

1 **Supplementary Materials for**
2 **Nitrogen Fixation in a Non-Equilibrium Spatially Distributed**
3 **Electric Field**

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Supplementary Note 1:

We perform *in situ* measurements using the HC-PCF based PTS diagnostic system to directly verify the reaction pathways under different electric field (EF) strength. Fiber I and II are placed in the high and low EF regions (Supplementary Fig. 22), respectively, to quantify the spatial distribution of NO, NO₂, and O₃ concentrations at 10 kV and 500 sccm (Supplementary Fig. 23). In this measurement, flow goes through the high EF region (Fiber I) and low EF (Fiber II) in turn. The concentrations of NO and NO₂ in the low EF region are higher than those in the high EF region, reflecting the accumulation of NO_x from the high EF region to the low EF region over reaction time in this measurement. It is well known that N₂(v) is mainly produced below 100 Td in a low EF and further promotes the NO_x formation in this region. However, the O₃ concentration is slightly higher in the high EF region than in the low EF region, indicating that O₃ is mainly produced in the high EF region, while is not significantly formed in the low EF. In addition, O₃ in the low EF is mainly produced through the transit from the high EF, and it is also consumed in the low EF to oxidize NO. These measurements experimentally verify that the SD-EF strategy can achieve the coexistence of N₂(v) and O₃ sub-mechanisms within a single reactor.

Supplementary Note 2:

In the SD-EF strategy, the kinetic enhancement arises from the electric field distribution rather than from the temperature variation. We design a nanosecond-pulsed discharge experiment in a closed DBD reactor at 30 kPa and 7 kV to explore the suppression of reverse reactions, as shown in Supplementary Fig. 24. The time-resolved measurements of NO and NO₂ concentrations ((Supplementary Fig. 25) are performed using our HC-PCF-based PTS method with “plasma on” for 300 s and with “plasma off” for another 300 s after the discharge switch. The transient measurement resolution is within 100 ms. The NO_x concentrations initially increase in plasma and then reaches a steady state near 250 s. When discharge ceases at 300 s, the NO concentration decreases while NO₂ slightly increases, indicating further formation of NO₂ from NO. However, the total NO_x concentration decreases, indicating the presence of reverse reactions and the reduction of NO_x to N₂. Therefore, the on/off mode in plasma does not completely suppress reverse reactions. Moreover, we have measured the internal temperatures in plasma on and plasma off, which are 18.5 °C and 21.3 °C, respectively. The small temperature difference above indicates that the thermal effect is minimal.

Supplementary Note 3:

The HC-PCF-based PTS system offers high detection sensitivity and compact size, relatively high temporal resolution, strong resistance to electromagnetic interference, and capability for *in situ* monitoring in both gas and liquid phases.

However, the main limitation arises from molecule diffusion, which restricts the response speed. As a result, the system is unsuitable for extremely fast transient phenomena or detection of short-lived radical species, because its response time is on the order of seconds to minutes. Future studies on enabling rapid exchange of species inside and outside the optical fiber are expected to address this issue.

Supplementary Note 4:

Photothermal spectroscopy (PTS) detects signals through the photothermal effects generated by absorbed light energy. Compared to DRIFTS and Raman spectroscopy, PTS offers three main advantages (Rev. Sci. Instrum., 2001, 72, 1937–1955; Appl. Phys. B, 2011, 110, 163–175):

i) **Higher sensitivity and lower detection limits:** PTS does not rely on the radiative scattering or absorption strength of molecules. Instead, it detects the local temperature rise induced by non-radiative relaxation processes, producing strong signals even for molecules with weak adsorption. In contrast, direct infrared absorption spectroscopy is limited by strong laser output and detector saturation, while Raman spectroscopy suffers from inherently weak scattering intensity, making it difficult to achieve comparable sensitivity even with enhancement techniques.

ii) **Broader dynamic range and stronger resistance to interference:** The PTS signal depends on variations in medium properties, making it less susceptible to background noise. Conversely, direct infrared absorption spectroscopy is often affected by laser output fluctuation, and Raman signals are easily overwhelmed by fluorescence backgrounds.

iii) **Wider applicability:** PTS is particularly suitable for non-infrared-active or weakly scattering molecules because detection does not rely on a molecular dipole moment. Any absorption or scattering process that generates a thermal effect can be measured, allowing PTS to identify species with weak infrared absorption, providing measurable signals in systems that are otherwise spectroscopically challenging.

These characteristics make PTS particularly suitable for highly sensitive *in situ* detection of trace species in plasma environments under strong electromagnetic fields.

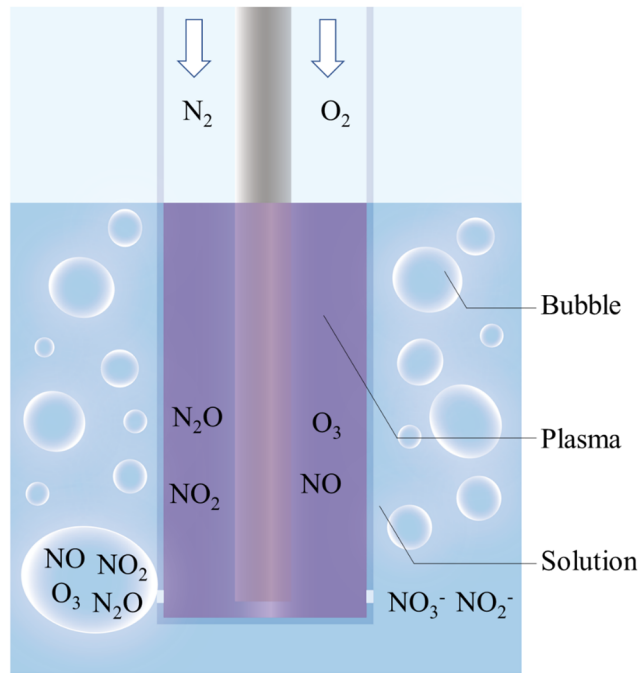
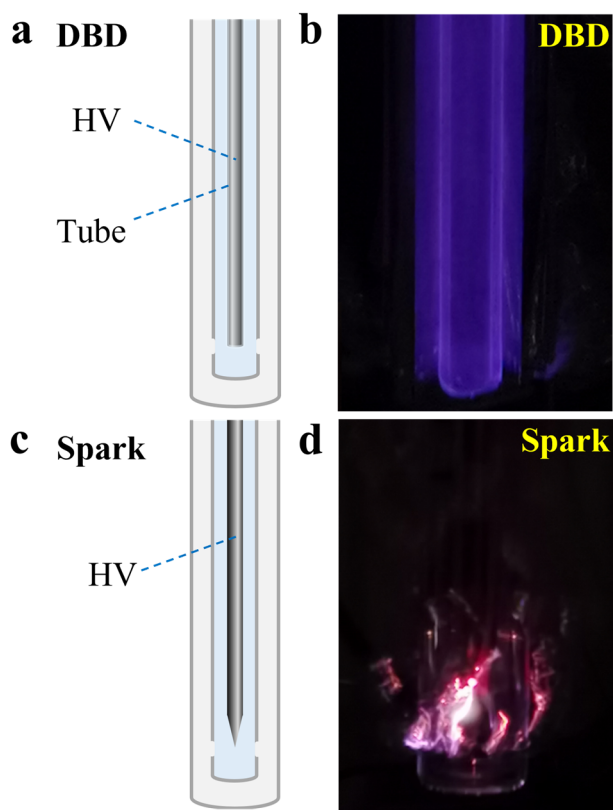


Fig. S1 Schematic of the nitrogen fixation process by plasma bubble reactor.



