Supporting information

Boosting methanol production via plasma catalytic CO_2 hydrogenation over MnO_x/ZrO_2 catalyst

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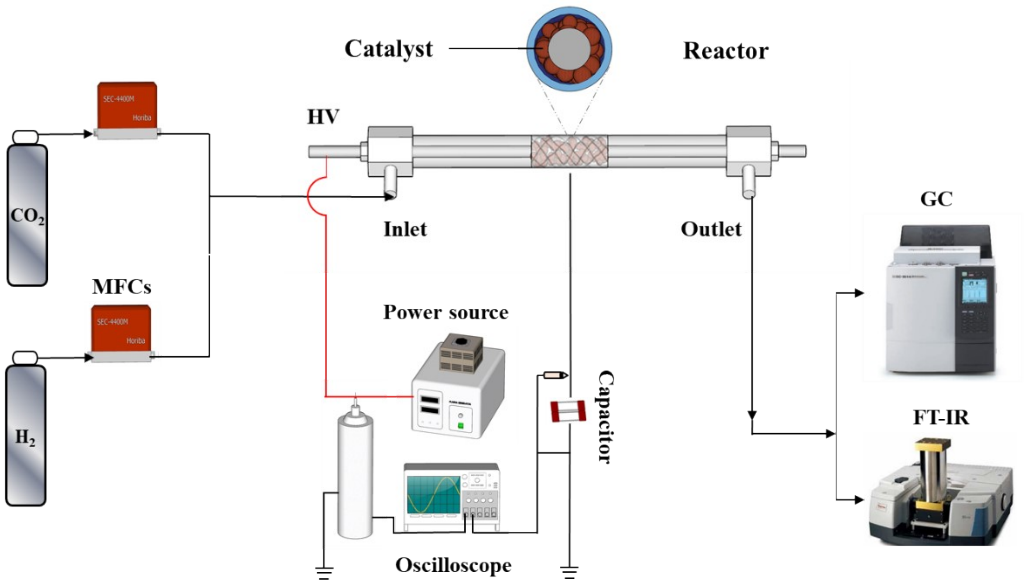


