Molecular Additives Improve Selectivity of CO_2 Photoelectrochemical Reduction over Gold Nanoparticles on Gallium Nitride

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Table of Contents

Materials 2
Experimental Methods 2
Figure S1: Optical absorption measurements and Mott-Schottky plot 4
Figure S2: XPS characterization 5
Figure S3: Device fabrication 6
Figure S4: A Nyquist plot 7
Figure S5: Chronopotentiometry 8
Figure S6: Chronoamperometry 9
Figure S7: Faradaic Efficiency 10
Figure S8: SEM 11
Figure S9: SEM 12
Figure S10: XPS 13
Figure S11: Cross-sectional SEM 14
Table S1: Hall measurements 15
Table S2: ICP-MS 15
References 16

Supporting Information

Materials

Pt foil (99.99 % Pt, 25 mm × 25 mm × 0. 05 mm, Sigma-Aldrich), potassium carbonate (99.995 %, Thermo Scientific), ammonium hydroxide solution (ACS reagent, 28 – 30 % NH_3 basis, Honeywell), nitric acid (GR ACS, Sigma-Aldrich), and hydrochloric acid (ACS reagent, ca. 37 % solution in water, Acros Organics) were used as received, unless stated otherwise. Selemion AMV anion-exchange membrane was purchased from AGC Engineering Co. CO_2 (research grade), Ar (ultra-high purity) were purchased from Airgas. Silver colloidal suspension (SPI Flash-Dry) was purchased from SPI Supplies. Loctite EA 9460 UV-resistant epoxy was purchased from Henkel. Water was purified by a Milli-Q Advantage A10 Water Purification System (Millipore) with specific resistance of 18.2 MΩ·cm at 25 °C.

Experimental Methods

Synthesis of p-GaN and Au/p-GaN photocathodes

Commercial p-GaN (4.5 ± 0.5 μm, c-axis 0001 orientation, Mg doping concentration of (3-7) x 10^{18} cm^{-3}) on sapphire (430 ± 25) was purchased from Pam-Xiamen. Prior to depositing metals via electron-beam (E-beam) vapor deposition, p-GaN wafers were cleaned in ethanol and water (30 s sonication each) and dipped into a 30 vol.% NH_4OH solution for 30 s. Then the wafers were rinsed with ultrapure water, mounted onto an E-beam substrate holder, and dried with nitrogen gas. 20 nm Ni and 20 nm Au were deposited sequentially at a base pressure of ca. 1 x 10^{-7} Torr and a deposition rate of 0.5 Å s^{-1} (Ni) and 1.0 Å s^{-1} (Au) using a shadow mask. 1.5 nm Au was then deposited under the same conditions with another shadow mask to avoid co-depositing Au onto Ni/Au. For solid-state current-voltage measurements, Ni/Au and Au contacts (d = 1 mm^2) were deposited using 20 nm/20 nm Ni/Au and 200 nm Au.

Solid-state current-voltage and Hall measurements

Electrical measurements were conducted under an optical microscope using piezoelectric microcontact probes (Imina Technologies, miBots™) to electrically address the contact pads on the p-GaN substrate. The current-voltage (I-V) behavior was then collected through a Keithley 236 source-meter unit and operated with custom-built software. Hall measurements were performed on a Lakeshore Cryotronics M91 Fast Hall System.

X-ray photoelectron measurements

XPS data were collected using a Kratos Axis Nova system with a base pressure of 1 × 10^{-9} Torr. The X-ray source was a monochromatic Al Kα line at 1486.6 eV. Data were analyzed using CasaXPS. Spectral energy for all spectra were calibrated using the C1s peak (284.8 eV).

Optical absorption measurements

Optical absorption measurements were collected in transmission and reflection modes on Cary 5000 spectrometer in the 300 – 800 nm range with 0.1 s time per data point and 1 nm data interval. Prior to performing measurements, beam was aligned using reference samples. Baseline correction was applied using 0 % and 100 % transmission and reflection standards.

Scanning electron microscopy measurements

SEM measurements were performed on Nova NanoSEM 450 using 10 kV high voltage and a spot size of 3.

