RSC Advances

Supplementary Information

A Self-Boosting Microwave Plasma Strategy Tuned by Air Pressure for High-Efficient and Controllable Surface Modification of Carbon

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Theoretical calculation and model simulation

Fig. S2 illustrated the key part of the experimental setup where the carbon fiber cloth was treated and possible gas discharge occurred. In this paper, the calculation domain was simplified in two dimensions as shown in **Fig. S3** based on the microwave field distribution characteristics. For a standard rectangular waveguide WR430, the microwave working frequency (2.45GHz) and its dimensions decided together that TE_{10} mode was the only propagating mode in the waveguide. In this electromagnetic mode, the microwave electric field only had a z-component (E_z) that depends on x and y coordinates, which was accordingly independent of the z coordinate. This made it reasonable to model microwave propagation and reflection in the waveguide in x-y plane ($z = a/4$) as shown in **Fig. S3**. In **Fig. S3**, AD=312 mm and AB=109.2 mm. The inner diameter of the glass tube is 19 mm and the carbon fiber cloth has the size of $10\ mm \times 10\ mm$.

The microwave field distribution in the computational domain can be described by the Helmholtz equation as follows:

$$\nabla \times \left(\mu_r^{-1} \nabla \times \vec{E}\right) - k_0^2 \left(\varepsilon_r - \frac{j\sigma}{\omega \varepsilon_0}\right) \vec{E} = 0 \qquad \text{Eq. (A.1)}$$

$\vec{E}$ is the microwave electric field. μ_r, ε_r and σ are the relative permeability, the relative permittivity and the electric conductivity respectively of the medium in the waveguide. k_0 and ε_0 are the wave number and the permittivity in free space respectively. For the carbon fiber cloth, its complex permittivity is 33.7-j*40.7. It is worth noting that the plasma introduced by the microwave breakdown in the quartz tube has the equivalent conductivity σ_p as shown in Eq. (A.2)* MERGEFORMAT (3), when it is regarded as a conductive medium.

$$\sigma_p = \frac{n_e q^2}{m_e \left(v_m + j\omega\right)} \qquad \text{Eq. (A.2)}$$

In this equation, n_e indicates the electron number density and v_m is the electron collision frequency with the neutrals and ions. m_e and q are respectively the elementary mass and the charge of a single electron.

For the electromagnetic boundary conditions on the edges of the computation domain in **Fig. S3**, the microwave excitation on AB can be described by the Eq. (A.3)* MERGEFORMAT (4), considering the field distribution of TE10 mode. Other edges (BC, CD and AD) are set as the perfect electric conductor (PEC) boundaries.

$$E_z = E_{10} \sin\left(\frac{\pi}{\mathrm{a}} \mathrm{y}\right) \qquad \text{Eq. (A.3)}$$

The amplitude E_{10} can be deduced from Eq. (A.4)* MERGEFORMAT (5) with the measured microwave power P_{10}, when the microwave propagates in TE_{10} mode.

$$P_{10} = \frac{abE_{10}^2}{4Z_{TE_{10}}} \qquad \text{Eq. (A.4)}$$

$Z_{TE_{10}}$ is the wave impedance of a TE10-mode microwave in the rectangular waveguide. In our case, $Z_{TE_{10}} = 120\pi/\sqrt{1-(\lambda/2a)^2} \cong 455\Omega$. When $P_{10} = 500W$, E_{10} is approximately equal to $1.23 \times 10^4\ V/m$. Other edges (BC, CD and AD) were set as the perfect electric conductor (PEC) boundaries.

The electron number density (n_e) change during the microwave breakdown can be characterized by a continuity equation as follows:

$$\frac{\partial n_e}{\partial t} - \nabla\left(D_{eff} n_e\right) = v_i n_e - r_e n_e^2 \qquad \text{Eq. (A.5)}$$

D_{eff} is the effective diffusivity of electrons, v_i is the ionization rate, and r_e is the electron recombination rate with ions. This equation is based on the plasma fluid model with the ambipolar diffusion approximation.[1] It has been successfully applied to explore the mechanism of discharge pattern formation under atmospheric pressure in a 110-GHz microwave air breakdown.[2,3] When linking the related parameters (D_{eff}, v_i and v_m) with gas pressure, the model can be extended to simulate other microwave discharges under low pressures at different electromagnetic frequencies.[4-6] The effective diffusivity of electrons was determined from the following Eq.* MERGEFORMAT (7) (A.6).[1]

$$D_{eff} = \frac{\alpha D_e + D_a}{1+\alpha}; \quad \alpha = v_i \frac{\varepsilon_0}{q n_e(\mu_e + \mu_i)} \qquad \text{Eq. (A.6)}$$