Fig. S1 Schematic diagram of the experimental setup

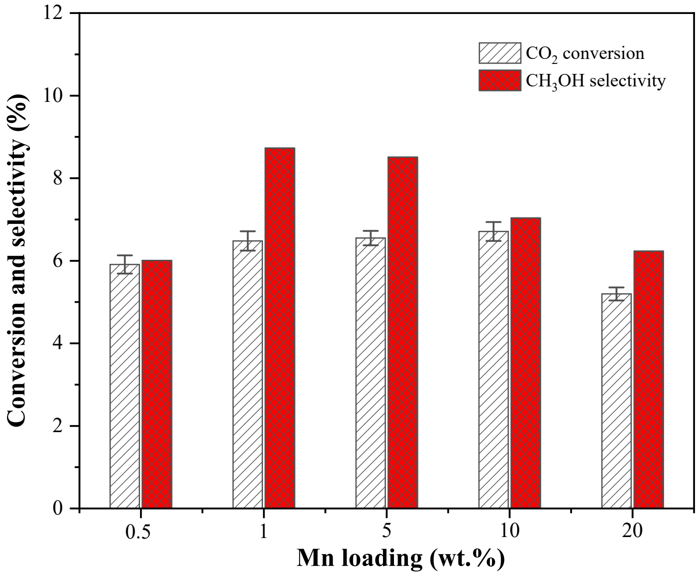


Fig. S2 The effect of Mn loading on the CO_2 conversion and CH_3OH selectivity

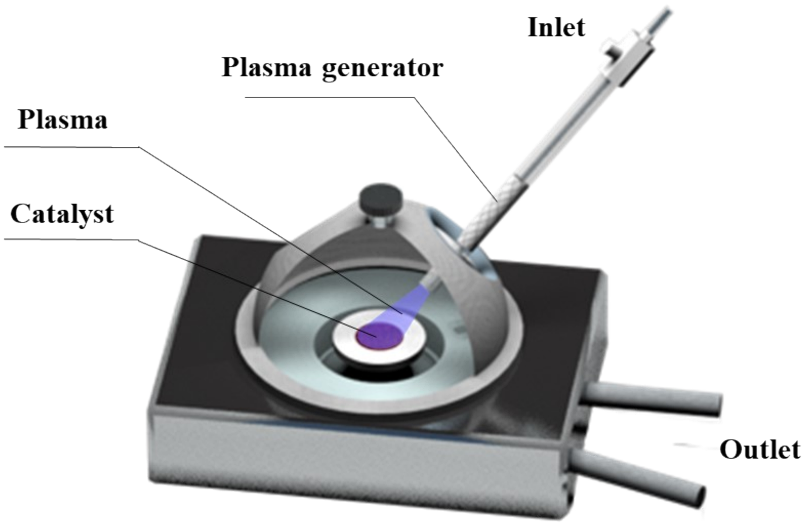


Fig. S3 Schematic diagram of the designed plasma-added DRIFT spectra cell

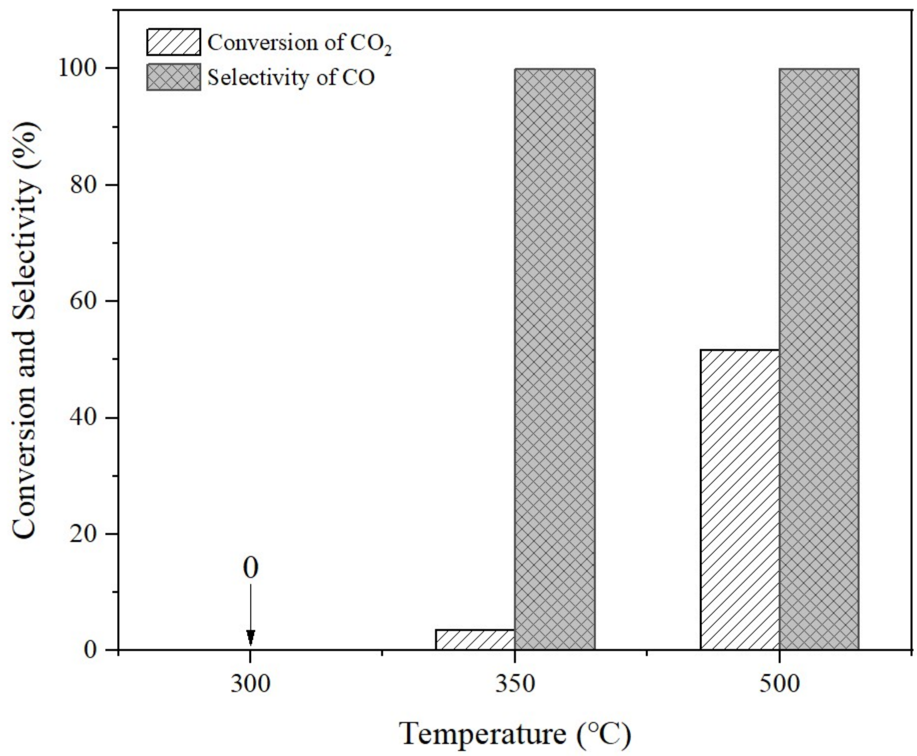


Fig. S4 The effect of temperature on CO_2 conversion and CO selectivity in thermal catalysis CO_2 hydrogenation reaction.

