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Supporting Information

Experimental

Materials

Copper and iron were separately used as the inner electrodes in the plasma experiments. The characteristic properties of the wires and the rod are summarized in Table S1. The surface area per 150 mm of wire/rod was calculated assuming a cylindrical wire/rod and was used for the measurement of the catalytic activity of a unified surface area for each element.

Plating of copper

An electroless plating (so-called a two-step method) was used for loading a copper film on the inner wall of the silica reactor. After the $SnCl_2$ sensitization followed by $PdCl_2$ activation, the inner wall of silica tube was treated at 343 K for 22 seconds with an aqueous mixture of $CuSO_4 \cdot 5H_2O$ 0.03 mol dm^{-3}, ethylene diamine tetra-acetic acid 0.07 mol dm^{-3}, and 37 % formaldehyde 1.8 ml dm^{-3}. Approximately 7-8 mg of Copper was planted on the silica surface after water-washing. This method was reported to possibly produce surface-remaining tin, palladium, and chloride which might influence the catalytic activity [*s1, s2*].

Reactor

The quartz tubular reactor is shown in Figure 1. The outer diameter and thickness of the quartz tube were 12.7 mm and 1.0 mm, respectively, unless otherwise stated. The outer side of the quartz reactor was surrounded by the outer electrode (the copper wire gauze of 80 mesh). A net electrode was employed to observe the state of the inner plasma. The inner electrode was connected to a high voltage power supply, and the outer electrode acted as a ground electrode.

A function generator and a high voltage power supply (Plasma Concept Tokyo Inc., Tokyo,

Japan, PCT-MBS-50A) were employed to power the reactor. The process's performance was analyzed by varying both the voltage and the frequency of the input power. The characteristic voltage *V(t)* and current *I(t)* curves were recorded using an oscilloscope (Iwatsu Electric Co., Ltd., Tokyo, Japan, DS-5412A) that was directly connected to the high voltage power supply, which included a high voltage probe and a series resistance. The power P(W) consumed within the plasma was determined from power calculations based on one period integration of the *V(t)I(t)* product. Figure S1 shows representative V-I. The energy efficiency is expressed as the ammonia production rate (μmol min^{-1}) per consumed unit of energy (W). The power of the plasma was dependent on the applied voltage and was approximately 2-100 W at V=2-5 kV. Therefore, the power density in the present experiments 0.148-7.42 W/cm^3.

Experimental run

All of the experiments were performed at atmospheric pressure without heating. A mixture of N_2 and H_2 was flowed into the reactor from the top of the reactor, and the exit gas was delivered to a diluted H_2SO_4 aqueous solution to gather the produced ammonia. The gas flow rates were controlled using mass flow controllers, and the concentration of ammonia was analyzed using an ion chromatograph (Shimadzu, Tokyo, Japan, LC-20AD_{sp} and CTO-20AC) that was equipped with an IC-C4 column and a conductivity detector (Shimadzu, CDD-10A_{VP}).

Typical reaction conditions included an applied voltage of 5 kV and a frequency of 50 kHz for the reaction port, which was 150 mm in length. A mixture of H_2/N_2 = 1 was flowed into the reactor at a flow rate of 100 ml min^{-1}. Wool-like copper wires (1.10 g) with a diameter of 0.08 mm were employed as the inner electrode unless otherwise stated. It is important to note that the amount of ammonia produced in the current reaction system frequently varied with the reaction

times and the number of runs. For changes in the production activity, the experiments were repeated until the production rates were stabilized, and the production rates or yields of ammonia were determined thereafter. The ammonia yield and production rate were calculated based on the nitrogen molecules supplied as follows:

Yield of ammonia (%) = 100 x conc. of NH_3 produced (mol min^{-1}) / 2 x conc. of N_2 supplied (mol min^{-1}) (1)

Production rate of ammonia (μmol min^{-1}) = amount of ammonia produced in the predetermined time (μmol) / sampling interval (min) (2)

Consumption energy of a Haber-Bosch process

The consumption energy of a current Haber-Bosh process is dependent on the process, for example the preparation method of hydrogen and the electricity cost, and is not disclosed due to industrial secrets. We have estimated the energy consumption from the prices of ammonia. The ammonia production in a large-scale Haber-Bosh process was roughly 127 or 80.5 g-NH_3/kW h for hydrogen produced from methane conversion or water electrolysis, which was much higher than the value reported in this manuscript.

