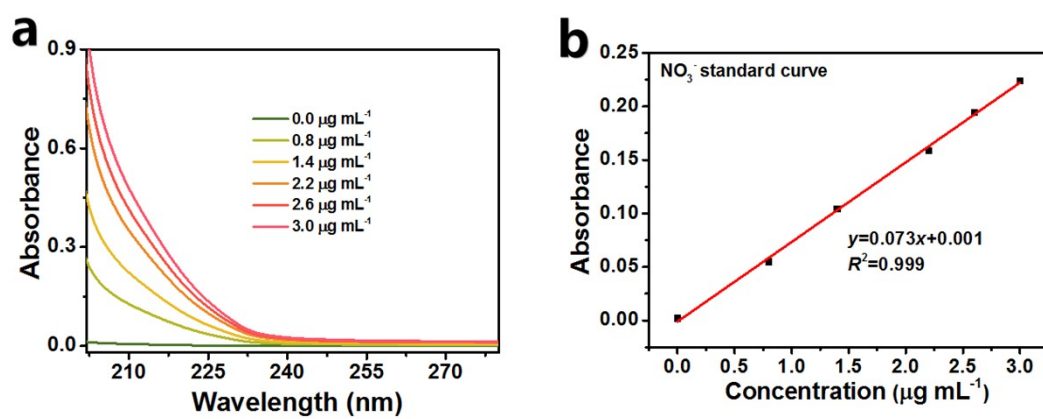


Fig S38. (a) UV-vis absorption spectra of NO_3^- assays after incubated for 20 min at ambient conditions. (b) Calibration curve used for calculation of NO_3^- concentrations.

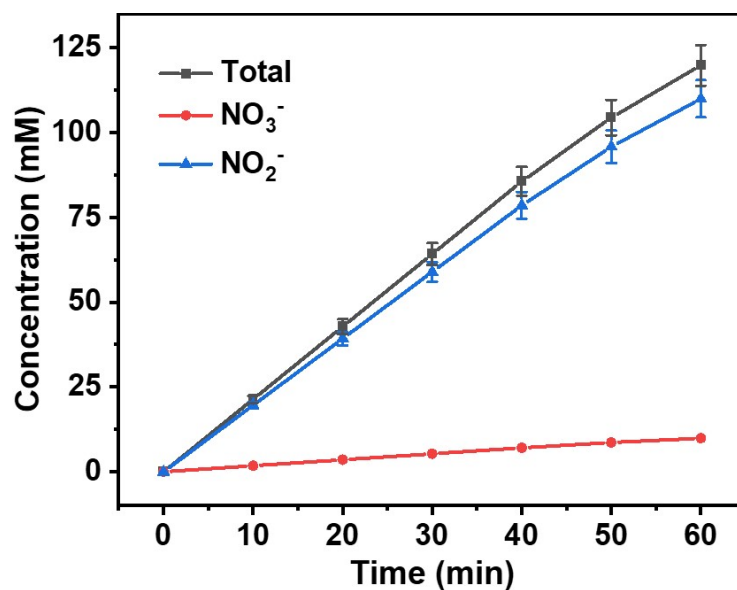


Fig S39. The NO_x⁻ concentration at different plasma reaction times.

It is seen that prolonged plasma discharge time linearly enhances NO_x⁻ concentration, with NO₂⁻ as the dominant species. The persistent NO₂⁻ selectivity (90.5%-92%) throughout extended operation underscores the effective alkaline (1.0 M KOH) absorption where high OH⁻ concentration kinetically inhibits NO₂⁻ oxidation by suppressing the disproportionation reaction.

