Photoinduced Surface Oxidation of GaN

Nanowires Facilitates Hydrogen Evolution

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SI1: Computational Model
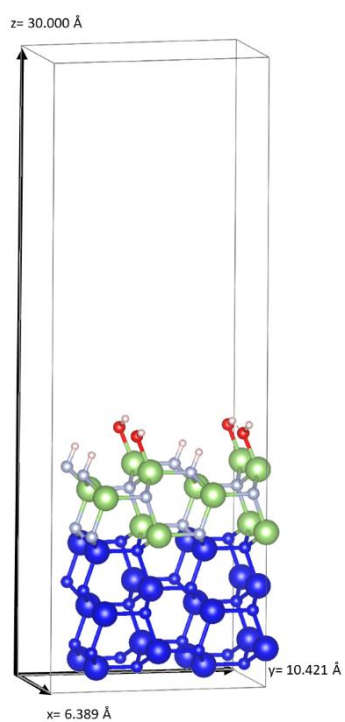

z= 30.000 Å

y= 10.421 Å

x= 6.389 Å

Figure S1: Full simulation box with the frozen atoms shown in dark blue.

SI2: Free Energies of the intermediates

Table S1: Free energies of reactants, products and intermediates in the water oxidation on pristine GaN. 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 (H_2, O_2) 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_2O	-14.55	+0.09	-14.46
Ga*-OH	-454.25	+0.36	-453.89
Ga*-O·	-448.23	+0.04	-448.19
Ga*-OOH	-485.51	+0.39	-458.12
Ga*-OO·	-453.42	+0.09	-453.33

Table S2: Free energies of reactants, products and intermediates in the surface oxidation of GaN. Given are the electronic energies in implicit solvent, free energy corrections obtained through optimization and frequency analysis in vacuo, total Gibbs free energy in eV. Note that for the molecules in gas phase (H_2, O_2, NO) 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 [eV]
H_2	-6.77	-0.04	-6.82
O_2	-9.87	-0.45	-10.31
H_2O	-14.55	+0.09	-14.46
NO	-12.28	-0.54	-12.82
N*-H	-454.25	+0.42	-453.83
N*·	-448.36	+0.09	-448.27
N*-OH	-459.16	+0.46	-458.70
N*-O·	-453.92	+0.11	-453.80
O*-H	-452.11	+0.39	-451.72
O*	-449.22	+0.08	-449.14

Table S3: *Free energies of reactants, products and intermediates in the water oxidation on surface oxidized GaN. Given are the electronic energies in implicit solvent, free energy corrections obtained through optimization and frequency analysis in vacuo, total Gibbs free energy in eV. Note that for the molecules in gas phase (H_2, O_2) 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 [eV]
H_2	-6.77	-0.04	-6.82
O_2	-9.87	-0.45	-10.31
H_2O	-14.55	+0.09	-14.46
Ga*-OH	-433.80	+0.33	-433.46
Ga*-O·	-427.79	+0.03	-427.76
Ga*-OOH	-437.93	+0.41	-437.52
Ga*-OO·	-432.79	+0.09	-432.69

Table S4: *Free energies of reactants, products and intermediates in the hydrogen evolution on pristine GaN. Given are the electronic energies in implicit solvent, free energy corrections obtained through optimization and frequency analysis in vacuo, total Gibbs free energy in eV. Note that for the H_2, 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 [eV]
H_2	-6.77	-0.04	-6.82
H_2O	-14.55	+0.09	-14.46
Ga*-OH	-454.25	+0.36	-453.89
Ga*·	-442.22	+0.00	-441.22
Ga*-H	-446.12	+0.19	-445.93

Table S5: *Free energy of the intermediates on potential proton reduction on the nitrogen site. Electronic energies, apart from H_2 are determined with implicit solvent, free energy corrections are obtained through optimization and frequency analysis in vacuo. The total Gibbs free energies are given in eV. The reaction Gibbs free energy of the reactions are shown below, suggesting that proton reduction does not happen on the nitrogen site.*

| Intermediate	Electronic Energy [eV]	Free energy correction [eV]	Gibbs free Energy [eV]
H_2	-6.77	-0.04	-6.82
N*-H	-454.25	+0.32	-453.93
N*·	-448.36	+0.00	-448.36
Reaction	**ΔG [eV]**		
N*-H + H$^+$+e → N* · + H$_2$	+2.16		
N*· + H$^+$ + e$^-$ → N*-H	-2.16		