Photoelectrochemical characterization of p-GaN and Au/p-GaN and CO_2 PEC measurements

All electrochemical experiments were performed in a three-electrode configuration with the p GaN or Au/p-GaN photocathode as the working electrode, a Pt metal counter electrode, and a leakless Ag/AgCl reference electrode (eDAQ, 2 mm OD) in 0.1 M $KHCO_3$ (pH 6.8) electrolyte. The electrolyte was made by sparging 50 mM K_2CO_3 with CO_2 for 12 h. Prior to each measurement the CO_2-saturated 0.1 M $KHCO_3$ solution was additionally sparged with CO_2 for at least 1 h. All electrode potentials were converted to the reversible hydrogen electrode (RHE) scale through the following equation: E vs. RHE = E vs. Ag/AgCl + (0.059 V pH^{-1} x pH) + Ref V. Ref V was obtained for each experiment by calibrating the Ag/AgCl electrode with respect to the HydroFelx hydrogen reference electrode. Linear sweep voltammograms were recorded with 20 mV/s steps. Details of a two-compartment compression cell can be found somewhere else.[1] Prior to each use, the cell was soaked in a 10 vol.% HNO_3 solution, thoroughly rinsed with ultrapure water, boiled in water for 15 min, and dried in an oven at 80 - 100 °C. The light source is provided by a mercury-xenon lamp (6291 Hg(Xe) Arc Lamp is 200 watt and has a 0.5 x 1.5 mm effective arc size) operating with an IR filter. Potentiostatic electrochemical impedance spectroscopy (PEIS) measurements were conducted in the frequency range 200 kHz – 500 mHz with a 10-mV sinusoidal amplitude. Photoelectrochemical CO_2 reduction measurements were conducted in the same cell using 5 sccm of CO_2 or Ar with Au/p-GaN or bare p-GaN as a working electrode, Pt foil as a counter electrode, and a leakless Ag/AgCl reference electrode. Gas-phase products from the cell passed through a liquid trap and then to an Agilent GC (7890A) with Molsieve 5A and Hayesep columns. Products were detected using a thermal conductivity detector (TCD) and flame ionization detector (FID) equipped with a methanizer (Jetanizer by Activated Research Company). Quantitative analysis of gaseous products was based on calibration with five different gas standards.

Synthesis and deposition of molecular additives

Diphenyliodonium triflate (**Add**) was synthesized according to the previously reported procedures.[2] For *in-situ* deposition experiments, the additive was added to 0.1 M $KHCO_3$ solution and PEC CO_2RR CA experiments were conducted in the 10 mM additive solutions under full-spectrum light illumination at -0.2 V vs RHE. Add was additionally pre-deposited by exposing photocathodes to the conditions described above for 1, 5, and 10 min, rinsing the photocathodes with ultrapure water, and replacing the additive solution with the fresh 0.1 M $KHCO_3$ electrolyte. Each pre-deposition experiment was done with a new photocathode sample.

