Supporting Information

Enhanced nitrogen fixation using DBD plasma with continuous flowing water and TiO_2 photocatalytic coupled system

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1. Measurement of NO_3^- and TN (total nitrogen) concentrations

1.1 Analysis of the samples

NO_3^- : First, the acidic environment is created by taking 50 mL of water sample and adding l mL hydrochloric acid solution of 1 mol/L into 100 mL volumetric bottle. Then 3-5 mL sulfamic acid of 50 g/L is added to the solution, and the solution is diluted to the 100 mL calibration mark with water for the measurement of nitric acid. A UV-Vis spectrophotometer is used to measure the absorbance at a wavelength of 210 nm with a quartz colorimetric cup and reagent blank as reference. Then the wavelength is adjusted to 275 nm, and the absorbance is measured again with the reagent blank as a reference.

TN: The TN concentration in the water sample is measured using the alkaline potassium persulfate digestion ultraviolet spectrophotometry method. The measurement principle involves the oxidation of nitrogen-containing species in the sample solution by alkaline potassium persulfate in an acidic environment (R1-R3), resulting in the formation of nitrate ions. Subsequently, the test sample solution is added to a quartz cuvette, while another quartz cuvette containing pure water is taken as a control, and the absorbance at 210 nm and 275 nm wavelength are measured by a UV-vis spectrophotometer [1].

$$K_2S_2O_8 + H_2O \rightarrow 2\ KHSO_4 + \frac{1}{2}O_2 \tag{R1}$$

$$\frac{1}{2}O_2 + NO_2^- \rightarrow NO_3^- \tag{R2}$$

$$2\ O_2 + NH_4^+ \rightarrow NO_3^- + H_2O + 2H^+ \tag{R3}$$

1.2 Standard curve drawing

A UV-Vis spectrophotometer (Beijing Puxi General Instrument Co., Ltd., TU-1901) is used to determine the absorbance A_{210} and A_{275} at the wavelength of 210 nm and 275 nm, respectively, and the absorbance A is corrected according to formula (S1).

$$A = A_{210} - 2A_{275} \tag{S1}$$

The NO_3^- and TN content are proportional to the corrected absorbance A based on the formulas (S2, S3), in which Y stands for concentration (mg/L).

