

# Insights into the mechanisms of plasma physicochemical characteristics on ultralong-lasting plasma-activated water: The influence of DC power polarity on RONS generation

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The gas temperature, electron excitation temperature, and electron density measurements were based on the emission spectra. In this study, Czerny-Turner type monochromator (MS7504i, SOL Instruments) with a grating of 3600 lines mm<sup>-1</sup> and intensified charge-coupled device cameras (ICCD, DH334T, Andor) were used to record the optical emission spectra. The light generated by DC pin-water discharge reactor was focused after passing through a planoconvex lens, and then transmitted to the spectrometer by optical fibers.

## S1 Determination of gas temperature

The gas temperature is correlated to the thermal translational energy with the same order of magnitude as the energy separation between rotational levels. Gas kinetic collisions occur frequently during the discharge, leading to a dynamic balance between translational and rotational motions. Therefore, the gas temperature can be estimated by the rotational temperature that is measurable by emission spectra. The rotational temperatures were obtained from the emission spectrum of N<sub>2</sub> (C-B (0-2), 380nm) using Specair 2.2. In detail, the spectrum profiles at different gas temperatures were first obtained by fitting with Specair software. Then, based on the least squares method and MATLAB, the fitted spectral line closest to the experimental spectrum was selected, whereby the temperature of fitted curve was approximated to the actual gas temperature.

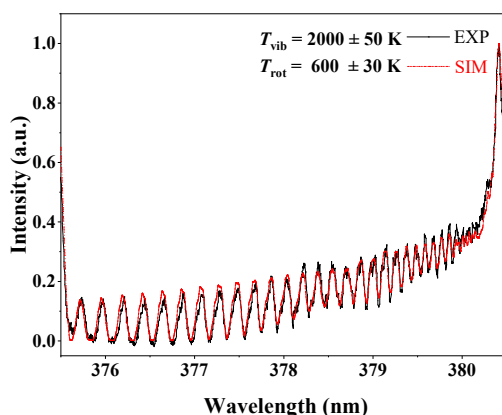


Fig. S1 The fitting of the emission spectrum

## S2 Determination of electron excitation temperature

The electron excitation temperature ( $T_{exc}$ ) can be obtained from the intensity ratio of  $H_\alpha$  and  $H_\beta$  based on the assumption that the excited states of hydrogen are Boltzmann distributed,

$$\frac{I_\alpha}{I_\beta} = \frac{A_\alpha g_\alpha \lambda_\beta}{A_\beta g_\beta \lambda_\alpha} \exp\left(-\frac{E_\alpha - E_\beta}{k_B T_{exc}}\right) \quad (1)$$

where  $I_\alpha$  and  $I_\beta$  are the integrated intensities of  $H_\alpha$  and  $H_\beta$ ;  $A_\alpha$ ,  $g_\alpha$ ,  $\lambda_\alpha$ ,  $E_\alpha$ , and  $A_\beta$ ,  $g_\beta$ ,  $\lambda_\beta$ ,  $E_\beta$  are the transition probability, the statistical weight, the wavelength, and the excitation energy of  $H_\alpha$  and  $H_\beta$ , respectively; and  $k_B$  is the Boltzmann constant, which is 0.695 cm<sup>-1</sup> K<sup>-1</sup>. Using the constants cited in Ref. 1, the  $T_{exc}$  can be calculated as follows:

36 
$$T_{\text{exc}} = \frac{7.67 \times 10^3}{\ln\left(\frac{I_{\alpha}}{I_{\beta}}\right) - 0.87} \quad (2)$$

### 37 **S3 Determination of electron density**

38 The  $n_e$  can be calculated with the Stark broadening of  $H_{\beta}$  (486.1 nm), using the following equation:

39 
$$n_e = 10^{17} \times \left(\frac{\Delta\lambda_s}{4.8}\right)^{1.46808} \quad (3)$$