Figures

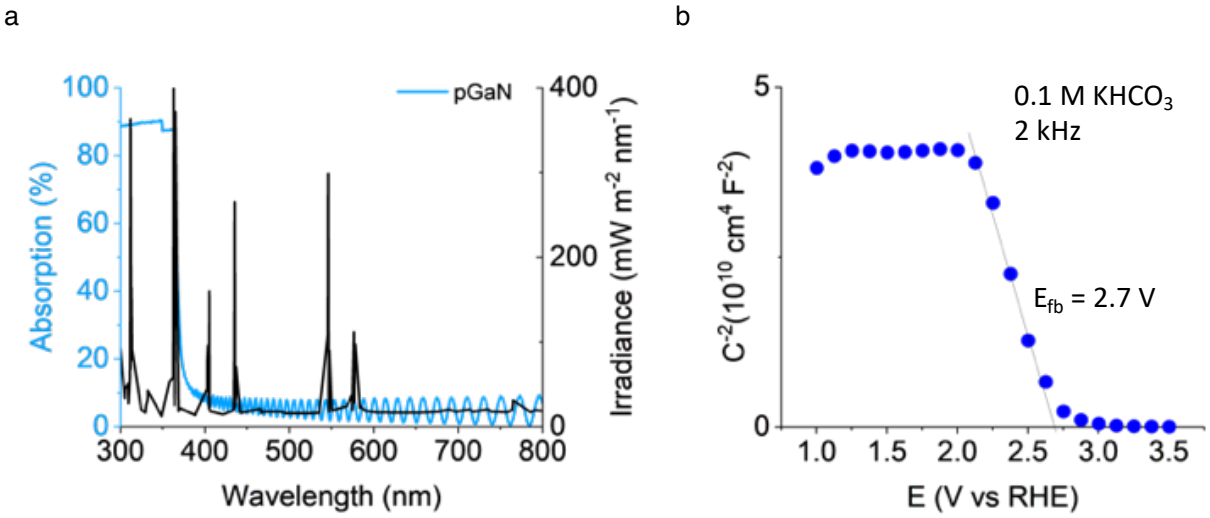

Figure S1. a) Optical absorption of p-GaN substrate, demonstrating absorption in the UV region. The less than 100 % above-the-bandgap absorption is due to the surface reflectivity. Fringes in the visible regime are due to Fabry-Pérot interferences within the GaN/sapphire layer; b) Mott-Schottky plot of electrochemical impedance data of bare p-GaN photocathodes obtained at 2 kHz. The negative slope confirms the p-type character of the GaN substrate. Fitting the data using a Mott-Schottky equation yields a flat-band potential of 2.7 V vs RHE.

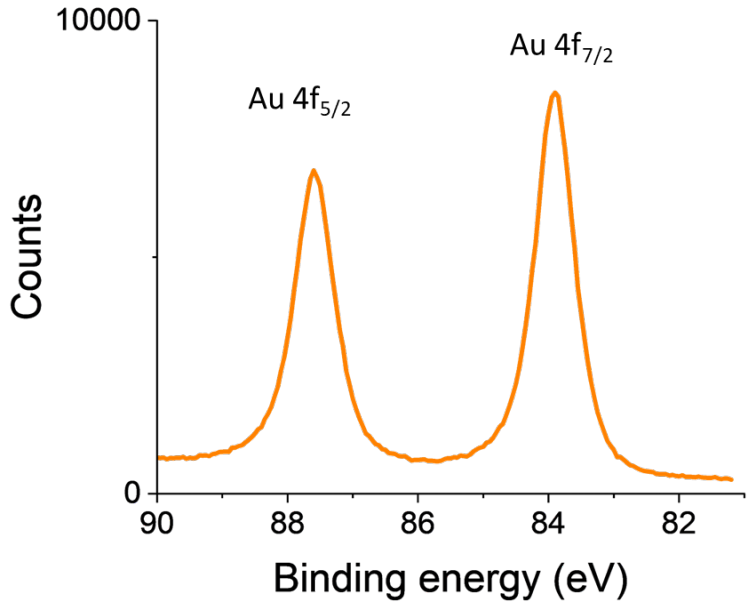

Figure S2. XPS characterization of Au/p-GaN confirming metallic Au (Au 4f5/2 and Au 4f7/2 of 87.6 and 84 eV, respectively).