References

s1) Z-C. Liu, Q-G. He, P. Hou, P=F Xiao, N-Y. He, Z-H. Lu, *Colloids Sur. A: Physicochem. Eng. Aspects* **2005**, *257-258*, 283.

s2) W. Wang, Q. Li, J. Zhai, *Surf. Interface Anal.* **2013**, *45*, 4756.

Table S1. Properties of metal rods or wires employed in the current plasma experiments.

Metal	Density /g cm^{-3}	Diameter /mm	Surface area of a 150 mm rod or wire /cm^2	Supply source
Cu	8.96	8 (rod)	37.7	Iwasaki Corp.
		0.12	0.57	Ohsato Corp.
		0.08	0.38	Nippon Steel Wool Co., Ltd.
Fe	7.87	0.14	0.66	Nippon-clever Co. Ltd.

Table S2. Dependency of ammonia yield on the shape of the electrode.[a)]

Shape of inner copper electrode	Silica tube /mm		Diameter of electrode /mm	Distance between inner electrode and silica wall /mm	Surface area of copper /cm^2	H_2/N_2 ratio /-	NH_3 yield /%
	Outer diameter	Inner diameter					
Rod 	20.0	16.1	16.0	0.05	75.4	3	0.40
	22.0	18.7	16.0	1.35	75.4	3	0.57
	25.0	21.0	16.0	2.50	75.4	3	0.54
	28.0	24.5	16.0	4.25	75.4	3	—[b)]
	30.0	26.0	16.0	5.00	75.4	3	—[b)]
	12.7	10.7	8.0	1.35	37.7	3	0.90
	12.7	10.7	8.0	1.35	37.7	1	0.83
Cylindrical wire gauze 	12.7	10.7	0.12 (wire)	0.85	863[c)]	3	3.4
	12.7	10.7	0.12 (wire)	0.85	863[c)]	1	2.7
Wool-like 	12.7	10.7	0.08 (wire)	1.57[d)]	61.3[e)]	3	3.5
	12.7	10.7	0.08 (wire)	1.57[d)]	61.3[e)]	1	2.6

[a)] Reaction conditions: applied voltage, 5 kV; frequency, 50 kHz; electrode length, 150 mm; total flow rate, 100 ml min^{-1}; H_2/N_2=1-3. [b)] The yields of ammonia could not be determined due to unsettled plasma. [c)] The wire gauze of 80 mesh was made of a copper wire with a 0.12 mm diameter. Total weight of used copper was 23.2 g. [d)] Average distance. [e)] Wool-like copper of 1.10 g was used for the experiment.