NO_3^-: $$Y = 15.85881 \times A - 0.23728 \tag{S2}$$

TN: $$Y = 42.99584 \times A + 0.214785 \tag{S3}$$

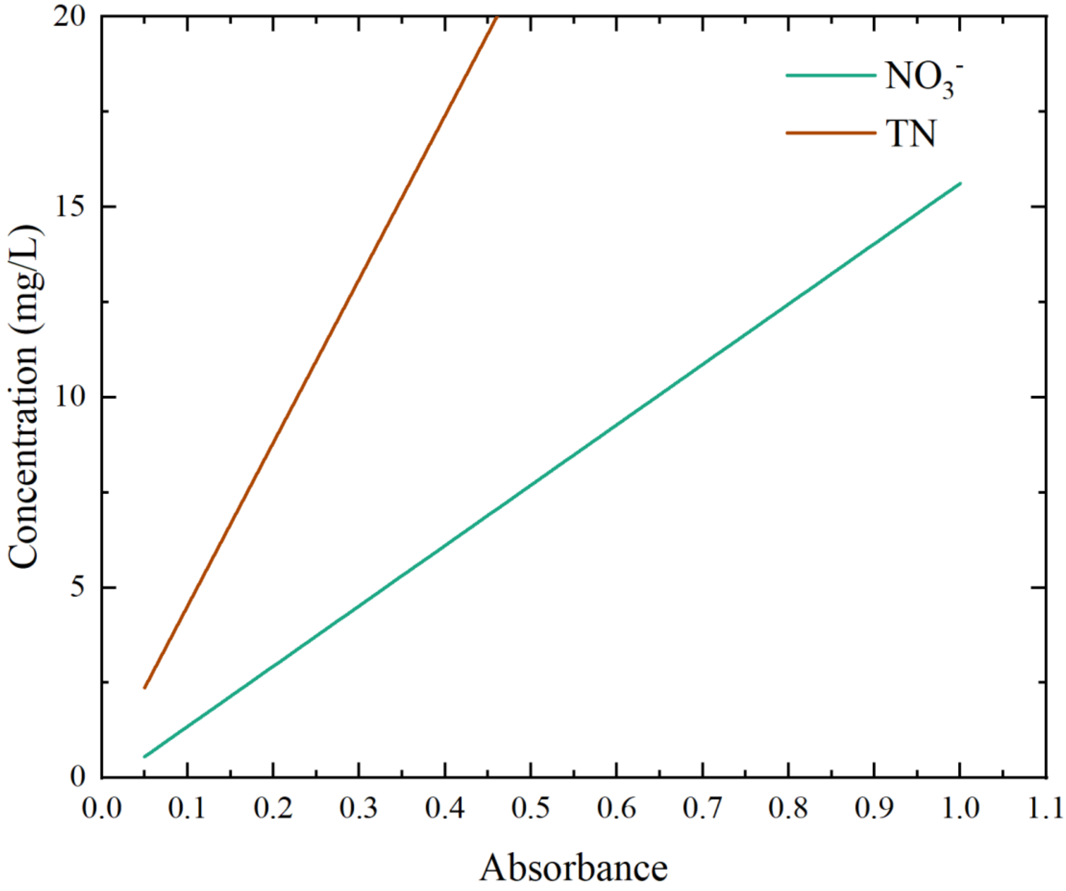
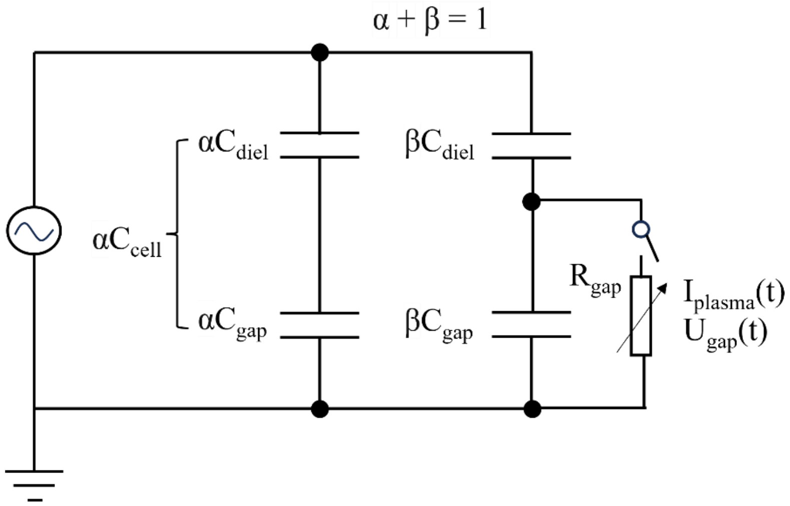


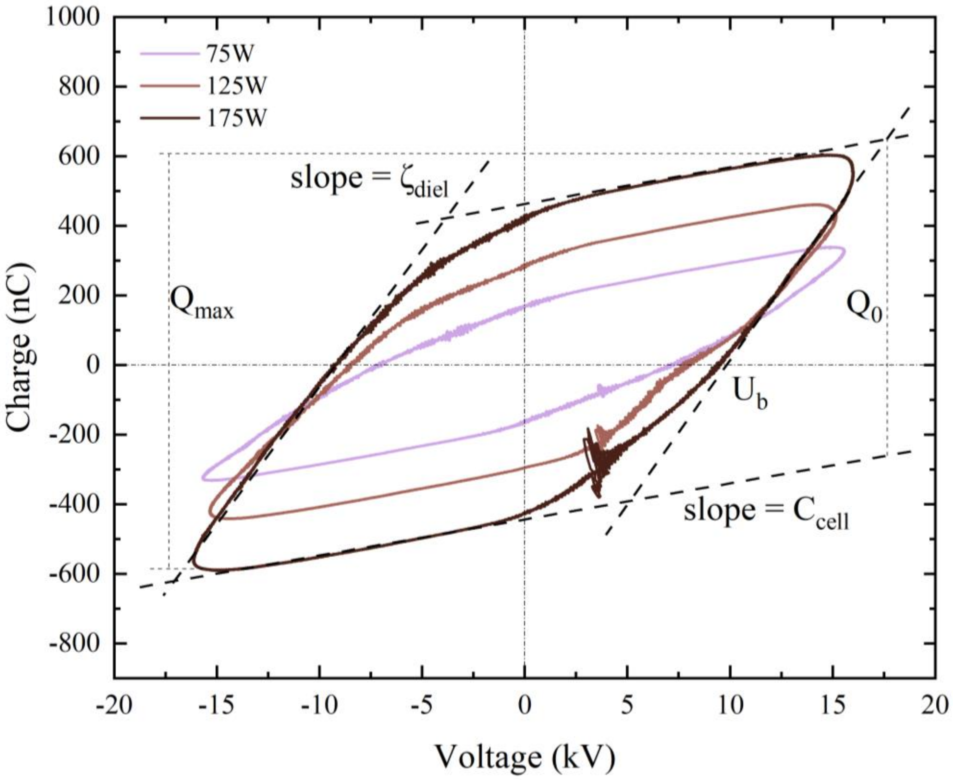
Figure S1 Standard curve of NO_3^- and TN concentrations as a function of their absorbance