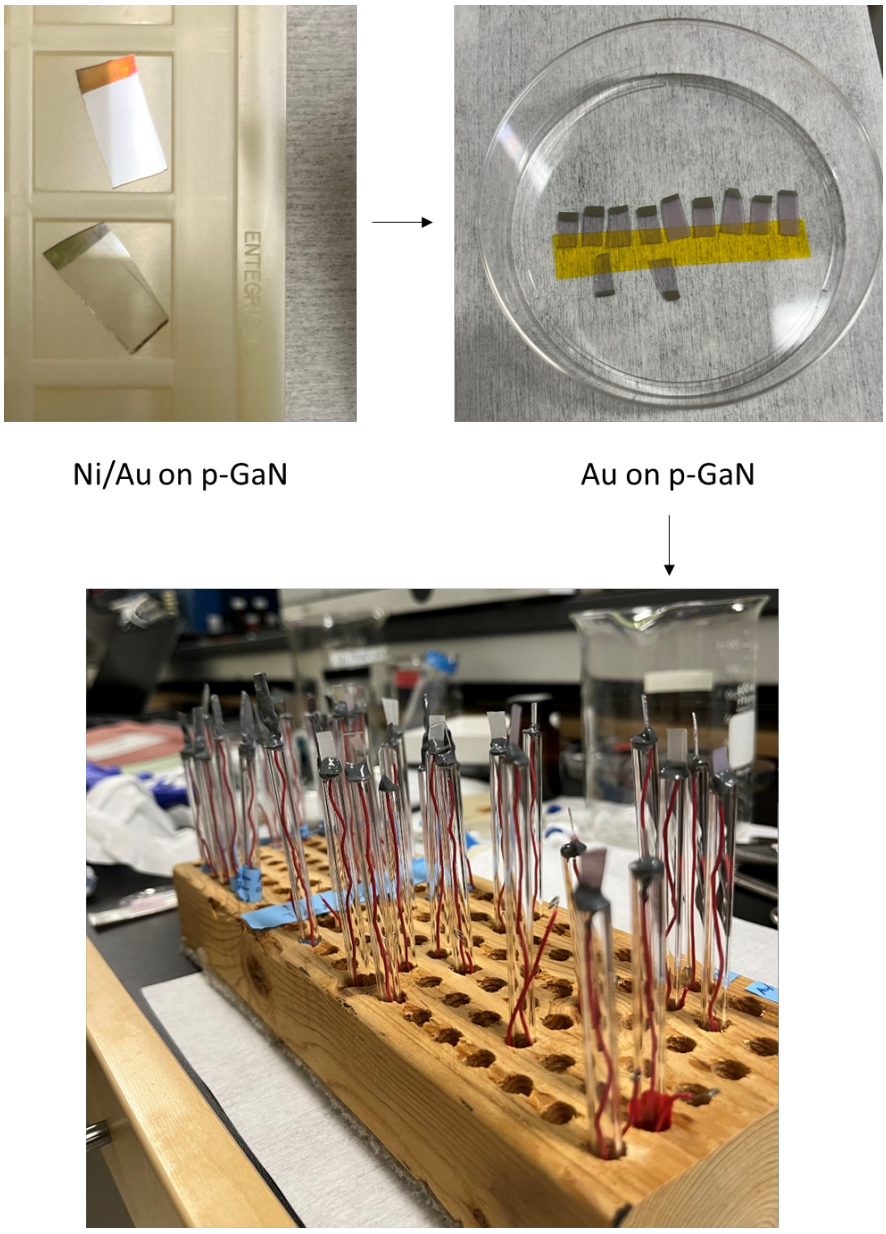

Figure S3. Nickel-gold (Ni/Au) and Au are deposited via electron-beam physical vapor deposition and annealed at 300 °C in air. Working photoelectrodes were made by connecting the Ni/Au ohmic contact to metallic wires using a silver paste and UV-resistant epoxy.

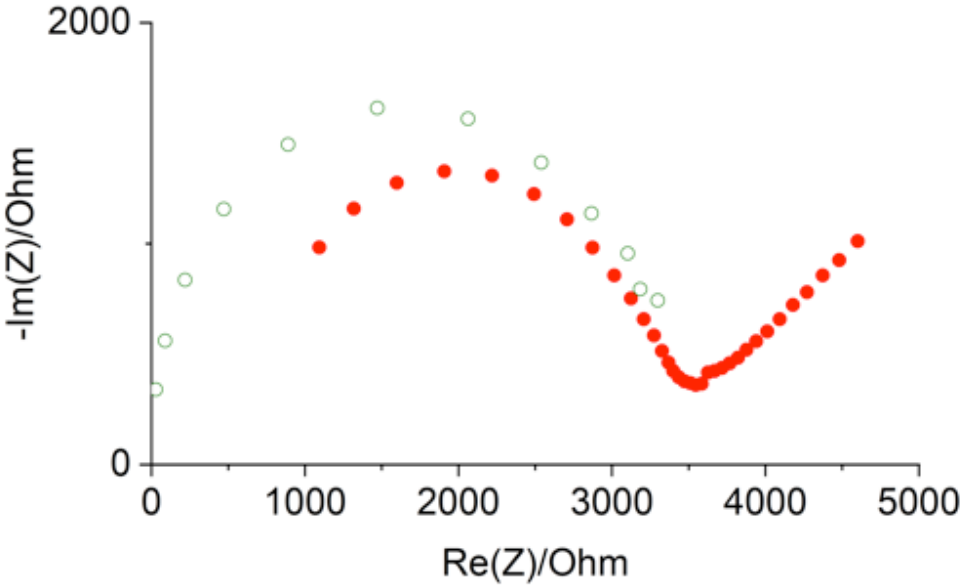

Figure S4. A Nyquist plot demonstrating the solution resistance of Au/p-GaN without the ohmic contact (1 kΩ) and with (30 Ω).

