

# Nitrogen fixation in a non-equilibrium spatially distributed electric field

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Nitrogen fixation heavily relies on the energy-intensive Haber-Bosch process, necessitating renewable alternatives. Here, we introduce a non-equilibrium spatially distributed electric field (SD-EF) strategy for nitrogen fixation in ambient air plasma. The optimized SD-EF strategy gives a  $\text{NO}_x^-$  yield of 9.8 mmol/h, tripling that of a uniform electric field and the  $\text{N}_2$  conversion is three times higher than most discharge configurations at similar or lower energy consumptions. This high  $\text{NO}_x^-$  yield is achieved through simultaneously activating two beneficial kinetic networks via SD-EF by having both high and low electric fields present:  $\text{O}_3$  and vibrational excitation of  $\text{N}_2$  ( $\text{N}_2(\text{v})$ ) sub-mechanisms, which are revealed by developing a photonic crystal fiber diagnostic for in-situ quantification of molecules and ions ( $\text{NO}$ ,  $\text{NO}_2$ ,  $\text{N}_2\text{O}$ ,  $\text{O}_3$ ,  $\text{NO}_3^-$ , and  $\text{NO}_2^-$ ) in gas-liquid plasma. The establishment of the SD-EF strategy, coupled with in-situ gas-liquid diagnostics, is broadly applicable to plasma-assisted nitrogen fixation and holds promise for other plasma-assisted chemical conversion processes.

Nitrogen fixation is essential for fertilizer production, nitrogenous chemical synthesis, and sustainable fuel production for transportation. The conventional nitrogen fixation route involves the Haber-Bosch (H-B) process by synthesizing ammonia ( $\text{NH}_3$ ) from nitrogen ( $\text{N}_2$ ) and hydrogen ( $\text{H}_2$ ) under high temperatures ( $> 350^\circ\text{C}$ ) and high pressures ( $> 200\text{ atm}$ ),  $\text{N}_2 + 3\text{H}_2 \rightleftharpoons 2\text{NH}_3$  ( $R_1$ )<sup>1</sup>, and  $\text{NH}_3$  is then used for the synthesis of other nitrogenous chemicals<sup>2</sup>. The H-B process revolutionized nitrogen fixation and is considered among the most important discoveries of the 20<sup>th</sup> century. However, this process consumes around 1–2% of the total global energy production because of the required high temperatures and pressures and large quantities of  $\text{H}_2$ , which is typically obtained from steam reforming of natural gas that contributes up to 1.2% of global carbon dioxide emissions<sup>3</sup>. To minimize the environmental impact of carbon emissions, increasing attention has been devoted to biological, photocatalytic, and electrified nitrogen fixation<sup>4–6</sup>. Among these processes, biological nitrogen fixation converts atmospheric  $\text{N}_2$  into  $\text{NH}_4^+$  through symbiotic and free-living nitrogen fixation microorganisms<sup>7–9</sup>. Photocatalytic nitrogen fixation uses solar energy and water to drive  $\text{NH}_3$  synthesis on catalytic surfaces such as transition-metal-based<sup>10</sup>, plasmonic metal<sup>11,12</sup>, and carbon-based materials<sup>13</sup>. Electrified nitrogen fixation utilizes

renewable electricity to achieve nitrogen fixation under ambient conditions via an environmentally friendly way, such as through electrocatalytic or non-thermal plasma (NTP) strategies<sup>2,14–16</sup>. It should be noted that the electrified nitrogen fixation is considered to hold substantial promise for practical deployment because of its compatibility with rapidly expanding distributed renewable power grids<sup>4</sup>. However, conventional electric nitrogen fixation, such as electrocatalysis or direct  $\text{N}_2$  reduction from  $\text{H}_2\text{O}$  and  $\text{H}_2$  by NTP suffers from a high energy consumption and a low nitrogen fixation yield due to a high activation energy of  $\text{N}_2$ <sup>17–23</sup>.

As an alternative, direct  $\text{N}_2$  oxidation by  $\text{O}_2$  through the reaction  $\text{N}_2 + x\text{O}_2 \rightarrow 2\text{NO}_x$  ( $R_2$ ) is another industrial nitrogen fixation method via the Birkeland-Eyde process. But the thermodynamic equilibrium composition for direct  $\text{N}_2$  oxidation severely limits  $\text{NO}_x$  yield at moderate temperatures. Even if  $\text{NO}_x$  products form in a non-equilibrium plasma, decomposition back into much more stable  $\text{N}_2$  and  $\text{O}_2$  will be favored once the gas equilibrates at low temperature. To address this challenge, a plasma bubble reactor integrating plasma generation and water absorption is designed. The schematic of plasma bubble reactor is shown in Supplementary Fig. 1. In this configuration, gas bubbles are formed within a liquid phase, and plasma discharge occurs either

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inside the bubbles or at the gas–liquid interface, producing abundant radicals and reactive species that drive chemical reactions under mild conditions. This approach has been explored for nitrogen fixation and ammonia synthesis<sup>24–28</sup>. However, the nitrogen fixation yield and the energy consumption are still far from the H-B benchmark<sup>29</sup>. A major challenge hindering progress is the lack of kinetic understanding of the complex plasma-assisted catalysis process at the gas–liquid interface.

For plasma-assisted nitrogen fixation in  $N_2$ , the rate-controlling step(s) for nitrogen fixation is poorly understood because of the complex coupling reaction networks of the  $N_2$  and  $O_2$  excitations in air plasma<sup>30</sup>. It is known that NTP generates a large number of free radicals and vibrationally excited molecules, which are considered capable of promoting  $NO_x$  synthesis<sup>31</sup>. But there is a lack of direct research on the effects of NTP types on nitrogen fixation and a need for accurate in situ diagnostics of the gas–liquid interface under high electromagnetic fields in plasma. Fiber optics offers a promising solution for *operando* quantifying key characteristics, such as temperature, pressure, and species in gas and liquid in plasma, due to their compact size (diameter  $\sim 125\ \mu\text{m}$ ), high temporal sensitivity, time–resolved response, and immunity to electromagnetic interference<sup>32–35</sup>.

In this work, we employ a plasma bubble reactor to fix nitrogen from air by using spark and dielectric barrier discharge (DBD). Novel in situ fiber diagnostics with hollow-core photonic crystal fibers (HC-PCF) based photothermal spectroscopy (PTS) are used for the first time to simultaneously quantify key molecules ( $NO$ ,  $NO_2$ , and  $O_3$ ) and ions ( $NO_3^-$  and  $NO_2^-$ ) in plasma in both the gas phase and aqueous solution. HC-PCF achieves a temporal resolution of 1 Hz and a detection limit of 10 ppm for the species above, and exhibits an excellent resistance to high electromagnetic fields. Furthermore, we identify two different beneficial reaction networks for nitrogen fixation in different electric field strengths, that is, the  $N_2(v)$  sub-mechanism in a low electric field and the  $O_3$  sub-mechanism in a high electric field. Guided by the kinetic results, we establish a non-equilibrium spatially distributed electric field (SD-EF) strategy for nitrogen fixation in air plasma. SD-EF enables the coexistence of a lower electric field for the vibrational excitation of  $N_2$  and a higher electric field for the dissociative excitation of  $O_2$  by employing a dielectric barrier with varied thickness. This new strategy provides an energy efficiency of 1.6 kWh/mol and a  $NO_x^-$  yield of 9.8 mmol/h, which is three times higher  $NO_x^-$  yield than the uniform electric field at a similar energy consumption. We believe the SD-EF strategy to simultaneously activate multiple beneficial kinetic networks, coupled with in situ gas–liquid diagnostics, will be broadly useful for plasma-assisted nitrogen fixation, as well as other plasma catalysis processes.