40 where  $\Delta\lambda_s$ ,  $n_e$  are the full width at half maximum (FWHM) of Stark broadening in nm and the electron density in  
41  $\text{cm}^{-3}$ , respectively. The FWHMs of  $H_{\beta}$  can be divided into Doppler broadening ( $\Delta\lambda_D$ ), van der Waals  
42 broadening( $\Delta\lambda_{\text{vdw}}$ ), resonance broadening ( $\Delta\lambda_R$ ), instrumental broadening( $\Delta\lambda_i$ ), and  $\Delta\lambda_s$ . The FWHM of  $\Delta\lambda_i$  is 0.02  
43 nm in this study, and the FWHMs of  $\Delta\lambda_D$  can be calculated as follows:

44 
$$\Delta\lambda_D = 7.16 \times 10^{-7} \lambda_0 \sqrt{T_g/M} \quad (4)$$

45 where  $\lambda_0$  is the central wavelength of  $H_{\beta}$  in nm and  $M$  is the atomic mass of hydrogen. In atmospheric air, the  
46 equation can be simplified as follows:

47 
$$\Delta\lambda_D = 3.48 \times 10^{-4} \sqrt{T_g} \text{ (nm)} \quad (5)$$

48 The FWHMs of  $\Delta\lambda_{\text{vdw}}$  can be calculated by the equation

49 
$$\Delta\lambda_{\text{vdw}} = 8.18 \times 10^{-12} \lambda_0^2 (\bar{\alpha} R^2)^{0.4} N_o T_g^{0.3} / \mu \quad (6)$$

50 Where  $\bar{R}^2$  is the difference of the mean square radius of hydrogen between the upper and lower levels,  $\bar{\alpha}$  is the  
51 average polarizability of air in  $\text{cm}^3$ ,  $\mu$  is the reduced mass of the H-O<sub>2</sub> system, and  $N_o$  is the number density of air  
52 in  $\text{cm}^{-3}$ . When all these parameters are substituted into Eq. (6),  $\Delta\lambda_{\text{vdw}}$  is obtained approximately as

53 
$$\Delta\lambda_{\text{vdw}} = \frac{3.9}{T_g^{0.7}} \text{ (nm)} \quad (7)$$

54 According to Djurović and Konjević<sup>2</sup> the FWHMs of  $\Delta\lambda_R$  are written as follows:

55 
$$\Delta\lambda_R = 8.61 \times 10^{-14} \frac{g_1}{g_R} \lambda^2 \lambda_R f_R N_H \quad (8)$$

56 where  $g_1$  and  $g_R$  are the statistical weights of the ground state and the upper resonance level, respectively;  $\lambda$  and  
57  $\lambda_R$  are the observed and resonance wavelengths, respectively;  $f_R$  is the absorption oscillator strength of the upper  
58 level of resonance transition; and  $N_H$  is the number density of ground state H atoms in  $\text{cm}^{-3}$ . In pin-water discharge,  
59 H atoms are sourced by the dissociation of water vapor, which results in a low  $N_H$ , and thus  $\Delta\lambda_R$  for  $H_{\beta}$  is negligibly  
60 small and can be excluded from calculation.

### 61 **S4 Determination of absolute OH density**

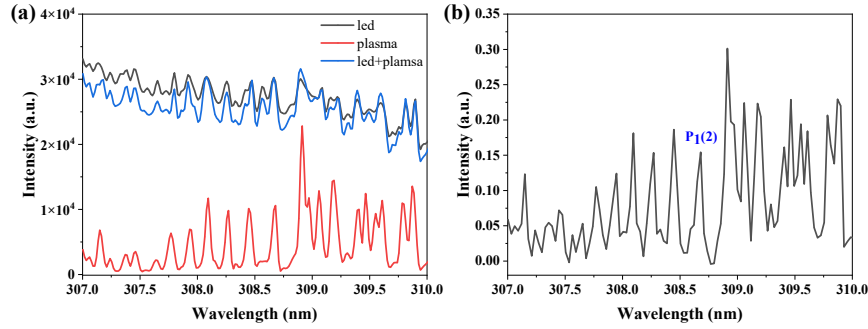
62 The OH density was determined from measurements of the ultraviolet absorption spectroscopy system by using  
63 the Beer-Lambert law. The optical system consists of AvaSpect-2048-8 spectrometer and a UV light source. The  
64 spectrometer with 5  $\mu\text{m}$  wide slit has 8 channels covered the range from 270 nm to 900 nm, those channels have  
65 a grating of more than 1800 lines/mm and a minimum resolution of 0.1 nm. The light source is a UV light emitting  
66 diode with maximum intensity around 310 nm and 10 nm-FWHM (full width at half maxima). In order to perform  
67 absorption measurements, a light path which allow the UV probe beam to cross the plasma axially is set. The light  
68 is focused by a UV-lens (Focal length: 75 mm), delivered by an optical fiber, detected by the spectrometer, and  
69 analyzed by computer. When the optical system is used to measure the emission spectrum of needle-water  
70 discharge plasma, the light would be off. And when acquiring absorption spectra, the light source would be on. In  
71 order to reduce the measurement errors of OES, every spectrum was the average of fifty shots.

