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Supplementary Materials for

Catalyst-free, highly selective synthesis of ammonia from nitrogen and water by a plasma electrolytic system

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Equation for faradaic efficiency calculation for NH₃ from NH₃ measurements

$$\text{Faradaic efficiency (\%)} = \frac{\text{Experimentally measured } NH_3 \text{ concentration}}{\text{Faradaic } NH_3 \text{ concentration}} \, x \, 100$$

Equation for instantaneous faradaic efficiency calculation for NH₃ from H₂ measurements

$$\text{Instantaneous faradaic efficiency (\%)} = \left(1 - \frac{\dot{V}C_{H2}Fz}{(1000000 - C_{H2})I}\right) x \, 100$$

where $\dot{V}$ is the nitrogen flow rate through the cell, C_{H2} is the ppm hydrogen measured, F is Faraday's constant, z is the number of electrons and equal to 2 for hydrogen, and I is the plasma current in mA.

Equation for faradaic NH₃ concentration

$$\text{Faradaic } NH_3 \text{ concentration} = \frac{Q}{F \, zV}$$

where Q is the total charge, F is Faraday's constant, z is the number of electrons and equal to 3 for the NH₃ reaction, and V is the volume of the solution and equal to 20 ml.

Equation for energy consumption

$$\text{Energy consumption} = \frac{VI}{\dot{m}_{NH_3}}$$