## Results

### Optic fiber diagnostics in plasma

A plasma reactor (Fig. 1a) is used for the nitrogen fixation experiments, featuring a central high voltage electrode and a quartz cylinder that has 12 micro holes with a diameter of 0.4 mm near the sealed base. The entire reactor is immersed in a water-filled cylindrical vessel, which simultaneously serves as an absorber vessel and ground electrode. Air is introduced into the reactor through a three-way plastic joint, where discharge occurs in the region between the high-voltage electrode and the water-immersed section of the reactor wall (purple area in Fig. 1a). The micro holes allow reactive species generated by the plasma to flow into the water, forming bubbles and enabling the dissolution of  $NO_x$  species into the liquid. The detailed description is given in the Methods. Moreover, two types of discharge configurations, DBD and spark modes, are used for nitrogen fixation. The discharge images are included in Supplementary Fig. 2a and b, respectively. The typical voltage and current waveforms of the DBD and spark modes are shown in Supplementary Fig. 3. Spark is characterized by a low electric field, high gas temperature, and high electron density, whereas DBD is

characterized by a high electric field, low gas temperature, and low electron density.

We use photothermal spectroscopy (PTS) through hollow-core photonic crystal fibers (HC-PCF) to quantify in situ stable species in plasma. After drilling holes in the HC-PCF, the processed HC-PCF is not only suitable for the gas phase but also for the liquid phase. This has been verified by our optic mode analysis (Supplementary Fig. 4). Our results show that the light can transmit well in our HC-PCF. Fiber optic probes are placed at different locations within the reactor, each labeled to indicate its measurement position. Position I refers to the bottom of the quartz tube of the reactor, where the probe measures the  $NO$ ,  $NO_2$ ,  $N_2O$ , and  $O_3$  concentrations in the gas phase before absorption. Position II is located within the absorption solution, enabling measurement of dissolved  $NO_2^-$  and  $NO_3^-$  species. Position III is situated at the reactor outlet above the liquid surface, where the  $NO$ ,  $NO_2$ ,  $N_2O$ , and  $O_3$  concentrations are monitored after gas–liquid interaction. The specific arrangements of Position I, II, and III are shown in Fig. 1a. The measurement principle of the HC-PCF based PTS is shown in Fig. 1b. The molecules diffuse into the interior of the PCF through the micro holes made by focused ion beam on the PCF, and then absorb photons at specific wavelengths from a beam of pump light within the PCF. Due to the photothermal effect of different excited molecules, a periodic heat release appears in the central core of the fiber and changes the local temperature and the refractive index of the filling medium. Meanwhile, a beam of probe light is introduced into the PCF along with the pump light. Then the probe light reflects back at the other end of the fiber. The optical phase change between the reflected and incoming probe lights linearly corresponds to the change in the refractive index or local temperature. Hence, the species concentrations of interest can be in situ quantified by measuring the optical phase change of probe light according to their different photothermal effects. The detailed measurement method is described in the Methods.

The calibrations of gaseous species and ions, such as  $NO$ ,  $NO_2$ ,  $N_2O$ ,  $O_3$ ,  $NO_3^-$ , and  $NO_2^-$  are detailed in the Methods. Here, we show the calibration curves of  $NO_2$  and  $NO_3^-$  in Fig. 1c, d as an example to indicate the excellent linear response of the HC-PCF based PTS to the  $NO_2$  concentration. Subsequently, the transient evolutions of  $NO$ ,  $NO_2$ , and  $O_3$  concentrations before absorption in the solution (Position I) are measured using the HC-PCF based PTS with a temporal resolution of 1 Hz (Fig. 1e). After the power is on, the gas concentrations of these species before absorption continuously increase after a delay of around 600 s before reaching equilibrium due to the gas diffusion into PCF and the gas temperature fluctuation in plasma. Therefore, the steady-state species quantification by using the HC-PCF based PTS is employed after 600 s in each experiment.

### Kinetic mechanisms of $N_2(v)$ and $O_3$ in plasma-assisted nitrogen fixation

The  $NO$ ,  $NO_2$ ,  $N_2O$ , and  $O_3$  concentrations in Position I are separately measured in DBD and spark by using the HC-PCF based PTS (Fig. 2a). The spark mode produces a higher  $NO$  concentration than that in the DBD mode. However, the spark mode forms negligible  $O_3$ , which is around 1800 ppm in the DBD mode. Both modes produce little  $N_2O$ , indicating that  $N_2O$  in air plasma is not a major nitrogen-containing product. The  $NO_x^-$  concentration in Position II is measured by using the HC-PCF based PTS after 600 s (Fig. 2b). The  $NO_x^-$  concentration of DBD is 2.0 mmol/L, which is similar to the situation in spark (2.2 mmol/L). But the selectivity of  $NO_x^-$  to  $NO_3^-$  is 97.5 % using DBD, while it is 39.9 % using spark.

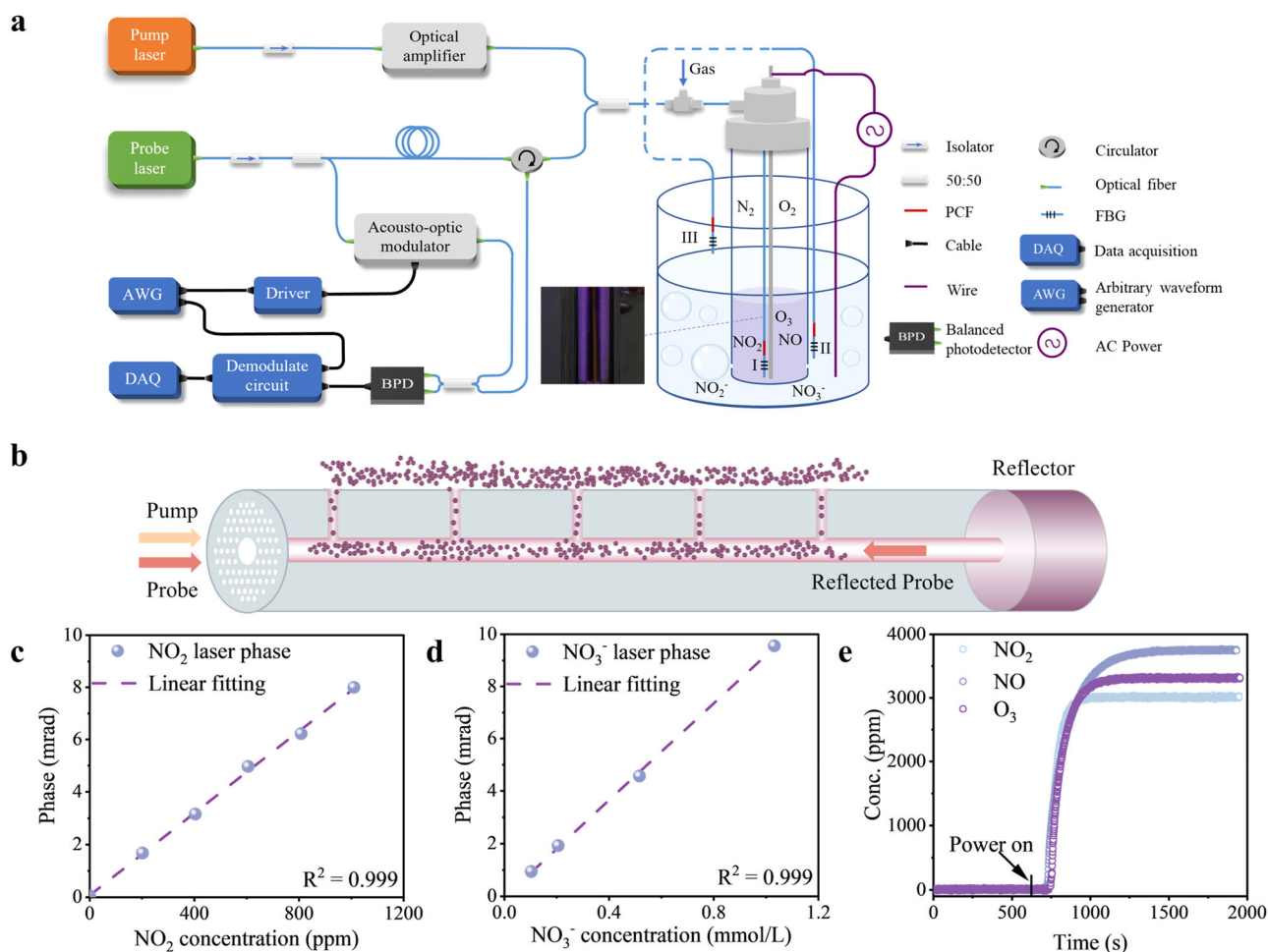
Furthermore, the  $NO$ ,  $NO_2$ ,  $N_2O$ , and  $O_3$  concentrations in Position III are separately quantitatively detected in DBD and spark by using the HC-PCF based PTS (Fig. 2c). After absorption, the  $NO_2$  concentrations in DBD and spark are 589 ppm and 563 ppm, respectively. As for the absorption performance of  $NO$ , the  $NO$  concentration clearly