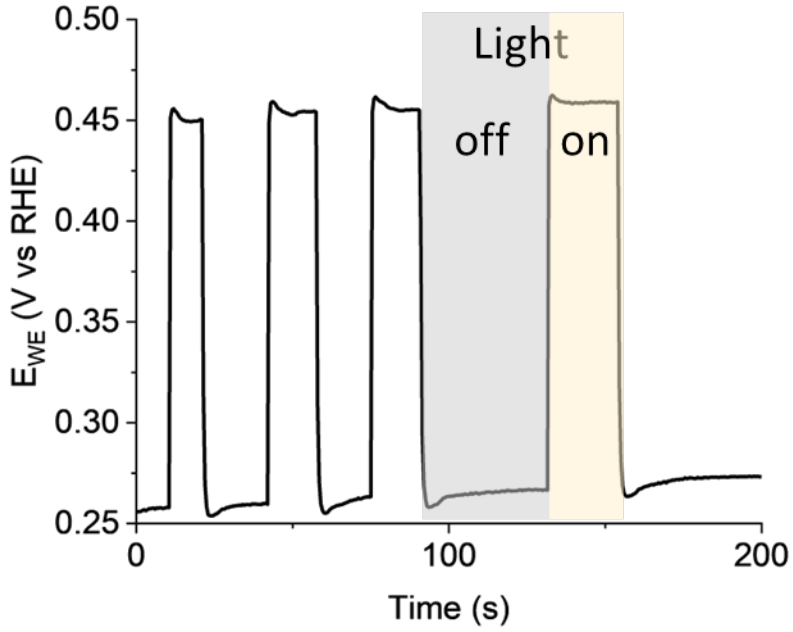

Figure S5. Chronopotentiometry of the open-circuit voltage (V_{oc}) from p- GaN photocathodes under Hg-Xe lamp full-spectrum illumination. The positive shift in V_{oc} upon UV light exposure confirms the p-type character of GaN.

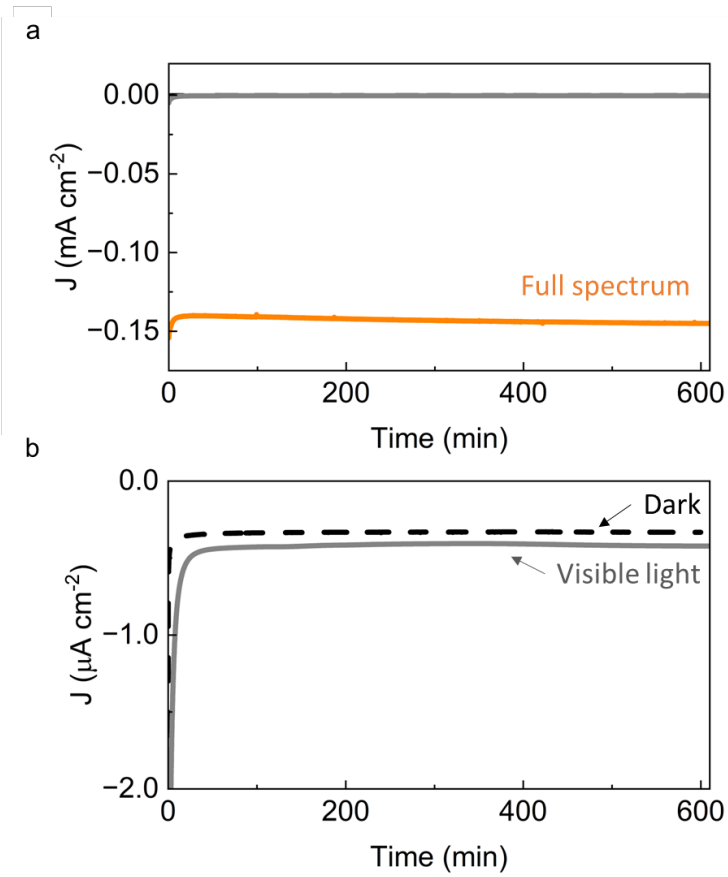

Figure S6. a) CA at -0.2 V with Au/p-GaN under dark, visible light and the full-spectrum illumination; b) CA at -0.2 V with Au/p-GaN under dark and visible light illumination. Note the difference in the y-axis units.