D_e and μ_e are the free diffusivity and the mobility of electrons respectively, which have the so-called Einstein's relation as $D_e = \mu_e T_e[eV]$. μ_e is determined from the equation $\mu_e = q/(m_e v_m)$, where the electron collision frequency (v_m) depends on the gas pressure (*P* in Torr) as $v_m = 5.3 \times 10^9 P[Torr]$.[7] μ_i is the free mobility of ions, which is approximately taken as $\mu_i \cong \mu_e/200$.[1] D_a is the ambipolar diffusion coefficient that can be calculated by $D_a = \left(\mu_i/\mu_e\right)D_e$. Reference 6 and the recombination rate (r_e) approximately equals to 3×10^{-14}.[8] The electron ionization rate v_i and electron temperature T_e strongly depend on the effective field E_{eff} that is generally determined by the following Eq. (A.7)* MERGEFORMAT (8).

$$E_{eff} = \sqrt{\frac{E_{rms}{}^2}{1+\frac{\omega^2}{v_m^2}}} \qquad \text{Eq. (A.7)}$$

E_{rms} is the effective value of the microwave electric field in the unit of V/m. With different E_{rms}/P data and the above Eq. (A.7)* MERGEFORMAT (8), v_i can be either estimated by the empirical formulas based on experimental data[6] or obtained by solving the Boltzmann equation with the Bolsig+ solver.[9] In this paper, the empirical formulas based on the references[10,11] were applied to calculate v_i as shown in Eq. (A.8)* MERGEFORMAT (9).

$$\begin{cases} \frac{v_i}{P} = \left(1.32 + 0.054\,E_{eff}/P\right) \times \exp(-208P/E_{eff}) \times 10^7 & (30 \le \frac{E_{eff}}{P} \le 54) \\ \frac{v_i}{P} = \left(5 + 0.19\,E_{eff}/P\right) \times \exp(-273.8P/E_{eff}) \times 10^7 & (54 \le \frac{E_{eff}}{P} \le 120) \\ \frac{v_i}{P} = 5.48\sqrt{E_{eff}/P} \times \exp(-359P/E_{eff}) \times 10^7 & (120 \le \frac{E_{eff}}{P} \le 3000) \end{cases}$$

Eq. (A.8)

$T_e[eV]$ can be estimated from the following equation.[12]

$$T_e[\mathrm{eV}] = \left[2.1 \times 10^{-3}\frac{E_{eff}}{P}\left(91 + \frac{E_{eff}}{P}\right)\right]^{1/3} \qquad \text{Eq. (A.9)}$$

The initial value of n_e was assumed to be $1 \times 10^{13}/m^3$ and the modelling time of microwave discharge was set to be 1000 ns. The input microwave power was set to be

500 W, indicating it had an amplitude of $1.23 \times 10^4\ V/m$. The calculation was implemented in a software named COMSOL Multiphysics on a computer having 72GB of RAM and 2 processors with 32 cores. The mesh structure has 48708 elements and it took approximately 12 minutes to complete one calculation.

