

Supplementary Information (SI) for
Structural response of metal-organic frameworks to non-thermal
plasma treatment and its effect on CO₂ adsorption and conversion
performance

Yue Liu,^a Linghe Song,^a Juntai Tian,^a Shanshan Shang,^a Peirong Chen,^{abc} Junliang
Wu,^{abc} Daiqi Ye*^{abc}

^a *School of Environment and Energy, South China University of Technology,
Guangzhou, Guangdong 510006, China*

^b *National Engineering Laboratory for VOCs Pollution Control Technology and
Equipment, Guangzhou Higher Education Mega Centre, Guangzhou, Guangdong
510006, China*

^c *Guangdong Provincial Engineering and Technology Research Centre for
Environmental Risk Prevention and Emergency Disposal, South China University
of Technology, Guangzhou Higher Education Mega Centre, Guangzhou,
Guangdong 510006, China*

* Corresponding Author

E-mail: cedqye@scut.edu.cn

1. Experimental section

1.1. Chemicals

The primarily used chemicals and reagents including zirconium tetrachloride (ZrCl_4), copper nitrate hydrate ($\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$), zinc nitrate hexahydrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), 1,4-dicarboxybenzene (H_2BDC), 4,4'-biphenyldicarboxylic acid (H_2BPDC), 1,3,5-benzenetricarboxylic acid (H_3BTC), 2-methylimidazole (2-MeIM), *N,N*-dimethylformamide (DMF), acetic acid, methanol and anhydrous ethanol were obtained from Aladdin Co., Ltd., without further purification before used.

1.2. Synthesis of Cu-BTC

For Cu-BTC,¹ the 0.42 g of H_3BTC (2 mmol) was dissolved in a 24 mL mixture of ethanol and deionized water (v/v=1/1), and then the 0.875 g of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (3.62 mmol) was added to the mixture. After a thorough stir, the clear blue solution was transferred to a teflon-lined autoclave, and heated at 120 °C for 12 h. The formed blue crystalline powder was filtered and washed with a 50 mL mixture of ethanol and deionized water (v/v=1/1) for three times.

1.3. Synthesis of Zr-BDC and Zr-BPDC

For Zr-BDC,² the 1.456 g of ZrCl_4 (6.27 mmol), the 1.038 g of H_2BDC (6.27 mmol), acetic acid (11.25 mL) and deionized water (675 μL) were dissolved in 50 mL DMF and then transferred to a 100 mL teflon-lined autoclave, heated at 120 °C for 24 h. The centrifugally collected sediment was suspended in DMF for 2 hours (2 times), and washed three times with anhydrous ethanol over 24 h period. Finally, all synthesized MOFs were activated under a dynamic vacuum overnight at 80 °C. The

synthesis method of Zr-BPDC was consistent with Zr-BDC, except that the organic ligand was replaced with H₂BPDC.

1.4. Synthesis of Zn-MeIM

For preparation of Zn-MeIM,³ 2-MeIM methanol solution (0.82 g, 25 mL) and Zn(NO₃)₂·6H₂O methanol solution (0.75 g, 25 mL) were rapidly mixed and stirred at room temperature. After stewing for 3 h, the white deposition was collected by centrifugation (8000 rpm, 3 min), and washed with methanol for three times, and the white products were obtained.

2. Additional experimental results

Table S1 The major peaks found in the infrared band of the MOFs and the structure's composition.

MOFs	Wavenumber (cm ⁻¹)	Peak assignment	Literature value (cm ⁻¹)
Cu-BTC	1625, 1563	ν_{as} (COO-)	1550-1645 ⁴
	1445, 1368	ν_s (COO-)	1368 ⁴ , 1445 ⁴
Zr-BDC	1658	ν (C=O)	1657 ⁵
	1579	ν_{as} (COO-)	1579 ⁶
	1402	ν_s (COO-)	1402 ⁶
	1509	C=C	1509 ⁶
	665	O-H	665 ⁵
Zn-MeIM	1579	ν (C=N)	1578.7 ⁷
	1145, 994	ν (C-N)	1145 ⁴ , 994 ⁷

Table S2 The BET parameters of Zr-BDC and Cu-BTC before and after NTP-assisting CO₂ conversion.