2. Plasma electrical characteristics

2.1 Discharge parameters



(a)



(b)

Figure S2 Equivalent circuit of DBD reactor (a) and typical Q–V plot of DBD (b).

Figure S2 shows the equivalent circuit of a DBD reactor and the Q-V plot, which is also known as the Lissajous figure. The total capacitance of the DBD reactor C_{cell} without plasma discharge is composed of the dielectric capacitance C_{diel} and the gap capacitance C_{gap}. Peeters et al. [2] proposed an equivalent circuit model, as shown in Fig. S2(a). In this model, the electrode area of the planar reactor is divided into non-discharging and discharging area components with fractions α and β, respectively. The actual measured slopes are called the total capacitance of the DBD reactor C_{cell} and the effective dielectric capacitance ζ_{diel}.

The C_{diel} mentioned above can be calculated according to the plate capacitance calculation formula (S4):

$$C_{diel} = \frac{\varepsilon A}{d} \tag{S4}$$

Here, ε represents the dielectric constant, A is the opposite area between the two planar electrodes, and d is the thickness of the dielectric barrier.

The capacitance C_{cell} is calculated as a series connection of gas gap C_{gap} and dielectric barrier C_{diel} capacitances:

$$C_{cell} = \frac{C_{diel}C_{gap}}{C_{diel}+C_{gap}} \tag{S5}$$

The specific value of C_{Cell} can be calculated from Fig. S2(b) and C_{diel} can be calculated according to formula (S4), so C_{gap} can be known. U_b is the breakdown voltage in Fig. S2(b).

2.2 Calculation of mean electric field

The following equation was used to approximate the mean electric field (E):

$$E(\mathrm{kV\ m^{-1}}) = \frac{U_b(\mathrm{kV})}{d_{gap}(\mathrm{m})} \tag{S6}$$

where d_{gap} is the gas gap.

2.3 Calculation of reduced electric field strength

The reduced electric field was obtained using the calculated E and neutral particle density N, which can be estimated by the ideal gas equation of state.

2. 4 Electron temperature

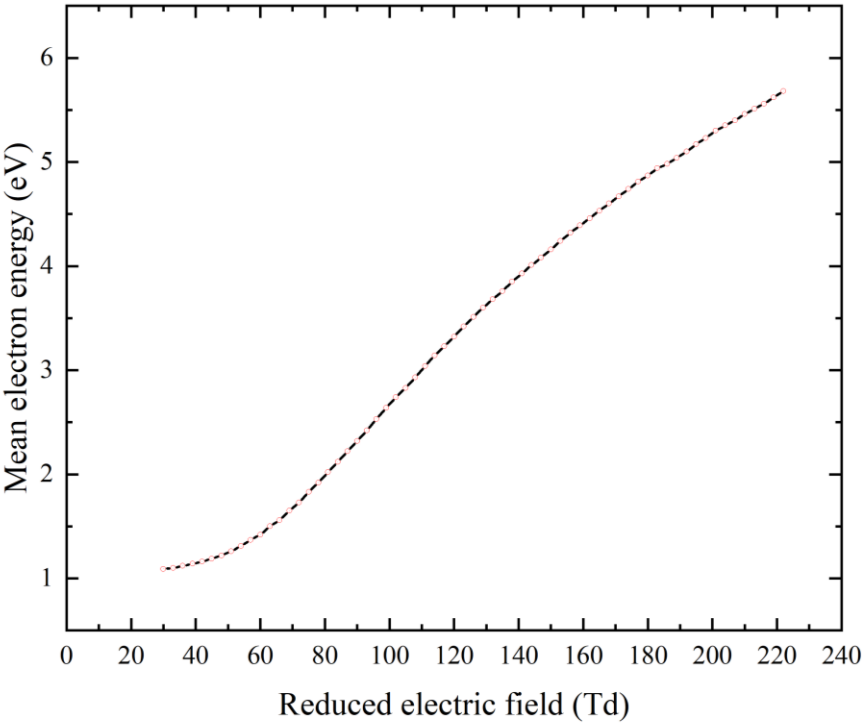


Figure S3 The relationship between the mean electron energy and the reduced electric field