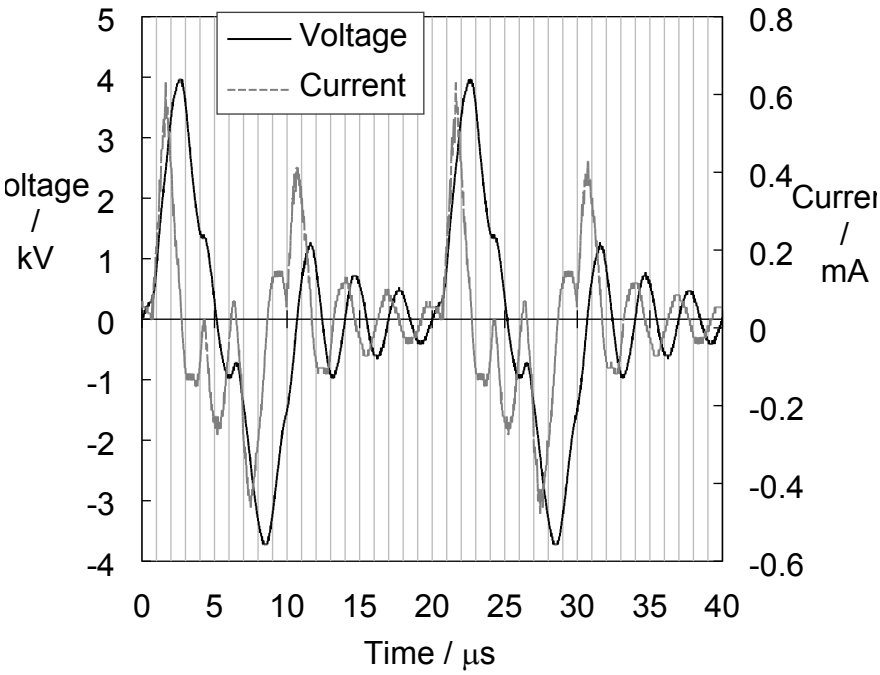

Figure S1. Waveform of applied voltage and current on the present apparatus. Reaction conditions: applied voltage, 5 kV; frequency, 50 kHz; electrode length, 150 mm; wool-like copper, 61.3 cm^2 (1.10 g); total flow rate, 100 ml min^{-1}; H_2/N_2=1.

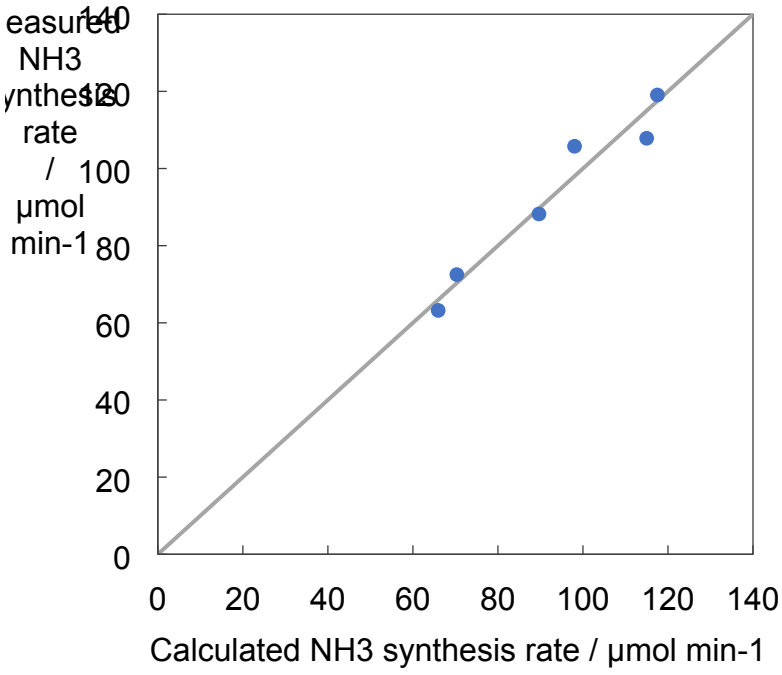

Figure S2. Comparison of measured ammonia synthesis rates with calculated ones using α=0.77 and β=1.16 determined by a least squares method for Equation 1 and the data of Figure 4.