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86 **Fig. S2 Discharge phenomena in the reactor.** **a, b**, Schematic (**a**) and digital image (**b**) of the
 87 DBD. **c, d**, Schematic (**c**) and digital image (**d**) of the spark. In DBD, uniform discharge fills
 88 the entire quartz tube and the micro discharges are almost invisible to the naked eye. In the
 89 spark, the arc generates from the pin of the central stainless steel, and then extends to the bubble
 90 from the holes in the bottom of the reactor.

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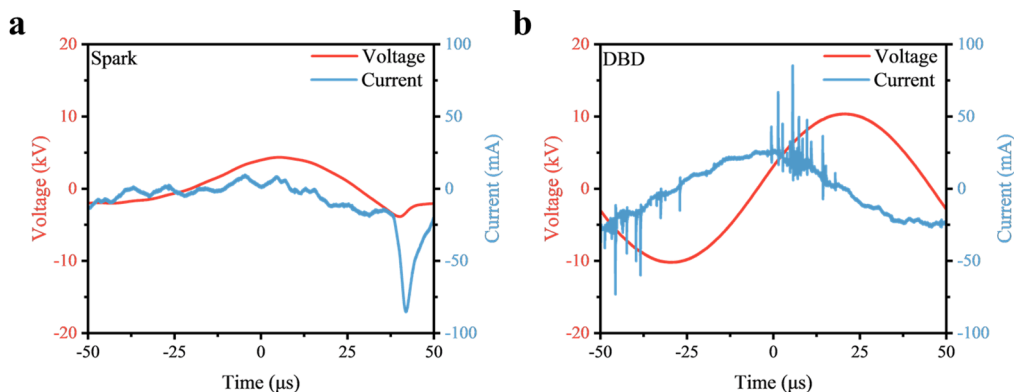


Fig. S3 Typical electrical characteristics of the discharge. a, b, Voltage and current measurements of spark **(a)** and DBD **(b)**. (Reaction condition for Fig. S2a: $N_2/O_2 = 2:8$, Frequency: 10 kHz, Voltage of spark: 5 kV; Reaction condition for Fig. S2b: $N_2/O_2 = 2:8$, Frequency: 10 kHz, Voltage of DBD: 10 kV). In DBD, the voltage and current curves exhibit a sinusoidal shape, with typical peak values of 10 kV and 25 mA, respectively. However, there are some minor peaks reaching up to 85 mA in the current curve, which are considered as micro-discharges. For the I-V curve of the spark discharge mode, abrupt changes occur, with a peak voltage of 5 kV and a peak current of 84 mA during the air breakdown.

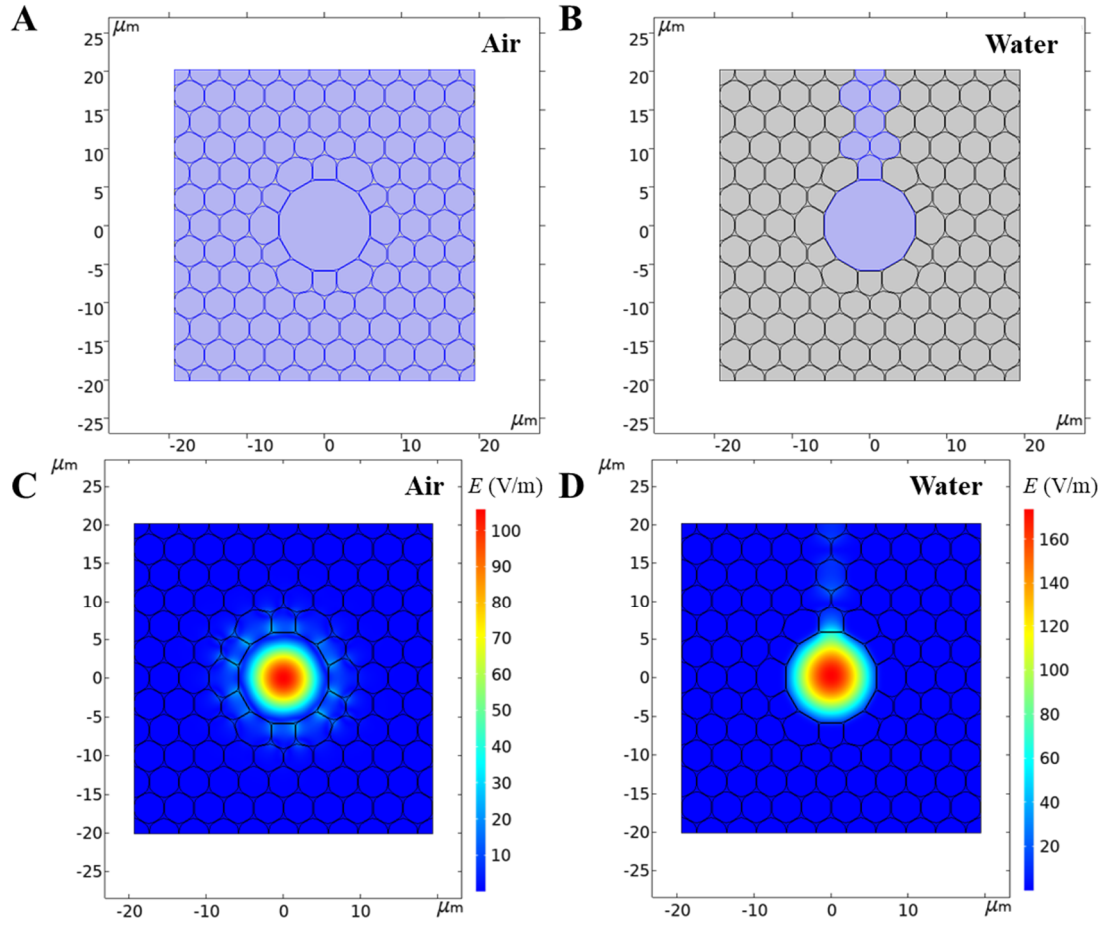


Fig. S4 Light field power simulation in the PCF. a, b, Simulation structure diagram of the (a) HC-PCF without water and (b) HC-PCF with water. **c, d,** Light field power distribution of the HC-PCF without water (c) and HC-PCF with water (d). The laser can be effectively restricted to transmit with and without water. Furthermore, the effective refractive indices of the HC-PCF without water and with water are 1.012 and 1.330, respectively.