where V and I are the plasma voltage and current in the electrolytic system, respectively, and I is calculated from the total charge divided by the time, Q/t, and $\dot{m}_{NH_3}$ is the NH₃ production rate. Using units of kV for V, A for I, and kg/h for $\dot{m}_{NH_3}$ gives the energy consumption in kWh/kg.
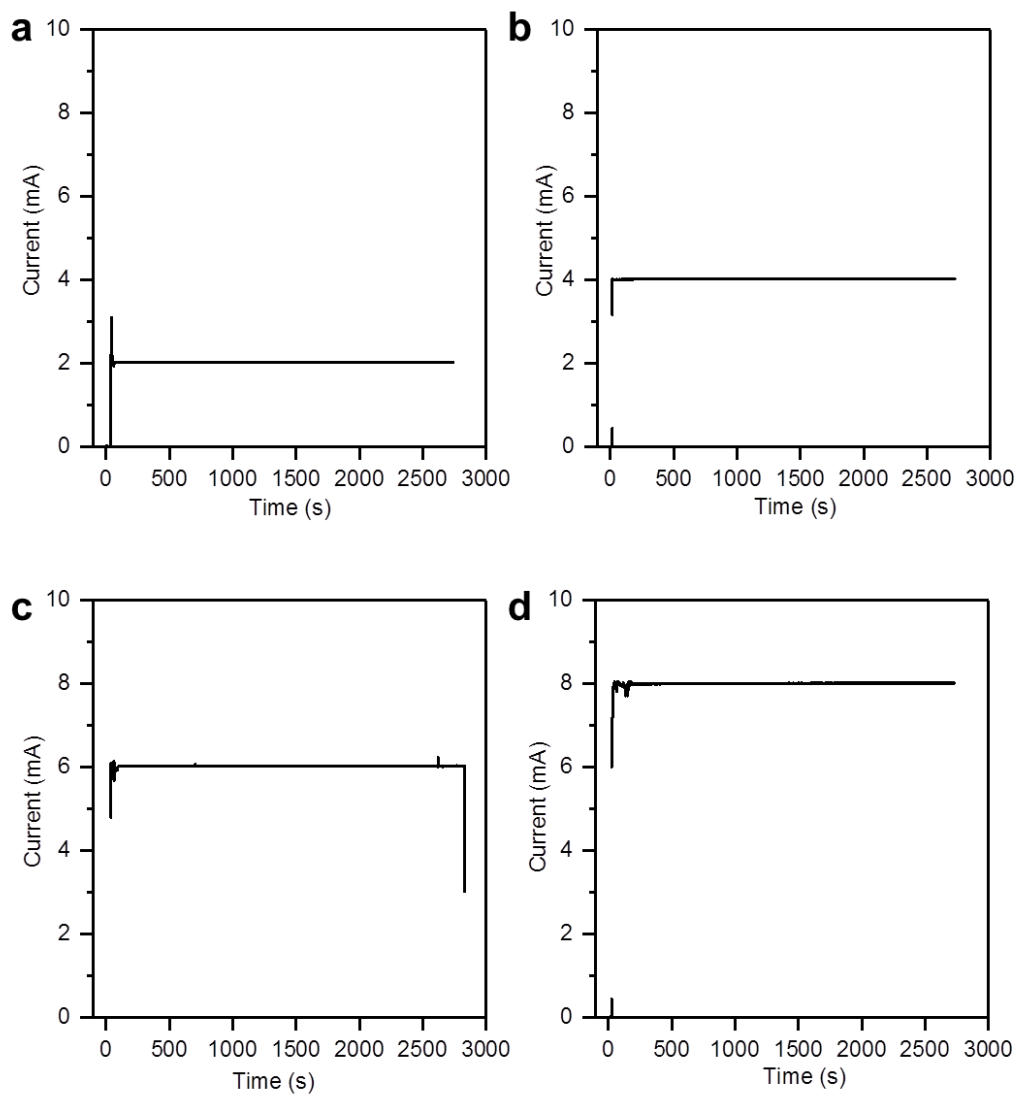
Fig. S1. Representative current waveforms measured in the plasma electrolytic system during NH$_3$ synthesis. The current was integrated over the process time to obtain the total charge, $Q = \int I(t)dt$. For the four examples shown, the total charges were (a) 5448, (b) 10858, (c) 16717, and (d) 21647 mAs, respectively.
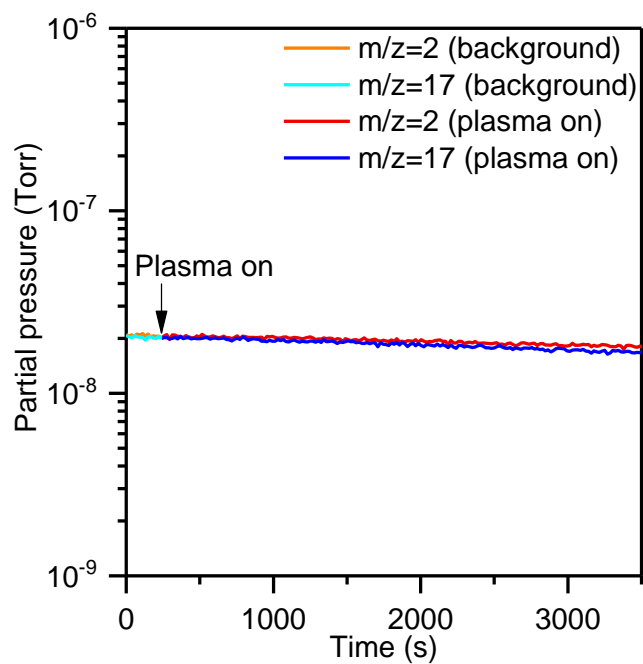
Fig. S2. RGA measurements of mass/charge ratio (m/z) = 2 and 17, corresponding to H_2 and NH_3 partial pressure, at 2 mA in a plasma electrolytic reactor by analyzing exhaust gas from cell as a function of time. The background signal was obtained for 240 s before turning on the plasma.
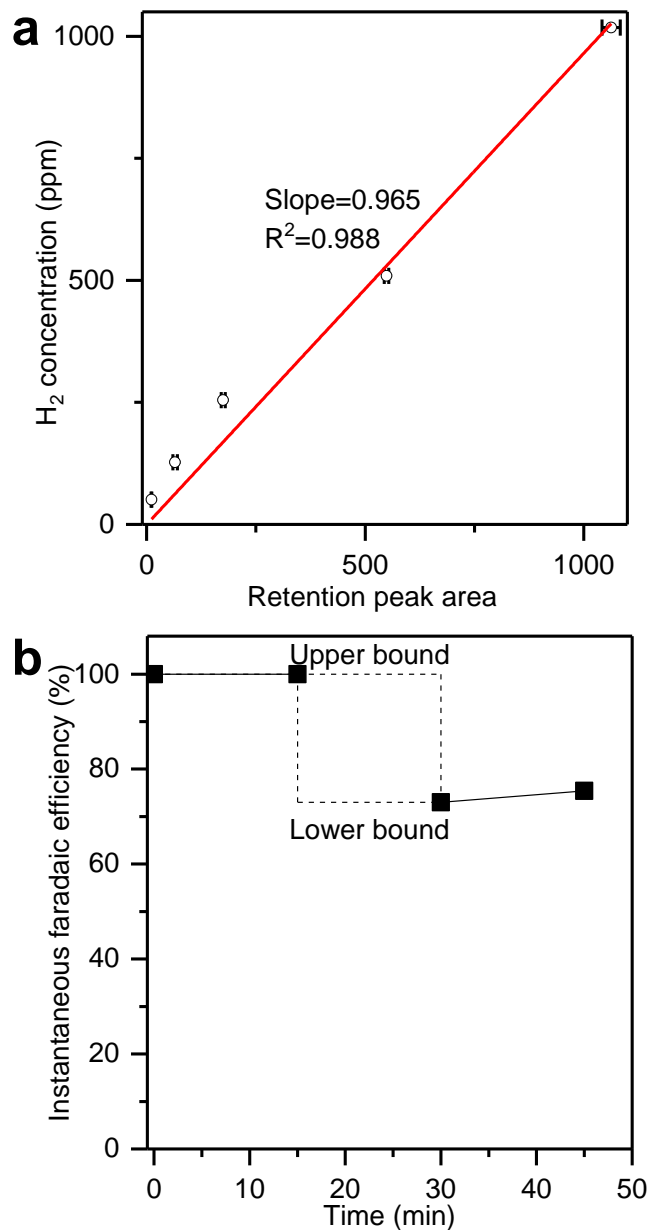
Fig. S3. H_2 production in the plasma electrolytic system. (a) Gas chromatography (GC) calibration of H_2 retention peak area and H_2 concentration. (b) Instantaneous faradaic efficiency from GC measurements of H_2 as a function of time, assuming the rest of the current goes towards NH_3 production. Two step functions are shown for estimating the cumulative faradaic efficiency which represent the lower and upper bound.
