Supporting Information

Photoelectrochemical Urea Synthesis from Nitrate and Carbon Dioxide on GaN Nanowires

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Experimental section

Fabrication of photocathodes

n⁺-p Si wafer was fabricated via a thermal diffusion process using phosphorus and boron dopants in (100) p-type Si wafer. Phosphorus and boron dopants were spin-coated on each front and back side of the polished Si wafer, followed by thermal annealing at 950 °C under nitrogen atmosphere for 4 h. N-type GaN nanowires (NWs) were grown on n⁺-type front side of n⁺-p Si substrate by plasma-assisted molecular-beam epitaxy (MBE) under nitrogen richcondition with a N₂ flow rate of 1.0 standard cubic centimeter per minute (sccm) at temperature of 790 °C for ~2 h. The forward plasma power was 350 W and Ga flux beam equivalent pressure (BEP) was 5×10^{-8} Torr. Ag and Au cocatalysts were loaded onto GaN NWs by photodeposition in an aqueous solution containing metal precursors, methanol sacrificial reagent (11 ml), and water (55 ml). Amounts of loaded metal cocatalysts were controlled by using 1, 10, and 100 µl of 0.2 M AgNO₃ (Sigma-Aldrich) or 0.4 M HAuCl₄ (Sigma-Aldrich) as the metal precursors. GaN/Si wafer on a Teflon holder was put in the bottom of a reactor. Then, the reactor was covered by quartz lid and evacuated for 5 min using a rotary pump. A 300 W Xe lamp (Cermax, PE300BUV) was used as a light source to irradiate the chamber for 30 min. Metal ions were reduced to metal nanoparticles (NPs) on the surface of GaN NWs during light illumination. After the photodeposition, the samples were rinsed with deionized water and dried by air blowing.

Characterizations

The scanning electron microscopy (SEM) was performed using a field-emission scanning electron microscope (MIRA3 TESCAN) with 10 kV acceleration voltage and 15 mm working distance. The scanning-transmission electron microscopy (STEM) and energy dispersive X-ray spectroscopy (EDS) images were collected at 200 kV using JEOL 3100R05 Double Cs Corrected TEM/STEM with a 200 kV accelerating voltage which generated the high-angle annular dark field scanning transmission electron microscopy (HAADF-STEM) images. The X-ray photoelectron spectroscopy (XPS) was measured using a Kratos Axis Ultra XPS with a monochromatic Al Kα source.

Photoelectrochemical measurement

Photoelectrochemical measurement was performed in an H-type cell separated by a Nafion membrane with a three-electrode system using a potentiostat (Biologic SP-300). The Nafion

membrane was pretreated by heating it in H₂O₂ (5%) aqueous solution at 80 °C for 1 h and deionized water at 80 °C for 1 h, respectively, followed by treatment in 0.05 M H₂SO₄ for 1 h and stored in deionized water. Ag/AgCl filled with 3 M KCl was used as the reference electrode and Pt wire was used as the counter electrode. The electrolytes used for measurements was an aqueous solution of 0.5 M KNO₃ (Sigma-Aldrich) and 0.5 M KHCO₃ (Sigma-Aldrich) prepared by dissolving the solid salts in deionized water. The electrolyte was saturated with Ar or CO₂ gas by purging the gas for 30 min prior to measurement. pH values of the electrolytes were measured using a pH meter (Mettler Toledo). The measured potentials (V_{Ag/AgCl}) (V) were converted to the reversible hydrogen electrode (V_{RHE}) (V) by using the Nernst function: $V_{RHE} = V_{Ag/AgC1} + 0.197 + 0.0591 \times pH$. The electrolyte volume in the cathodic compartment of H-cell was 8 ml and continuosly stirred during the reaction. The light source used for the illumination was LCS-100 (ORIEL) and the light intensity with AM 1.5G filter was calibrated by adjusting the distance from the sample to the light source. Linear sweep voltammetry curves were recorded at a rate of 100 mV/s. Chronoamperometric (CA) measurement was conducted at each potential for 1 h. All measurements were conducted at ambient pressure and room temperature. After CA measurement, 1 ml of gas produced in the reaction chamber was injected into the gas chromatographs (Shimadzu GC-2010 plus and Shimadzu GC-8A) to quantify the H₂ and CO products, respectively. Meanwhile, the electrolyte was collected for further spectrocolorimetric measurement of urea, NH₃, NO₂⁻, and N₂H₄ products.