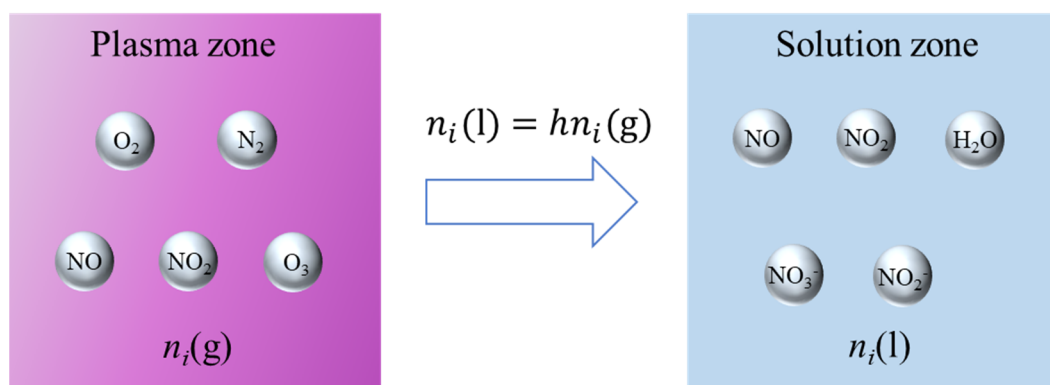


Fig. S5 Schematic of the simulation model for plasma discharge and solution absorption.

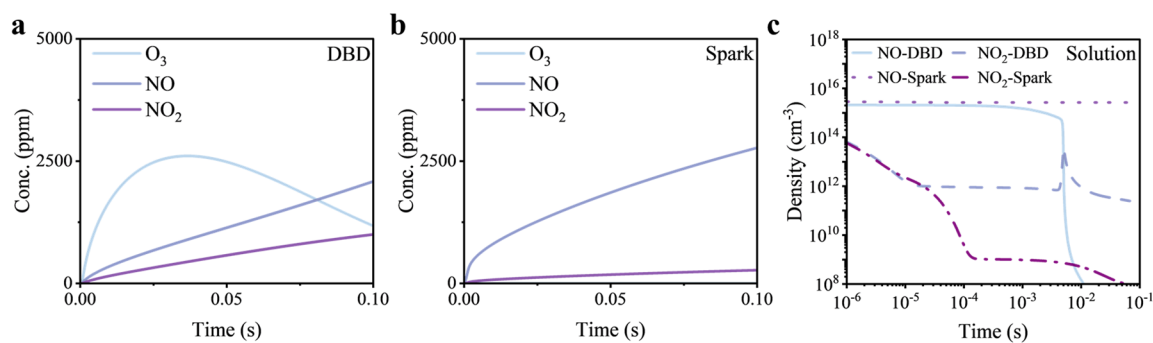


Fig. S6 Numerical simulations for key species concentrations in NO_x generation and dissolution. **a**, Temporal evolution of O₃, NO, and NO₂ concentrations in DBD. **b**, Temporal evolution of O₃, NO, and NO₂ concentrations in spark. **c**, Temporal evolution of NO and NO₂ densities in DBD and spark. (Simulation condition for Fig. S3a: Power: 10 W, Frequency: 10 kHz; Simulation condition for Fig. S3b: Power: 10 W, Frequency: 10 kHz) The O₃ concentration in DBD is 1175 ppm, unlike the absence of O₃ in spark at 0.1 s. However, the NO_x concentrations in spark is 3042 ppm, respectively, which are significantly higher than those in DBD. In the NO_x dissolution process, we find that NO can be absorbed well in DBD, but the absorption of NO is poor in spark. As for NO₂, both discharge modes have a good NO₂ absorption due to its good solubility.

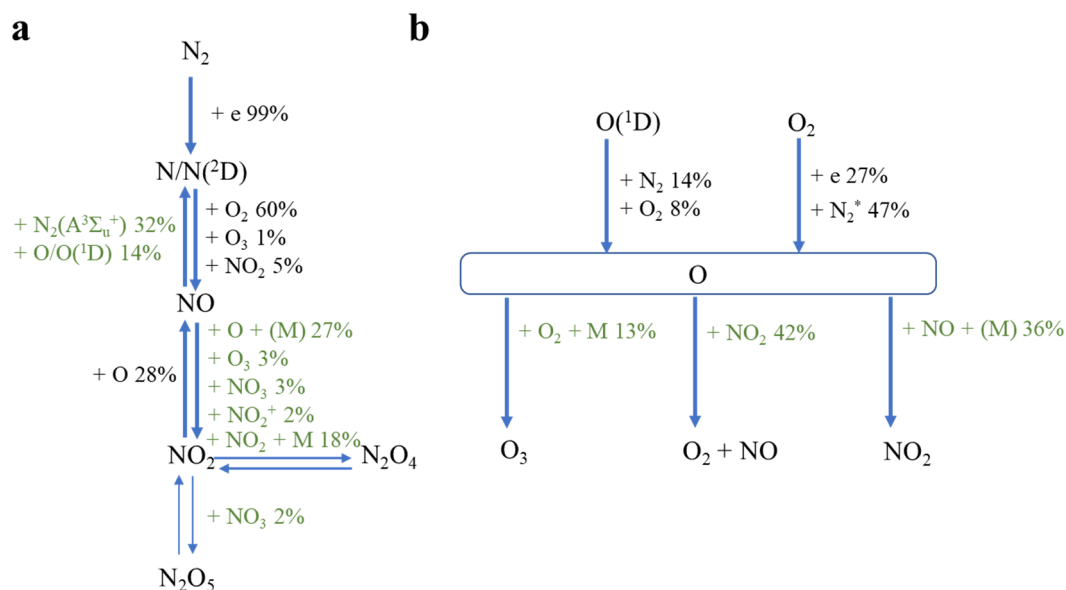


Fig. S7 Kinetics of plasma-assisted nitrogen fixation in DBD. a, Path flux analysis of N in DBD. **b,** Path flux analysis of O in DBD. N_2^* is the electronic excitation of N_2 , include $N_2(A^3\Sigma_u^+)$, $N_2(B^3\Pi_g)$, $N_2(a^1\Sigma_u^-)$, and $N_2(C^3\Pi_u)$. The percentages with black (green) color indicate the contributions accounting for the total species production (consumption). N and O radicals are initially produced by direct electron impact dissociation $e + N_2 \rightarrow e + N + N(^2D)$ (RS1), $e + O_2 \rightarrow e + O + O(^1D)$ (RS2), and $e + O_2 \rightarrow e + O + O$ (RS3). Subsequently, NO is formed from the reaction $N + O_2/O_3 \rightarrow NO + O/O_2$ (RS4), while O radicals generate O_3 through a three-body reaction $O + O_2 + M \rightarrow O_3 + M$ (RS5). It is noted that NO still needs O radicals or O_3 to produce NO_2 , thereby establishing a competitive relationship between O_3 and NO. This underscores the key role of O radicals in nitrogen fixation. However, excessive O radicals are not necessary for optimizing nitrogen fixation performance. Excessive O radicals reduce NO_2 back to NO and O_2 , limiting the yield of NO_2 . Thus, despite the substantial generation of O radicals in the DBD, NO remains the predominant product in the NO_x .

