Electronic Supplementary Material (ESI) for Reaction Chemistry & Engineering.

Plasma nitrogen fixation in the presence of a liquid interface

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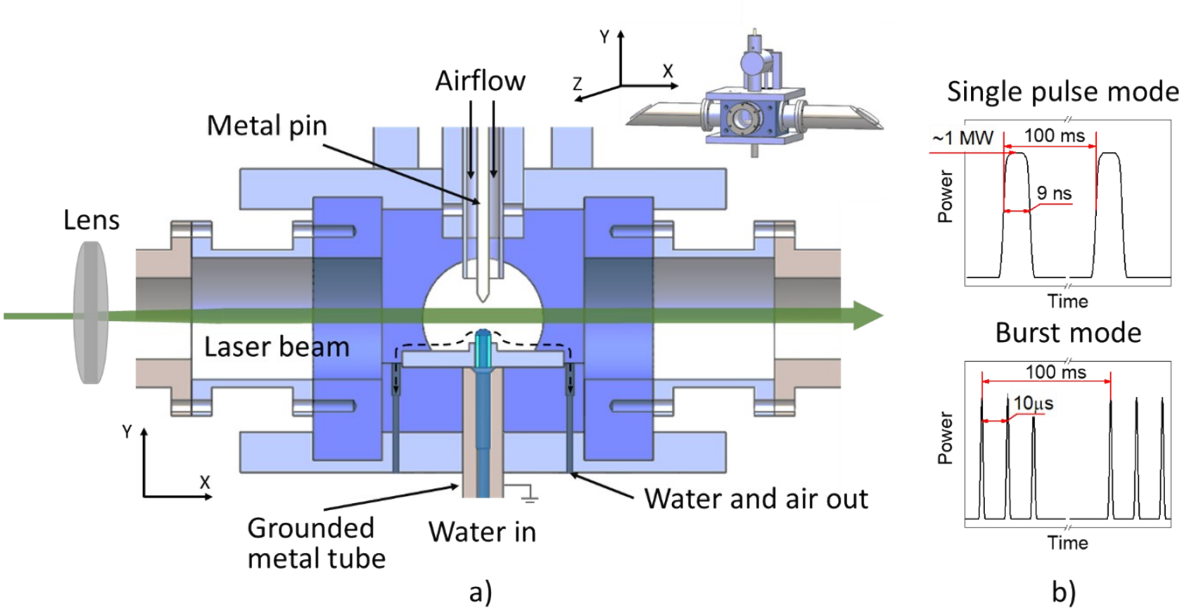

Fig. S1. Schematic view of the experimental setup (a) and visual explanation of the investigated frequency modes (b).

The voltage and current waveforms were measured using a Tektronix P6015A high voltage probe (75 MHz bandwidth, 4.7 ns rise time) and current measurement shunt (CS-10/500, Megaimpulse, 1 ns rise time), respectively. The measured signals were recorded using an oscilloscope with a bandwidth of 600 MHz (LeCroy WaveRunner 64Xi). The phase shift between the voltage and current waveforms was measured connecting a non-inductive resistor as a load and was found to be 3.2 ns. Accordingly, the energy deposited into the main discharge pulse was estimated using the following equation:

$$E = \int_{t_0}^{t_1} (I \cdot U)\, dt \ \ [J] \qquad (1)$$

where t_0 and t_1 define the time interval of the first positive current pulse, and I and U are the current and the voltage, respectively.

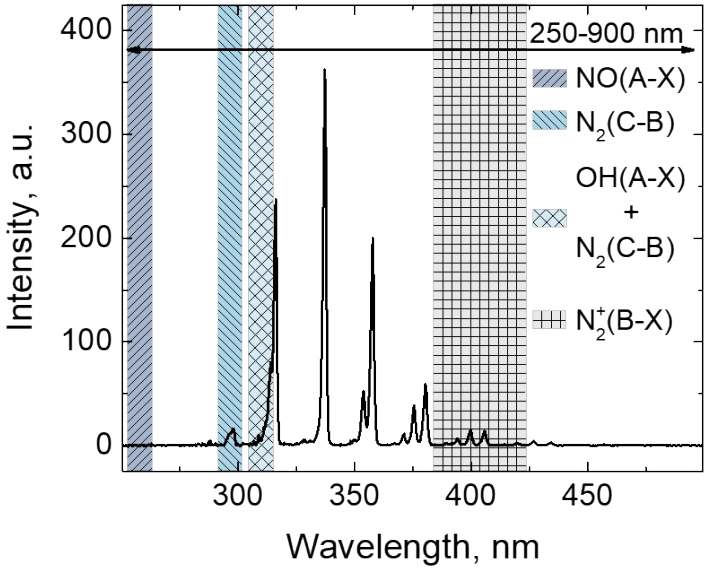

Fig. S2. Overview of the optical emission spectra with marked regions that correspond to the optical filters transparency.