MOFs	NTP treatments	BET surface area (m ² g ⁻¹)			Pore volume (cm ³ g ⁻¹)			Average pore diameter (nm)
		Total	Mesopore	Micropore	Total	Mesopore	Micropore	
Cu-BTC	None	1487	183	1304	0.61	0.11	0.50	1.63
Cu-BTC	9 W	1141	132	1009	0.48	0.09	0.39	1.69
Cu-BTC	18 W	565	59.3	506	0.28	0.08	0.19	1.96
Cu-BTC	25 W	595	66.0	529	0.29	0.09	0.20	1.94
Zr-BDC	None	1139	113	1025	0.45	0.07	0.38	1.58
Zr-BDC	9 W	1131	114	1018	0.45	0.07	0.37	1.59
Zr-BDC	18 W	999	101	897	0.40	0.07	0.33	1.60
Zr-BDC	25 W	1022	106	916	0.41	0.08	0.34	1.61

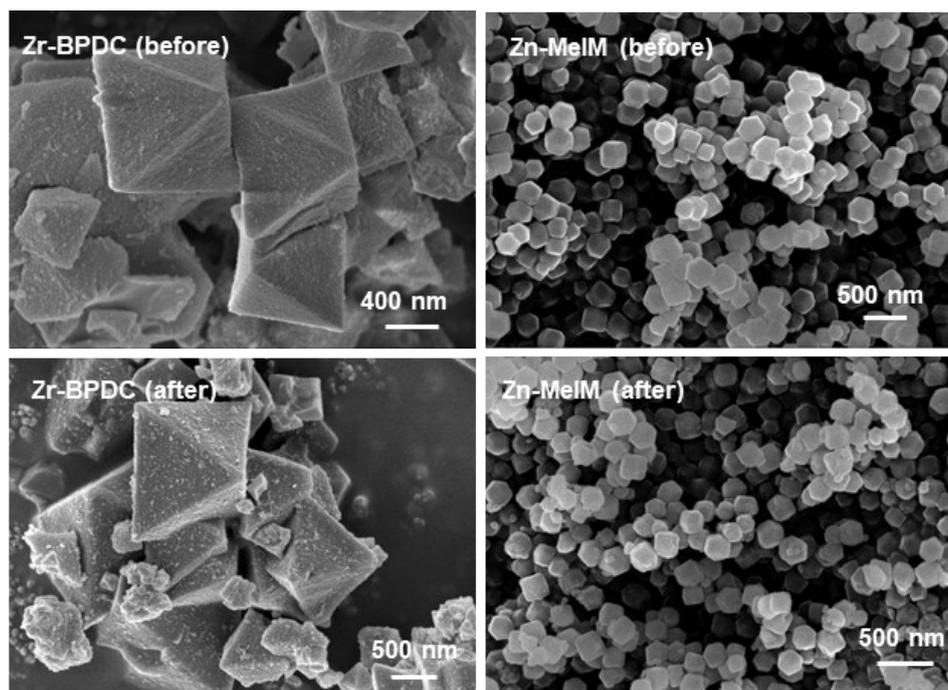


Fig. S1. SEM images of Zr-BPDC and Zn-MeIM before and after the Ar plasma treatment (at 12 W for 2 h).