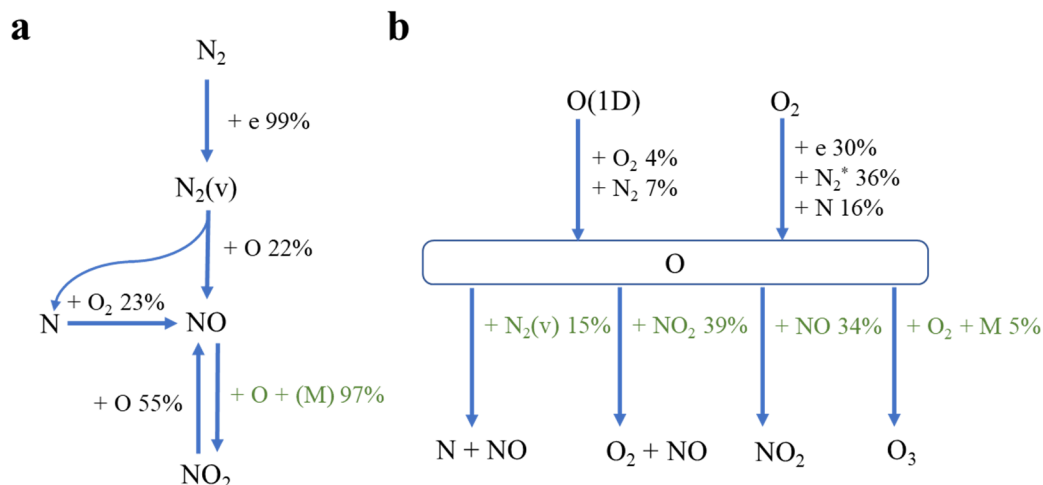


Fig. S8 Kinetics of plasma-assisted nitrogen fixation in spark. **a**, Path flux analysis of N in spark. **b**, Path flux analysis of O in spark. N_2^* is the electronic excitation of N_2 , include $N_2(A^3\Sigma_u^+)$, $N_2(B^3\Pi_g)$, $N_2(a'^1\Sigma_u^-)$, and $N_2(C^3\Pi_u)$. The percentages with black (green) color indicate the contributions accounting for the species total production (consumption). The electron impact reactions of N_2 are no longer primarily resulting in dissociation. Instead, they predominantly produce vibrationally excited $N_2(v)$. Meanwhile, approximately 80% of NO is produced by the reaction $O + N_2(v) \rightarrow NO + N$ (RS6). However, the accumulated N radical is harmful to the NO_x generation, which can reduce NO to N_2 by the reaction $NO + N \rightarrow N_2 + O$ (RS7). Furthermore, due to the low electric field intensity, the electron dissociation of O_2 is insufficient, causing the lower concentrations of NO_2 and O_3 .

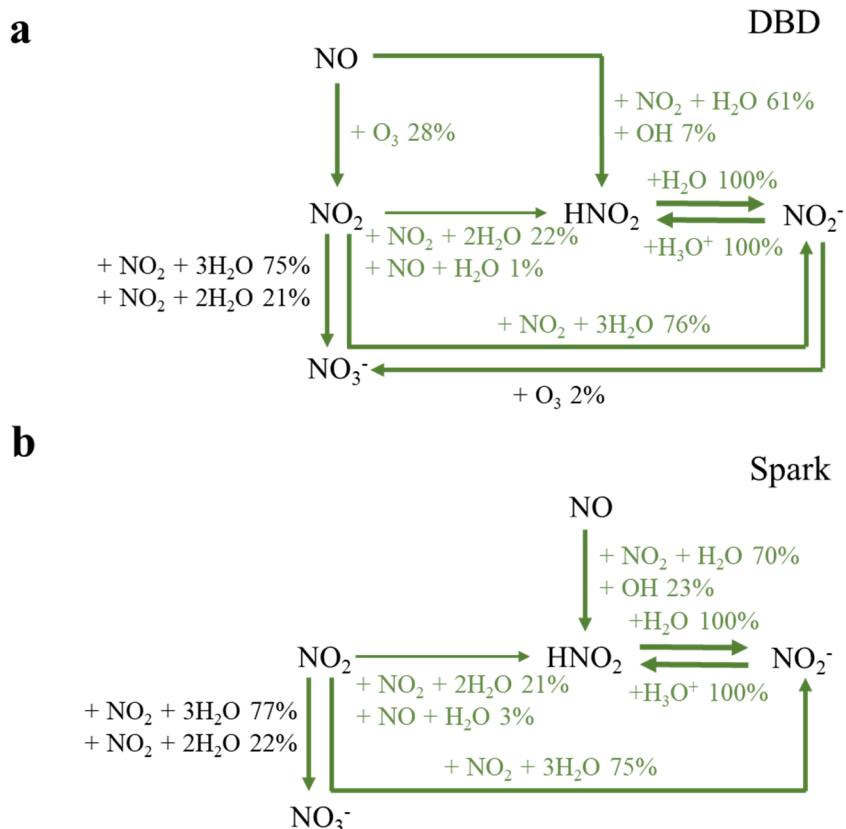


Fig. S9 Kinetics of NO_x dissolution in DBD and spark. a, Reaction pathways for NO_x dissolution in DBD. **b,** Reaction pathways for NO_x dissolution in spark. The percentages with black (green) color indicate the contributions accounting for the species total production (consumption). In DBD, NO(aq) has a low reactivity with H₂O, but can be consumed through NO(aq) + NO₂(aq) + H₂O(aq) → 2HNO₂(aq) (RS8). Interestingly, O₃ which has previously been considered as non-beneficial in plasma-assisted nitrogen fixation, has been found to be utilizable in the liquid phase, facilitating the conversion of NO(aq) to NO₂(aq). Therefore, despite the low solubility and reactivity of NO in water, a large amount of NO is still absorbed in DBD. Otherwise, NO₂(aq) demonstrates favorable reactivity with H₂O, with 50% of NO₂ utilized in NO₃⁻ production, while the remaining 50% contributes to NO₂⁻ formation. Moreover, NO₂⁻(aq) also can be oxidized to NO₃⁻(aq) by O₃(aq), resulting in a lower concentration of NO₂⁻(aq) and a higher concentration of NO₃⁻(aq) in the final products, which agrees with our experimental results. Furthermore, in spark mode, there's a lack of O₃, causing the lower NO absorption efficiency in the spark mode than that in DBD.