Determination of urea

The concentration of urea was spectrocolorimetrically determined by diacetylmonoxime method.¹ 1 ml of electrolyte was collected from the cathodic compartment. Then, 2 ml acid-ferric solution (prepared by mixing 100 ml phosphoric acid, 300 ml sulfuric acid, 600 ml deionized water, and 100 mg ferric chloride) and 1 ml diacetylmonoxime (DAMO)-thiosemicarbazide (TSC) solution (prepared by dissolving 5 g DAMO and 100 mg TSC in 1,000 ml deionized water) were added. The solution was heated to 90 °C and maintained for 30 min before the UV-vis measurment. After cooling to room temperature, the concentration of urea was recorded by absorbance at a wavelength of 526 nm. For the calibration, urea (Sigma-Aldrich) standard solutions with known concentration was used (Figure S3a).

Determination of NH3

The concentration of NH₃ product was spectrocolorimetrically determined by the indophenol blue method.² 1 ml of electrolyte was collected from the cathodic compartment and mixed with 1 ml of a 1 M NaOH (Sigma-Aldrich) solution containing 5 wt% salicylic acid (Sigma-Aldrich) and 5 wt% sodium citrate (Sigma-Aldrich). Then, 0.5 ml of 0.05M NaClO (Sigma-Aldrich) and 0.1 ml of 1 wt% C₅FeN₆Na₂O (Sigma-Aldrich) solution were added and stored more than 2 h in dark. When the solution has changed color to yellowich green, UV-vis measurement was carried out using Varian 50-Bio. The concentration of NH₃ was determined by absorbance at a wavelength of 655 nm. For the calibration, NH₄Cl (Sigma-Aldrich) standard solutions with known concentration was used (Figure S3b).

Determination of N2H4

1.5 g of $C_9H_{11}NO$ (Sigma-Aldrich) and 7.5 ml of HCl (Sigma-Aldrich) were added into 75 ml of ethanol (Sigma-Aldrich) as the color agent.³ Then 1 ml of the electrolyte was mixed with 1 mL of color reagent. The absorbance at a wavelength of 455 nm was recorded by UV-vis spectrometer to determinte the concentration of N₂H₄. For the calibration, hydrazine hydrate (Sigma-Aldrich) standard solutions with known concentration was used (Figure S3c).

Determination of NO2⁻

0.2 g of N-(1-naphthyl) ethylenediamine dihydrochloride (Sigma-Aldrich), 4 g of paminobenzenesulfonamide (Sigma-Aldrich), and 10 ml of phosphoric acid (Sigma-Aldrich) were added into 50 ml of deionized water as the color reagent.⁴ Then 2.5 ml of the diluted electrolyte were mixed with 0.05 ml of color reagent. The absorbance at a wavelength of 540 nm was recorded by UV-vis spectrometer to determinte the concentration of NO₂⁻. For the calibration, KNO₂ (Sigma-Aldrich) standard solutions with known concentration was used (Figure S3d).

Computational Details

DFT calculations were performed using the Vienna Ab initio Simulation Package (VASP.5).⁵⁻⁷ The PBE functional was used to assume the exchange and correlation terms,⁸⁻⁹ while the dispersive interactions were included using the DFT-D3 methodology developed by Grimme et al., including the BJ-damping function.⁹⁻¹⁰ Projected-augmented Wave potentials (PAW) where used to describe the core electrons, including the d-electrons for gallium.¹¹⁻¹² A Gaussian smearing was employed, using a σ value of 0.1 eV. An energy cutoff of 550 eV was

used for the plane waves, while the convergence criteria were 10^{-6} eV and 0.02 eV/Å for energy and forces respectively. The unit cell, constructed first from bulk GaN, then rotated such that the m-plane is perpendicular to the z direction, used 8 layers, with the lowest four layers frozen in bulk geometry, while the upper four were allowed to relax to the new surface environment. The optimized lattice vectors in x and y correspond to 6.393 Å and 10.422 Å respectively, while the box was expanded in z to 30.000 Å to ensure a vacuum layer between the mirror images. A Monckhorst-Pack type k-grid was used with sample Brillouin zone, using 3x3x1 k points.¹³ In Figure S6, a view of the simulation box is given. Geometry optimizations were followed up by frequency calculations to determine the enthalpic and entropic correction terms for the Gibbs free energy. This was done using the harmonic approximation, using the vaspkit1.3 post-processing package at 298 K and 1 atm pressure.¹⁴ For the internal energy term, optimizations were repeated using the VASPSol extension, to model implicit water using a dielectric constant of 80.0.¹⁵ The Ag(111) surface, experimentally determined to be the predominant facet of the Ag nanoparticles adsorbed on the GaN nanowires, was modelled in a similar way. The surface was constructed from a bulk optimization, with the (111) surface normal adjusted to the z-axis. The vectors spanning the box corresponded to a (8.14, 0.00, 0.00), b (-4.07, 7.05, 0.00) and z (0.00, 0.00, 35.00) in Å, including vacuum spacing in z. A total of four 3×3 layers were used, with the bottom two layers fixed according to the bulk geometry and the upper layers allowed to relax to model surface reconstruction effects. All settings previously described were also used for Ag 3 \times 3 \times 1 k-point grid, and 550 eV cutoff energy, Gaussian smearing, convergence criteria of 10⁻⁶ eV for energy and 0.02 eV Å⁻¹ for forces). An optimization of the intermediates in vacuum was followed by a frequency calculation and optimization in implicit water, as described above. The VESTA program was used to visualize the optimized structures.¹⁶



