Electronic Supplementary Material (ESI) for Chemical Communications

Supplementary Materials:

1. Optical emission spectroscopy (OES)
2. OES of H_2 and H_2-CH_3OH
3. The attribution of H_2 OES

1. Optical emission spectroscopy (OES)

OES（SP 2758, produced by Princeton instrument company）studies were carried out in the 200-1000 nm range. Light emitted from the plasma was collected and directed to a monochromator with a fiber optic cable. The accuracy of the position of the emission lines in the spectra was 0.1 nm.

The reaction conditions of H_2-CH_3OH discharge using double dielectric barrier discharge (DDBD) reactor in plasma diagnosis were as follows: H_2 = 0, 20, 40, 60, 80, 100 mL/min, CH_3OH = 0.02 (liquid) mL/min, input power = 11 W.

The reaction conditions of H_2 discharge in plasma diagnosis were as follows: H_2 = 100 mL/min, input power = 11 W.

2. OES of H_2 and H_2-CH_3OH

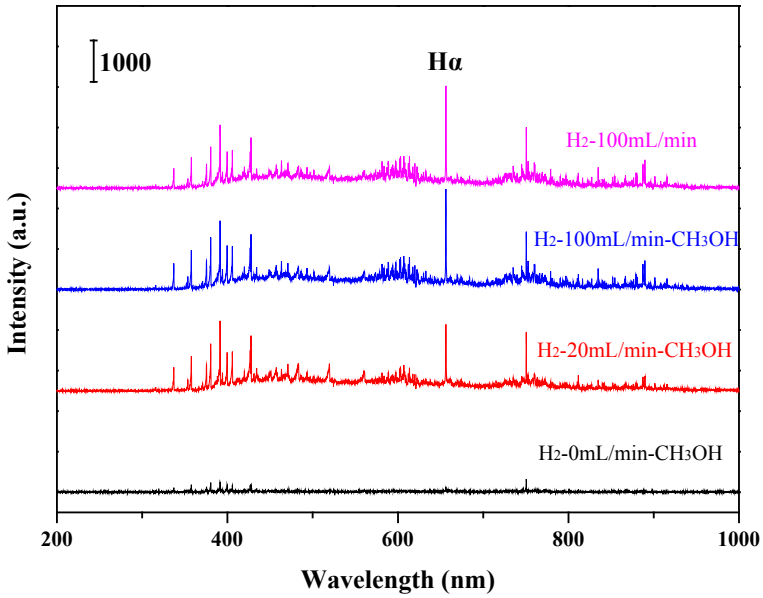

Fig. S1. OES (wavelength: 200~1000nm) of H_2 and H_2-CH_3OH non-equilibrium plasma in the double dielectric barrier discharge (DDBD) reactor with different H_2 content; (H_2 flow rate = 0, 20, 100 mL/min, CH_3OH liquid flow rate = 0.02 mL/min, 1 atm, input power = 11 W, 300 G/mm grating, exposure time = 1.0 s.)

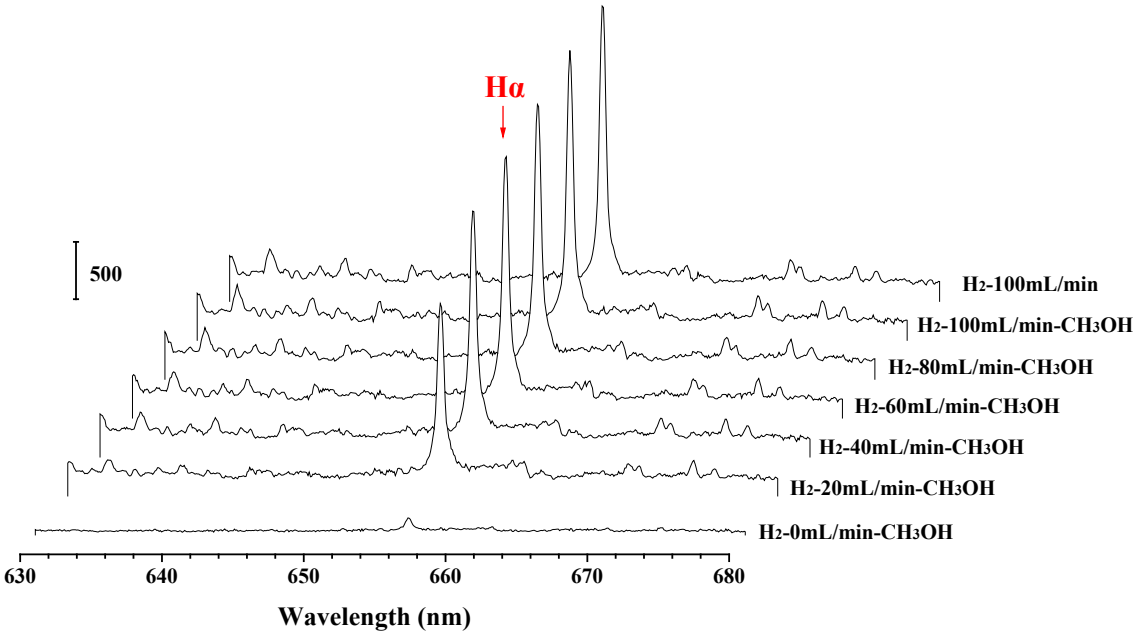

Fig. S2. OES (wavelength: 630~680nm) of H_2 and H_2-CH_3OH non-equilibrium plasma in the double dielectric barrier discharge (DDBD) reactor with different H_2 content; (H_2 flow rate = 0, 20, 40, 60, 80, 100 mL/min, CH_3OH liquid flow rate = 0.02 mL/min, 1 atm, input power = 11 W, 300 G/mm grating, exposure time = 1.0 s.)

3. The attribution of H_2 OES

There are two important emission bands in the range of about 380-550 nm and about 580-650 nm, and an intensive emission line at 656.3 nm. These emissions correspond to the radiative dissociation continuum of the H_2 molecule ($a^3\sum_g^+ \rightarrow b^3\sum_u^+$), the Fulcher transition of the H_2 molecule ($d^3\prod_u^+ \rightarrow a^3\sum_g^+$) and the H_α line ($3d^2D \rightarrow 2p^2P^0$), respectively [1]. The $b^3\sum_u^+$ state of H_2 is a repulsive state which produces two ground state H atoms spontaneously. Thus the radiative dissociation continuum and the Fulcher transition constitute relay channels for ground state H formation [H_2 ($a^3\sum_g^+$) → H_2 ($b^3\sum_u^+$) → H (1S) + H (1S) and H_2 ($d^3\prod_u^+$) → H_2 ($a^3\sum_g^+$) → H_2 ($b^3\sum_u^+$) → H (1S) + H (1S)].

[1]. U. Fantz, B. Schalk, K. Behringer, *New J. Phys.* **2000**, 2, 7.1.