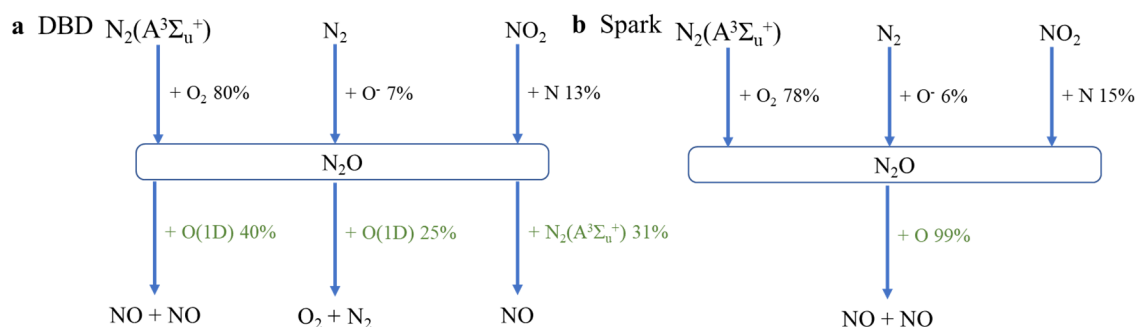


Fig. S10 0-D simulated Path flux analysis of N_2O in (a) DBD and (b) spark. The percentages with black (green) color indicate the contributions accounting for the species total production (consumption). N_2O is mainly produced through reaction $\text{N}_2(\text{A}^3\Sigma_u^+) + \text{O}_2 \rightarrow \text{N}_2\text{O} + \text{O}$. But the electronic excitation of N_2 requires a high electric field strength (> 130 Td), so low electric field is not suitable for the generation of N_2O in spark discharge. Meanwhile, the abundance of O radical promotes the conversion of N_2O into NO through reaction $\text{N}_2\text{O} + \text{O}/\text{O}(^1\text{D}) \rightarrow 2\text{NO}$, leading to a low N_2O concentration in the DBD mode. Overall, N_2O plays a minor role in plasma-assisted nitrogen fixation.

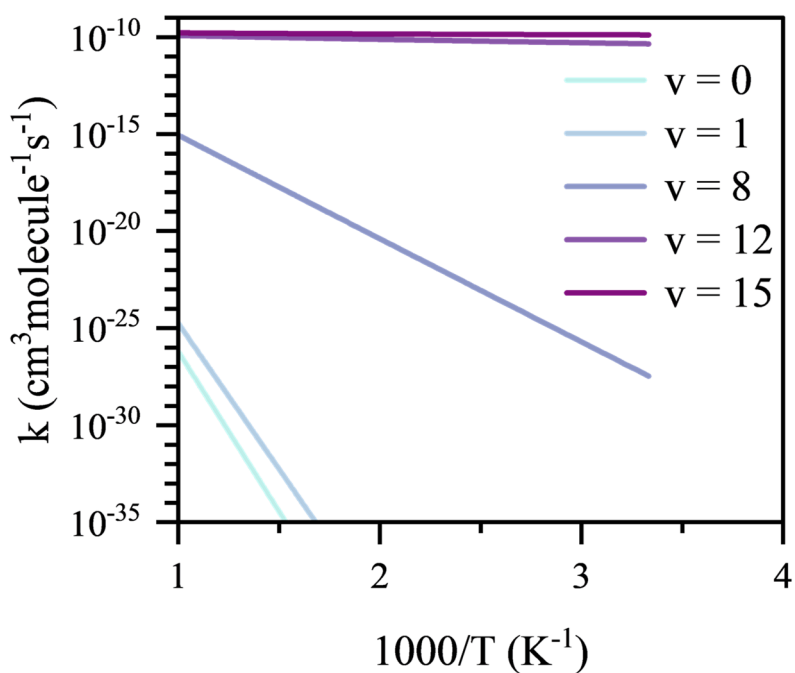
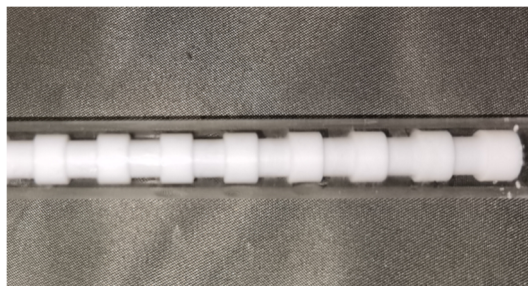


Fig. S11 Reaction rate $\text{O} + \text{N}_2(v) \rightarrow \text{NO} + \text{N}$ (RS6) against temperature under different vibrational levels. The chemical reactions of $\text{N}_2(v)$ are estimated by the semi-empirical formula from the Fridman-Macheret model. The reaction rate of $\text{N}_2(v=15)$ and $\text{N}_2(v=12)$ is 1.38×10^{-10} and $6.23 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, respectively, which are 13–40 orders of magnitude higher than those of $\text{N}_2(v=0)$, $\text{N}_2(v=1)$, and $\text{N}_2(v=8)$.



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184 **Fig. S12 Photograph of non-uniform thickness of the dielectric.** The central high-voltage
185 electrode is wrapped in this dielectric made of polytetrafluoroethylene.

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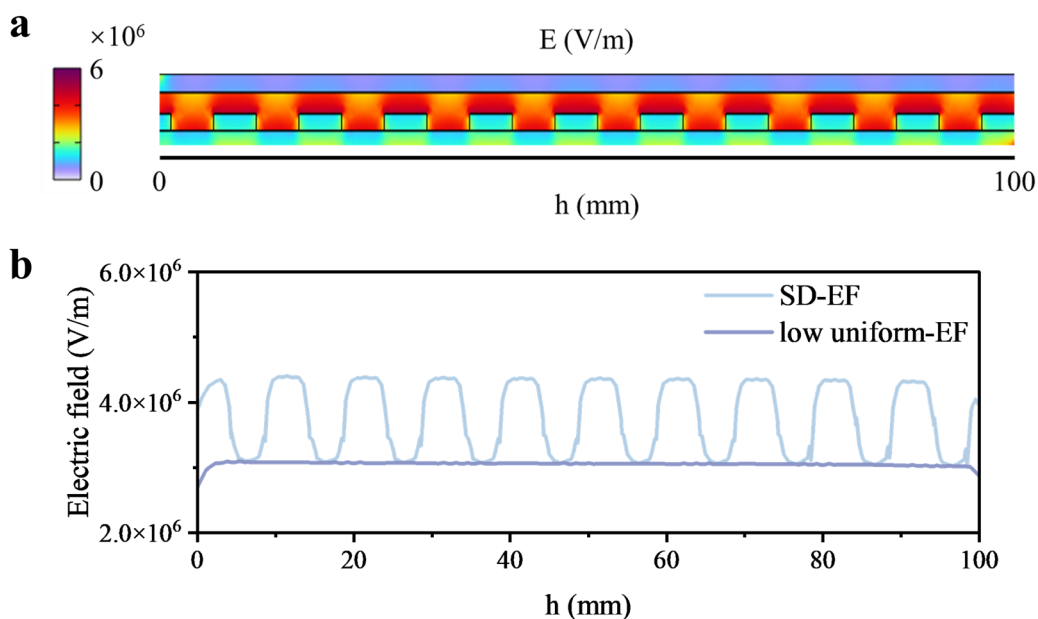


Fig. S13 Simulation of the electric field distribution of the SD-EF and low uniform-EF under the constant voltage. **a**, Electric field distribution of center section in the reactor in the SD-EF. **b**, The electric field distribution at a height of 0.5 mm from the inner wall of the quartz tube in SD-EF and low uniform-EF. (Simulation condition: Voltage: 10 kV). The simulation result shows that there are a higher electric field at the narrower gap and a lower electric field at the thicker gap. Furthermore, the higher electric field is approximately 1.5 times that of the lower electric field.