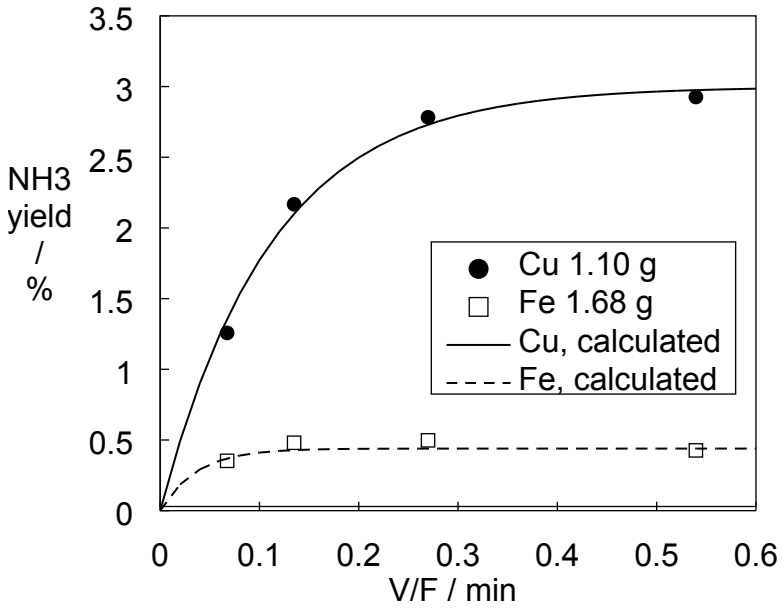

Figure S3. Change in ammonia yield as a function of the transit time (V/F) using a wool-like copper (closed circle) or iron (open square) electrode. Reaction conditions: applied voltage, 5 kV; frequency, 50 kHz; electrode length, 150 mm; wool-like metal electrode, 61.3 cm^2 (1.10 g of Cu or 1.69 g of Fe); volume of reaction port (V), 13.49 ml (the volumes of employed electrodes (0.12 ml) was neglected in the calculation); total flow rate (F), 25-200 ml min^{-1}; H_2/N_2=0.5.

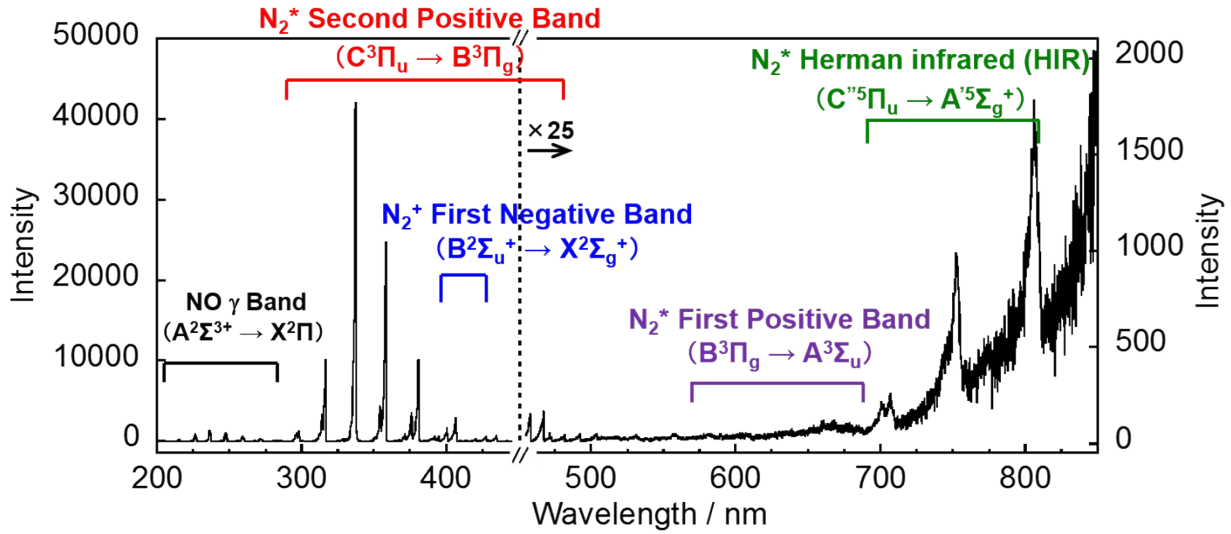

Figure S4. Emission spectra of plasma-activated nitrogen on a copper-wool electrode. Assignments of the spectra were based on the references shown in the main text.[16] Reaction conditions: applied voltage, 5 kV; frequency, 50 kHz; electrode length, 150 mm; wool-like metal electrode, 61.3 cm^2 (1.10 g of Cu); total flow rate of N_2, 100 ml min^{-1}; N_2=100 %.