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A DFT Study of Plasma-Catalytic Ammonia Synthesis: Effect of Electric Field, Excess Electrons and Catalyst Surface on N_2 Dissociation

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Table S1 Catalyst surface dimensions: X is the horizontal length of the surface, Y is the vertical length, and S is the surface area. $\boldsymbol{\sigma}$(1e) is the surface charge density when one electron is added to the surface, and $\boldsymbol{\sigma}$(2e) is the surface charge density for two electrons.

Surface	X [Å]	Y [Å]	S [Å^2]	$\boldsymbol{\sigma}$(1e)[C/m^2]	$\boldsymbol{\sigma}$(2e)[C/m^2]
Ru(0001) terrace	13.745	14.284	196.336	0.081	0.162
Ru(0001) step	13.745	14.284	196.336	0.081	0.162
Ni(211)	12.190	14.930	181.998	0.088	0.176

Table S2 The bond length, angle and adsorption energy of N_2 molecules on the terrace Ru (0001) surface under the combined effect of electric fields and excess electrons. In order to distinguish two N atoms, the lower N atom that forms a bond with the surface is identified as the N_I atom, while the higher is N_{II} atom.

Voltage [V]	r(N_I-Ru) [Å]	r(N_I-N_{II}) [Å]	Angle(N-slab) [°]	E_{abs} [eV]
0V	1.965	1.137	92.284	-0.90
10V	1.941	1.144	92.708	-1.00
20V	1.922	1.154	93.517	-1.20
30V	1.905	1.167	94.982	-1.55
10V+1e	1.928	1.150	93.313	-1.14
20V+1e	1.910	1.162	93.814	-1.42
30V+1e	1.892	1.179	96.720	-1.85
0.03V+1e	1.948	1.142	92.584	-0.96
0.03V+2e	1.934	1.147	93.171	-1.06

Table S3 The bond length, angle and adsorption energy of N_2 molecules on the stepped Ru (0001) surface under the combined effect of electric fields and excess electrons. In order to distinguish two N atoms, the lower N atom that forms a bond with the surfaces is identified as the N_I atom, while the higher is N_{II} atom.

Voltage [V]	$r(N_I\text{-Ru})$ [Å]	$r(N_{II}\text{-Ru})$ [Å]	$r(N_I\text{-}N_{II})$ [Å]	E_{abs} [eV]
0V	2.053	2.064	1.318	-1.36
10V	2.058	2.063	1.324	-1.39
20V	2.064	2.061	1.329	-1.43
30V	2.074	2.060	1.334	-1.46
10V+1e	2.061	2.061	1.327	-1.41
20V+1e	2.070	2.060	1.332	-1.41
30V+1e	2.081	2.059	1.337	-1.46
0.03V+1e	2.055	2.063	1.322	-1.39
0.03V+2e	2.058	2.061	1.325	-1.40

Table S4 The bond length, angle and adsorption energy of N_2 molecules on the Ni (211) surface under the combined effect of electric fields and excess electrons. In order to distinguish two N atoms, the lower N atom that forms a bond with the surface is identified as the N_I atom, while the higher is N_{II} atom.

Voltage [V]	r(N_I-Ni) [Å]	r(N_I-N_{II}) [Å]	Angle(N-slab) [°]	E_{abs} [eV]
0V	1.770	1.138	115.255	-1.08
10V	1.754	1.145	114.312	-1.28
20V	1.744	1.155	114.580	-1.57
10V+1e	1.744	1.153	113.669	-1.67
20V+1e	1.737	1.166	113.733	-2.18
0.03V+1e	1.757	1.144	114.587	-1.29
0.03V+2e	1.745	1.150	114.045	-1.46

Table S5 The bond length, angle and the dissociative adsorption energy of N atoms on the terrace Ru(0001) surface under the combined effect of electric fields and excess electrons.

Voltage [V]	*r*(N-Ru) [Å]	*h*(N-slab) [Å]	Angle(N-Ru-N) [°]	E_{abs} [eV]
0	1.969	0.906	100.186	-2.45
10	1.977	0.920	99.572	-2.57
20	1.983	0.933	98.993	-2.66
30	1.990	0.948	98.410	-2.76
10V+1e	1.980	0.925	99.324	-2.66
20V+1e	1.987	0.939	98.718	-2.75
30V+1e	1.995	0.953	98.117	-2.85
0.03V+1e	1.974	0.910	99.906	-2.56
0.03V+2e	1.976	0.914	99.696	-2.67

Table S6 The bond length, angle and the dissociative adsorption energy of N atoms on the stepped Ru (0001) surface under the combined effect of electric fields and excess electrons. In order to distinguish two N atoms, the lower N atom that forms a bond with the surfaces is identified as the N_I atom, while the higher is N_{II} atom.