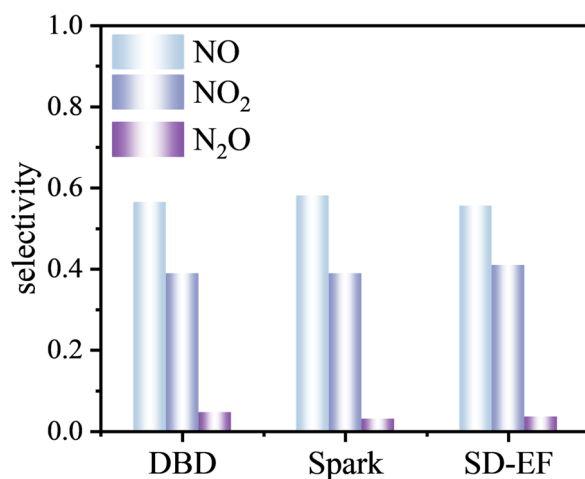
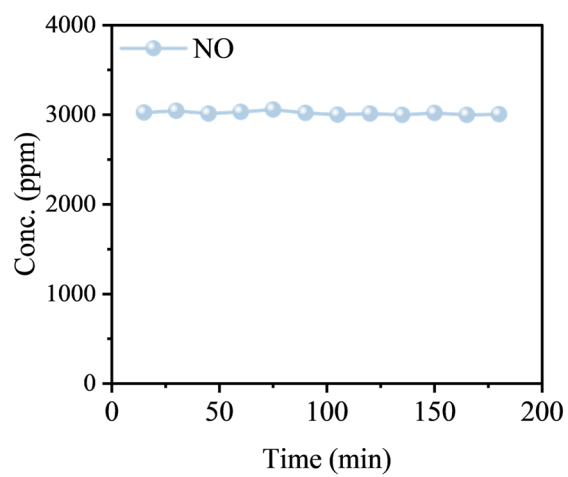


Fig. S14 Comparison of selectivities for the conversion of N₂ to NO, NO₂, and N₂O between different discharge modes. In DBD, the selectivities are 56.5% for NO, 38.9% for NO₂, and 4.6% for N₂O, respectively. In spark discharge, the selectivities are approximately 58.1% for NO, 38.8% for NO₂, and 3.0% for N₂O, respectively. In SD-EF, the selectivities are 55.6% for NO, 40.9% for NO₂, and 3.5% for N₂O.



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204 **Fig. S15 Evolution of the NO concentration during a 3-hour operation test in the SD-EF.**

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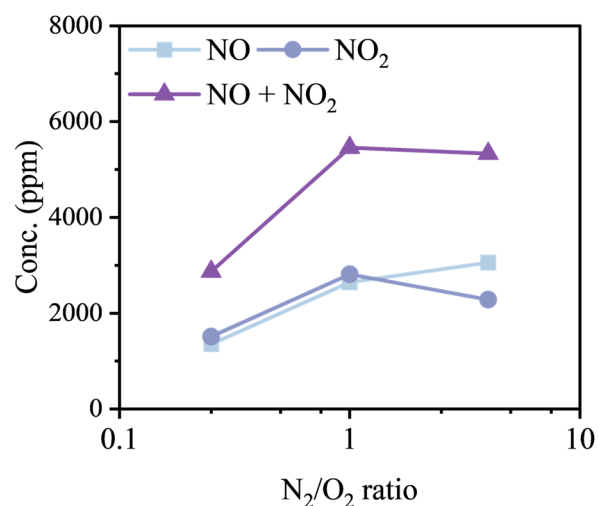


Fig. S16 NO and NO₂ concentrations at different N₂/O₂ ratios in SD-EF. The optimal N₂/O₂ ratio for NO₂ generation is 4:1, reaching 2813 ppm, compared to 2280 ppm at a 0.5 N₂/0.5 O₂ ratio. However, the overall NO_x concentration (the sum of NO and NO₂) shows little difference between a 0.5 N₂/0.5 O₂ ratio (5334 ppm) and a 0.8 N₂/0.2 O₂ ratio (5455 ppm).

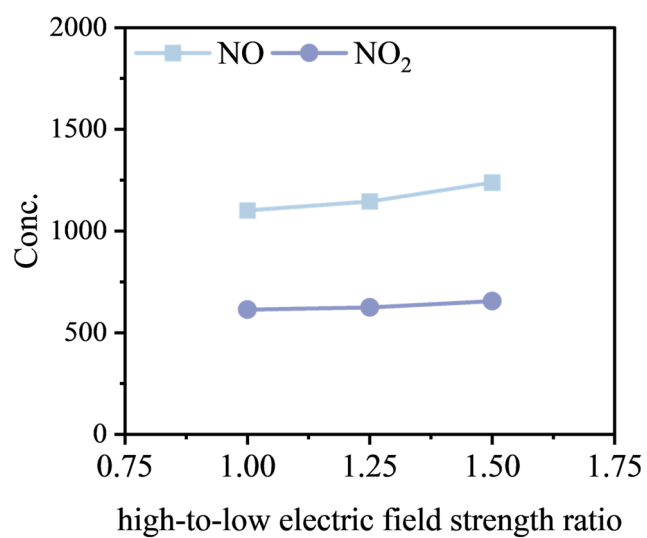


Fig. S17 Numerical simulation of SD-EF under different high-to-low electric field strength ratios.

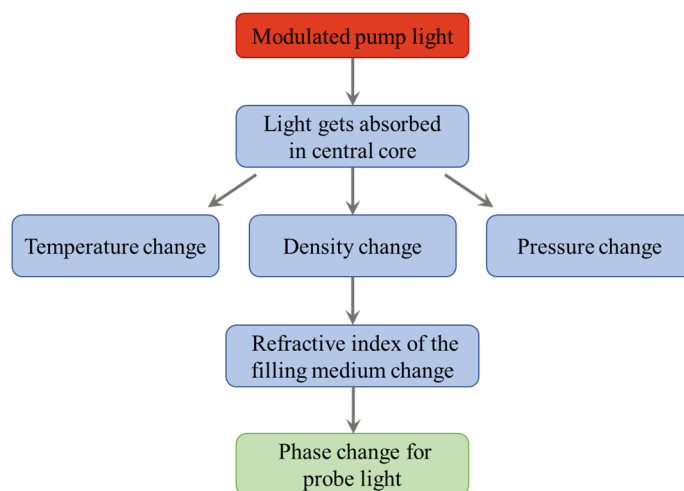


Fig. S18 Schematic of the basic principle of hollow-core photonic crystal fiber based photothermal spectroscopy (HC-PCF). When an intensity modulated pump light travels in the PCF, it interacts with the filling medium in the central core and gets absorbed by the molecules of the target substance. According to the principle of the photothermal effect, a periodic heat source appears in the central core, modulating the local temperature and the refractive index of the filling medium. A beam of probe light is introduced in the PCF simultaneously, and its optical phase is modulated by the periodic thermal source.