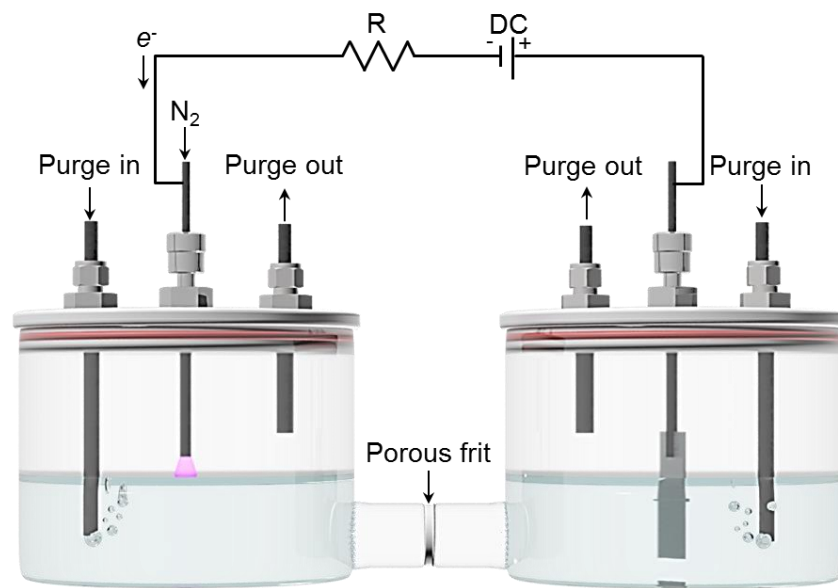
Fig. S4. Schematic of the hybrid plasma electrolytic system in a split H-cell geometry.
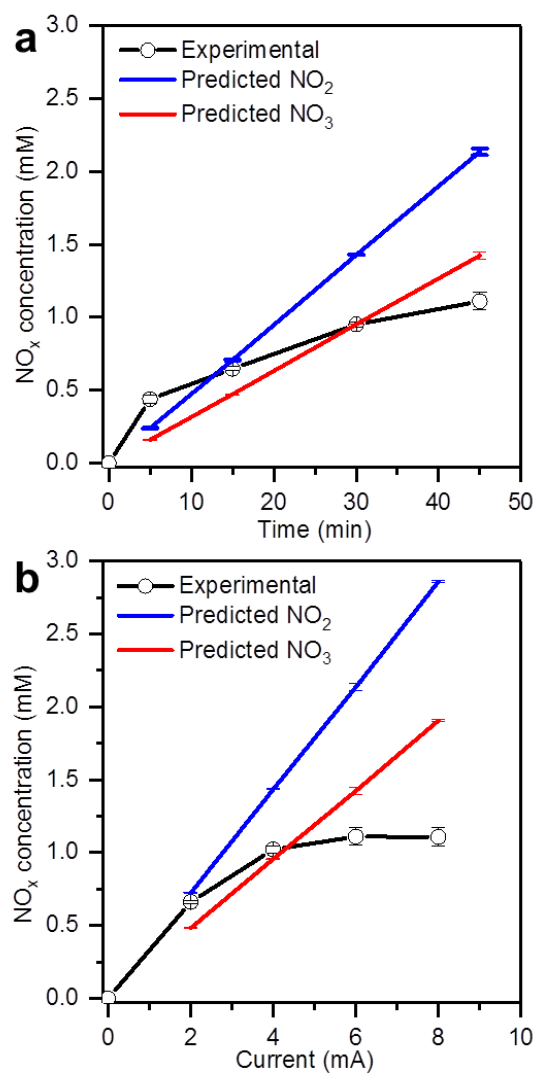
Fig. S5. Comparison of NO$_x$ produced with that predicted from O$_2$ gas evolution in plasma electrolytic system.
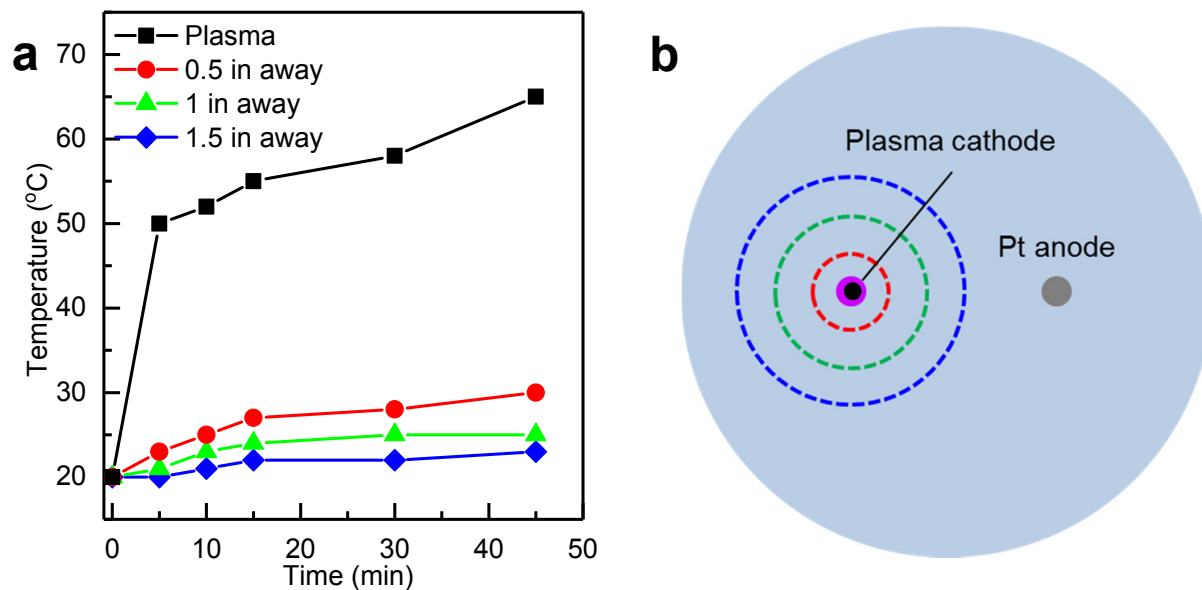
Fig S6. Heating of solution in the plasma electrolytic system. (**a**) Temperature measurements of solution surface as a function of position and time at 6 mA. (**b**) A color-coded illustration of the radially symmetric positions shown in (**a**) at which the temperature was measured with respect to the position of the plasma cathode and Pt anode.
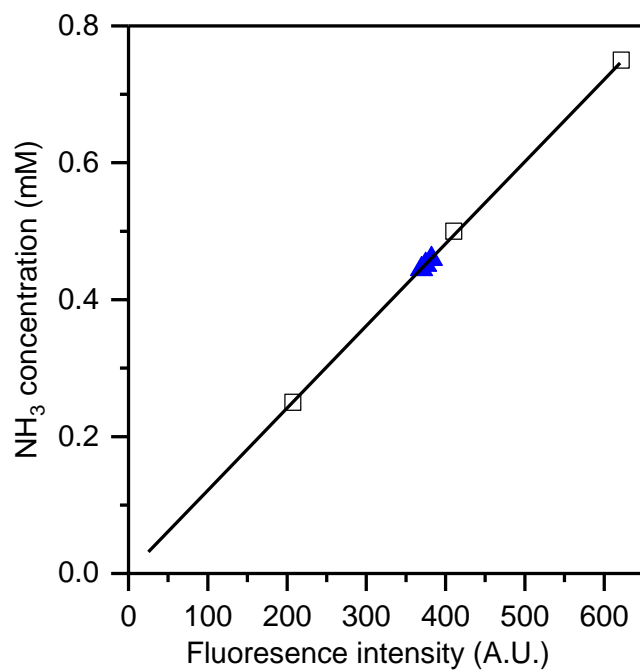
Fig. S7. Representative fluorescence assay calibration used to determine NH₃ produced. The empty black square data points correspond to control solutions and filled blue triangle data points correspond to solutions synthesized in the plasma electrolytic system.
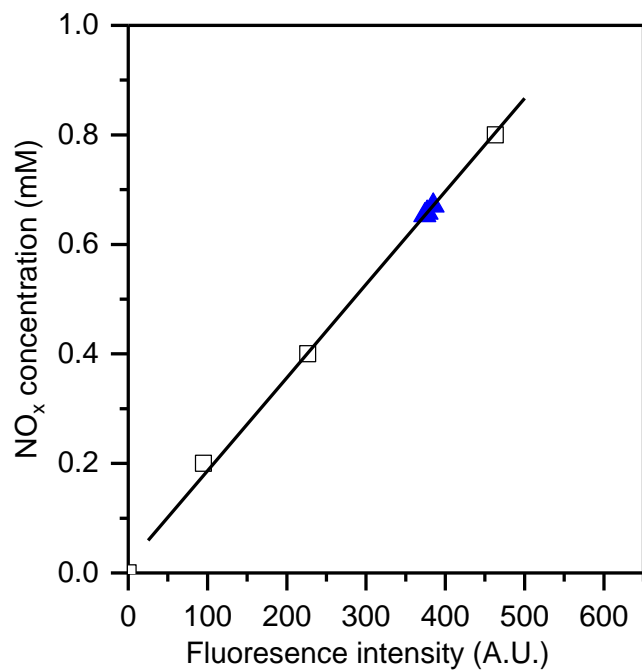
Fig. S8. Representative fluorescence assay calibration used to determine NO$_x$ produced. The empty black square data points correspond to control solutions and the filled blue triangle data points correspond to solutions synthesized in the plasma electrolytic system.