Voltage [V]	$r(N_I\text{-Ru})$ [Å]	$r(N_{II}\text{-Ru})$ [Å]	E_{abs} [eV]
0V	1.914	1.954	-2.33
10V	1.920	1.957	-2.40
20V	1.926	1.961	-2.48
30V	1.933	1.965	-2.54
10V+1e	1.923	1.958	-2.43
20V+1e	1.930	1.962	-2.49
30V+1e	1.938	1.966	-2.55
0.03V+1e	1.917	1.955	-2.39
0.03V+2e	1.921	1.956	-2.40

Table S7 The bond length, angle and the dissociative adsorption energy of N atoms on the Ni (211) surface under the combined effect of different applied electric fields and excess electrons.

Voltage [V]	*r*(N-Ni) [Å]	E_{abs} [eV]
0V	1.757	-1.56
10V	1.764	-1.77
20V	1.774	-1.92
10V+1e	1.772	-1.92
20V+1e	1.780	-2.07
0.03V+1e	1.762	-1.74
0.03V+2e	1.768	-1.87

Table S8 Surface partial charges of N_2 molecules adsorbed on the surface of Ru (0001) terraces under the combined effect of electric fields and excess electrons. N_I is the N atom that forms a bond with the surface metal atom, and N_{II} atom is the one away from the surface.

Voltage [V]	Bottom [e]	Top [e]	N_I [e]	N_{II} [e]	N_2 [e]
0	-0.549	-1.066	0.58	-0.098	0.482
10V	0.239	-1.777	0.606	-0.197	0.409
20V	1.039	-2.476	0.626	-0.304	0.322
30V	1.83	-3.15	0.639	-0.425	0.214
10V+1e	-0.268	-2.241	0.62	-0.267	0.353
20V+1e	0.53	-2.927	0.636	-0.383	0.253
30V+1e	1.34	-3.595	0.646	-0.521	0.125
0.03V+1e	-1.061	-1.539	0.598	-0.162	0.436
0.03V+2e	-1.572	-2.002	0.614	-0.227	0.387

Table S9 Surface partial charges of N_2 molecules adsorbed on the surface of the Ru(0001) steps under the combined effect of electric fields and excess electrons. N_I is the N atom that forms a bond with the surface metal atom, and N_{II} atom is the one away from the surface.

Voltage [V]	Bottom [e]	Top [e]	N_I [e]	N_{II} [e]	N_2 [e]
0	-0.575	-0.485	-0.008	-0.001	-0.009
10V	0.299	-1.279	-0.038	-0.057	-0.095
20V	1.171	-2.156	-0.066	-0.115	-0.181
30V	2.045	-3.021	-0.093	-0.174	-0.267
10V+1e	-0.245	-1.775	-0.055	-0.089	-0.144
20V+1e	0.635	-2.649	-0.082	-0.148	-0.23
30V+1e	1.519	-3.521	-0.108	-0.209	-0.317
0.03V+1e	-1.12	-0.9	-0.025	-0.032	-0.057
0.03V+2e	-1.665	-1.385	-0.042	-0.063	-0.105

Table S10 Surface partial charges of N_2 molecules adsorbed on the surface of the Ni (211) under the combined effect of electric fields and excess electrons. N_I is the N atom that forms a bond with the surface metal atom, and N_{II} atom is the one away from the surface.

Voltage [V]	Bottom [e]	Top [e]	N_I [e]	N_{II} [e]	N_2 [e]
0	-0.245	-0.933	0.801	-0.134	0.667
10V	0.413	-1.518	0.828	-0.234	0.594
20V	1.082	-2.091	0.844	-0.343	0.501
10V+1e	-0.073	-1.963	0.844	-0.319	0.525
20V+1e	0.601	-2.52	0.851	-0.439	0.412
0.03V+1e	-0.747	-1.39	0.824	-0.212	0.612
0.03V+2e	-1.236	-1.832	0.841	-0.294	0.547

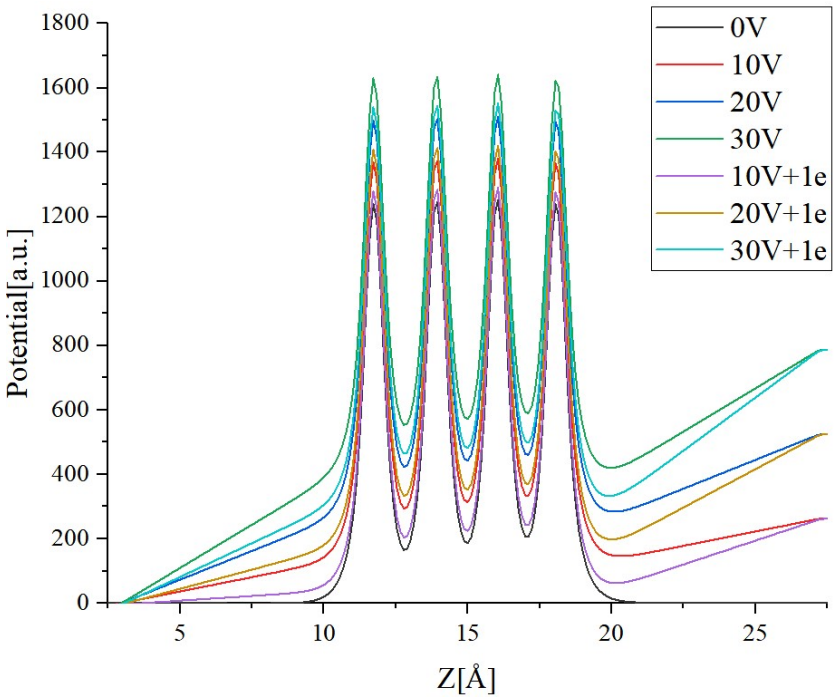

Fig.S1 Electric potential distribution of the terrace Ru (0001) surface under the combined effect of electric fields and excess electrons.