Table S6: *Free energies of reactants, products and intermediates in the hydrogen evolution on oxidized GaN. Given are the electronic energies in implicit solvent, free energy corrections obtained through optimization and frequency analysis in vacuo, total Gibbs free energy in eV. Note that for H_2, 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 [eV]
H_2	-6.77	-0.04	-6.82
H_2O	-14.55	+0.09	-14.46
Ga*-OH	-433.80	+0.33	-433.46
Ga*·	-421.10	+0.00	-421.10
Ga*-H	-425.79	+0.19	-425.60

Table S7: *Free energies of reactants, products and intermediates in the following oxidation step after initial surface oxidation. Given are the electronic energies in implicit solvent, free energy corrections obtained through optimization and frequency analysis in vacuo, total Gibbs free energy in eV. Given in green are the atoms that were displaced in the frequency calculation. Below are the potentials for oxidation on the nitrogen and oxygen site respectively.*

Intermediate	Electronic Energy [eV]	Free energy correction [eV]	Gibbs free Energy [eV]
H_2	-6.77	-0.04	-6.82
Ga*-OH	-449.22	+0.34	-448.88
Ga*-O·	-443.19	+0.00	-443.19
N*-H	-449.22	+0.32	-448.90
N*·	-443.39	+0.00	-443.39
*OH → *O·		N*H→ N*·	
2.28 V		2.10 V	

SI3: Pathways including molecular oxygen
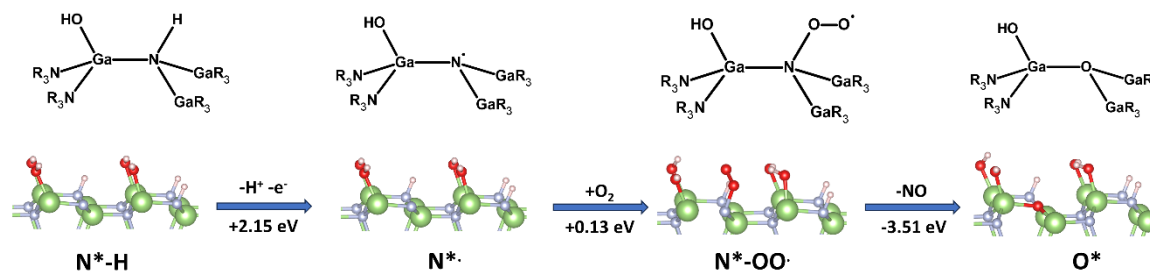
Scheme S1: *Possible oxidation pathway including molecular oxygen. After oxidation on the N surface site, diatomic oxygen attacks at the site, forming N*-OO radical, significantly weakening the Ga-N bond. An oxygen atom then inserts into that bond, expelling NO and forming the GaO* final structure, with integrated oxygen.*

Table S8: *Free energies of reactants, products and intermediates in the surface oxidation of GaN involving molecular oxygen. Given are the electronic energies in implicit solvent, free energy corrections obtained through optimization and frequency analysis in vacuo, total Gibbs free energy in eV. Note that for the molecules in gas phase (H_2, O_2, NO) the electronic energies were determined in vacuo. Given in green are the atoms that were displaced in the frequency calculation.*