Table S1A. Summary of NH$_3$ produced by plasma electrolytic synthesis for the following configurations: N$_2$ both flowing through the cathode tube where the plasma is normally generated and bubbled through the solution to purge, but no electrical power applied, Ar as both the supply gas in the plasma and purge gas, Ar as the supply gas in the plasma and N$_2$ as the purge gas, and N$_2$ as both the supply gas in the plasma and purge gas. The faradaic efficiencies are calculated when the NH$_3$ produced was non-zero. The current was 6 mA, the processing time was 45 min, and the reaction volume was 20 ml in all cases.

No plasma + N$_2$ purge

	NH$_3$ produced (mM)	NH$_3$ produced (mg)
Trial 1	0.000	0.000
Trial 2	0.000	0.000
Trial 3	0.000	0.000
Average		**0.000±0.000**

Ar plasma + Ar purge

	NH$_3$ produced (mM)	NH$_3$ produced (mg)
Trial 1	-0.002	0.000
Trial 2	0.001	0.000
Trial 3	0.000	0.000
Average		**0.000±0.000**

Ar plasma + N$_2$ purge

	NH$_3$ produced (mM)	NH$_3$ produced (mg)	Total charge (mAs)	Faradaic NH$_3$ conc. (mM)	Faradaic efficiency (%)
Trial 1	0.022	0.007	16254	2.81	0.8
Trial 2	0.172	0.059	16227	2.80	6.1
Trial 3	0.067	0.023	16198	2.80	2.4
Trial 4	0.003	0.001	16394	2.83	0.1
Trial 5	0.144	0.049	16252	2.81	5.1
Trial 6	0.029	0.010	16228	2.80	1.0
Average		**0.025±0.018**			**2.58±1.85**

N₂ plasma + N₂ purge

	NH$_3$ produced (mM)	NH$_3$ produced (mg)	Total charge (mAs)	Faradaic NH$_3$ conc. (mM)	Faradaic efficiency (%)
Trial 1	0.919	0.313	16240	2.86	32.1
Trial 2	0.889	0.303	16314	2.87	30.9
Trial 3	0.902	0.307	16387	2.89	31.2
Trial 4	0.929	0.317	16288	2.87	32.4
Trial 5	0.919	0.313	16322	2.88	31.9
Trial 6	0.926	0.315	16263	2.87	32.3
Trial 7	0.896	0.305	16253	2.81	31.9
Trial 8	0.902	0.307	16227	2.80	32.2
Trial 9	0.908	0.309	16199	2.80	32.5
Trial 10	0.990	0.337	16394	2.83	35.0
Average		**0.313±0.006**			**32.2±0.6**

Table S1B. Summary of one-sample and two-sample t tests carried out on datasets in table S1A.

One-Sample t
Test of $\mu = 0.00$ vs $\mu \neq 0.00$

	Algebraic Mean	St. Deviation	95% Lower Bound	Probability
N$_2$ plasma	0.313	0.010	0.306	0.000
Ar plasma+ N$_2$	0.025	0.024	0.000	0.050

Two-Sample t
Test of $\mu_1 - \mu_2 = 0$

	Difference	95% Lower Bound	95% Upper Bound	Probability
N$_2$ plasma vs. Ar plasma+N$_2$	0.288	0.263	0.313	0.000

Table S2A. Summary of NH$_3$ produced and faradaic efficiencies by plasma electrolytic synthesis after different processing times. The current was 6 mA and the reaction volume was 20 ml in all cases.

t=5 min

	NH$_3$ produced (mM)	NH$_3$ produced (mg)	Total charge (mAs)	Faradaic NH$_3$ conc. (mM)	Faradaic efficiency (%)
Trial 1	0.206	0.070	1838	0.317	64.9
Trial 2	0.073	0.025	1862	0.322	22.8
Trial 3	0.339	0.116	1832	0.317	107.1
Trial 4	0.150	0.051	1866	0.322	46.5
Average		**0.065±0.033**			**60.3±30.9**

t=15 min

	NH$_3$ produced (mM)	NH$_3$ produced (mg)	Total charge (mAs)	Faradaic NH$_3$ conc. (mM)	Faradaic efficiency (%)
Trial 1	0.335	0.114	5508	0.951	35.2
Trial 2	0.285	0.097	5532	0.956	29.8
Trial 3	0.324	0.110	5493	0.949	34.2
Trial 4	0.346	0.118	5519	0.935	37.1
Trial 5	0.461	0.157	5511	0.933	49.4
Trial 6	0.359	0.122	5541	0.938	38.2
Average		**0.120±0.015**			**37.3±4.9**

t=30 min

	NH$_3$ produced (mM)	NH$_3$ produced (mg)	Total charge (mAs)	Faradaic NH$_3$ conc. (mM)	Faradaic efficiency (%)
Trial 1	0.574	0.196	11026	1.905	30.2
Trial 2	0.602	0.205	11038	1.907	31.6
Trial 3	0.529	0.180	11014	1.902	27.8
Trial 4	0.572	0.195	11030	1.905	30.0
Average		**0.194±0.009**			**29.9±1.3**

t=45 min

	NH$_3$ produced (mM)	NH$_3$ produced (mg)	Total charge (mAs)	Faradaic NH$_3$ conc. (mM)	Faradaic efficiency (%)
Trial 1	0.919	0.313	16567	2.86	32.1
Trial 2	0.889	0.303	16643	2.87	30.9
Trial 3	0.902	0.307	16717	2.89	31.2
Trial 4	0.929	0.317	16615	2.87	32.4
Trial 5	0.919	0.313	16651	2.88	31.9
Trial 6	0.926	0.315	16590	2.87	32.3
Trial 7	0.896	0.305	16253	2.81	31.9