The electron temperature T_e was calculated using the Boltzmann solver “BOLSIG+” [3], in which the reduced electric field was given as the input parameter, and collision cross sections were obtained from the SIGLO database on LXcat website.

3. Supplemental results of OES

3.1 Optical properties of air plasma

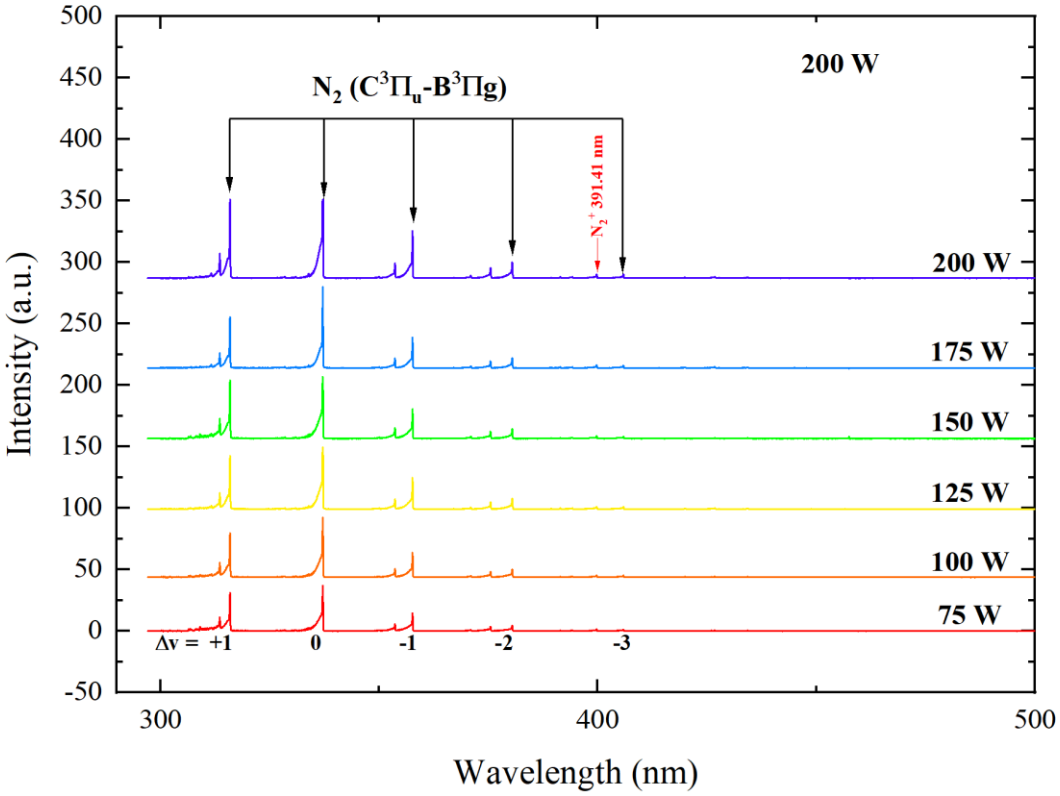
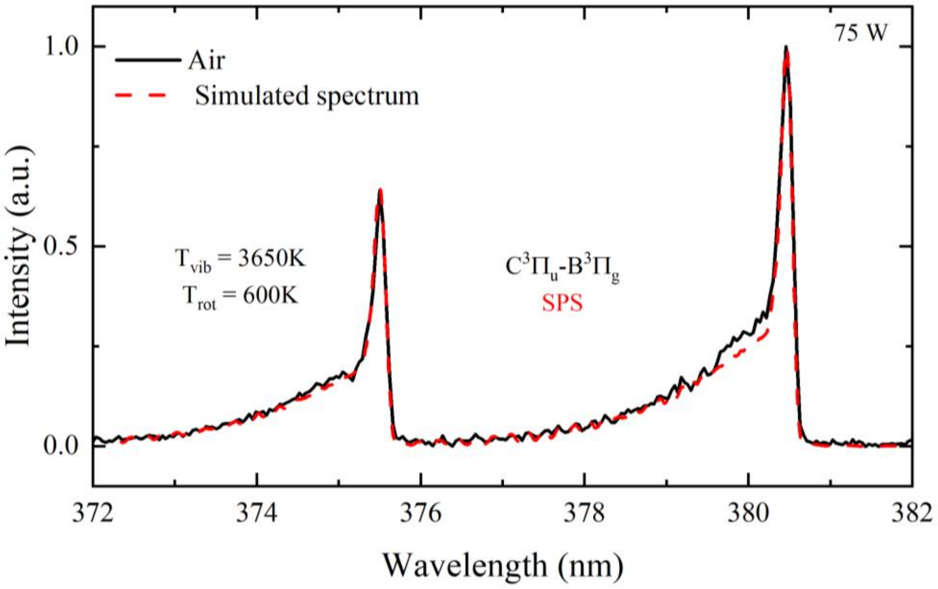