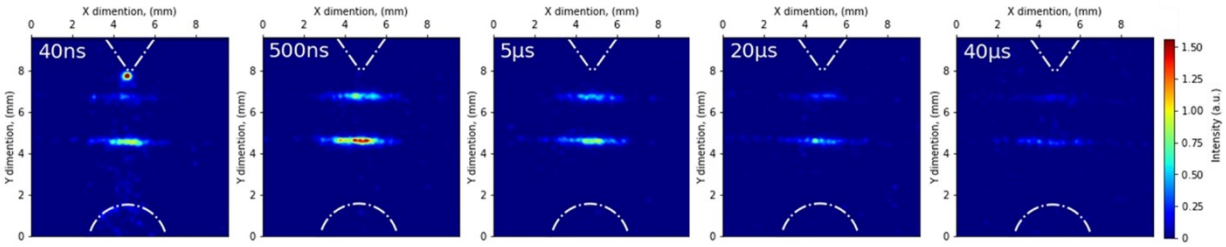

Fig. S3. Spatial resolved TALIF profiles of O aotms. The images are match cuts of TALIF measurements at two positions in the discharge gap.

O atoms kinetics:

Phase I, shown in Fig 3a, represents the time range when O atoms generation was dominant. Aside from O_2 dissociation by electron impact reaction, a major contribution into O atoms formation is a set of reactions with electronically excited $N_2(B^3\Pi_g, C^3\Pi_u)$ states:[1]

$$N_2\left(B^3\Pi_g, C^3\Pi_u\right) + O_2 \rightarrow N_2(X) + O\left(^3P\right) + O\left(^3P, ^1S\right) \quad \text{(R1)}$$

It is noteworthy that at atmospheric pressure, high electronically excited $N_2(B^3\Pi_g, C^3\Pi_u)$ states have the lifetime of $\tau < 5$ ns, while N_2 ($A^3\Sigma_u^+$) state has the $\tau \approx 60$ ns.[2] O atoms' prolonged growth during 100's of ns is explained by periodically appearing corona discharge (see Fig. S3) that can effectively generate $N_2(A^3\Sigma_u^+)$ and, consequently, form O atoms as follows:[3]

$$N_2\left(A^3\Sigma_u^+\right) + O_2 \rightarrow N_2(X) + O\left(^3P\right) + O\left(^3P\right) \quad \text{(R2)}$$

Interestingly, despite $N_2(a'^1\Sigma_u^-)$ can also be generated in the discharge; these states are effectively quenched by H_2O and therefore were not considered as a possible route of O atoms formation.[4]

Time-resolved ICCD images shown in Fig. 4S demonstrate that the pulsed corona is generated nearby the pin electrode. Moreover, with increasing applied voltage, this effect becomes more pronounced. It defines a nonlinear increase in the O atoms' density of 2.8 times, increasing the pulse energy by 1.5 times, as shown in Fig 3a.

The main recombination pathway of the O atoms is the O_3 generation in three-body reactions during phase II.

$$O(^3P) + O_2 + M \rightarrow O_3 + M \quad \text{(R3)}$$

The measurements show that the detected TALIF signal has a long tail up to ~50 ms (Fig. 3a, dashed lines with empty dots). This is attributed to artificial $O(^3P)$ atoms generation because of laser-induced photodissociation of

O_3 and well correlated with the gas phase removal by the coming air. The same artifact was observed by Oda et al., and the correction has been made to the overall O number density accordingly to the proposed methodology.[5]