Trial 8	0.902	0.307	16227	2.80	32.2
Trial 9	0.908	0.309	16199	2.80	32.5
Trial 10	0.990	0.337	16394	2.83	35.0
Average		**0.313±0.006**			**32.2±0.6**

t=300 min

	NH_3 produced (mM)	NH_3 produced (mg)	Total charge (mAs)	Faradaic NH_3 conc. (mM)	Faradaic efficiency (%)
Trial 1	4.68	1.594	108648	18.77	24.9

Table S2B. Summary of one-sample and two-sample t tests carried out on datasets in table S2A.

One-Sample t on NH_3 production
Test of $\mu = 0.00$ vs $\mu \neq 0.00$

	Algebraic Mean	St. Deviation	95% Lower Bound	Probability
5 min	0.065	0.038	0.005	0.021
15 min	0.120	0.020	0.099	0.000
30 min	0.194	0.010	0.178	0.000
45 min	0.312	0.016	0.305	0.000

Two-Sample t on NH_3 production
Test of $\mu_1 - \mu_2 = 0$

	Difference	95% Lower Bound	95% Upper Bound	Probability
5 vs. 15 min	0.054	-0.003	0.112	0.059
15 vs. 30 min	0.074	0.051	0.097	0.000
30 vs. 45 min	0.118	0.102	0.133	0.000

One-Sample t on FE
Test of $\mu = 0.00$ vs $\mu > 0.00$

	Algebraic Mean	St. Deviation	95% Lower Bound	Probability
5 min	60.3	35.6	18.4	0.021
15 min	37.3	6.59	31.9	0.000
30 min	29.9	1.56	28.1	0.000
45 min	32.1	1.70	31.5	0.000

Two-Sample t on FE
Test of $\mu_1 - \mu_2 = 0$

	Difference	95% Lower Bound	95% Upper Bound	Probability
5 vs. 15 min	23.0	-80.4	34.3	0.291
15 vs. 30 min	7.42	0.23	14.6	0.045
30 vs. 45 min	2.24	-0.175	4.66	0.062

Table S3A. Summary of NH$_3$ produced and faradaic efficiencies by plasma electrolytic synthesis at different currents. The processing time was 45 min and the reaction volume was 20 ml in all cases.

I=1 mA	NH$_3$ produced (mM)	NH$_3$ produced (mg)	Total charge (mAs)	Faradaic NH$_3$ conc. (mM)	Faradaic efficiency (%)
Trial 1	0.456	0.155	2709	0.468	97.4
Trial 2	0.470	0.160	2705	0.467	100.7
Trial 3	0.465	0.158	2700	0.466	99.8
Trial 4	0.463	0.158	2732	0.472	98.1
Average		**0.158±0.002**			**99.0±1.3**

I=2 mA	NH$_3$ produced (mM)	NH$_3$ produced (mg)	Total charge (mAs)	Faradaic NH$_3$ conc. (mM)	Faradaic efficiency (%)
Trial 1	0.849	0.289	5438	0.939	90.4
Trial 2	0.939	0.320	5483	0.947	99.1
Trial 3	0.944	0.322	5448	0.941	100.3
Trial 4	1.017	0.346	5798	1.002	101.5
Trial 5	1.050	0.358	5690	0.983	106.8
Trial 6	1.043	0.355	5643	0.975	107.0
Average		**0.332±0.020**			**100.9±4.6**

I=3 mA	NH$_3$ produced (mM)	NH$_3$ produced (mg)	Total charge (mAs)	Faradaic NH$_3$ conc. (mM)	Faradaic efficiency (%)
Trial 1	0.586	0.199	8132	1.405	41.7
Trial 2	0.514	0.175	8189	1.415	36.3
Trial 3	0.431	0.147	8072	1.394	30.9
Average		**0.174±0.025**			**36.3±5.1**

I=4 mA	NH$_3$ produced (mM)	NH$_3$ produced (mg)	Total charge (mAs)	Faradaic NH$_3$ conc. (mM)	Faradaic efficiency (%)
Trial 1	0.674	0.230	11121	1.921	35.1
Trial 2	0.714	0.243	11156	1.927	37.1
Trial 3	0.664	0.226	11015	1.903	34.9
Trial 4	0.724	0.247	11049	1.909	37.9
Trial 5	0.664	0.226	11076	1.913	34.7
Trial 6	0.719	0.245	11076	1.902	37.8
Average		**0.236±0.007**			**36.3±1.1**

I=6 mA

	NH$_3$ produced (mM)	NH$_3$ produced (mg)	Total charge (mAs)	Faradaic NH$_3$ conc. (mM)	Faradaic efficiency (%)
Trial 1	0.919	0.313	16567	2.86	32.1
Trial 2	0.889	0.303	16642	2.87	30.9
Trial 3	0.902	0.307	16717	2.89	31.2
Trial 4	0.929	0.317	16615	2.87	32.4
Trial 5	0.919	0.313	16650	2.88	31.9
Trial 6	0.926	0.315	16591	2.87	32.3
Trial 7	0.896	0.305	16253	2.81	31.9
Trial 8	0.902	0.307	16227	2.80	32.2
Trial 9	0.908	0.309	16199	2.80	32.5
Trial 10	0.990	0.337	16394	2.83	35.0
Average		**0.313±0.006**			**32.2±0.6**

I=8 mA

	NH$_3$ produced (mM)	NH$_3$ produced (mg)	Total charge (mAs)	Faradaic NH$_3$ conc. (mM)	Faradaic efficiency (%)
Trial 1	0.962	0.328	22063	3.81	25.2
Trial 2	0.900	0.307	22152	3.83	23.5
Trial 3	0.953	0.325	22111	3.82	25.0
Trial 4	0.877	0.299	22028	3.81	23.0
Trial 5	0.961	0.327	22037	3.81	25.2
Trial 6	0.882	0.300	22047	3.81	23.2
Average		**0.314±0.010**			**24.2±0.8**

Table S3B. Summary of one-sample and two-sample t tests carried out on datasets in table S3A.