Figure S1. HAADF-STEM image of Ag/GaN NWs scarped from the Si substrate. Locally segregated Ag NPs showed a bright contrast compared to GaN NWs because of the atomic number difference between Ag (47) and Ga (31).



Figure S2. High-resolution STEM images of Ag30/GaN NW at different locations. Ag NPs were randomly anchored on the surface of GaN NW. Ag NPs were determined to be polycrystalline, predominantly consisting of Ag (111) planes.



Figure S3. X-ray diffraction patterns of Ag3/GaN/Si, Ag30/GaN/Si, and Ag300/GaN/Si photoelectrodes. Ag (111) was observed in Ag30/GaN/Si and Ag300/GaN/Si and Ag (200) was only observed in Ag300/GaN/Si.



Figure S4. (a) Ga $2p_{3/2}$, (b) N 1s, and (c) Ag 3d XPS spectra of Ag3/GaN/Si, Ag30/GaN/Si, and Ag300/GaN/Si photocathodes. Ga $2p_{3/2}$ peaks were deconvoluted with Ga-O and Ga-N bonds. N 1s peaks were separated into N-H and N-Ga bonds with Ga LMN Auger peaks. The Ag 3d peaks consisted mostly of metallic Ag⁰ with little oxidized Ag⁺ states. The atomic ratio was calculated by integration of Ga $2p_{3/2}$, N 1s, and Ag 3d peaks, followed by multiplying the atomic sensitivity factors of each element.

The bonding states of GaN NWs and Ag NPs were investigated by X-ray photoelectron spectroscopy (XPS) analysis. Ga $2p_{3/2}$ spectra were deconvoluted into a major Ga-N peak and a minor Ga-O peak (Figure S4a). In the N 1s spectra, peaks for N-Ga and N-H along with Ga LMN Auger peaks were observed (Figure S4b). Ag 3d XPS spectra of Ag3, Ag30, and Ag300 cocatalysts were deconvoluted by metallic Ag⁰ and oxidized Ag⁺ states (Figure S4c).



Figure S5. Ag 3d XPS spectra of (a) Ag3/GaN/Si, (b) Ag30/GaN/Si, and (c) Ag300/GaN/Si photocathodes, normalized for intensity.



Figure S6. UV-visible absorbance spectra and calibration curves of (a) urea, (b) NH₃, (c) N_2H_4 , and (d) NO_2^- in 0.5 KNO₃ aqueous electrolytes.



Figure S7. (a,c) Faradaic efficiency and (b,d) production rate of products on photoelectrodes with different amounts of Ag NPs. The measurements were carried out at -0.3 and -0.6 V_{RHE} in CO₂-saturated 0.5 M KNO₃ aqueous electrolyte under AM 1.5 G one-sun illumination.



Figure S8. Tilt-view SEM image of Ag/GaN/Si photoelectrodes after the reaction. The microstructure of the Ag/GaN/Si photoelectrode remained unchanged after the stability test.



Figure S9. (a) Ga 3d, (b) N 1s, and (c) Ag 3d XPS spectra of Ag30/GaN/Si photocathode before and after the stability test. There were no observable alterations in surface chemical compositions. The Ag/(Ga+N) ratio (\sim 0.2) remained unchanged after the stability test, indicating that the Ag cocatalysts were securely anchored on the GaN nanowires.



Figure S10. Production rate of H_2 , CO, NH₃, NO₂⁻, and urea for GaN/Si photocathode. The measurements were carried out in (a) Ar-saturated 0.5 M KNO₃ and (b) CO₂-saturated 0.5 M KHCO₃. There was no urea production in either condition.