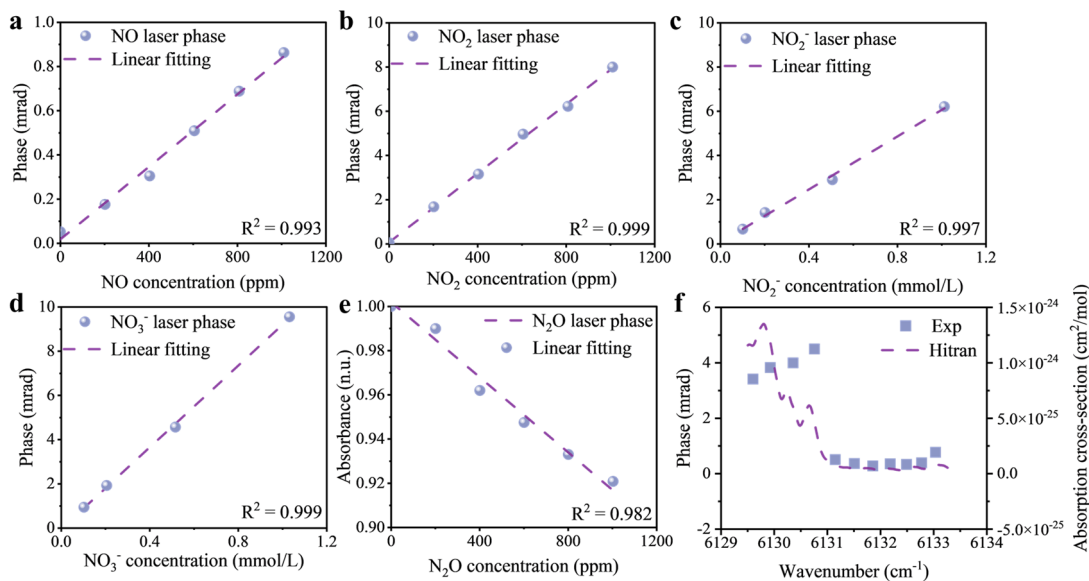


Fig. S19 In situ HC-PCF measurements for the quantification of the key products. a-d The modulation phase derived from photothermal spectra against the concentration for NO (a), NO₂ (b), NO₃⁻ (c), and NO₂⁻ (d). These curves all have a high degree of linearity. e, The absorbance derived from absorption spectra against the concentration for N₂O. The R-squared is 0.98, which is lower than the R-squared of the former. f, The modulation phase derived from photothermal spectra against the wavelength of pump light. The phase changes within a certain wavelength range are basically consistent with the database Hitran of absorption cross-sections.

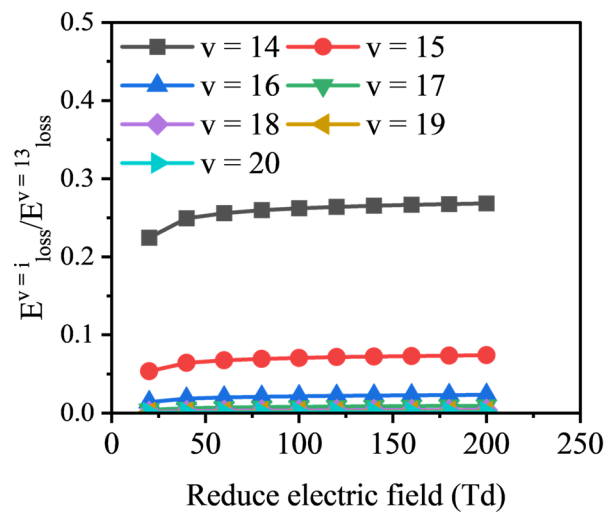


Fig. S20 Ratio of the energy loss coefficients of N_2 ($v = 14-20$) to that of N_2 ($v = 13$) for a $0.8 N_2/0.2 O_2$ mixture as a function of E/N .

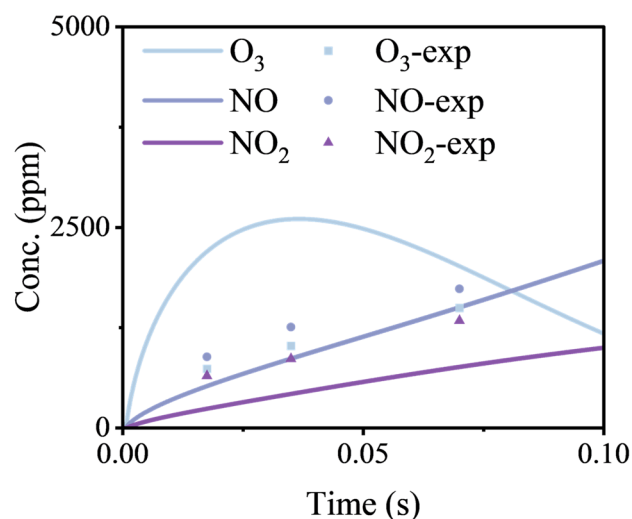


Fig. S21 Experimental results and model predictions of O₃, NO, and NO₂ concentrations at varying residence times in DBD. Our model agrees with the experimental data regarding the predicted NO and NO₂ concentrations. However, this model has a bias in predicting O₃ concentration, which is attributed to the inaccuracy of the estimated temperature. Moreover, the temperature does not change uniformly when the discharge region is long, leading to errors in predicting O₃ concentrations. (Simulation condition: Power: 10 W, Frequency: 10 kHz).

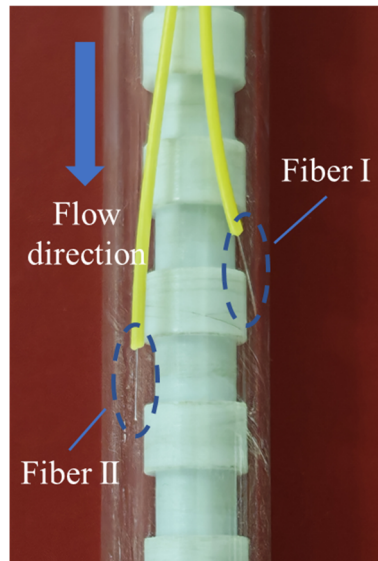


Fig. S22 Schematic diagram of the position for detecting optical fibers. Fiber I and II are placed in the high and low electric field regions

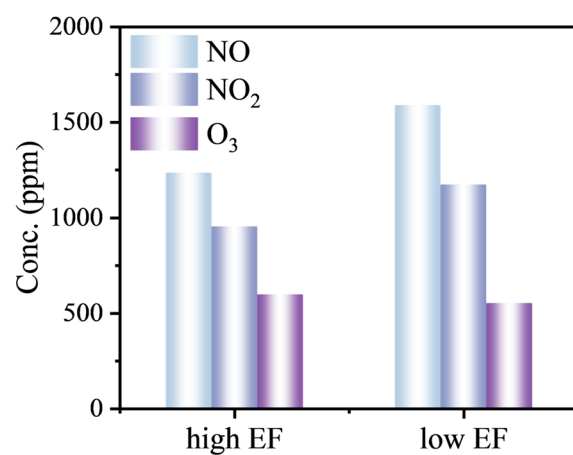


Fig. S23 Concentrations of NO, NO₂, and O₃ in the low and high electric fields.