One-Sample t on NH$_3$ production
Test of $\mu = 0.00$ vs $\mu > 0.00$

	Algebraic Mean	St. Deviation	95% Lower Bound	Probability
1 mA	0.158	0.002	0.155	0.000
2 mA	0.332	0.027	0.310	0.000
3 mA	0.174	0.026	0.130	0.004
4 mA	0.236	0.010	0.228	0.000
6 mA	0.313	0.010	0.307	0.000
8 mA	0.314	0.014	0.303	0.000

Two-Sample t on NH₃ production
Test of $\mu_1 - \mu_2 = 0$

	Difference	95% Lower Bound	95% Upper Bound	Probability
1 vs. 2 mA	0.174	0.146	0.202	0.000
2 vs. 3 mA	0.158	0.106	0.210	0.001
3 vs. 4 mA	0.062	-0.005	0.130	0.058
4 vs. 6 mA	0.077	0.065	0.088	0.000
6 vs. 8 mA	0.002	-0.013	0.016	0.819

One-Sample t on FE
Test of $\mu = 100$ vs $\mu < 100$

	Algebraic Mean	St. Deviation	95% Upper Bound	Probability
1 mA	99.0	1.51	100.7	0.000
2 mA	1.01	6.12	105.9	0.000
3 mA	36.3	5.39	45.4	0.000
4 mA	36.2	1.52	37.5	0.000
6 mA	32.2	1.08	32.9	0.000
8 mA	24.2	1.06	25.1	0.000

One-Sample t on FE
Test of $\mu = 0$ vs $\mu > 0.00$

	Algebraic Mean	St. Deviation	95% Lower Bound	Probability
1 mA	99.0	1.51	97.2	0.000
2 mA	1.01	6.12	95.8	0.000
3 mA	36.3	5.39	27.2	0.004
4 mA	36.2	1.52	35.0	0.000
6 mA	32.2	1.08	31.6	0.000
8 mA	24.2	1.06	23.3	0.000

Two-Sample t on FE
Test of $\mu_1 - \mu_2 = 0$

	Difference	95% Lower Bound	95% Upper Bound	Probability
1 vs. 2 mA	1.88	-8.59	4.84	0.505
2 vs. 3 mA	64.6	53.5	75.6	0.000
3 vs. 4 mA	0.00	-13.6	13.7	0.986
4 vs. 6 mA	4.00	2.38	5.63	0.000
6 vs. 8 mA	8.05	6.82	9.28	0.000

Table S3C. Summary of H₂ produced in plasma electrolytic reactor by analyzing exhaust gas using GC.

		I=1 mA		
Time (min)	Peak area	H$_2$ concentration (ppm)	Instantaneous faradaic efficiency (%)	Cumulative faradaic efficiency (%)
15	0	0	100	100
30	0	0	100	100
45	6	6	90.2	95.1-100

		I=2 mA		
Time (min)	Peak area	H$_2$ concentration (ppm)	Instantaneous faradaic efficiency (%)	Cumulative faradaic efficiency (%)
15	0	0	100	100
30	34	33	73.0	86.5-100
45	31	30	75.4	77.9-95.9

Table S4A. Summary of NH₃ produced and faradaic efficiencies by plasma electrolytic synthesis in a split cell. The reaction volume was 20 ml in all cases.

6 mA, 5 min

	NH$_3$ produced (mM)	NH$_3$ produced (mg)	Total charge (mAs)	Faradaic NH$_3$ conc. (mM)	Faradaic efficiency (%)
Trial 1	0.042	0.014	1803	0.312	13.5
Trial 2	0.216	0.074	1804	0.312	69.3
Trial 3	0.114	0.039	1789	0.309	36.8
Average		**0.042±0.028**			**39.9±26.4**

6 mA, 15 min

	NH$_3$ produced (mM)	NH$_3$ produced (mg)	Total charge (mAs)	Faradaic NH$_3$ conc. (mM)	Faradaic efficiency (%)
Trial 1	0.391	0.133	5417	0.936	41.8
Trial 2	0.287	0.098	5402	0.933	30.8
Trial 3	0.447	0.152	5489	0.948	47.2
Trial 4	0.382	0.130	5391	0.931	41.0
Trial 5	0.322	0.110	5393	0.932	34.5
Trial 6	0.362	0.123	5402	0.933	38.8
Average		**0.124±0.014**			**39.0±4.3**

6 mA, 30 min

	NH$_3$ produced (mM)	NH$_3$ produced (mg)	Total charge (mAs)	Faradaic NH$_3$ conc. (mM)	Faradaic efficiency (%)
Trial 1	0.617	0.210	10811	1.868	33.0
Trial 2	0.592	0.202	10842	1.873	31.6
Trial 3	0.533	0.182	10781	1.862	28.6
Average		**0.198±0.014**			**31.1±2.1**

6 mA, 45 min

	NH$_3$ produced (mM)	NH$_3$ produced (mg)	Total charge (mAs)	Faradaic NH$_3$ conc. (mM)	Faradaic efficiency (%)
Trial 1	0.874	0.298	16265	2.81	31.1
Trial 2	0.935	0.318	16171	2.79	33.5
Trial 3	0.930	0.317	16180	2.79	33.3
Average		**0.311±0.011**			**32.6±1.2**

| | **4 mA, 45 min** | | | | |
	NH$_3$ produced (mM)	**NH$_3$ produced (mg)**	**Total charge (mAs)**	**Faradaic NH$_3$ conc. (mM)**	**Faradaic efficiency (%)**
Trial 1	0.691	0.235	10791	1.86	37.1
Trial 2	0.651	0.222	10834	1.87	34.8
Trial 3	0.686	0.234	10885	1.88	36.5
Average		**0.230±0.007**			**36.1±1.1**

Table S4B. Summary of two-sample t tests carried out on datasets in table S4A (and tables S2A and S3A).