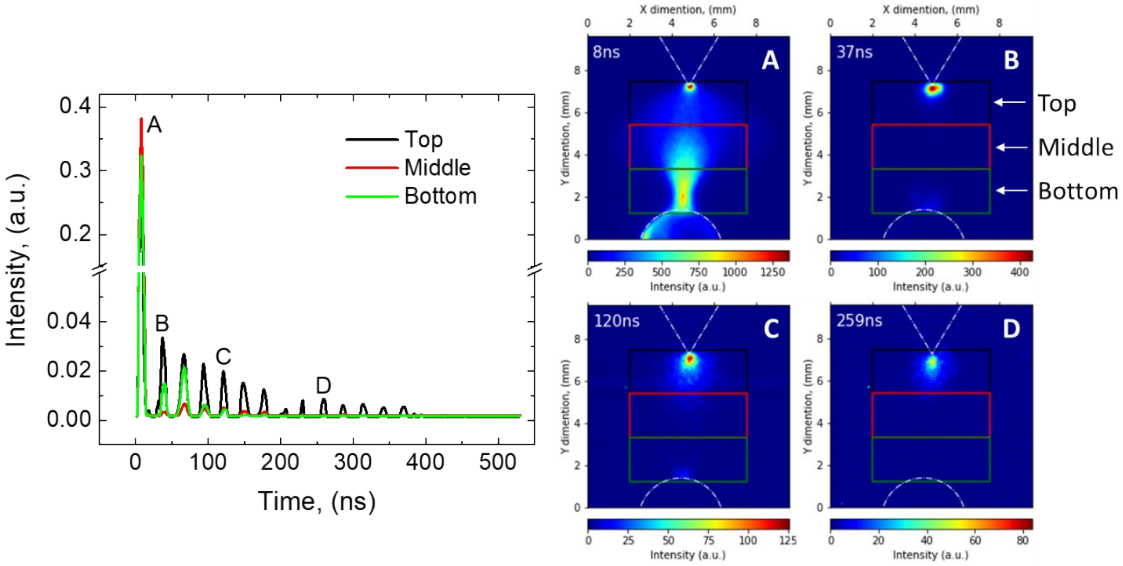

Fig. S4. Time-resolved emission intensity of the NRP discharge at 3 positions in the gap for the pulse energy of 3.4 mJ. The first intense peak (image A) represents the main pulse; the following peaks (images B-D) depict periodically appearing pulsed corona. The images were made with an exposure time of 5 ns.

Table S1. A set of reactions responsible for O atoms, OH, and NO radicals generation and loss and their characteristic times estimated using experimentally obtained number densities for the pulse energy of 3.4 mJ.

	Reaction	k(298K), m^3s^{-1}	τ^a	Ref.
	O atoms			
(R1)	$N_2(B^3\Pi_g, C^3\Pi_u) + O_2 \rightarrow \rightarrow N_2(X) + O(P) + O(P,^1S)$	3×10^{-16}	~6.5 ns	4
(R2)	$N_2(A^3\Sigma^+_u) + O_2 \rightarrow N_2(X) + O(P) + O(P)$	1.7×10^{-18}	~114 ns	4
(R3)	$O(^3P) + O_2 + N_2 \rightarrow O_3 + N_2$	1.89×10^{-45b}	~124 µs	4
	$O(^3P) + O_2 + O_2 \rightarrow O_3 + O_2$	1.71×10^{-45b}	~509 µs	4
	OH radicals			
(R4)	$N_2(a'^1\Sigma^-_u) + H_2O \rightarrow N_2(X) + H + OH$	3.00×10^{-16}	-	4
(R5)	$O(^1D) + H_2O \rightarrow OH + OH$	2.20×10^{-16}	-	6
(R6)	$N(^4S) + OH \rightarrow NO + H$	5.06×10^{-17}	~25 µs	6
(R7)	$OH + OH \rightarrow H_2O_2$	$2.1\pm0.5\times10^{-17}$	~59±12 µs	6
(R8)	$OH + NO + N_2 \rightarrow HNO_2 + N_2$	7.46×10^{-43b}	~64 µs	6
	$OH + NO + O_2 \rightarrow HNO_2 + O_2$	7.46×10^{-43b}	~234 µs	6
(R9)	$OH + OH + N_2 \rightarrow H_2O_2 + N_2$	6.92×10^{-43b}	~95 µs	6
	$OH + OH + O_2 \rightarrow H_2O_2 + O_2$	6.92×10^{-43b}	~347 µs	6
	NO radicals			
(R10)	$N_2(A^3\Sigma^+_u) + O(P) \rightarrow NO + N(^2D)$	7.00×10^{-18}	~643 ns	4
(R11)	$N(^4S) + NO \rightarrow N_2 + O(P)$	$2.7\pm0.6\times10^{-17}$	~35±8 µs	6
(R12)	$O_3 + NO \rightarrow NO_2 + O_2$	$1.9\pm0.3\times10^{-20}$	~49±8 ms	6

[a]The characteristic time (τ) was estimated as $\tau = (k \times n)^{-1}$, where k is a reaction rate constant, and n is a number density of the involved species obtained in this work (O atoms, OH, and NO radicals) or theoretically estimated (N_2, O_2) based on the ideal gas law. [b]Three body reactions with reaction rate in $m^6\ s^{-1}$.

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