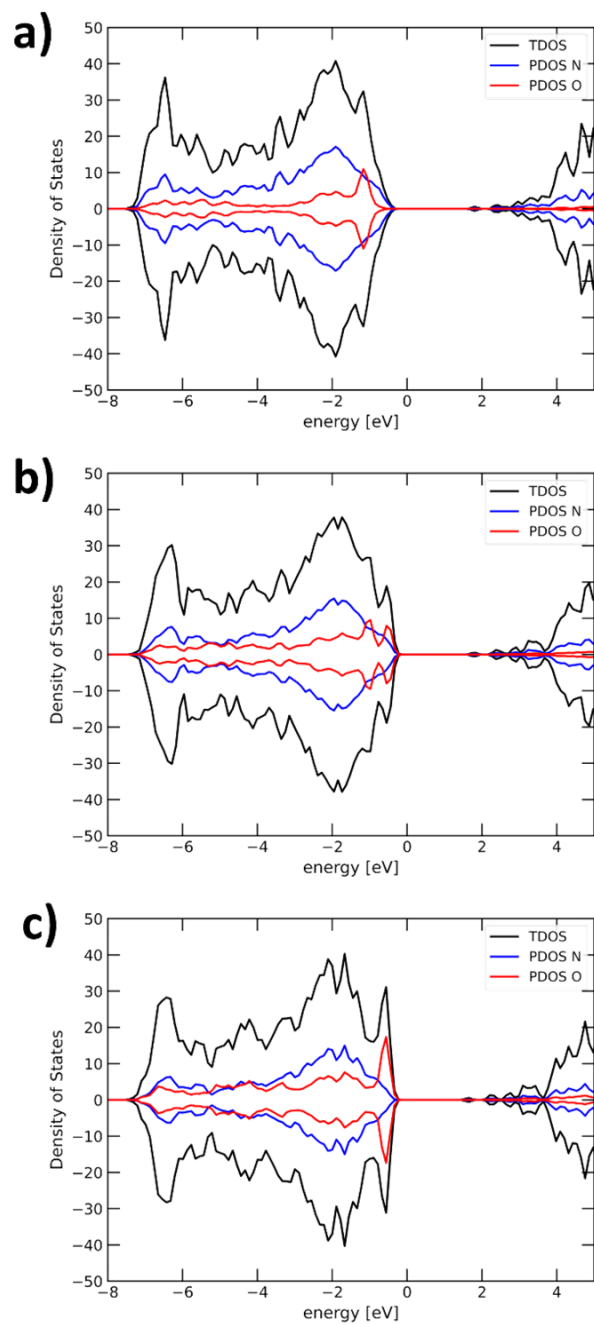| Intermediate	Electronic Energy [eV]	Free energy correction [eV]	Gibbs free Energy [eV]
H_2	-6.77	-0.04	-6.82
O_2	-9.87	-0.45	-10.31
NO	-12.28	-0.54	-12.82
N*-H	-454.25	+0.42	-453.83
N*·	-448.36	+0.09	-448.27
N*-OO·	-458.65	+0.20	-458.46
N*-O·	-453.92	+0.11	-453.80
O*	-449.22	+0.08	-449.14

SI4: Density of States

Figure S2: *Total Density of states (black) and projected density of states on nitrogen (blue) and oxygen (red) for a) pristine GaN surface, b) partially oxidizes GaN surface, c) fully oxidized GaN surface.*

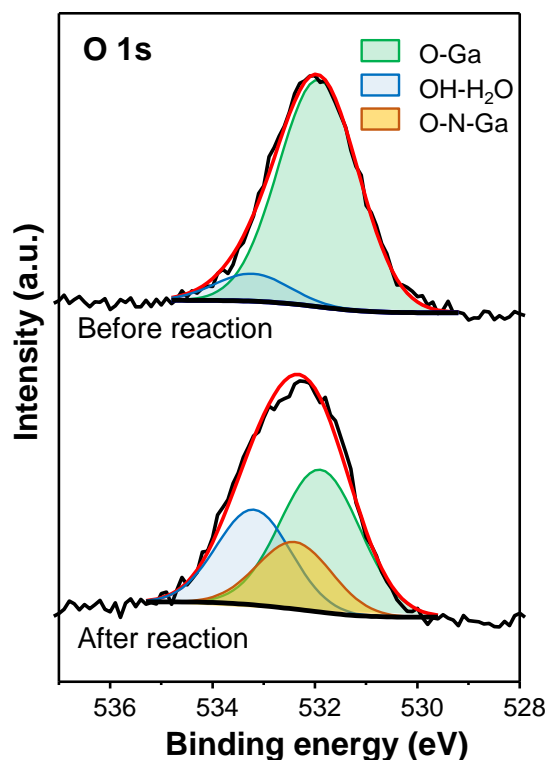## SI5: XPS spectra of GaN nanowires before and after photoelectrochemical reaction