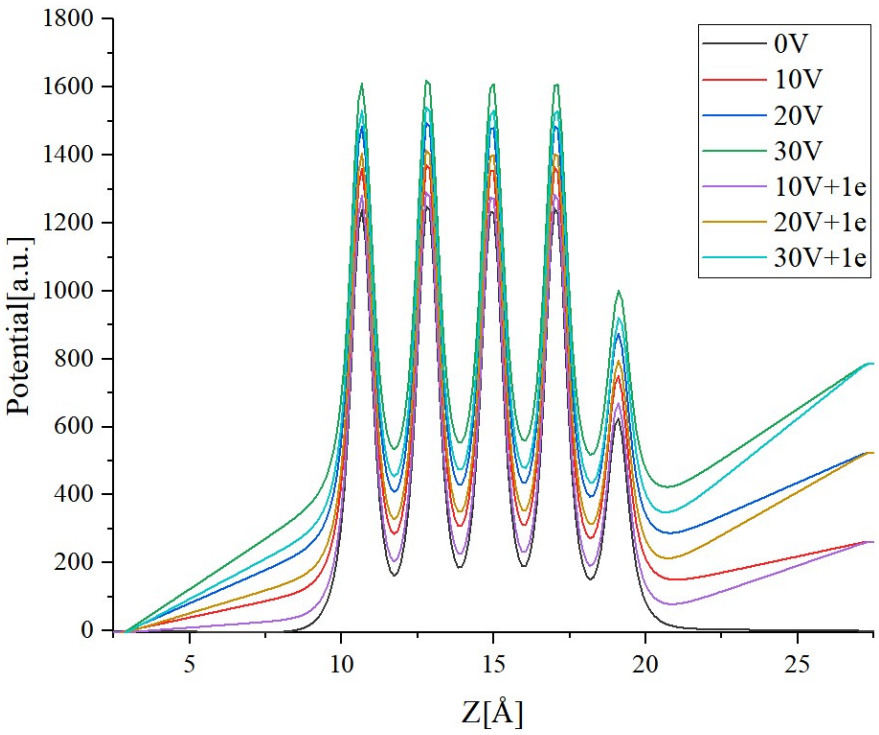

Fig.S2 Electric potential distribution of the stepped Ru (0001) surface under the combined effect of electric fields and excess electrons.

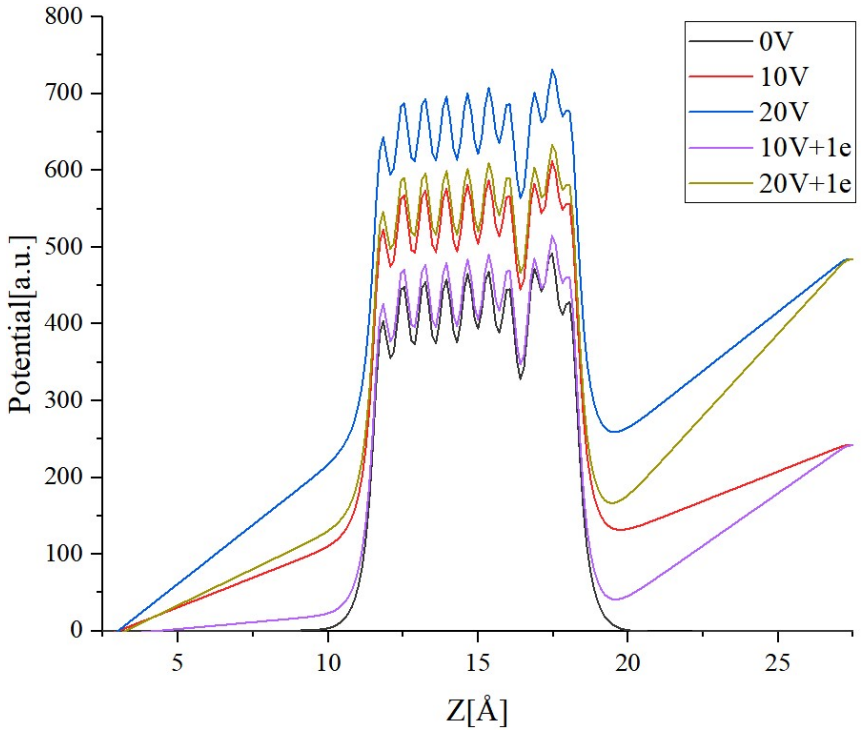

Fig.S3 Electric potential distribution of the Ni (211) surface under the combined effect of electric fields and excess electrons.