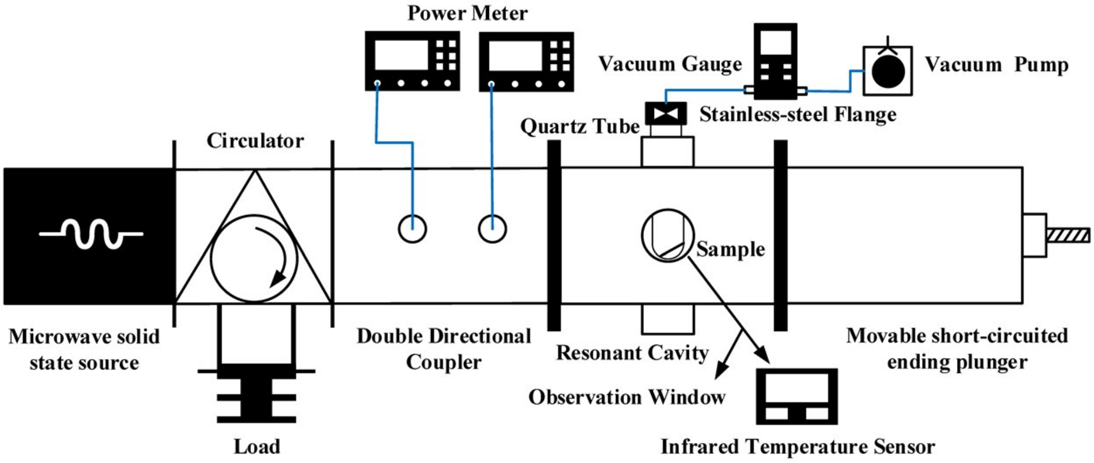

Fig. S1 Schematic illustration of the microwave air plasma device for surface modification of carbon fiber cloth