Figure S3: *O 1s core-level X-ray photoelectron spectroscopy spectra of GaN nanowires before and after photoelectrochemical reaction for 10 h at -0.4 V_{RHE} under 1 sun light.*

Before the reaction, the O 1s spectrum exhibited a relatively sharp profile, deconvoluted into a major O-Ga peak and a minor surfaced-adsorbed $OH-H_2O$ peak (Figure S3). However, after conducting the reaction for 10 hours under light, the O 1s spectrum broadened. This broadening attributed to an increase in the intensity of the $OH-H_2O$ peak, indicating an elevated number of OH or H_2O species adsorbed on the GaN NWs during the reaction in the aqueous electrolyte. More interestingly, there was a decrease in the intensity of the O-Ga peak and the emergence of a new O-Ga-N peak.
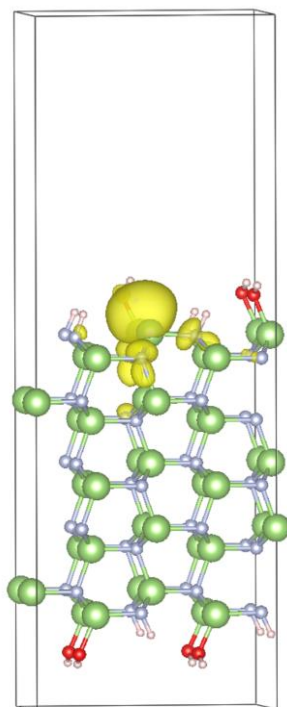
SI6: Spin density on free Gallium site

Figure S4: *Spatial localization of spin density on the free Gallium as active site in the hydrogen evolution reaction.*

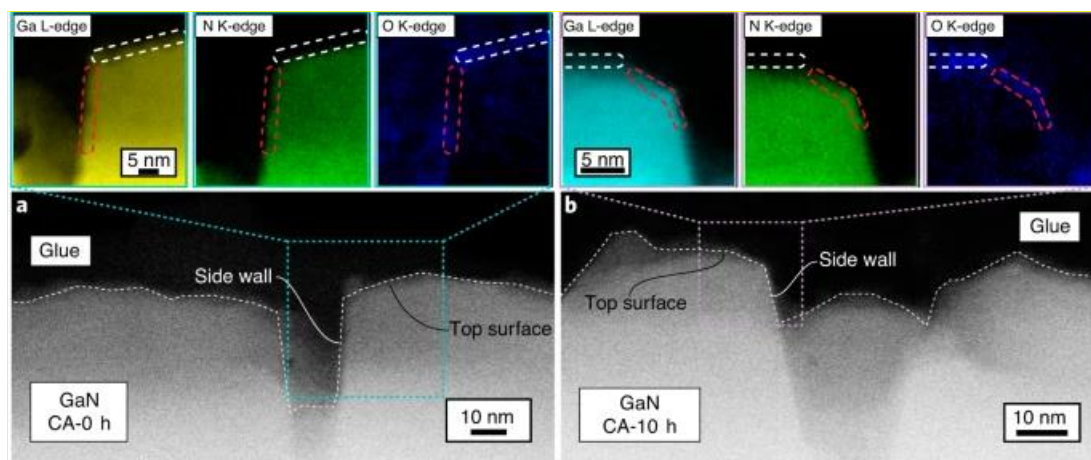*SI7: STEM images adapted from Nat. Mater. 20, 1130 (2021).*

Figure S5. (a) STEM image of CA-0 h surface with insets (left to right) showing the EELS mappings of Ga L-edge, N K-edge and O K-edge. (b) STEM image of CA-10 h surface with insets (left to right) showing the EELS mappings of Ga L-edge, N K-edge and O K-edge. Adapted with permission from Nat. Mater. 20, 1130 (2021).[1]

(1) Zeng, G.; Pham, T. A.; Vanka, S.; Liu, G.; Song, C.; Cooper, J. K.; Mi, Z.; Ogitsu, T.; Toma, F. M. Development of a Photoelectrochemically Self-Improving Si/GaN Photocathode for Efficient and Durable H2 Production. *Nat. Mater.* **2021**, *20* (8), 1130–1135. https://doi.org/10.1038/s41563-021-00965-w.