Two-Sample t on NH$_3$ production
Test of $\mu_1 - \mu_2 = 0$

	Difference	95% Lower Bound	95% Upper Bound	Probability
6-5 single vs. split	0.028	-0.072	0.128	0.437
6-15 single vs. split	0.005	-0.021	0.030	0.692
6-30 single vs. split	0.004	-0.035	0.028	0.726
6-45 single vs. split	0.002	-0.030	0.033	0.837
4-45 single vs. split	0.004	-0.012	0.020	0.535

Table S5A. Summary of NH$_3$ produced and faradaic efficiencies by plasma electrolytic synthesis at different pH values. The pH was controlled by the concentration of sulfuric acid. "MC" refers to the main reaction cell and "Trap" refers to a second trapping vessel where the gas exhaust from the main reaction cell was bubbled through a solution of sulfuric acid at pH=2. The reaction volume was 20 ml in all cases.

pH=2	NH$_3$ produced (mM)	NH$_3$ produced (mg)	Total charge (mAs)	Faradaic NH$_3$ conc. (mM)	Faradaic efficiency (%)
Trial 1	1.116	0.380	16252	2.81	39.8
Trial 2	1.146	0.390	16227	2.80	40.9
Trial 3	1.104	0.376	16199	2.78	39.5
Trial 4	1.154	0.393	16395	2.83	40.8
Average		**0.385±0.007**			**40.2±0.6**

pH=5.5	NH$_3$ produced (mM)	NH$_3$ produced (mg)	Total charge (mAs)	Faradaic NH$_3$ conc. (mM)	Faradaic efficiency (%)
Trial 1	0.884	0.301	16252	2.81	31.5
Trial 2	0.821	0.280	16227	2.80	29.3
Trial 3	0.834	0.284	16198	2.80	29.8
Trial 4	0.796	0.271	16395	2.83	28.1
Average		**0.284±0.011**			**29.7±1.2**

pH=7	NH$_3$ produced (mM)	NH$_3$ produced (mg)	Total charge (mAs)	Faradaic NH$_3$ conc. (mM)	Faradaic efficiency (%)
Trial 1 (MC)	0.134	0.045	16290	2.81	4.7
Trial 1 (Trap)	0.041	0.014	16290	2.81	1.5
Trial 2 (MC)	0.066	0.022	16231	2.80	2.3
Trial 2 (Trap)	0.105	0.036	16231	2.80	3.7

Table S5B. Summary of one-sample and two-sample *t* tests carried out on datasets in table S5A. "MC" refers to the main reaction cell and "Trap" refers to a second trapping vessel where the gas exhaust from the main reaction cell was bubbled through a solution of sulfuric acid at pH=2.

One-Sample t on NH$_3$ production
Test of $\mu = 0$ vs $\mu > 0.00$

	Algebraic Mean	St. Deviation	95% Lower Bound	Probability
pH 2.0 (MC)	0.385	0.008	0.375	0.000
pH 3.5 (MC)	0.313	0.010	0.307	0.000
pH 5.5 (MC)	0.284	0.013	0.269	0.000
pH 7 (MC)	0.034	0.016	-0.039	0.104
pH 7 (Trap)	0.025	0.015	-0.043	0.131

Two-Sample t on NH$_3$ production
Test of $\mu_1 - \mu_2 = 0$

	Difference	95% Lower Bound	95% Upper Bound	Probability
2.0 (MC) vs. 3.5 (MC)	0.072	0.060	0.085	0.000
3.5 (MC) vs 5.5 (MC)	0.029	0.048	0.009	0.015
5.5 (MC) vs 7.0 (MC)	0.250	0.083	0.417	0.033
7.0 (MC) vs 7.0 (Trap)	0.009	-0.210	0.192	0.668

One-Sample t on FE
Test of $\mu = 0$ vs $\mu > 0.00$

	Algebraic Mean	St. Deviation	95% Lower Bound	Probability
pH 2.0 (MC)	40.22	0.708	39.39	0.000
pH 3.5 (MC)	32.24	1.080	31.62	0.000
pH 5.5 (MC)	29.67	1.404	28.02	0.000
pH 7 (MC)	3.55	1.700	-4.030	0.104
pH 7 (Trap)	2.60	1.610	-4.560	0.131

Two-Sample t on FE
Test of $\mu_1 - \mu_2 = 0$

	Difference	95% Lower Bound	95% Upper Bound	Probability
2.0 (MC) vs 3.5 (MC)	7.978	6.844	9.113	0.000
3.5 (MC) vs 5.5 (MC)	2.569	0.402	4.736	0.030
5.5 (MC) vs 7.0 (MC)	26.13	8.470	43.79	0.034
7.0 (MC) vs 7.0 (Trap)	0.950	-20.04	21.93	0.669

Table S6A. Summary of NH$_3$ produced and faradaic efficiencies by plasma electrolytic synthesis in the presence of NO$_3$ and NO$_2$ scavengers. The concentration of NO$_3$ and NO$_2$ was controlled by NaNO$_3$ and NaNO$_2$. The reaction volume was 20 ml in all cases.