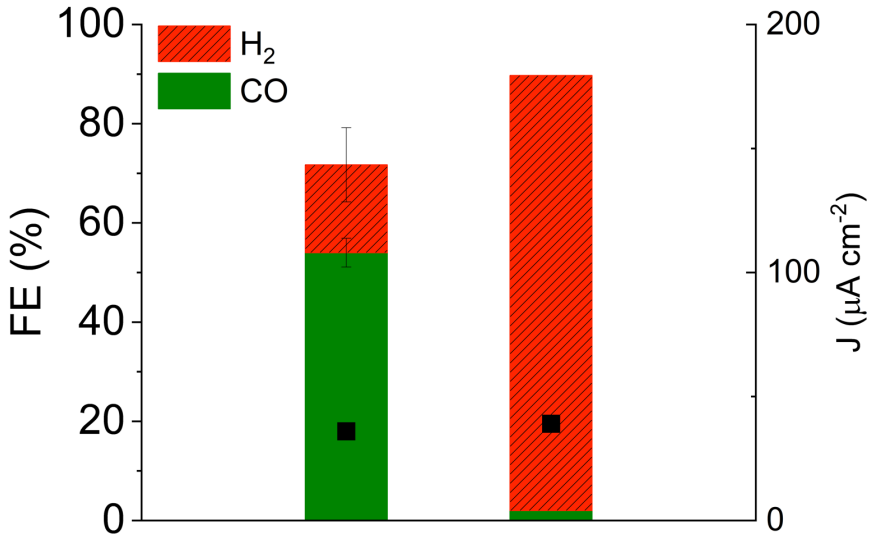

Figure S7. CO FE (bar graphs) and current density (black squares) of Au/p-GaN with *in-situ* deposited **Add** under CO_2 and Ar -0.2 V vs RHE under full-spectrum light illumination.

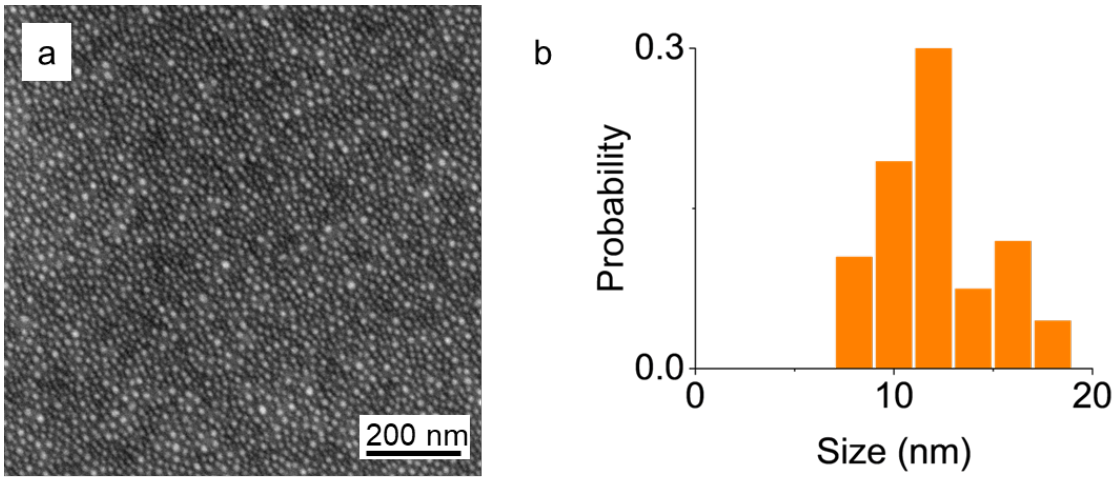

Figure S8. SEM (a) and particle size distribution (b) of Au/p-GaN after PEC CO_2RR at -0.2 V RHE under full-spectrum light illumination.