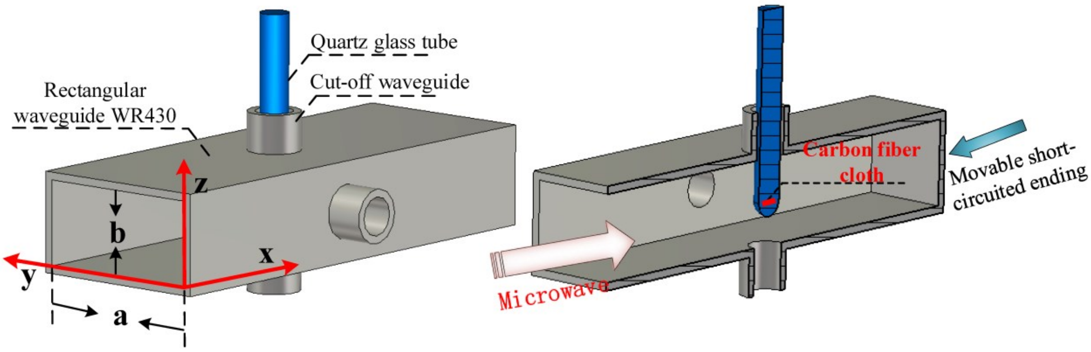

Fig. S2 Schematic presentation of the key part of the experimental setup

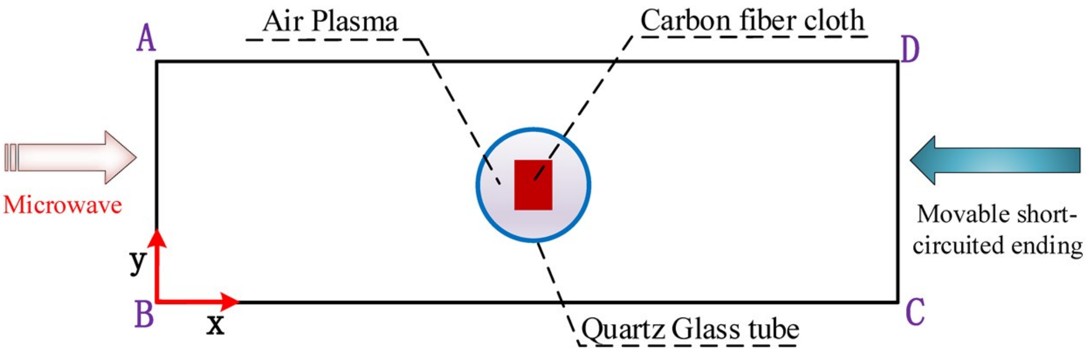

Fig. S3 Computational domain

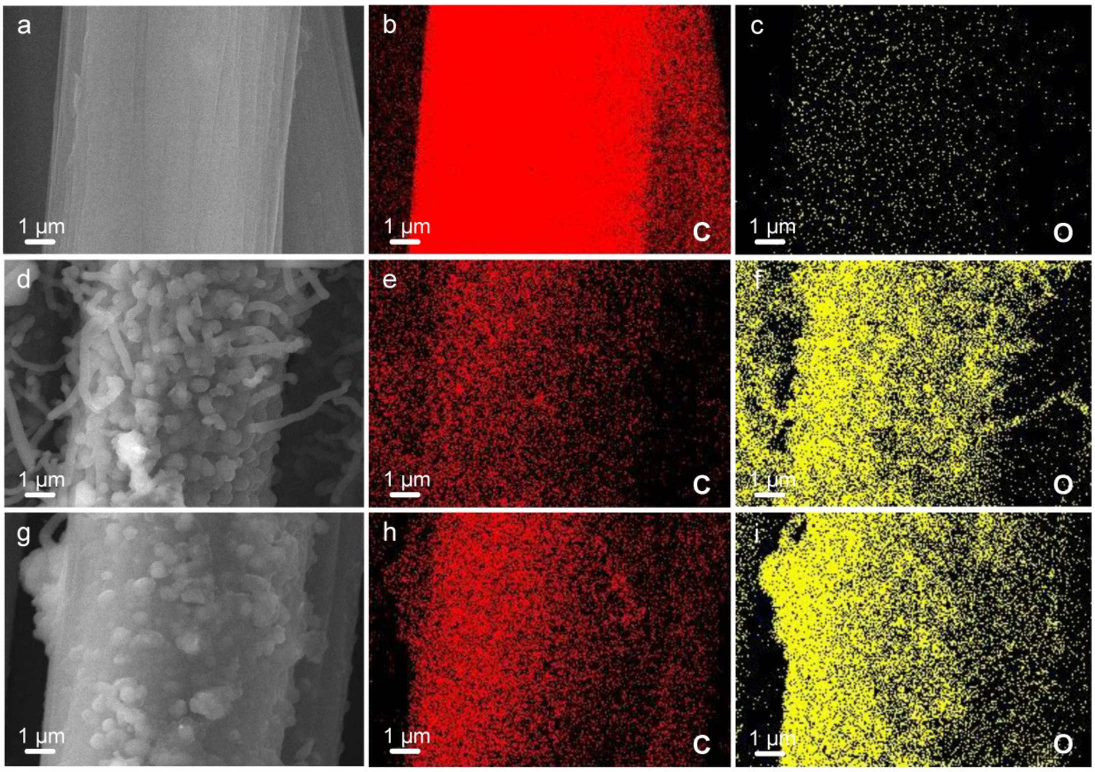

Fig. S4 FESEM (a) and EDS Mapping of C (b), O (c) element of CFC-pristine; FESEM (d) and EDS Mapping of C (e), O (f) element of CFC-8000Pa; FESEM (g) and EDS Mapping of C (h), O (i) element of CFC-80Pa.

References

1 G. Q. Zhu, J. -P. Boeuf and B. Chaudhury, *Plasma Sources Sci. Technol.*, 2011, **20**,

035007.

2 Y. Hidaka, E. M. Choi, I. Mastovsky, M. A. Shapiro, J. R. Sirigiri, R. J. Temkin, G. F. Edmiston, A. A. Neuber and Y. Oda, *Phys. Plasmas*, 2009, **16**, 055702.

3 J. -P. Boeuf, B. Chaudhury and G. Q. Zhu, *Phys. Rev. Lett.*, 2010, **104**, 015002.

4 V. E. Semenov, E. I. Rakova, V. P. Tarakanov, M. Y. Glyavin and G. S. Nusinovich, *Appl. Phys. Lett.*, 2011, **98**, 161504.

5 V. E. Semenov, E. I. Rakova, V. P. Tarakanov, M. Y. Glyavin and G. S. Nusinovich, *Phys. Plasmas*, 2015, **22**, 092308.

6 P. C. Zhao, L. X. Guo and P. P. Shu, *Phys. Plasmas*, 2016, **23**, 092105.

7 B. Chaudhury and J. -P. Boeuf, *IEEE Trans. Plasma Sci.*, 2010, **38**, 2281-2288.

8 K. Kourtzanidis, J. P. Boeuf, F. Rogier, *Phys. Plasmas*, 2014, **21**, 123513.

9 G. J. M. Hagelaar and L. C. Pitchford, *Plasma Sources Sci. Technol.*, 2005, **14**, 722.

10 A. W. Ali, *Laser Part. Beams.*, 1988, **6**, 105-117.

11 T. Tang, C. Liao and W. Lin, *Prog. Electromagn. Res.*, 2010, **14**, 207-220.

12 W. Woo and J. S. DeGroot, *Phys. Fluids.*, 1984, **27**, 475-487.