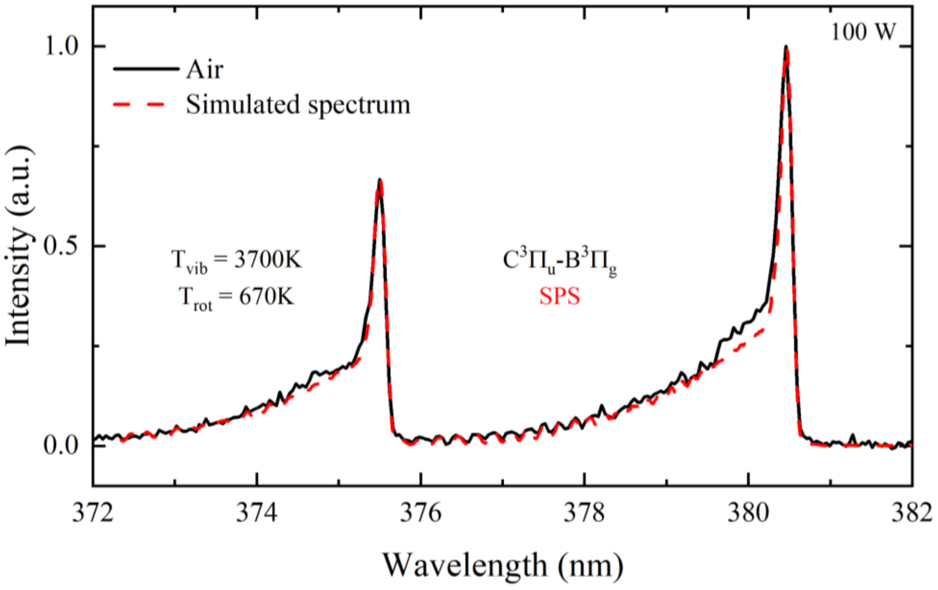
Figure S4 Variation of measured emission spectrum with the input power

Figure S4 shows the variation of measured emission spectrum with input power, since the excited species are also important to the formation of NO_x. As demonstrated in Fig. S4, upon increasing input power, the emission intensity of N_2(C-B) significantly enhances, indicating the enhancement of electron impact excitation, which may enhance excitation-induced dissociation of N_2. The rise of N_2^+ emission intensity with increasing power may denote there exist more electrons contributing to the nitrogen fixation at a larger input power, which is consistent with the variations of maximum transferred charge presented in table 1 of the main paper, subsequently stimulating a higher synergistic chemistry in both gas phase and liquid phase that actuates an efficient nitrogen fixation process.