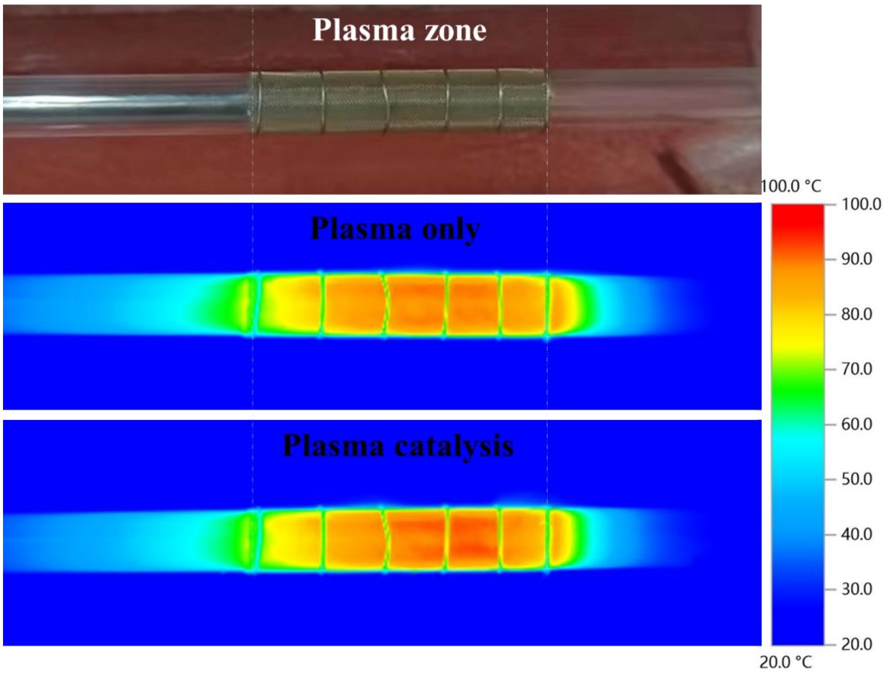
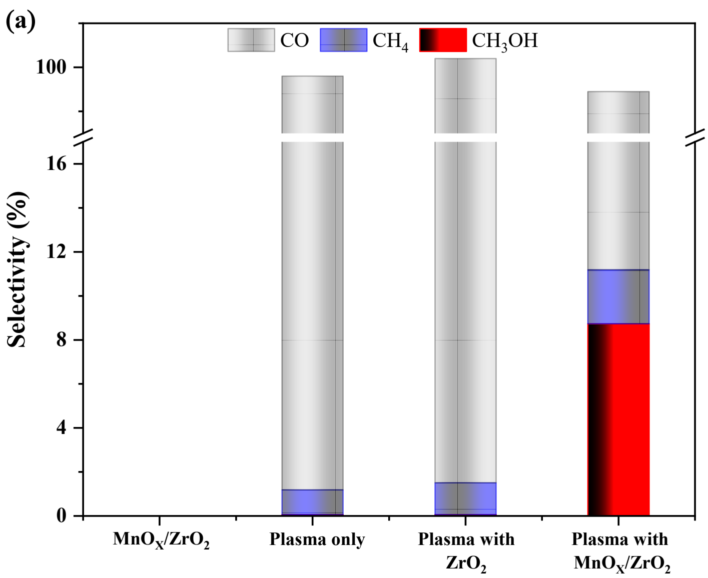
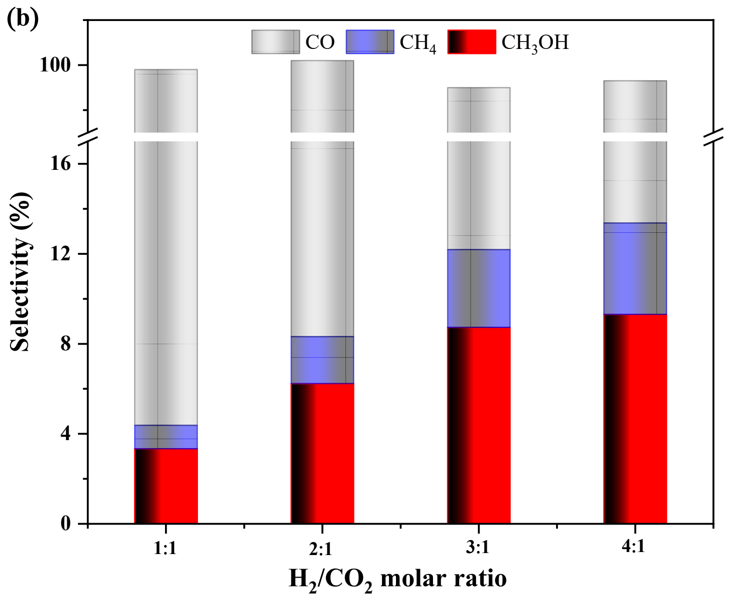


Fig. S5 The reactor temperature distribution of plasma only and plasma catalysis after 3-h discharge