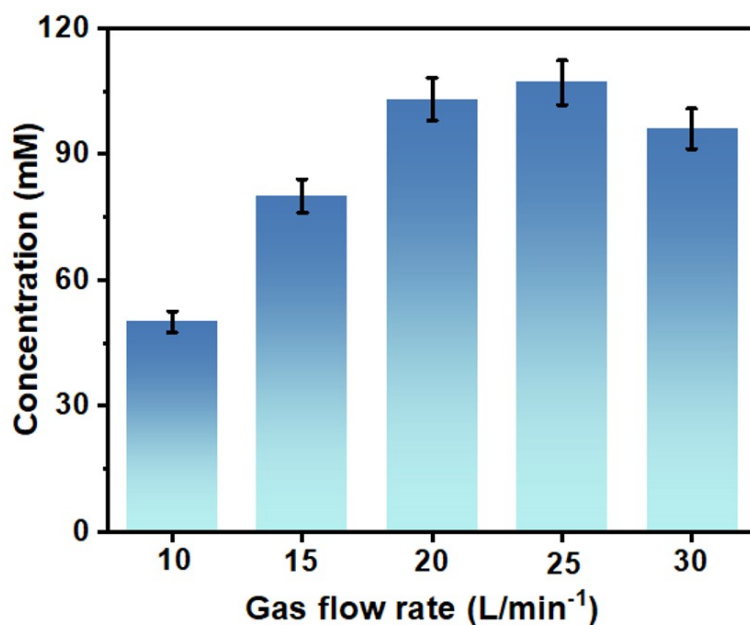


Fig S40. The NO_2^- concentration at different gas flow rates.

It is seen that the air flow rate significantly impacts NO_x^- yield. At 25 L/min , the system achieves peak NO_x^- yield of 118.8 mM after 60 min. This flow rate balances sufficient residence time for radical interactions and effective heat dissipation to prevent NO_2^- degradation. Lower flow rates ($<15 \text{ L/min}$) cause overheating and NO_2^- oxidation, while higher flow rates ($>25 \text{ L/min}$) reduce radical collisions and NO_x formation efficiency.

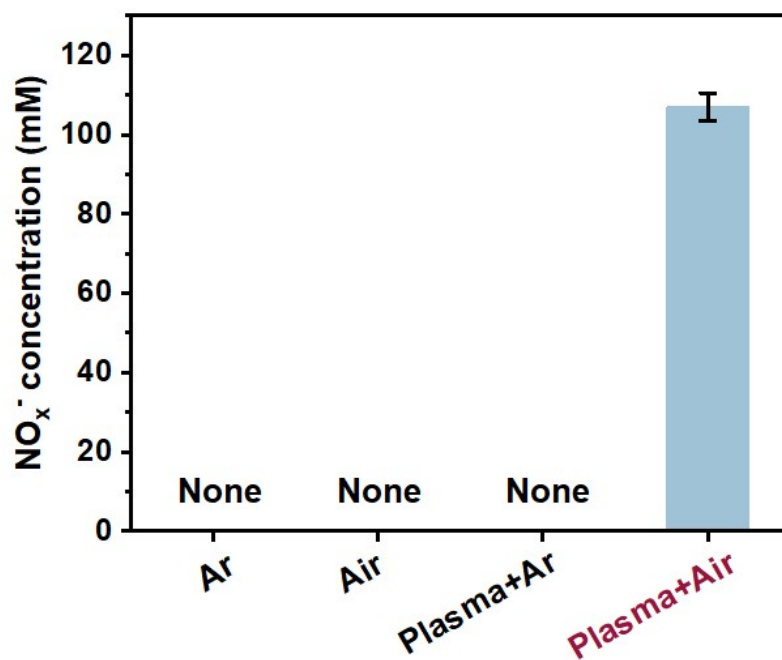


Fig. S41. Amounts of produced NO_x^- on under different conditions.

Control experiments confirm that plasma activation is essential, as NO_x^- is undetectable under Ar-plasma or non-plasma conditions.