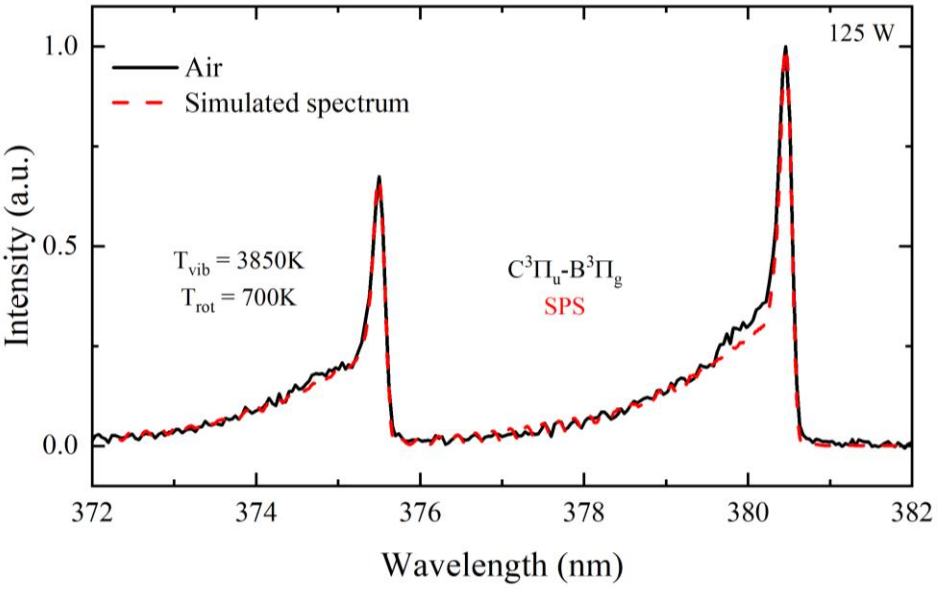
3.2 Rotational and vibrational temperature measurement



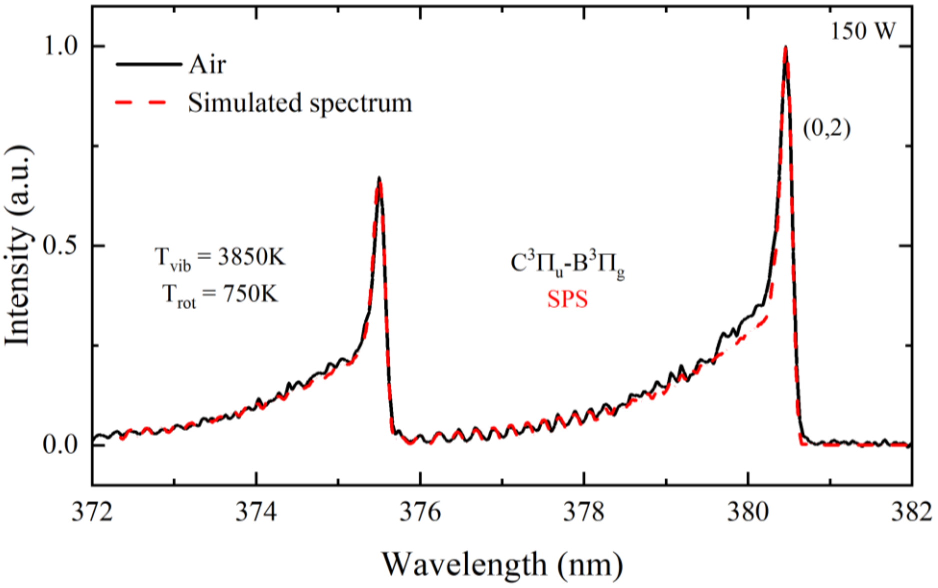
(a)



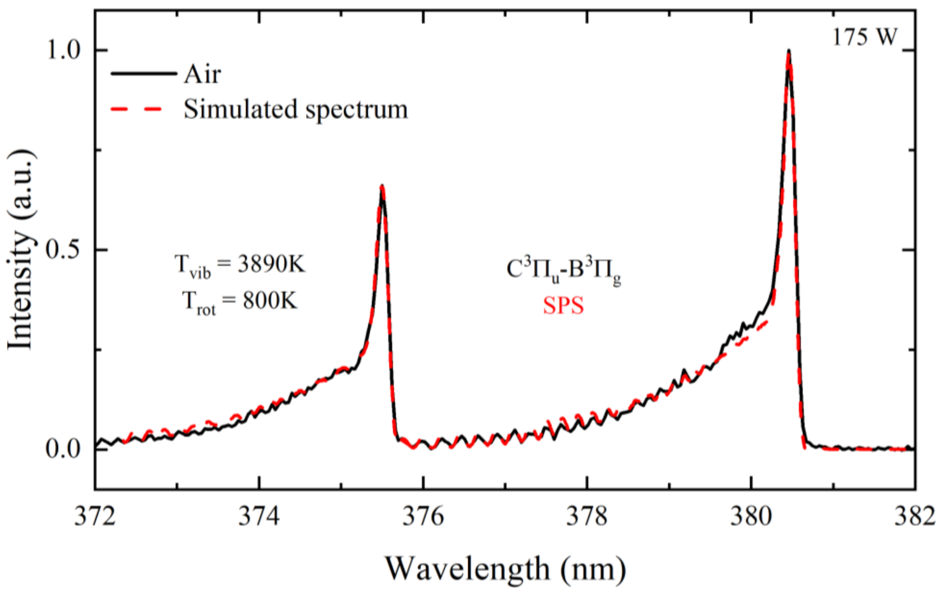
(b)