decreases to 1083 ppm in DBD, but the absorption of NO is limited in spark. To evaluate the performance of the NO<sub>x</sub> absorption, the NO<sub>x</sub> absorption rate is defined as the difference between 1 and the ratio of the NO<sub>x</sub> concentration after and before absorption. The NO<sub>2</sub> absorption ratio is similar between the different discharge modes, while the NO absorption ratio in DBD with O<sub>3</sub> is higher than that in spark without O<sub>3</sub> (Fig. 2d). In general, considering the requirement of O radical for the synthesis of NO<sub>x</sub> and O<sub>3</sub>, we postulate that sufficient O radical concentration is crucial for enhancing N<sub>2</sub> fixation performance through oxidizing NO.

To understand this discrepancy between the two discharge modes, the electron energy transfer to vibrational (v), ionizing (ion), dissociative (dis), and electronic (ele) excitations of N<sub>2</sub> and O<sub>2</sub> is calculated under varied reduced electric fields (E/N) in Fig. 2e, which is consistent with previous work<sup>36</sup>. The energy loss fractions are calculated by BOLSIG +<sup>37</sup> and computational details are in the Methods. This analysis reveals that electron energy predominantly transfers to the vibrational excitation of N<sub>2</sub> under a low E/N, which is in the range of spark mode. In the DBD mode, however, the energy of transferring to the N<sub>2</sub>(v) channel diminishes, while the N<sub>2</sub>(dis) and O<sub>2</sub>(dis) channels are dominant to form N, O, and O<sub>3</sub>, which agrees with our experimental

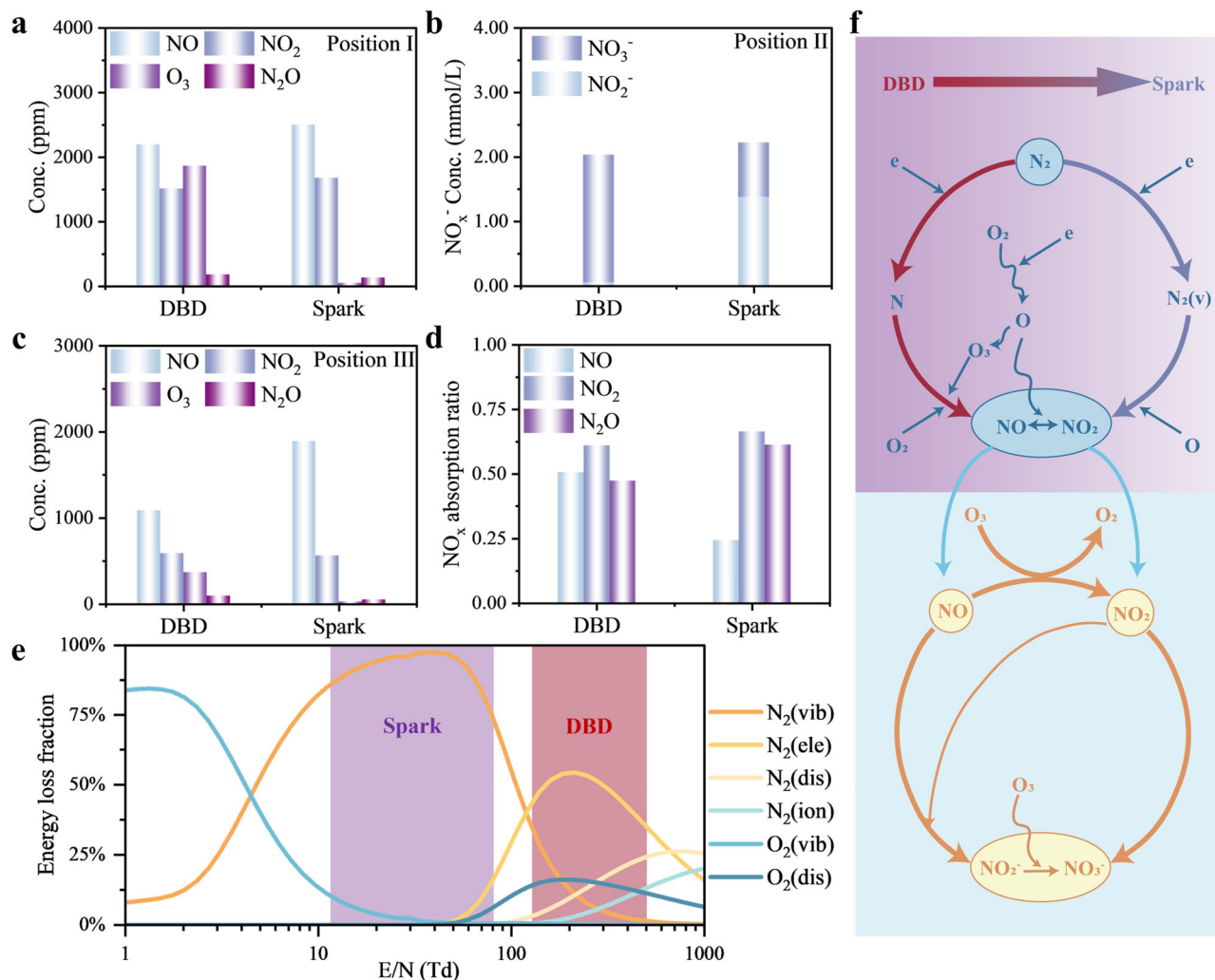
observation of higher O<sub>3</sub> but lower NO<sub>2</sub><sup>-</sup> concentrations in the DBD mode in Fig. 2b. Therefore, the kinetic discrepancy in nitrogen fixation under different configurations is attributed to the shift in the electron energy deposition.

To explore the reaction pathway for N<sub>2</sub> fixation, we perform zero-dimensional (0D) numerical simulations of plasma discharge and gas absorption in solutions in DBD and spark discharge, respectively. The model neglects gas flow and bubble dynamics, focusing instead on the temporal evolution of plasma chemistry. The physical simulation scheme, illustrated in Supplementary Fig. 5, simplifies the process into two stages: a zero-dimensional plasma discharge stage and a zero-dimensional absorption stage in solution. The reaction times for both stages are determined by the gas residence time in the plasma region and the bubble residence time in the solution, both estimated as 0.1 s in this study. The two stages are coupled through Henry's law to account for gas-liquid mass transfer. This calculation is conducted using ZDPlasKin<sup>38</sup> with a validated N<sub>2</sub>/O<sub>2</sub> plasma chemistry set, tracking the temporal evolution of gas temperature and species densities, including vibrationally and electronically excited states, radicals, molecules, ions, and electrons. The nitrogen fixation kinetics explicitly incorporates the vibrational dynamics, accounting for impact



**Fig. 1 | Setup of the HC-PCF based PTS inside the reactor. a** Schematic of the experimental setup. The platform involves three parts: plasma discharge system, gas distribution system, and the HC-PCF based PTS diagnostic system. **b** Schematic of the HC-PCF based PTS. **c,d** Calibration curves of the NO<sub>2</sub> (c) and the NO<sub>3</sub><sup>-</sup> (d) concentrations using the HC-PCF based PTS. These module phases have good linear responses with an R-squared of 0.99. **e** Evaluation of NO, NO<sub>2</sub>, and O<sub>3</sub> concentrations during 1800 s. The plasma power is turned on at 600 s. Position I refers to the bottom of the quartz tube of the reactor, where the probe measures the NO,

NO<sub>2</sub>, N<sub>2</sub>O, and O<sub>3</sub> concentrations in the gas phase before absorption. Position II is located within the absorption solution, enabling measurement of dissolved NO<sub>2</sub><sup>-</sup> and NO<sub>3</sub><sup>-</sup> species. Position III is situated at the reactor outlet above the liquid surface, where the NO, NO<sub>2</sub>, N<sub>2</sub>O, and O<sub>3</sub> concentrations are monitored after gas-liquid interaction. (Reaction condition: Total flow rate: 500 ml/min, N<sub>2</sub>/O<sub>2</sub> = 2:8, Voltage: 15 kV, Frequency: 10 kHz, Discharge type: DBD, Volume of absorption solution: 200 ml).