72 There are four spectra needed to record to determine the fractional absorption  $A(\lambda)$ :

$$A(\lambda) = 1 - \frac{I_{L+p}(\lambda) - I_P(\lambda)}{I_L(\lambda) - I_B(\lambda)} = 1 - \frac{I(\lambda)}{I_0(\lambda)} \quad (9)$$

73

74 where  $I_{L+p}(\lambda)$  is the emission spectra from both the UV light source and plasma,  $I_P(\lambda)$  is the emission of plasma (UV  
75 light off),  $I_L(\lambda)$  is the UV light emission and  $I_B(\lambda)$  is the recorded background intensity (both light and plasma are  
76 off).  $I(\lambda)$  is the transmitted radiation,  $I_0(\lambda)$  is the incident radiation.<sup>3</sup> These spectrums and the corresponding  
77 absorption spectrum are presented on Fig. 2(a) and (b).



78

79 Fig. S2 (a) Different spectrum intensities in the range 307 nm-310 nm from the led, led + plasma, plasma. The dark  
80 background has been preprocessed. (b) Absorption spectrum obtained from the positive column of the discharge  
81 with the water cathode.

82 The line integrated absorption of a specific transition along the light path can be obtained by the Beer-Lambert  
83 law:<sup>4</sup>

$$W = \int A(\lambda)d\lambda = \int 1 - \exp(-h\lambda B\varphi(\lambda)n_iL)d\lambda \quad (10)$$

84

85 where  $h$  is the Planck constant.  $B$  is the absorption coefficient,  $\varphi(\lambda)$  is the normalized line profile,  $n_i$  is the OH  
86 density in the specific level of the ground state,  $L$  is the absorption path length, which is approximately equal to  
87 the diameter of positive column corresponds to the position in the middle of the electrode gap.

88 To obtain the OH ground state density, rotational spectral lines  $P_1(2)$  were chosen since it is well isolated in the  
89 spectrum (see Fig. 3(b)). The line profile is mainly composed by the Doppler Broadening ( $w_D$  (pm)) and van der  
90 Waals broadening ( $w_L$  (pm)). The Doppler line width for the  $P_1(2)$  transition (in pm) is calculated from

$$w_D = 7.16 \times 10^{-7} \lambda \sqrt{\frac{T}{M}} \quad (11)$$

91

92 where  $M = 17$  is the molecular weight of OH,  $T$  is the gas temperature. And the van der Waals broadening line  
93 width (in pm) is calculated from

$$w_L = \frac{\lambda^2}{c} 1.71 \times 10^{-3} \left(\frac{T}{296}\right)^{-0.7} \quad (12)$$

94

95 Thus, the experimental line shape,  $\varphi(\lambda)$ , can be considered as a Voigt function. The total ground state OH(X)  
96 density  $n_{tot}$  in both  $^2\Pi_{3/2}$  and  $^2\Pi_{1/2}$  states can be calculated by  $n_{J''} = f_{J''} n_{tot}$ . From which  $f_{J''}$  is the fraction of  
97 population in the  $J''$  rotational level, calculated from:

$$f_{J''} = \frac{2(2J'' + 1)}{Q_{rot}(T)} \exp\left(-\frac{E_{J''}}{kT}\right) \quad (13)$$

98

99 where  $J''$  is the lower level rotational number, is the energy of the rotational level,  $Q_{rot}$  is the rotational partition  
100 function and  $k$  is the Boltzmann constant.

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## 102 Reference

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