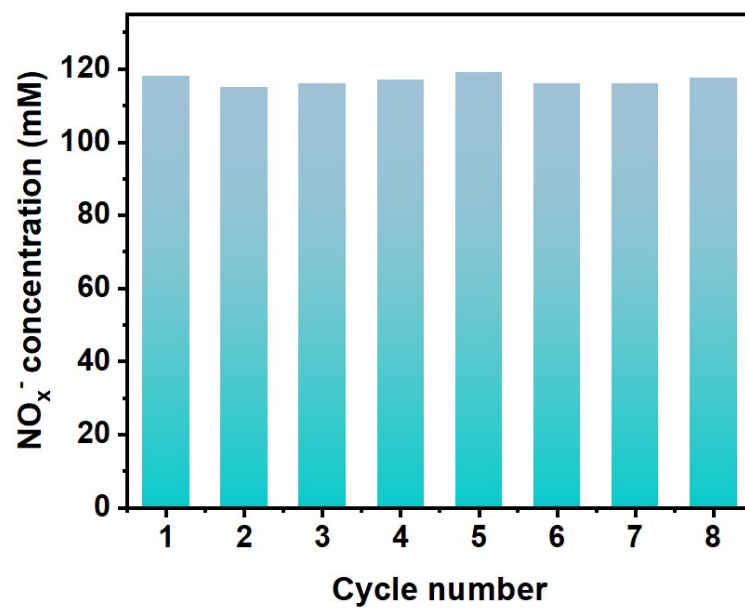


Fig. S42. Cyclic stability tests of plasma-derived NO_x^- production (each cycle for 60 min continuous discharge).

Table S1. Ag K-edge EXAFS fitting results of Ag₁-TiO_{2-x}

Sample	Shell	CN	R (Å)	σ^2 (10 ⁻³ Å)	$ \Delta E_0 $ (eV)	R factor
Ag ₁ /TiO _{2-x}	Ag-O	1.9	2.02	5.9	7.8	0.009

CN is the coordination number, R is interatomic distance, σ^2 is Debye-Waller factor, ΔE_0 is edge-energy shift, R factor is used to value the goodness of the fitting.

Table S2. Comparison of the optimum urea yield rate and FE_{urea} for the recently reported state-of-the-art electrocatalysts at ambient conditions.

Catalyst	N/C source	Urea yield rate (mmol h ⁻¹ g ⁻¹)	FE_{urea} (%)	Potential (V vs REH)	Ref.
In (OH)₃-S	NO ₃ ⁻ + CO ₂	8.88	53.4	-0.6 V	7
Fe(a)@C-Fe₃O₄/CNTs	NO ₃ ⁻ + CO ₂	22.3	16.5	-0.65 V	8
Fe-Ni	NO ₃ ⁻ + CO ₂	20.2	17.8	-1.5 V	9
Vo-CeO₂	NO ₃ ⁻ + CO ₂	15.71	/	-1.6 V	1
F-CNT	NO ₃ ⁻ + CO ₂	6.36	18	-0.65 V	10
m-Cu₂O	NO ₃ ⁻ + CO ₂	29.2	9.43	-1.3 V	11
Vo-InOOH	NO ₃ ⁻ + CO ₂	9.87	51	-0.5 V	12
CuWO₄	NO ₃ ⁻ + CO ₂	1.64	70.1	-0.2 V	13
Vo-SiO₂-6	NO ₃ ⁻ + CO ₂	15.16	60.6	-0.6 V	14
Cu SACs	NO ₃ ⁻ + CO ₂	29.97	28	-0.9 V	15
MoO_x/C	NO ₃ ⁻ + CO ₂	23.83	27.7	-0.6 V	16
AgI/TiO_{2-x}	NO ₃ ⁻ + CO ₂	61.6	66.1	-0.7 V	This work
AgI/TiO_{2-x}	Plasma-derived NO_x⁻ + CO₂	74.6	75.7		

Table S3. Comparison of the NO_x⁻ yield rate and specific energy consumption for the recently reported state-of-the-art non-thermal plasma.

Plasma discharge system	Feeding gas	Absorption solution	NO _x ⁻ yield rate (mmol h ⁻¹)	NO ₂ ⁻ Selectivity (%)	SEC (KW h mol ⁻¹)	Ref.
Rotating gliding arc plasma jet	Air	0.1 M KOH	9.06	99.34	23.18	17
Double reactor glow and spark discharge with Raschig rings	Air	0.01 M H ₂ SO ₄	2.97	27.03	3.79	18
Dielectric Barrier Discharge	Air	H ₂ O	0.13	2.44	23.08	19
Jet-type plasma	Air	1 M NaOH	55.29	98.75	11.18	20
spark discharge	Air	H ₂ O	2.7	--	6.3	21
pulsed high-voltage plasma discharge	Air	1 M NaOH	118.8	90.5	0.857	This work

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