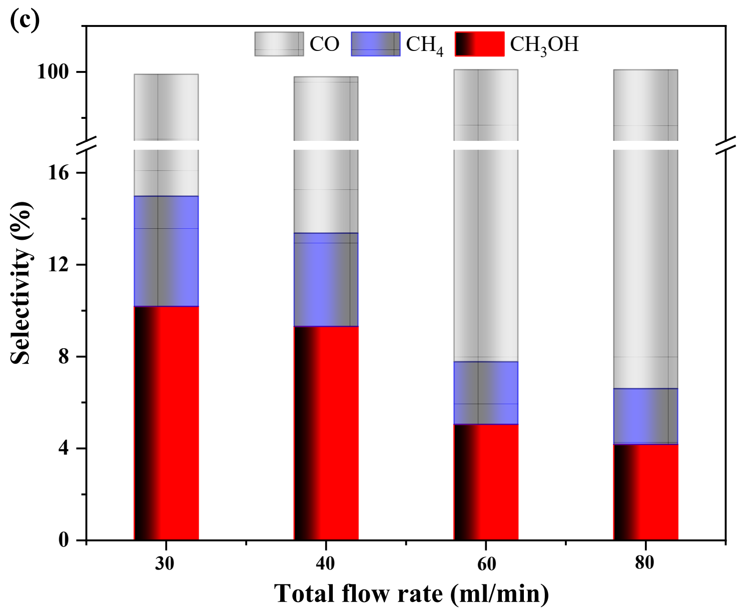


Fig. S6 (a) The products selectivities comparison of thermal catalysis, plasma only and plasma catalysis reaction routes for CO_2 hydrogenation to methanol; The effects of (b) H_2/CO_2 molar ratio and (c) total flow rate on products selectivities

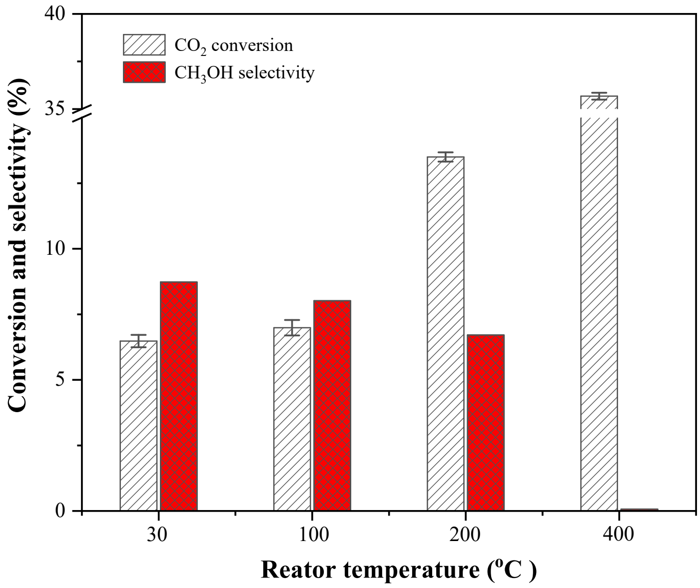


Fig. S7 The effect of reactor temperature on CO2 conversion and methanol selectivity

Conditions: $H_2/CO_2 = 3$, total flow rate of 40 mL/min, power of 5 W, 1wt.% MnO_x/ZrO_2.