Figure S11. Production rate of H_2 , CO, NH₃, NO₂⁻, and urea for Ag/GaN/Si photocathode. The measurements were carried out in (a) Ar-saturated 0.5 M KNO₃ and (b) CO₂-saturated 0.5 M KHCO₃. There was no urea production in either condition.



Figure S12. ¹H NMR spectra after the urea synthesis in 0.5 M K¹⁵NO₃ and K¹⁴NO₃ aqueous electrolytes. (a) Low magnification spectrum of K¹⁵NO₃ electrolyte. (b) High magnification spectra of K¹⁵NO₃ and K¹⁴NO₃ electrolytes.

We conducted an isotope labeling test using CO₂-saturated 0.5 M K¹⁵NO₃ and 0.5 M K¹⁴NO₃ aqueous electrolytes. The reactions were carried out on Ag/GaN/Si photoelectrodes at -0.3 V_{RHE} for 1 hour, and the electrolytes were collected post-reaction. We utilized Varian Vnmrs 500 for ¹H nuclear magnetic resonance (NMR) analysis. In the K¹⁵NO₃ electrolyte, the abundant water molecules led to a large peak centered at ~4.5 ppm, which overlapped with the urea peaks (Figure S12a).¹⁷ Consequently, the urea peaks (~5.7 ppm) were embedded within the water signal shoulder, making quantification challenging. Instead, we focused on the ammonium peaks (~6.9 ppm), which exhibited distinct doublet and triplet peaks when using ¹⁵NO₃⁻ and ¹⁴NO₃⁻ sources, respectively (Figure S12b). Although the NH₄⁺ peak intensity was low due to the low faradaic efficiency of NH₃ (< 20%), it is important to note that most of the ¹⁵NH₄⁺ originated from ¹⁵NO₃⁻.



Figure S13. Tilt-view SEM images of Au/GaN/Si photocathodes with different loading amounts of Au cocatalysts.



Figure S14. (a) Ga $2p_{3/2}$, (b) N 1s, and (c) Au 4f XPS spectra of Au6/GaN/Si, Au60/GaN/Si, and Au600/GaN/Si photocathodes. The Au 4f peaks consisted mostly of metallic Au⁰ with negligible amount of oxidized Au⁺ states. (d) Surface Au/GaN ratio obtained from XPS measurement.



Figure S15. (a) LSV curves and (b) faradaic efficiency and production rate of urea for Au6/GaN/Si, Au60/GaN/Si, and Au600/GaN/Si photocathodes.



Figure S16. (a) Faradaic efficiency and (b) production rate of photoelectrochemical urea synthesis reaction for Au60/GaN/Si. The measurements were conducted in CO₂-saturated 0.5 M KNO₃ at applied cathodic bias. (c) Stability test of Au60/GaN/Si at -0.2 V_{RHE} . Each cycle was conducted for 1 hour.



Figure S17. (a) Si 2p XPS spectra of Si, Ag/Si, and Au/Si photocathodes. (b) Ag 3d spectrum of Ag/Si and (c) Au 4f spectrum of Au/Si.



Figure S18. (a) LSV curves of Si, Ag/Si, and Au/Si photocathodes. The photocurrent density was much lower than the GaN/Si photocathodes. (b) Faradaic efficiency of urea for Ag/Si and Au/Si photocathodes. The measurement was carried out in CO₂-saturated 0.5 M KNO₃ under one-sun illumination.



Figure S19. Simulation box used with all frozen atoms shown in dark blue. Large green atoms represent gallium and the small light blue atoms are the nitrogen. Periodic Boundary Conditions are employed in all 3 dimensions.



Figure S20. Free energy profile of different possible pathways after the initial C-N bond formation. The first reduction on the C terminus (red) is energetically favored versus the reduction on the N terminus (blue). After this initial step, that is slightly uphill, reductions on the N terminus (blue) are energetically downhill and favored over coupling with NO₂ (green) and adsorbed *NH₂ (cyan) up until the *OC-NH intermediate. The last reduction on the N terminus is uphill in energy and slightly more demanding than coupling with *NH₂. Once the N terminus is fully reduced, coupling with both NO₂ and *NH₂ is favorable, the latter more so than the former. However, most favorable is coupling of the *OC-NH intermediate with *NH₂ and simultaneous reduction given in along the blue/cyan dotted pathway.