125 W
Air
Simulated spectrum
Intensity (a.u.)
Wavelength (nm)
T_{vib} = 3850K
T_{rot} = 700K
$C^3\Pi_u$-$B^3\Pi_g$
SPS
0.0
0.5
1.0
372
374
376
378
380
382

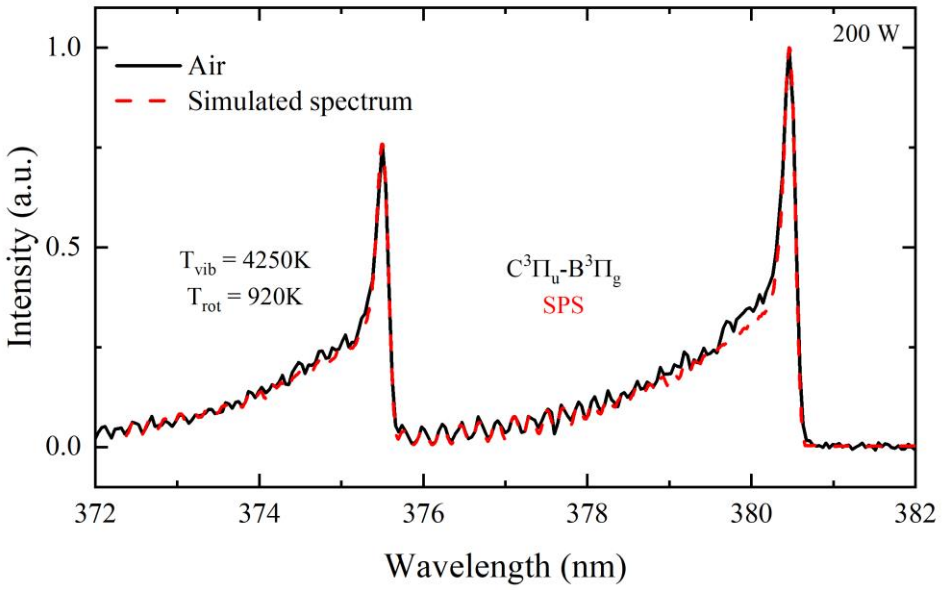
(c)


150 W
Air
Simulated spectrum
(0,2)
Intensity (a.u.)
Wavelength (nm)
T_{vib} = 3850K
T_{rot} = 750K
$C^3\Pi_u$-$B^3\Pi_g$
SPS
0.0
0.5
1.0
372
374
376
378
380
382

(d)



(e)



(f)

Figure S5 Fitting of experimentally measured spectra to simulated spectra

Based on the spectral information, the rotational temperature T_{rot} and vibrational temperature T_{vib} can be determined by fitting the N_2 second positive system ($C^3\Pi_u$-$B^3\Pi_g$, SPS, $\Delta v = -2$). Fig. S5 shows the comparison of fitting curves between the experimental and simulated intensities by the Specair 2.2 program at different power values, indicated in the right upper corner of the figures [4].

References

[1] Armstrong F A J. Determination of Nitrate in Water Ultraviolet Spectrophotometry. Analytical Chemistry. 1963, 35(9): 1292-1294.

[2] Peeters F J J, Van de Sanden M C M. The influence of partial surface discharging on the electrical characterization of DBDs. Plasma Sources Science and Technology. 2014, 24(1): 015016.

[3] Hagelaar G J M, Pitchford L C. Solving the Boltzmann equation to obtain electron transport coefficients and rate coefficients for fluid models. Plasma sources science and technology. 2005, 14(4): 722-733.

[4] Laux C O, Spence T G, Kruger C H, et al. Optical diagnostics of atmospheric pressure air plasmas. Plasma Sources Science and Technology. 2003, 12(2):125-138.