10 mM NO$_3$					
	NH$_3$ produced (mM)	NH$_3$ produced (mg)	Total charge (mAs)	Faradaic NH$_3$ conc. (mM)	Faradaic efficiency (%)
Trial 1	0.779	0.265	5409	0.934	83.3
Trial 2	0.797	0.272	5437	0.939	84.9
Trial 3	0.727	0.248	5402	0.933	77.9
Average		**0.261±0.011**			**82.0±3.5**

100 mM NO$_3$					
	NH$_3$ produced (mM)	NH$_3$ produced (mg)	Total charge (mAs)	Faradaic NH$_3$ conc. (mM)	Faradaic efficiency (%)
Trial 1	0.553	0.188	5379	0.929	59.5
Trial 2	0.568	0.194	5409	0.934	60.8
Trial 3	0.584	0.199	5402	0.933	62.6
Average		**0.194±0.005**			**61.0±1.5**

1 M NO$_3$					
	NH$_3$ produced (mM)	NH$_3$ produced (mg)	Total charge (mAs)	Faradaic NH$_3$ conc. (mM)	Faradaic efficiency (%)
Trial 1	0.330	0.112	5419	0.936	35.3
Trial 2	0.314	0.107	5428	0.938	33.4
Trial 3	0.322	0.110	5411	0.935	34.5
Average		**0.110±0.003**			**34.4±0.8**

2 M NO$_3$					
	NH$_3$ produced (mM)	NH$_3$ produced (mg)	Total charge (mAs)	Faradaic NH$_3$ conc. (mM)	Faradaic efficiency (%)
Trial 1	0.211	0.072	5390	0.931	22.6
Trial 2	0.188	0.064	5392	0.932	20.1
Trial 3	0.136	0.046	5421	0.936	14.5
Average		**0.061±0.012**			**19.1±3.9**

10 mM NO$_2$					
	NH$_3$ produced (mM)	NH$_3$ produced (mg)	Total charge (mAs)	Faradaic NH$_3$ conc. (mM)	Faradaic efficiency (%)
Trial 1	0.376	0.133	5303	0.916	41.0
Trial 2	0.406	0.138	5338	0.922	44.1
Trial 3	0.389	0.133	5216	0.901	43.2
Average		**0.133±0.005**			**42.7±1.5**

1 M NO$_2$					
	NH$_3$ produced (mM)	NH$_3$ produced (mg)	Total charge (mAs)	Faradaic NH$_3$ conc. (mM)	Faradaic efficiency (%)
Trial 1	0.026	0.009	5314	0.918	2.9
Trial 2	0.037	0.013	5319	0.918	4.1
Trial 3	0.032	0.011	5030	0.869	3.7
Average	**0.032**	**0.011**			**3.6±5.7**

Table S6B. Summary of one-sample and two-sample t tests carried out on datasets in table S6A.

One-Sample t on NH$_3$ production
Test of $\mu = 0$ vs $\mu > 0.00$

	Algebraic Mean	St. Deviation	95% Lower Bound	Probability
No Scavenger	0.313	0.010	0.307	0.000
10 mM NO$_3$	0.261	0.012	0.240	0.000
10 mM NO$_2$	0.133	0.005	0.124	0.000
1 M NO$_3$	0.110	0.003	0.105	0.000
1 M NO$_2$	0.011	0.002	0.008	0.005

Two-Sample t on NH$_3$ production
Test of $\mu_1 - \mu_2 = 0$

	Difference	95% Lower Bound	95% Upper Bound	Probability
None vs. 10 mM NO$_3$	0.051	0.018	0.085	0.023
10 mM NO$_3$ vs. 10 mM NO$_2$	0.128	0.095	0.162	0.004
None vs. 1 M NO$_3$	0.203	0.195	0.211	0.000
10 mM NO$_3$ vs. 1 M NO$_3$	0.152	0.120	0.184	0.002
1 M NO$_3$ vs. 1 M NO$_2$	0.099	0.093	0.105	0.000

Table S7A. Summary of NO$_x$ produced by plasma electrolytic synthesis after different processing times and at different currents. The current was 6 mA in the time trials, the processing time was 45 min in the current trials, and the reaction volume was 20 ml in all cases.

	NO$_x$ produced (mM)			
	t = 5 min	t = 15 min	t = 30 min	t = 45 min
Trial 1	0.412	0.654	0.951	1.18
Trial 2	0.438	0.659	0.929	1.09
Trial 3	0.468	0.629	0.971	1.06
Average	**0.439**	**0.647**	**0.951**	**1.11**

	NO$_x$ produced (mM)			
	I = 2 mA	I = 4 mA	I = 6 mA	I = 8 mA
Trial 1	0.653	1.04	1.18	1.13
Trial 2	0.671	0.990	1.09	1.03
Trial 3	0.658	1.03	1.06	1.16
Average	**0.661**	**1.02**	**1.11**	**1.11**

Table S7B. Summary of one-sample and two-sample t tests carried out on datasets in table S7A.

One-Sample t on NOx production
Test of $\mu = 0$ vs $\mu > 0.00$

	Algebraic Mean	St. Deviation	95% Lower Bound	Probability
5 min	0.439	0.028	0.392	0.001
15 min	0.647	0.016	0.620	0.000
30 min	0.950	0.021	0.915	0.000
45 min	1.11	0.062	1.005	0.001

One-Sample t on NOx production
Test of $\mu = 0$ vs $\mu > 0.00$

	Algebraic Mean	St. Deviation	95% Lower Bound	Probability
2 mA	0.661	0.009	0.645	0.000
4 mA	1.02	0.028	0.974	0.000
6 mA	1.11	0.062	1.00	0.001
8 mA	1.11	0.068	0.992	0.001

Two-Sample t on NOx production
Test of $\mu_1 - \mu_2 = 0$

	Difference	95% Lower Bound	95% Upper Bound	Probability
5 vs. 15 min	0.208	0.149	0.267	0.002
15 vs. 30 min	0.303	0.255	0.352	0.000
30 vs. 45 min	0.159	-0.004	0.323	0.052

Two-Sample t on NO_x production
Test of $\mu_1 - \mu_2 = 0$

	Difference	95% Lower Bound	95% Upper Bound	Probability
2 vs. 4 mA	0.360	0.287	0.433	0.002
4 vs. 6 mA	0.089	-0.081	0.259	0.153
6 vs. 8 mA	0.003	-0.166	0.173	0.954

Table S8. Summary of voltages measured between the plasma cathode and the Pt anode as a function of the plasma current in the plasma electrolytic system. The plasma was formed in a flow of N_2 gas.

	1 mA	**2 mA**	**3 mA**	**4 mA**	**6 mA**	**8 mA**
			Voltage (V)			
Trial 1	508	510	503	498	510	505
Trial 2	509	514	506	509	502	514
Trial 3	503	504	511	506	499	501
Trial 4	511	501	508	508	507	497
Trial 5	506	503	512	503	501	501
Trial 6	513	507	501	508	503	499
Average	**508**	**507**	**507**	**505**	**504**	**503**