**Fig. 2 | Experimental and numerical research on the mechanism of the plasma-assisted nitrogen fixation.** **a** The NO, NO<sub>2</sub>, N<sub>2</sub>O, and O<sub>3</sub> concentrations before absorption (Position I) in DBD and spark. **b** The NO<sub>3</sub><sup>-</sup> and NO<sub>2</sub><sup>-</sup> concentrations in the solution (Position II) in DBD and spark. **c** The NO, NO<sub>2</sub>, N<sub>2</sub>O, and O<sub>3</sub> concentrations after absorption (Position III) in DBD and spark. **d** The absorption ratio of NO, NO<sub>2</sub>, and N<sub>2</sub>O using DBD and spark. **e** Energy loss fractions of electrons deposited into different molecular degrees of freedom for a 0.8 N<sub>2</sub>/0.2 O<sub>2</sub> mixture as a function of E/N. The region in purple indicates the corresponding E/N values of the spark

mode, and the region in red indicates the corresponding E/N values of the DBD mode (rot: rotational excitation, vib: vibrational excitation, ele: electronic excitation, dis: dissociation, and ion: ionization). **f** Schematic of the mechanism of the plasma-assisted nitrogen fixation in plasma and water. In plasma, the color of the reduced electric field intensity determines the strength of the reaction pathways. (Reaction condition in Fig. 2a–d: Total flow rate: 500 ml/min, N<sub>2</sub>/O<sub>2</sub> = 2:8, Frequency: 10 kHz, Voltage of DBD: 15 kV, Voltage of spark: 5 kV, Volume of absorption solution: 200 ml).

excitation, vibrational-translational relaxation, and vibrational-vibrational (V-V/V-V) exchanges based on the Schwartz-Slowsky-Herzfeld (SSH) theory<sup>39</sup>. Chemical abstraction reactions are described by the Fridman-Macheret  $\alpha$ -model<sup>40</sup>. The discharge power density is used to self-consistently determine the reduced electric field within the plasma. The details of the simulations are in the Methods, and the simulation results are included in Supplementary Figs. 6–10.

The simulations show that DBD produces a significant amount of O<sub>3</sub>, which assists NO<sub>x</sub> absorption in water by oxidizing NO, whereas spark produces more NO through the N<sub>2</sub>(v) channel with less NO<sub>x</sub> absorption in water. Both of these two plasma configurations are beneficial to nitrogen fixation in water, which validates our main experimental results above. In addition, we explore the N<sub>2</sub>O generation pathway (Supplementary Fig. 10), N<sub>2</sub>O is mainly formed through reaction N<sub>2</sub>(A<sup>3</sup>Σ<sub>u</sub><sup>+</sup>) + O<sub>2</sub> → N<sub>2</sub>O + O (R<sub>3</sub>). But the electronic excitation of N<sub>2</sub> requires a high electric field strength (> 130 Td), so low electric field is not suitable for the generation of N<sub>2</sub>O in spark discharge. Meanwhile, the abundance of O radical promotes the conversion of N<sub>2</sub>O into NO

through reaction N<sub>2</sub>O + O → 2NO (R<sub>4</sub>), leading to a low N<sub>2</sub>O concentration in the DBD mode. Overall, N<sub>2</sub>O plays a minor role in plasma-assisted nitrogen fixation.

Based on the results of the reaction pathways in Supplementary Figs. 7–10, we summarize the reaction pathway of plasma-assisted nitrogen fixation to NO<sub>x</sub><sup>-</sup> with two major sub-mechanisms: the O<sub>3</sub> sub-mechanism in DBD and the N<sub>2</sub>(v) sub-mechanism in spark, as shown in Fig. 2f. For the O<sub>3</sub> sub-mechanism at a high reduced electric field, O<sub>3</sub> is mainly produced from the dissociative excitation of O<sub>2</sub> in DBD. It is noted that the water layer primarily enables the transformation of NO and NO<sub>2</sub> into NO<sub>2</sub><sup>-</sup> and NO<sub>3</sub><sup>-</sup> rather than merely preventing their reduction. The high solubility of O<sub>3</sub> in the aqueous phase plays a crucial role in driving this overall conversion process, which contributes to the nitrogen fixation both through NO + O<sub>3</sub> → NO<sub>2</sub> + O<sub>2</sub> (R<sub>5</sub>) in the gas phase and NO<sub>2</sub><sup>-</sup> + O<sub>3</sub> → NO<sub>3</sub><sup>-</sup> + O<sub>2</sub> (R<sub>6</sub>) in the water solution. The present pathway explains the higher O<sub>3</sub> but lower NO concentrations in Fig. 2a and the much lower NO<sub>2</sub><sup>-</sup> concentration in Fig. 2b in the DBD plasma. For the N<sub>2</sub>(v) mechanism at a low reduced electric field, the

vibrational excitation of  $N_2$  is dominant for the  $N_2$  excitation in spark and contributes to the nitrogen fixation through  $N_2(v) + O \rightarrow NO + N$  ( $R_7$ ). The reaction rate increases significantly when the vibrational level of  $N_2(v)$  is over 12 (Supplementary Fig. 11). However, without the assistance of  $O_3$ , less NO is converted to  $NO_2$  and  $NO_3^-$ . The present pathway explains the higher NO concentration in Fig. 2a and the lower NO absorption ratio in Fig. 2d in the spark plasma. As a result, both the  $N_2(v)$  sub-mechanism at low E/N and the  $O_3$  sub-mechanism at high E/N are important for nitrogen fixation in the solution. The former provides reactive vibrationally excited  $N_2$  molecules for overcoming the large energy barrier of  $N \equiv N$  and producing NO, while the latter provides active oxidizers, O and  $O_3$ , to convert NO to  $NO_2$  and  $NO_2^-$  to  $NO_3^-$  for nitrogen fixation in the solution.

### Spatially distributed electric field strategy

Based on the reaction pathway analysis above, nitrogen fixation can be accelerated from the  $N_2(v)$  and the  $O_3$  sub-mechanisms at low and high reduced electric fields, respectively. Therefore, we propose a novel spatially distributed electric field (SD-EF) DBD strategy, where a non-equilibrium electric field is formed for the nitrogen fixation in DBD (Fig. 3a).

Here, we design a dielectric with non-uniform thickness to achieve SD-EF (Supplementary Fig. 12). This coaxial dielectric is made of polytetrafluoroethylene (PTFE) with periodic diameters of 6 and 8 mm (5 mm length for each). The formed plasma in the narrower gaps diffuses to the thicker gaps and reduces their breakdown voltages, achieving a spatially distributed stable discharge in the entire reactor in the plasma image of Fig. 3a. The thickness of the dielectric is specifically designed to achieve a low reduced electric field around 100 Td for the  $N_2(v)$  mechanism and a high reduced electric field around 150 Td for the  $O_3$  mechanism in DBD in the present experiments. We further simulate the distribution of the electric field strength within the reactor for SD-EF in Supplementary Fig. 13. It exhibits a higher reduced electric field at the narrower gap and a lower reduced electric field at the thicker gap. The detailed description is given in the Methods.