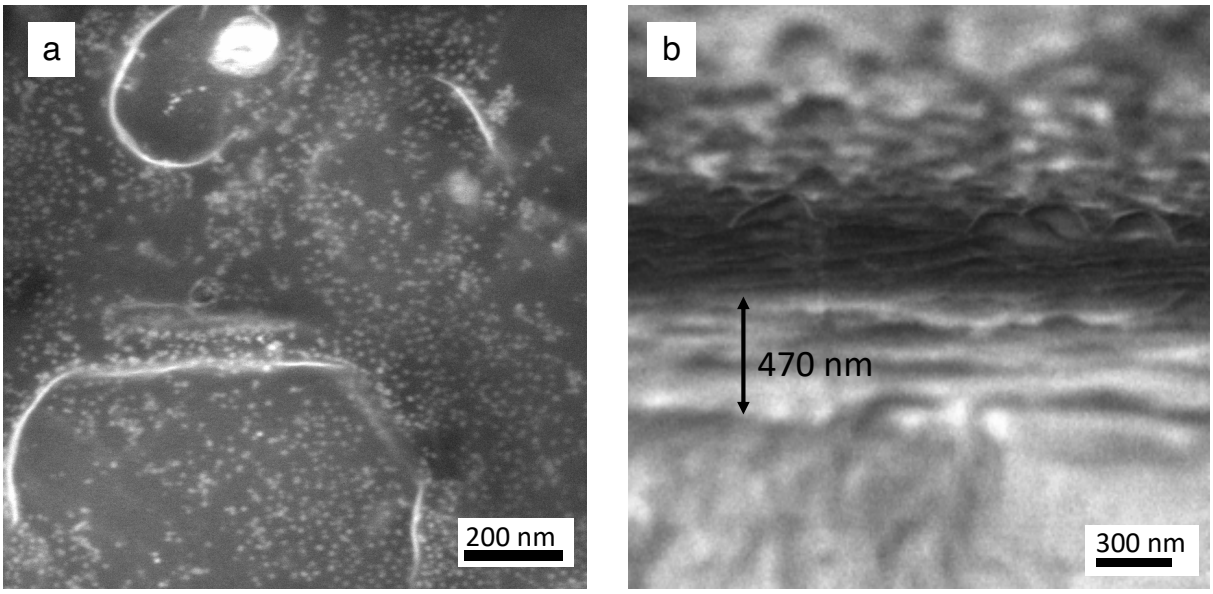

Figure S9. a-b) Representative SEM images of the 40-Add/Au/pGaN sample. Electrolysis conditions: full-spectrum light illumination, -0.2 V vs RHE.

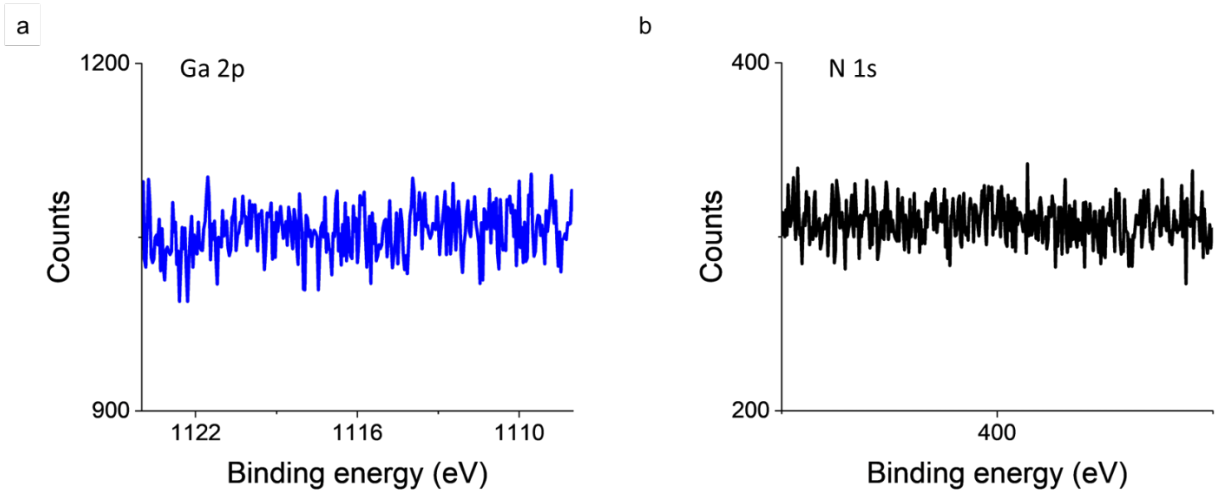

Figure S10. XPS characterization of the p-GaN sample with *in-situ* deposited **Add** after PEC CO_2RR at -0.2 V RHE under full-spectrum light illumination: a) Ga 2p; b) N 1s. The absence of Ga 2p and N 1s peaks suggests the additive thickness of at least 10 nm based on the electron escape depth.[3]