Nitrate Reduction to Ammonia



Figure S21. Free energy profile of the NO_3^- reduction to ammonia. With few exceptions, this is a downhill process. The most challenging step is the reduction of NO_2^- to NO, which requires 0.65 eV. This explains a large amount of NO_2^- side product.

Carbon Dioxide Reduction



Figure S22. Free energy profile of the CO_2 reduction to CO. Note the downhill character until adsorbed COO^- and the high barrier needed to reduce further to CO (black), while the C-N coupling from adsorbed COO^- and NO_2 to form the $O_2C-NO_2^-$ species (red) is favorable.

Carbon-Nitrogen bond formation



Figure S23. Free energy profile of different possible pathways to form the initial C-N bond. From NO₂, bonding to CO₂ from the gasphase with subsequent reduction is highly unlikely (blue), while both the coadsorbtion of reduced COO⁻ on the surface and radical coupling to form the C-N bond (green) and NO₂ reduction to NO₂⁻ (red) is favorable. With 0.65 eV, the subsequent coupling between NO₂⁻ and CO₂ (purple) is also unlikely due to the thermal character in comparison to the reduction to NO, that can be overcome by applying a reductive potential.



Figure S24. Free energy profile of C-N coupling for co-adsorbed *CO and *NO₂ on Ag (111), as well as from adsorbed *NO₂ and CO in the gas phase.

PEC/ EC	Electrode	Reactant	Electrolyte	Onset potential	FE _{uera}	Ref.
PEC	Ag/GaN/Si	NO ₃ ⁻ +CO ₂	0.5 M KNO ₃	-0.2 V _{RHE}	75.6% at -0.3 V _{RHE}	This work
EC	CoWO ₄	NO ₃ ⁻ +CO ₂	0.1 M KNO ₃	-0.1 V _{RHE}	70.1% at -0.2 V _{RHE}	17
EC	In(OH) ₃	NO ₃ ⁻ +CO ₂	0.1 M KNO3	-0.5 V _{RHE}	53.4% at -0.6 V _{RHE}	18
EC	InOOH	NO ₃ ⁻ +CO ₂	0.1 M KNO ₃	-0.4 V _{RHE}	51.0% at -0.5 V _{RHE}	19
EC	TiO ₂ -Nafion	NO ₃ ⁻ +CO ₂	0.1 M KNO ₃	N/A	40% at -0.98 V _{Ag/AgCl}	20
EC	Cu-Zn	NO ₃ ⁻ +CO ₂	0.2 M KHCO ₃ with 0.1 M KNO ₃	-1.35 V _{SCE}	9.28% at -1.02 V _{RHE}	21
EC	Diatomic Fe-Ni	NO ₃ ⁻ +CO ₂	0.2 M KHCO ₃ with 0.05 M KNO ₃	-1.1 V _{RHE}	17.8% at -1.5 V _{RHE}	22
EC	Cu-N-C	NO ₃ ⁻ +CO ₂	0.1 M KHCO ₃ with 0.1 M KNO ₃	-0.6 V _{RHE}	28% at -0.9 V _{RHE}	23
EC	Te-Pd	NO ₂ ⁻ +CO ₂	0.05 M KNO ₃	-1.0 V _{RHE}	12.2% at -1.1 V _{RHE}	24
EC	ZnO nanosheets	NO ₂ ⁻ +CO ₂	0.2 M NaHCO ₃ with 0.1 M NaNO ₂	-0.49 V _{RHE}	23.26% at -0.79 V _{RHE}	25
EC	Cu-TiO ₂	NO ₂ ⁻ +CO ₂	0.2 M KHCO ₃ with 0.02 M KNO ₂	-0.4 V _{RHE}	43.1% at -0.4 V _{RHE}	26
EC	Zn nanobelts	NO+CO ₂	0.2 M KHCO3	-0.72 V _{RHE}	11.26% at -0.92 V _{RHE}	27
EC	PdCu-TiO ₂	N ₂ +CO ₂	0.1 M KHCO3	-0.3 V _{RHE}	8.92% at -0.4 V _{RHE}	28
EC	Bi-BiVO ₄	N ₂ +CO ₂	0.1 M KHCO3	-0.3 V _{RHE}	12.55% at -0.4 V _{RHE}	29
EC	CuPc nanotubes	N ₂ +CO ₂	0.1 M KHCO3	-0.3 V _{RHE}	12.99% at -0.6 V _{RHE}	30
EC	PPy-Pt	N ₂ +CO ₂	0.1 M Li ₂ SO ₄ /0.03 M H ⁺	-0.1 V _{NHE}	7.1% at -0.225 V _{NHE}	31

Table S1. Performance and reaction condition comparison of electrochemical (EC) and photoelectrochemical (PEC) urea synthesis from recent literature.