We directly apply the SD-EF strategy to nitrogen fixation at the same flow and discharge conditions of the uniform DBD and spark experiments. Its main product concentrations are compared with those in DBD and spark before absorption (Fig. 3b) and in the water solution (Fig. 3c). Before the optimization of work conditions, it is observed in Fig. 3b that SD-EF enhances the  $NO_2$  yield by 34% and 49 % than spark and uniform DBD, respectively. But there is no significant difference in NO,  $NO_2$ , and  $N_2O$  selectivities between SD-EF, DBD, and spark discharge (Supplementary Fig. 14). Meanwhile, SD-EF keeps a similar level of  $O_3$  concentration around 1000 ppm with uniform DBD for NO oxidation and absorption in water, unlike the absence of  $O_3$  in the spark discharge. As shown in Fig. 3c, the SD-EF strategy produces 0.10 mmol/L  $NO_2^-$  and 2.81 mmol/L  $NO_3^-$ , which is an increase of 38% over uniform DBD and spark in nitrogen fixation in water, confirming the advantage of SD-EF over uniform DBD and spark. To assess the long-term stability of the SD-EF system, we conduct a 3 h SD-EF experiment, during which the NO concentration at Position I is monitored (Supplementary Fig. 15). The NO concentration stabilizes at approximately 3000 ppm, indicating that the SD-EF system maintains stable performance over short to moderate timescales.

To validate the discussion of kinetics on uniform DBD and non-uniform DBD, such as SD-EF, we simulate nitrogen fixation under different reduced electric fields in DBD at low uniform-EF (~100 Td), at high uniform-EF (~150 Td), and SD-EF in Fig. 3d–f. The low uniform-EF and the high uniform-EF refer to the reduced electric field at a thicker gap and a narrower gap of our SD-EF configuration at 15 kV. Due to the presence of both the  $N_2(v)$  and  $O_3$  mechanisms, SD-EF exhibits higher productions of NO around 1238 ppm and  $NO_2$  around 655 ppm at 0.1 s than that in uniform DBDs at 100 and 150 Td. Based on the preliminary

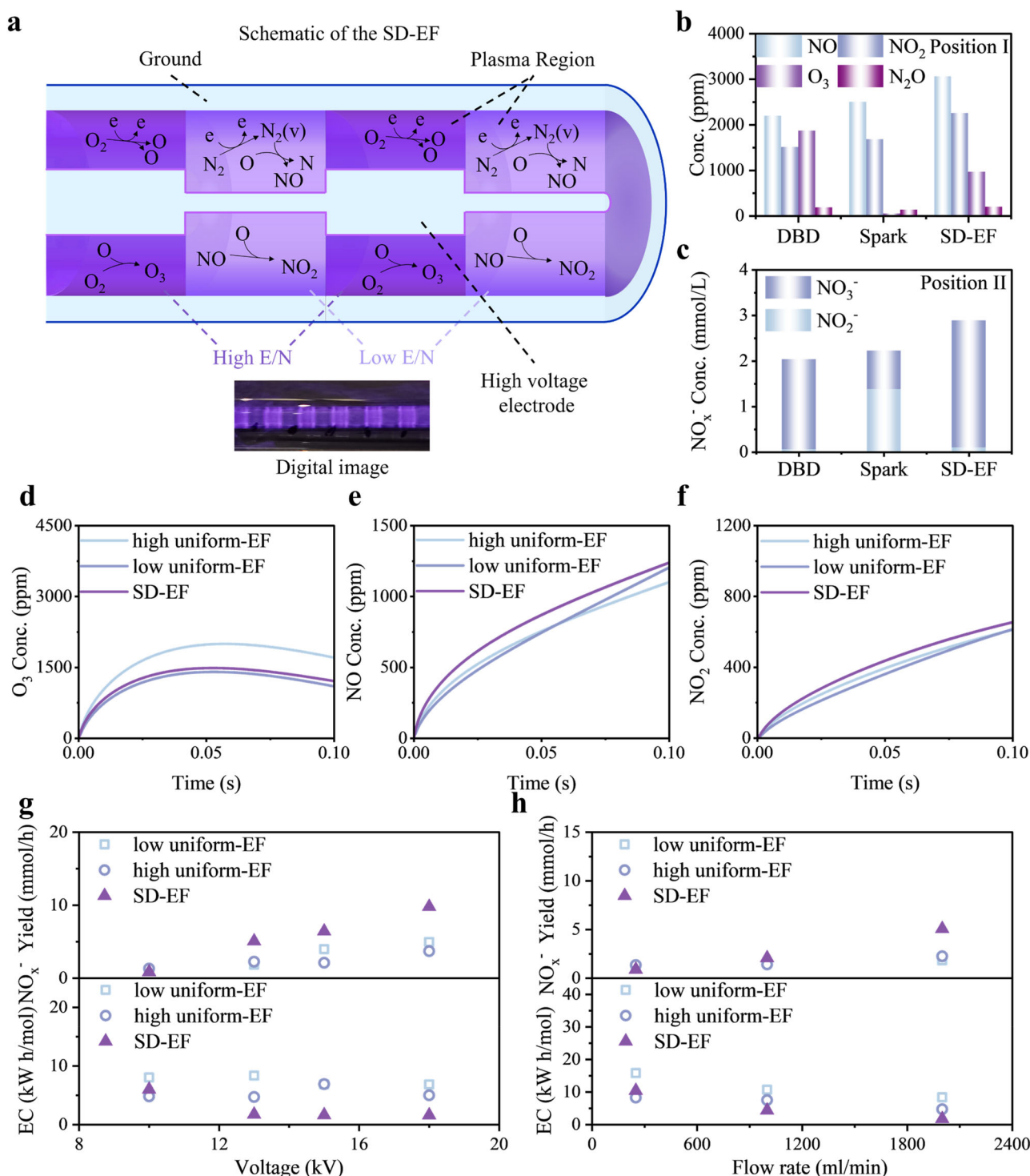
validation of SD-EF against experiments and simulations above, we further optimize the discharge and flow conditions of SD-EF, respectively, for the  $NO_x^-$  yield in water and energy consumption (EC) in Fig. 3g, h. A minimum EC around 1.6 kWh mol<sup>-1</sup>  $NO_x^-$  and a maximum  $NO_x^-$  yield around 9.8 mmol/h are achieved at 18 kV and 2 L/min flow rate in SD-EF, which is approximately three times the  $NO_x^-$  yield in a traditional DBD with a uniform electric field. In addition, it is seen from Fig. 3g, h that a higher voltage generally benefits  $NO_x^-$  yield in SD-EF, while it needs to be restricted with both low and high reduced electric field modes. The  $NO_x^-$  yield against time generally increases with the flow rate of reactants, while it decreases at a high flow rate level as the nitrogen fixation reactions are incomplete at a low residence time. We also investigate the effect of the  $N_2/O_2$  ratio; the results indicate that it has little influence on nitrogen fixation (Supplementary Fig. 16). Moreover, using air directly ( $N_2/O_2 = 4:1$ ) eliminates the need for gas separation, making it more practical for scalable applications.

Finally, we compare the performance of our proposed nitrogen fixation strategy with state-of-the-art results in the literature, including electrocatalytic nitrogen reduction reaction (eNRR) and various discharge configurations, such as DBD, spark, gliding arc, etc., as summarized in Supplementary Table 1. Since electrocatalysis typically produces  $NH_3$  rather than  $NO_x^-$ , the  $N_2$  conversion is used as a unified metric to quantify the performance of  $N_2$  fixation. After optimization, our proposed SD-EF strategy exhibits three times higher  $N_2$  conversion than most discharge configurations at similar or lower energy consumptions. Although the spark configuration achieves a higher  $N_2$  conversion than SD-EF, its energy consumption is approximately one order of magnitude higher. Moreover, SD-EF demonstrates a high  $NO_3^-$  selectivity of approximately 96.5% among  $NO_x^-$  in water solution (Fig. 3b). In contrast to previous studies conducted in alkaline solutions<sup>15,27,41</sup>, where  $NO_2^-$  is the main product. In addition to the plasma system, eNRR is also included in the comparison. Although the energy consumption of our proposed strategy is about 10 times higher than that of electrocatalysis, the  $N_2$  conversion is approximately 100 times higher. This indicates that our approach is more suitable for small-scale distributed nitrogen fixation.