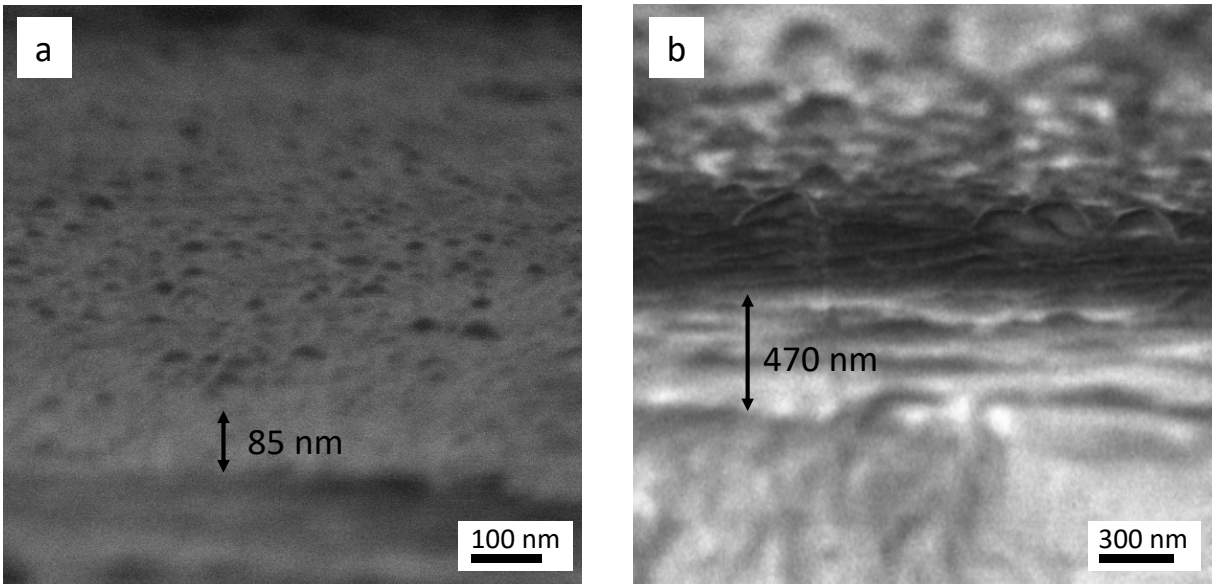

Figure S11. Cross-sectional SEM images of (a) 10-Add/Au/pGaN and (b) 40-Add/Au/pGaN. Electrolysis conditions: full-spectrum light illumination, -0.2 V vs RHE.

Tables

Table S1. Hall measurements of p-GaN. The obtained carrier concentration is consistent with the manufacturer's specification (> 10^{19} cm^{-3} Mg doping).

Mobility, $cm^2 V^{-1} s^{-1}$	**Sheet resistance, kΩ**	**Carrier concentration, cm^{-3}**
4.2	9	$8*10^{17}$

Table S2. ICP-MS results of blank 0.1 M KHCO3 electrolyte and post-electrolysis p-GaN and Au/p-GaN samples.

Sample	**Au, ppb**	**Ga, ppb**
Electrolyte (0.1 M $KHCO_3$)	0.00	0.01
p-GaN	0.01	0.02
Au/p-GaN	0.02	0.02

References

(1) Corson, E. R.; Creel, E. B.; Kim, Y.; Urban, J. J.; Kostecki, R.; McCloskey, B. D. A temperature-controlled photoelectrochemical cell for quantitative product analysis. *Review of Scientific Instruments* **2018**, *89* (5), 055112. DOI: 10.1063/1.5024802 (acccessed 7/11/2023).
(2) Bielawski, M.; Olofsson, B. High-yielding one-pot synthesis of diaryliodonium triflates from arenes and iodine or aryl iodides. *Chemical Communications* **2007**, (24), 2521-2523, 10.1039/B701864A. DOI: 10.1039/B701864A. Li, F.; Thevenon, A.; Rosas-Hernández, A.; Wang, Z.; Li, Y.; Gabardo, C. M.; Ozden, A.; Dinh, C. T.; Li, J.; Wang, Y.; et al. Molecular tuning of CO2-to-ethylene conversion. *Nature* **2020**, *577* (7791), 509-513. DOI: 10.1038/s41586-019-1782-2.
(3) Shinotsuka, H.; Tanuma, S.; Powell, C. J.; Penn, D. R. Calculations of electron inelastic mean free paths. X. Data for 41 elemental solids over the 50 eV to 200 keV range with the relativistic full Penn algorithm. *Surface and Interface Analysis* **2015**, *47* (9), 871-888. DOI: https://doi.org/10.1002/sia.5789.