Table S2. Free energies of reactants, products and intermediates. Given are the electronic energies in implicit solvent, free energy corrections obtained through optimization and frequency analysis in vacuo, total Gibbs free energy for all catalytic intermediates and reaction partners given in eV. Note that for the molecules in gas phase (H₂, O₂, CO₂, NO₂) the electronic energies were determined in vacuo. Given in green are the atoms that were displaced in the frequency calculation.

Intermediate	Electronic Energy [eV]	Free energy correction [eV]	Gibbs free Energy
H_2	-6.77	-0.04	-6.82
O_2	-9.87	-0.45	-10.31
H ₂ O	-14.55	+0.09	-14.46
CO ₂	-22.98	-0.26	-23.241
NH ₃	-19.75	+0.42	-19.33
HNO ₃	-29.00	-0.01	-29.02
HNO ₂	-23.10	-0.12	-23.23
NO ₂	-18.40	-0.40	-18.81
H ₂ NCONH ₂	-48.63	+0.91	-47.73
GaN	-387.91	+0.00	-387.91
GaN-NO ₃ -H ⁺	-419.53	+0.64	-418.90
GaN-NO ₂	-407.72	+0.17	-407.56
GaN-NO ₂ -COO ⁻ H ⁺	-435.47	+0.72	-434.75
GaN-O ₂ NCO ₂ -H ⁺	-436.49	+0.81	-435.68
GaN-OCNO ₂	-424.68	+0.47	-424.21
GaN-OCNOOH	-428.88	+0.73	-428.15
GaN-OCNO	-418.67	+0.38	-418.29
GaN-OCNHO	-423.65	+0.72	-422.92
GaN-OCNHOH	-428.02	+0.95	-427.08
GaN-OCNH	-417.88	+0.65	-417.23
GaN-H ₂ NCONH ₂	-437.73	+1.64	-436.09
GaN-ONCO ₂	-423.82	+0.35	-423.48
GaN-O ₂ NCONO ₂	-441.78	+0.56	-441.22
GaN-O2NCONOOH	-445.77	+0.96	-444.80
GaN-O ₂ NCONO	-436.15	+0.56	-435.60
GaN-O ₂ NCONHO	-440.44	+0.86	-439.57
GaN-O2NCONHOH	-444.39	+1.16	-443.23
GaN-O ₂ NCONH	-435.17	+0.83	-434.34
GaN-O ₂ NCONH ₂	-440.05	+1.05	-438.99
GaN-H ₂ NCONOOH	-443.77	+1.39	-442.37
GaN-H ₂ NCONO	-433.46	+1.02	-432.43
GaN-H ₂ NCONHO	-438.29	+1.30	-436.99
GaN-H2NCONHOH	-442.64	+1.71	-440.94
GaN-H ₂ NCONH	-432.95	+1.37	-431.58
GaN-NO ₂ -H ⁺	-413.52	+0.50	-413.02
GaN-NO	-401.47	+0.15	-401.32
GaN-NHO	-405.60	+0.48	-405.12
GaN-NHOH	-410.41	+0.65	-409.76
GaN-NH	-398.89	+0.39	-398.50
GaN-NH ₂	-403.50	+0.62	-402.88
GaN-H	-391.80	+0.31	-391.49
GaN-COO ⁻ H ⁺	-415.63	+0.19	-415.44
GaN-CO	-403.65	+0.19	-403.46
GaN-O ₂ NCO ₂	-430.65	+0.53	-430.13

Table S3. Free energies of Ag(111), *CO, *NO₂, *NO₂⁻ and *O₂N-CO adsorbed on Ag(111). Electronic energies in implicit solvent, free energy corrections obtained through optimization and frequency analysis in vacuo, total Gibbs free energy given in eV. Adsorption free energies, where applicable, are also provided. Given in green are the atoms that were displaced in the frequency calculation.

Intermediate	Electronic	Free energy	Gibbs free	Adsorption
	Energy [eV]	correction [eV]	Energy	Free Energy
Ag(111)	-105.50	+0.00	-105.50	
Ag-CO	-120.66	-0.04	-120.62	+0.06
Ag-NO ₂	-125.18	+0.11	-125.07	-0.77
$Ag-NO_2^H^+$	-128.48	+0.28	-128.21	+0.52
Ag-O ₂ N-CO	-138.70	+0.30	-138.40	

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