Based on the results above, SD-EF exhibits a higher  $NO_x^-$  yield, a higher  $NO_3^-$  selectivity, and a lower energy consumption than existing plasma configurations. The SD-EF strategy is fundamentally based on the modulation of kinetic networks and thus represents a general concept, independent of reactor type or power source. It can be adapted to other plasma-assisted nitrogen fixation systems, such as atmospheric pressure glow discharge plasma jet. Moreover, the strategy of the spatially non-equilibrium electricity field under kinetic networks provides an opportunity for plasma-assisted catalysis not only for nitrogen fixation, but also for other processes, such as  $CO_2$  conversion to methanol,  $H_2$  production from methane pyrolysis, and plastic recycling and upgrading. In addition, the time-resolved in situ optics by using HC-PCF also provides an important diagnostic approach of molecules and ions in gas and liquid phases under high electromagnetic fields for understanding their kinetic mechanisms.

### Discussion and conclusions

The work introduces a non-equilibrium spatially distributed electric field (SD-EF) strategy in a DBD to optimize nitrogen fixation in air plasma under ambient conditions, which is developed based on our understanding of two different beneficial kinetic networks,  $O_3$  sub-mechanism in a high reduced electric field and  $N_2(v)$  sub-mechanism in a low reduced electric field, respectively. To explore these mechanisms above, we developed an in situ fiber diagnostic technology with hollow-core photonic crystal fibers (HC-PCF) based photothermal spectroscopy (PTS) for simultaneous quantification of key molecules ( $NO$ ,  $N_2O$ ,  $NO_2$ , and  $O_3$ ) and ions ( $NO_3^-$  and  $NO_2^-$ ) in gas phase and aqueous solutions with a temporal resolution of 1 Hz and a detection limit of 10 ppm in the plasma-assisted nitrogen fixation process.



**Fig. 3 | The SD-EF strategy and its  $N_2$  fixation performance.** **a** Schematic of the SD-EF strategy. The digital image of the SD-EF is shown in the bottom.

**b** Comparison of  $NO_x^-$  concentration against different discharge configurations. **c** Comparison of  $NO$ ,  $NO_2$ , and  $O_3$  concentrations between the three different configurations. **d–f** Simulation results of the time evolutions of  $O_3$  (**d**),  $NO$  (**e**), and  $NO_2$  (**f**) concentrations with a pulsed energy density of  $0.5 \text{ mJ/cm}^3$  in the high uniform-EF, low uniform-EF, and SD-EF. **g, h** The  $NO_x^-$  yield and EC against voltage and flow rate. **i** Comparison of the  $N_2$  conversion and EC of this work with previous literature including eNRR, spark, DBD, gliding arc, and spark + DBD. (Reaction

condition for Fig. 3c, d: Total flow rate: 500 ml/min,  $N_2/O_2 = 2:8$ , Frequency: 10 kHz, Voltage of DBD: 10 kV, Voltage of spark: 5 kV, Voltage of SD-EF: 10 kV; Simulation condition for Fig. 3d–f: Reduced electric field of the high uniform-EF: 150 Td ( $0.5 \text{ mJ/cm}^3$  per pulse), Reduced electric field of the low uniform-EF: 100 Td ( $0.5 \text{ mJ/cm}^3$  per pulse), Reduced electric field of the SD-EF: 100 Td ( $0.125 \text{ mJ/cm}^3$  per pulse) and 150 Td ( $0.375 \text{ mJ/cm}^3$  per pulse); Reaction condition for Fig. 3h: Total flow rate: 500 ml/min,  $N_2/O_2 = 2:8$ , Frequency: 10 kHz; Reaction condition for Fig. 3i:  $N_2/O_2 = 2:8$ , Frequency: 10 kHz, Voltage: 18 kV, Total flow rate: 2000 ml/min, Volume of absorption solution: 200 ml).

In the  $O_3$  sub-mechanism,  $O_3$  is mainly produced from the dissociative excitation of  $O_2$  in the high reduced electric field. It contributes to the nitrogen fixation both through  $NO + O_3 \rightarrow NO_2 + O_2$  ( $R_5$ ) in the gas phase and  $NO_2^- + O_3 \rightarrow NO_3^- + O_2$  ( $R_6$ ) in aqueous solution, which is crucial for enhancing  $NO_x$  absorption and  $NO_3^-$  formation. For the  $N_2(v)$  sub-mechanism,  $N_2(v)$  is dominant for the  $N_2$  excitation in the low electric field and beneficial for the  $N_2$  fixation through  $N_2(v) + O \rightarrow NO + N$  ( $R_7$ ), in which the energy barrier is much less than the  $NO$  formation energy from ground  $N_2$ . The SD-EF strategy, which combines these two sub-mechanisms, achieves an energy efficiency of 1.6 kWh/mol, a  $NO_x^-$  yield of 9.8 mmol/h, and a  $NO_3^-$  selectivity of 96.5%. It achieves three times the  $NO_x^-$  yield of a traditional uniform DBD, positioning it as a leading contender in the field of nitrogen fixation.

Overall, we establish a non-equilibrium electric field strategy to selectively promote kinetic networks for plasma-assisted nitrogen fixation coupled with in situ gas-liquid diagnostics. This strategy has promise for nitrogen fixation from air by using distributed solar or wind electricity with a fast response and resistance to grid intermittence. Moreover, such a strategy guided by an understanding of kinetic networks is also applicable for plasma-assisted  $H_2$  production from methane pyrolysis,  $CO_2$  conversion to fuels, and plastic recycling and upgrading, etc. Lastly, this study reports a sensitive diagnostic approach for quantifying molecules and ions in situ in the gas phase and aqueous solution under high electromagnetic fields.

## Methods

### Plasma discharge system and gas distributions system

Experiments of plasma-assisted nitrogen fixation is conducted using a plasma reactor, as depicted in Fig. 1a. The plasma reactor is fabricated using a quartz tube (10.5 mm I.D., 12.7 mm O.D.) with one end sealed and a stainless-steel rod (4.0 mm dia.) at the reactor centre line as a high voltage electrode. 12 micro holes with a diameter of 400  $\mu m$  are positioned 1 mm above the sealed base, allowing for ventilation into water and facilitating gas-liquid interface for plasma generation. This reactor is submerged within a long gas cylinder (48.0 mm I.D., 52.0 mm O.D.) containing the deionized water. The water is regarded as an absorber and a ground electrode. The plasma is generated by an AC power supply (CTP 2000K), which generally set a discharge frequency of 10 kHz and a voltage of 10 kV in our experiments. High purity  $N_2$  and  $O_2$  are supplied from a pressurized gas cylinder, and the gas flow rates are controlled by mass flow controllers (Seven star CS200A), which are set to the flow rates of 2000 ml/min.