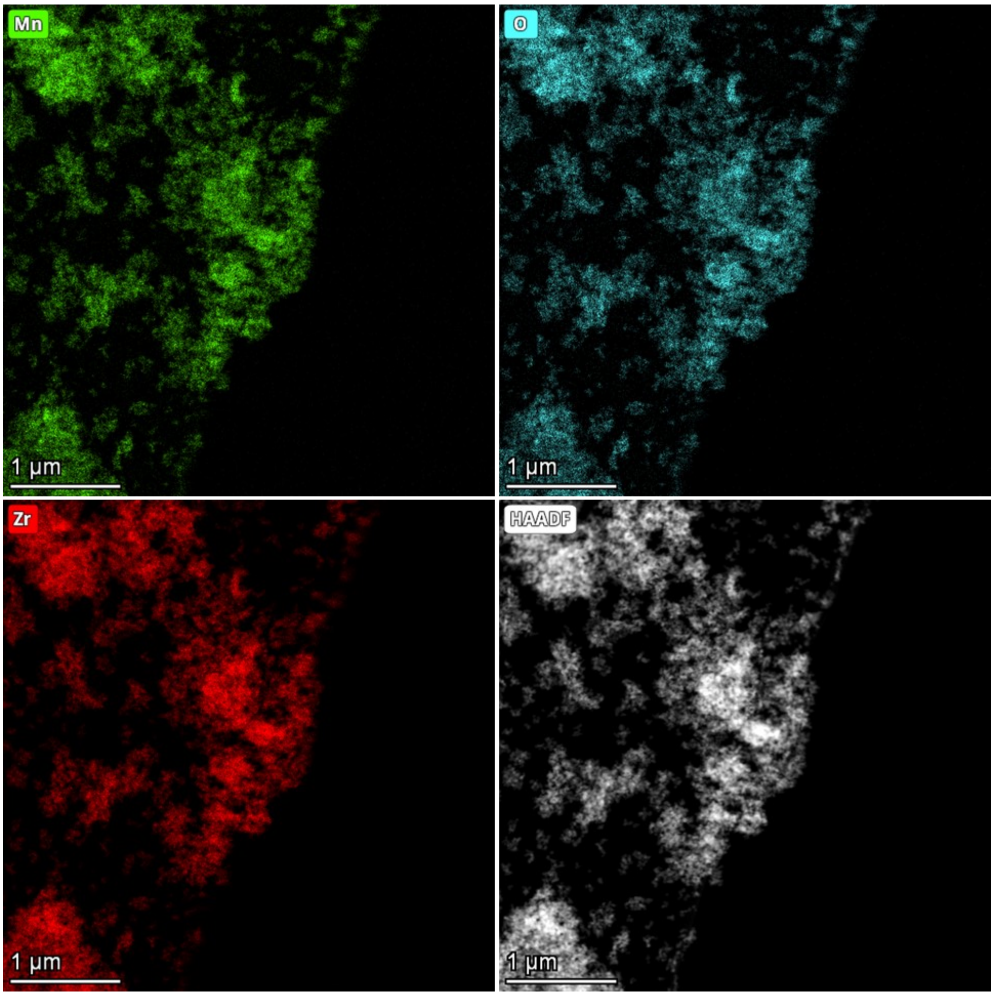
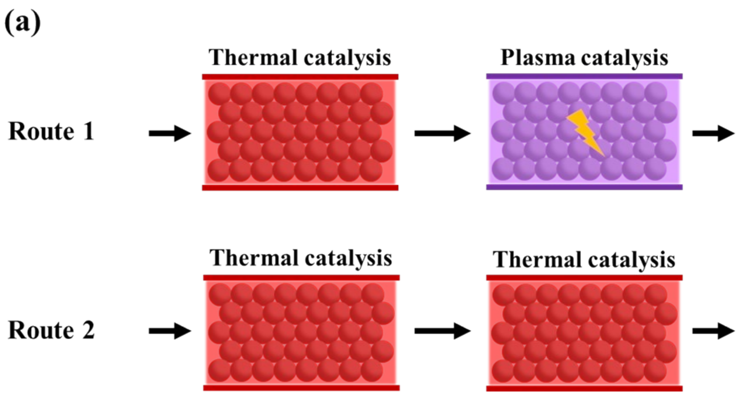


Fig. S8 The elemental mapping of MnO_x/ZrO_2 catalyst.