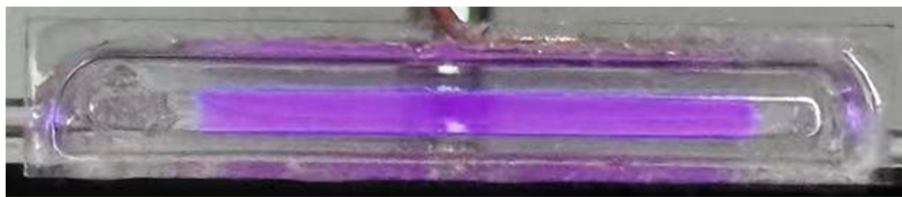


Fig. S24 Digital image of a closed flat DBD discharge reactor.

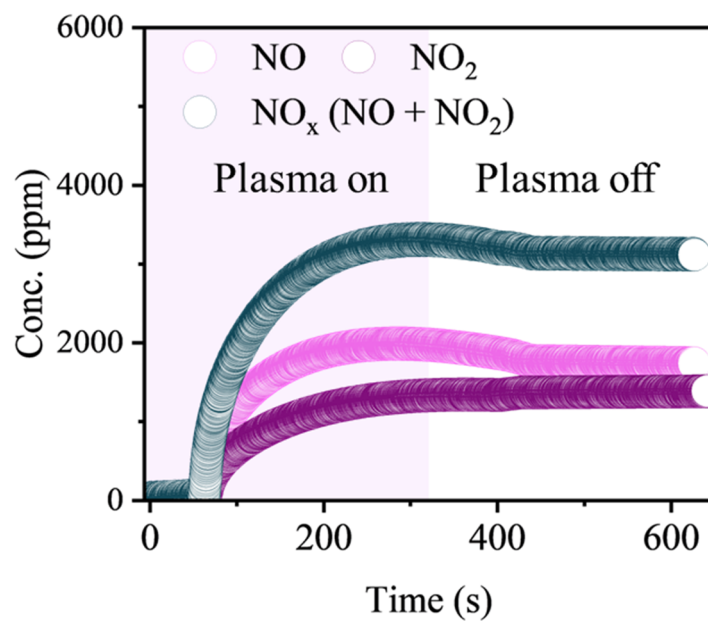


Fig. S25 Time resolved evolution of NO and NO₂ concentrations in the closed flat DBD discharge reactor.

Table S1 Comparison of the performance of N₂ fixation among various synthetic processes.

Synthetic process	Condition	Flow rate [mL/min]	NO ₃ ⁻ selectivity [%]	N ₂ conversion [%]	SEC [kWh/mol]	Refs.
Non-uniform DBD bubble	AC, Air, H ₂ O	2000	96.54	0.1157	1.61	This work
Spark bubble	Nanosecond Pulse, Air, H ₂ O	2000	90.00	0.0213	2.22	Ref. ¹
DBD bubble	Nanosecond Pulse, Air, H ₂ O	2000	75.00	0.0024	6.50	Ref. ¹
Double reactor glow and spark with Rasching rings	Microsecond Pulse, Air, 0.01 M H ₂ SO ₄	2000	72.97	0.0351	3.79	Ref. ²
Rotating gliding arc plasma jet	DC, Air, 0.1 M KOH	7000	0.66	0.0306	23.18	Ref. ³
DBD	AC, Air, 1 M H ₂ O	1000	98	0.0031	23.08	Ref. ⁴
Multi-Spark	AC, Air, H ₂ O	44	48	3.3349	16.1	Ref. ⁵
Multiple parallel spark	AC, Air, H ₂ O	200	100	0.8506	2.78	Ref. ⁶
eNRR	N ₂ , MOF-N-doped-C, graphite rod, 0.1 M KOH	20		0.0008	0.017 ^a	Ref. ⁷
eNRR	N ₂ , N-O-Bi ₂ O ₃ , Pt plate, 0.1 M HCl	25		0.0002	0.163 ^a	Ref. ⁸
eNRR	N ₂ , Pd/C, Pt gauze, 0.1 M PBS	10		0.0001	0.63 ^a	Ref. ⁹
eNRR	N ₂ , Cu ₁₄ NC _s , Pt wire, 0.1 M KOH	20		0.0002	0.38 ^a	Ref. ¹⁰

^a In the case of eNRR, energy calculated is based on the potential reported for the anode side (half-cell potential as the total cell potential was not reported. Also, energy required to generate ultra-pure nitrogen gas also was not considered.

Table S2 List of species introduced in the kinetic model for the N₂/O₂ gas mixture.

Type	Species
Ground-state neutral species	N ₂ , N, O ₂ , O, O ₃ , NO, N ₂ O, NO ₂ , NO ₃ , N ₂ O ₅
Positive ions	N ⁺ , N ₂ ⁺ , N ₃ ⁺ , N ₄ ⁺ , NO ⁺ , N ₂ O ⁺ , NO ₂ ⁺ , O ₂ ⁺ N ₂
Negative ions	e, O ⁻ , O ₂ ⁻ , O ₃ ⁻ , O ₄ ⁻
Excited nitrogen species	N ₂ (v = 1–15), N ₂ (A ³ Σ _u ⁺), N ₂ (B ³ Π _g), N ₂ (a' ¹ Σ _u ⁻), N ₂ (C ₃ Π _u), N(² D), N(² P)
Excited oxygen species	O ₂ (v = 1–4), O ₂ (a ¹ Δ _g), O ₂ (b ¹ Σ _g ⁺), O ₂ [*] , O(¹ D), O(¹ S)
Aqueous species	H, H ₂ , H ⁺ , H ⁻ , H ₂ ⁺ , H ₂ ⁻ , NH, HO ₂ ⁻ , H ₂ O, HO ₂ , OH, HNO, HNO ₃ , H ₂ O ₂ , HO ₂ NO ₂ , H ₃ O, ONOOH, H ₂ O ⁻ , ONOO ⁻ , OH ⁻ , O ₂ NO ₂ ⁻ , H ₃ O ⁺ , H ₂ O ⁺

267 **Supplementary References**

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