Three discharge modes, involving DBD, spark, and spatial-distributed electric field (SD-EF), are employed to investigate the effect of the electric field intensity. In the DBD mode, the high voltage electrode is enclosed within a quartz cylinder (6.0 mm O.D.) as a dielectric barrier. In the spark discharge mode, the stainless-steel rod is replaced by a stainless-steel needle. In the SD-EF configuration, the high voltage electrode is enclosed by a coaxial dielectric cylinder made of polytetrafluoroethylene (PTFE) featuring periodic diameters of 6 and 8 mm (each with a length of 5 m). The geometric parameters of the SD-EF configuration have been optimized to balance electric field modulation and gas residence time. The periodic alternation between the high and low electric fields influences the residence time of the gas within each region. It is noted that the characteristic lifetimes of intermediates such as  $N_2(v)$ ,  $O$ , and  $N$  are on the microsecond scale<sup>42</sup>, far shorter than the millisecond-level gas residence time in the SD-EF configuration. However, the characteristic lifetime of  $O_3$  is on a minute scale, which can transit through these electric field regions. The SD-EF strategy enables  $O_3$  generation in the regions of high electric field and its subsequent utilization in the regions of low electric field to oxidize  $NO$  to  $NO_2$  in the regions of low electric field. Moreover, the spatial electric field distribution is highly sensitive to the thickness and dielectric constant of dielectric barrier. Variations in dielectric thickness or permittivity primarily affect the local electric field gradient and

the spatial distribution of electric field strength, thereby influencing nitrogen fixation performance in SD-EF strategy. SD-EF simulations for different high-to-low electric field strength ratios (Supplementary Fig. 17) indicate that the performance of nitrogen fixation is optimized at a ratio of 1.5. Accordingly, we optimize the SD-EF strategy by selecting appropriate dielectric materials and adjusting the discharge gap to achieve a high-to-low electric field strength ratio of approximately 1.5 in this work.

### Electrical measurements of plasma discharge

The signals for the applied voltage and the applied current measured by a voltage probe (RIGOL RP1018H) and a current probe (Cybertek cp0030A), respectively, are recorded by an oscilloscope (SDS814X HD). The time-averaged discharge power is calculated from the measured discharge voltage and current with Eq. (1)

$$P = f \int_{t_0}^{t_0+T} u(t)i(t)dt \quad (1)$$

where  $P$  is the discharge power;  $f$  is the discharge Frequency;  $T$  is the discharge period time;  $u$  is the voltage; and  $i$  is the current. To ensure the accuracy of the power, all measurements are performed by taking the average over 20 cycles.

### Photothermal spectroscopy diagnostic system

The major species  $NO$ ,  $NO_2$ , and  $O_3$  in gas phase, as well as  $NO_3^-$  and  $NO_2^-$  in aqueous phase are measured by hollow core photonic crystal fiber (HC-PCF) based photothermal spectroscopy (PTS). Three PCFs serve as sensing units and are placed in the plasma reactor, in the water, and above the surface of water. The PCFs are processed with focused ion beam (FIB) to create surface micro-channels with the diameter of 5  $\mu m$  for molecule diffusion. The PCF in the plasma reactor is through the gas fitting that connects gas tube with quartz tube into the plasma reactor. For the PTS sensing system (Fig. 1a), an overview diagram of photothermal spectroscopy in a PCF is shown in Supplementary Fig. 18. The modulated pump light with the modulated frequency of 20 kHz emitted by the distributed feedback laser (Nanoplus DFB) is amplified by an optical amplifier and then directed into the PCF. After the pump light reaches the PCF, the molecules of the target substance absorb the pump light to induce a modulated photothermal effect. Additionally, another probe light is emitted by a RIO Orion™ laser and is split into two beams, which propagate through the sensing arm and the reference arm, respectively. The probe light transmitted in the sensing arm will be reflected by the fiber Bragg gratings (FBGs) distributed at the end of PCFs, whose central wavelengths are same with the wavelength of probe light. The probe lights transmitted in the sensing arm and reference arm are heterodyne interfered at the optical fiber coupler. The signal of the interference light is converted to electric signal using a photodetector (THORLABS PDB435C). Moreover, the optical phase information contains in electric signal is demodulated by a self-made demodulate circuit, and then gets recorded by a data acquisition card (PicoScope 6000E).

### Calibration of the key species

Concentrations of stable species are calibrated directly by a mixture with a known mole fraction of the molecule, such as  $NO$ ,  $NO_2$ ,  $NO_2^-$ ,  $NO_3^-$ , and  $N_2O$ . For different molecules, we use different pump light wavelengths.  $NO$ ,  $NO_2$ ,  $NO_2^-$ ,  $NO_3^-$ , and  $N_2O$  are measured at wavelengths of 1789.8, 1501.4, 1948.4, 1670.2, and 1521.17 nm, respectively. The calibrated curves can be found in Supplementary Fig. 19a–e. These species are measured by the HC-PCF based PTS, except for  $N_2O$ . Due to the lack of a corresponding tunable laser of the model, it is measured by the HC-PCF based absorption spectroscopy (ABS).  $O_3$  Concentrations is estimated using formula with the collected phase information.

By comparing with the absorption cross-section in HITRAN library and the measured phase curves near 1631.3 nm, we verified the feasibility of our method (Supplementary Fig. 19f).

### Calculation of the NO<sub>x</sub> absorption ratio

The NO<sub>x</sub> absorption ratio is calculated on the basis of the following equation:

$$\text{NO}_x \text{ absorption ratio} = 1 - \frac{C_{(\text{NO}_x)_{\text{III}}}}{C_{(\text{NO}_x)_{\text{I}}}} \quad (2)$$

where  $C_{(\text{NO}_x)_{\text{I}}}$  represent the concentrations of NO<sub>x</sub> (such as NO<sub>2</sub>, NO, and N<sub>2</sub>O) before absorption in the Position I;  $C_{(\text{NO}_x)_{\text{I}}}$  represent the concentrations of NO<sub>x</sub> (such as NO<sub>2</sub>, NO, and N<sub>2</sub>O) after absorption in the Position III.

### Calculation of the NO<sub>x</sub><sup>-</sup> yield

The NO<sub>x</sub><sup>-</sup> yield is calculated according to Eq. (4):

$$\text{NO}_x^- \text{ yield} = VC_{(\text{NO}_x^-)_{\text{II}}} / t \quad (3)$$

where  $V$  is the volume of solution;  $C_{(\text{NO}_x^-)_{\text{I}}}$  represent the concentration of NO<sub>x</sub><sup>-</sup> (such as NO<sub>2</sub><sup>-</sup> and NO<sub>3</sub><sup>-</sup>) in the solution in the Position II.

### Kinetic model

Numerical modelling for the time evolution of species densities in the plasma discharge and gas absorption is done using the open-source code ZDPlasKin<sup>38</sup>. The electron impact reaction rate constants and transport parameters are solved by the Boltzmann equation solver BOLSIG<sup>37</sup> incorporated in ZDPlasKin. The global equations are shown as follows,

$$dn_i/dt = \sum_j a_{ij} k_j \prod_l n_l^{\nu_l} \quad (4)$$

where  $n_i$  is the density of species  $i$ ,  $a_{ij}$  is the stoichiometric coefficients for the general reaction. The gas temperature ( $T_g$ ) is considered to be the experimentally measured temperature.

In order to simulate the processes of gas discharge and gas absorption, there are two kinetic modes incorporated into a plasma model and an aqueous solution model. There are 62 species in the plasma model, 971 reactions in the plasma model, 80 species in the aqueous solution model, and 163 reactions in the aqueous solution model. Detailed species information can be found in Supplementary Table 2. The plasma model is developed by Boagert's group<sup>43</sup>. However, the original model implements 24 vibrational levels for N<sub>2</sub> and 15 levels for O<sub>2</sub>, which is computationally demanding. Therefore, we reduced the vibrational levels for N<sub>2</sub> to 15 and the vibrational levels for O<sub>2</sub> to 8 based on another work<sup>44</sup>. To evaluate the deviation for the simplification of vibrational energy levels, we extend the model to include higher N<sub>2</sub> vibrational levels ( $v = 16-58$ ) using cross-section data from the Laporta database in LXCAT. The calculated ratios of energy loss coefficients for N<sub>2</sub>( $v = 14-20$ ) relative to N<sub>2</sub>( $v = 13$ ) are shown in Supplementary Fig. 20. The energy loss coefficients of N<sub>2</sub>( $v > 15$ ) are less than 3% of that for N<sub>2</sub>( $v = 13$ ), indicating that the concentration of N<sub>2</sub>( $v > 15$ ) is negligible. Moreover, according to the Fridman-Macheret  $\alpha$ -model, the reaction rate of N<sub>2</sub>( $v$ ) + O → NO + N becomes nearly constant for vibrational levels above  $v = 12$  (Supplementary Fig. 11). Therefore, the contribution of N<sub>2</sub>( $v > 15$ ) molecules to the formation of NO via N<sub>2</sub>( $v$ ) + O → NO + N is minimal. Overall, this simplification has negligible influence on the reaction mechanism and the conclusions of the study. Furthermore, we modified related reactions pertaining to vibrationally excited N<sub>2</sub>, that is, electron impact reaction, N<sub>2</sub> – O<sub>2</sub> vibrational-vibrational (VV) relaxations, N<sub>2</sub> – N and O<sub>2</sub> – O vibrational-

translational (VT) relaxations, and elementary reactions with vibrational energy.