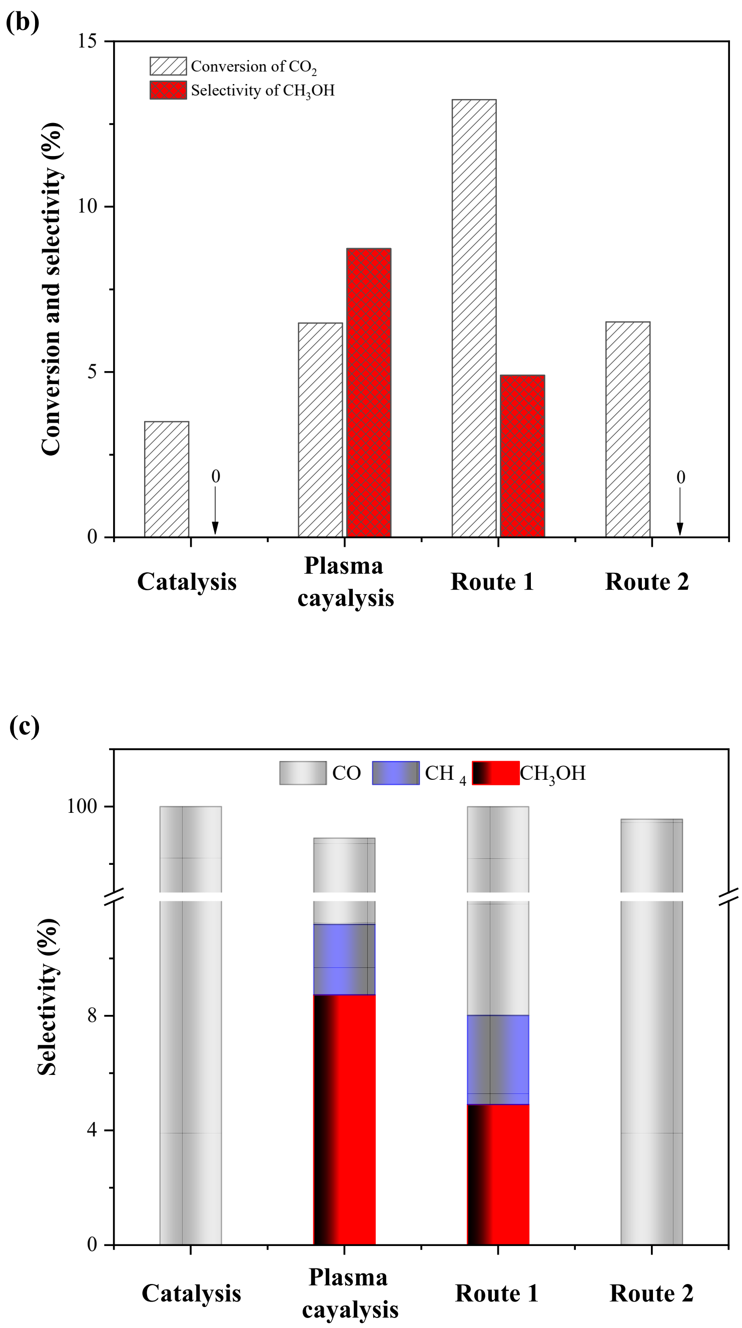


Fig. S9 (a) The schematic diagrams of Route 1 and 2; The comparison of thermal catalysis, plasma catalysis, Route 1 and Route 2: (b) CO_2 conversion and methanol selectivity, (c) products selectivities.

Two stages reactors were employed in Route 1 and 2. The first thermal catalysis reactor in both routes worked as a CO provider since its only product was CO. This reactor was conducted at 350 ^{o}C, in which the CO_2 conversion was 4% and a feed gas with ~1% CO was achieved. This CO-contained feed gas was then introduced to the plasma catalysis and thermal catalysis in Route 1 and 2, respectively.

Table S1 XPS analyses of MnO_x/ZrO_2 catalysts.

Sample	Mn^{2+} content (%)	Mn^{3+} content (%)	Mn^{4+} content (%)	$O_s/(O_l + O_s)$ (%)
Fresh	44.9	16.4	38.7	21.7
Reduced	50.1	14.5	35.4	22.8
Used	53.2	10.9	35.9	21.6

Table S2 The synergy factor of plasma catalytic CO_2 hydrogenation to methanol in literatures

Ref.	Feed gas	Product	Plasma	catalyst	Synergy factor
This work	H_2/CO_2	CH_3OH	DBD	MnO_x/ZrO_2	87
[1]	H_2/CO_2	CH_3OH	DBD	Cu/γ-Al_2O_3	12.8
[2]	H_2/CO_2	CH_3OH	DBD	Pt/film/In_2O_3	8.9
[3]	H_2/CO_2	CH_3OH	DBD	CuO/Fe_2O_3/QW	1.0
[4]	H_2/CO_2	CH_3OH	DBD	Cu/γ-Al_2O_3	1.6
[5]	H_2/CO_2	CH_3OH	DBD	Co_xO_y/MgO	1.4

Reference

[1] Cui Z, Meng S, Yi Y, et al. Plasma-catalytic methanol synthesis from CO_2 hydrogenation over a supported Cu cluster catalyst: Insights into the reaction mechanism. ACS Catalysis, 2022, 12(2): 1326-1337.

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[3] Joshi N, Loganathan S. Methanol synthesis from CO_2 using Ni and Cu supported Fe catalytic system: Understanding the role of nonthermal plasma surface discharge. Plasma Processes and Polymers, 2021, 18(5): 2000104.

[4] Wang L, Yi Y, Guo H, et al. Atmospheric pressure and room temperature synthesis of methanol through plasma-catalytic hydrogenation of CO_2. ACS Catalysis, 2018, 8(1): 90-100.

[5] Ronda-Lloret M, Wang Y, Oulego P, et al. CO_2 hydrogenation at atmospheric pressure and low temperature using plasma-enhanced catalysis over supported cobalt oxide catalysts. ACS Sustainable Chemistry & Engineering, 2020, 8(47): 17397-17407.