For the electron impact reactions, the cross sections of vibrational excitation, electronic excitation, dissociation, and ionization of N<sub>2</sub>, O<sub>2</sub>, N, and O are obtained from the Bigai database, Phelps database, and Morgan database of the LXCAT<sup>45</sup>. The relaxation rates for the N<sub>2</sub>( $v = 1$ ) and O<sub>2</sub>( $v = 1$ ) were based on Andrey et al.<sup>46</sup>. Other VV and VT relaxations are calculated based on Schwartz-Slowsky-Herzfeld (SSH) theory and approximations for the Morse oscillator model<sup>39</sup>.

Vibrational excitations play a critical role in the simulation of plasma. These rate coefficients are typically calculated from the corresponding rate coefficients of the collisions from the ground-state atoms by multiplying with an exponential factor according to the Fridman-Macheret  $\alpha$ -model<sup>40</sup>. In this work, the vibrational level of N<sub>2</sub> is up to 15 and a more elaborate description of the vibrational kinetics of N<sub>2</sub> and O<sub>2</sub> is added (i.e., vibrational-vibrational exchanges and vibrational-translational relaxation). In addition, the rate coefficients of the vibrationally excited species are determined according to the Fridman-Macheret model in which the activation energy is lowered by  $\alpha E_v$ , where  $\alpha$  is the vibrational efficiency to lower the activation barrier and  $E_v$  is the vibrational energy<sup>40</sup>. For the aqueous solution model, most of reactions are obtained from Leitz and Kushner<sup>47</sup>, and part of reactions are estimated by the gas phase reactions.

### Numerical Model

To predict the effective of N<sub>2</sub> fixation and analyze the reaction pathways, the simulation model includes the plasma discharge zone with electric field and the liquid zone without electric field. It is assumed that the gas diffusion can be ignored in bubbles of the water solution for simplifying the calculation. The initial mole fractions of dissolved post-discharge gas are directly calculated by Henry's law<sup>46</sup>.

For DBD, our discharge model is developed by Ju's group<sup>48</sup>. The reduced electric field intensity  $E/N$  in the discharge gap is estimated by

$$E/N = \frac{U_{app}}{L_g + d_q + \epsilon_{rq} N} \quad (5)$$

where  $U_{app}$  is the applied voltage,  $L_g$  is the discharge gap distance,  $d_q$  is the thickness of the quartz tube,  $N$  is the gas density, and  $\epsilon_{rq}$  is the relative dielectric constant of the quartz tube. The pulse duration  $t_d$  is determined by the periodic power density  $W$ , which can be obtained by

$$W = \int_0^{t_d} e N_e N^2 \mu (E/N)^2 dt \quad (6)$$

$$W = PT \quad (7)$$

where  $N_e$  is the electron number density,  $\mu$  is the electron mobility at a given reduced electric field,  $P$  is power in every pulse and  $T$  is the discharge periodic time.

For spark, we adapt the model of Boagert's group<sup>32</sup>. The power is assumed to be the constant. The reduced electric field is calculated by the following equations

$$\frac{E}{N} = \sqrt{\frac{P}{e N_e N^2 \mu}} \quad (8)$$

where  $E$  is the electric field;  $N$  is the gas density;  $P$  is discharge power;  $e$  is the electron charge;  $N_e$  is the electron number density;  $\mu$  is the electron mobility at a given reduced electric field. At the beginning of the calculation, an initial electron density of  $10^{10} \text{ cm}^{-3}$  is used. The initial corresponding  $E/N$  is calculated by equation. Then, the corrected  $E/N$  and electron density will be adapted from the input power density after a few timesteps.

To validate the  $O_2/N_2$  plasma chemistry for the predictions of NO,  $NO_2$ , and  $O_3$  mole fraction, the comparison with the experiment results is conducted in ZDPlasKin at a 0.8  $N_2/0.2 O_2$  DBD at 10 kV (Supplementary Fig. 21).

To get insight into the relationship between the  $N_2$  fixation with the reduce electric field, we use BOLSIG and the cross sections of  $N_2$  and  $O_2$  to calculate the fraction of electron energy transferred to different channels of excitation, as well as ionization and dissociation of  $N_2$  and  $O_2$ , in a 0.8  $N_2/0.2 O_2$  under different reduced electric field ( $E/N$ ), as shown in Fig. 2e.

To understand the mechanism of the plasma-assisted  $N_2$  fixation, we perform the simulations at a power of 10 W in the DBD and spark. The simulation results and reaction pathways are presented in Supplementary Figs. 6–10.

To study the importance of the energy distribution under the different reduced electric field, as shown in Fig. 3d–f. The high uniform-EF, low uniform-EF, and SD-EF are simulated under 0.5  $mJ/cm^3$  per pulse by fixing the reduced electric field of 100 Td, 150 Td, as well as 100 Td and 150 Td, respectively. In each pulse of the high uniform-EF and the low uniform-EF, the energy is only 0.5  $mJ/cm^3$ , and the discharge stops after the energy is applied. In addition, during a pulse of the SD-EF, 100 Td and 150 Td apply the deposition energy of 0.125 and 0.375  $mJ/cm^3$ , respectively, with no electric field applied during the rest of the time.

### Light field power simulation

To validate the feasibility of the optical transmission in the PCF, the optic mode of the HC-PCF is simulated by the Electromagnetic Waves, Frequency Domain (ewfd) module of COMSOL. We establish the simulation structures of the HC-PCF without water and with water for the gas phase and aqueous phase, respectively, as found in Supplementary Fig. 4a, b. In Supplementary Fig. 4a, air, whose refractive index is 1, is filled with the hollow-core region and the air holes within the cladding. The cladding is made of silicon dioxide with the refractive index of 1.44. In Supplementary Fig. 4b, air in the hollow-core region and the drilled holes is replaced with aqueous, while the rest air hole region is still filled with air. To simplify the simulation, the refractive index of aqueous is set to 1.333, the same as that of water. The simulation results of the HC-PCF without and with water are presented in Supplementary Fig. 4c, d.

### Electric field simulation

In this study, the electric field distribution in the SD-EF and low uniform-EF is simulated by the Electrostatic (es) module of COMSOL, and the simulation structures of the SD-EF and low uniform-EF are determined by our experimental configurations. To compare the discharge characteristics in the different configurations, we perform the simulations of the electric field distribution of the SD-EF and low uniform-EF. When the inner high voltage electrodes and the outer ground electrode are applied a voltage of 10 kV, the electric field distribution of the inner electrode center in the chamber is shown in Supplementary Fig. 13.

### Data availability

The authors declare that the data supporting this study are available within the paper and its supplementary information files. The authors declare that the data supporting this study are available within the paper and its supplementary information files. Source data are provided with this paper.

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## Author contributions

S.Y.G., Y.W., and H.Z. conceptualized the project. B.R.G., J.G.C., and H.Z. supervised the project. S.Y.G., Y.W., and Y.T.G. performed the plasma experiments. Y.W. designed the optical fiber diagnostic system and processed the photothermal spectra data. S.Y.G. did the numerical simulation. S.Y.G., Y.W., B.R.G., and H.Z. analyzed the data. S.Y.G. and Y.W. wrote the manuscript. All the authors discussed the data and commented on the paper.

## Competing interests

The authors declare no competing interest.

## Additional information

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