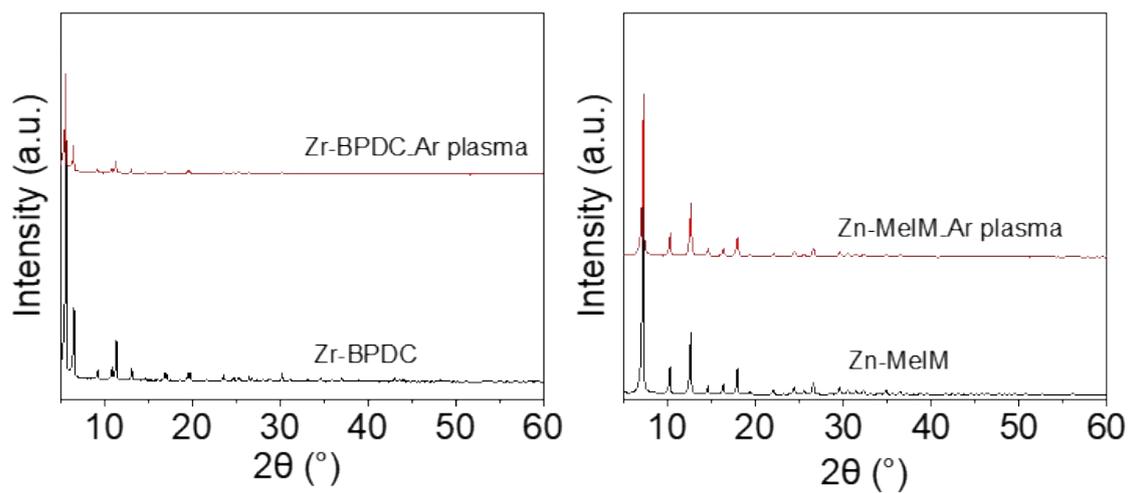


Fig. S2. XRD patterns of Zr-BPDC and Zn-MeIM before and after the Ar plasma treatment (at 12 W for 2 h).

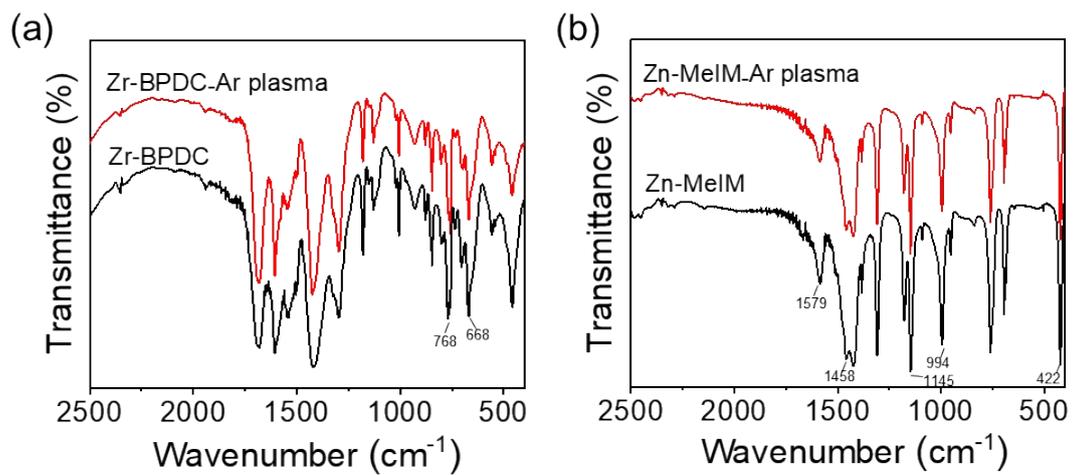


Fig. S3. FT-IR spectra of Zr-BPDC (a) and Zn-MeIM (b) after the Ar plasma treatment (at 12 W for 2 h).

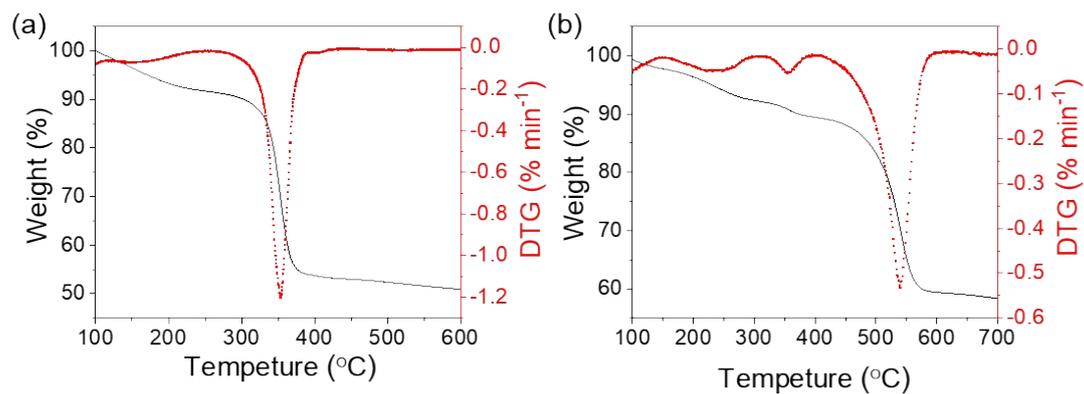


Fig. S4. TG/DTG of the synthetic (a) Cu-BTC and (b) Zr-BDC. Thermal gravimetric analysis (TGA) was fulfilled by a TGA 8000 thermogravimetric analyzer under a N₂ flow and a temperature increment of 10°/min from 30 °C to 700 °C.

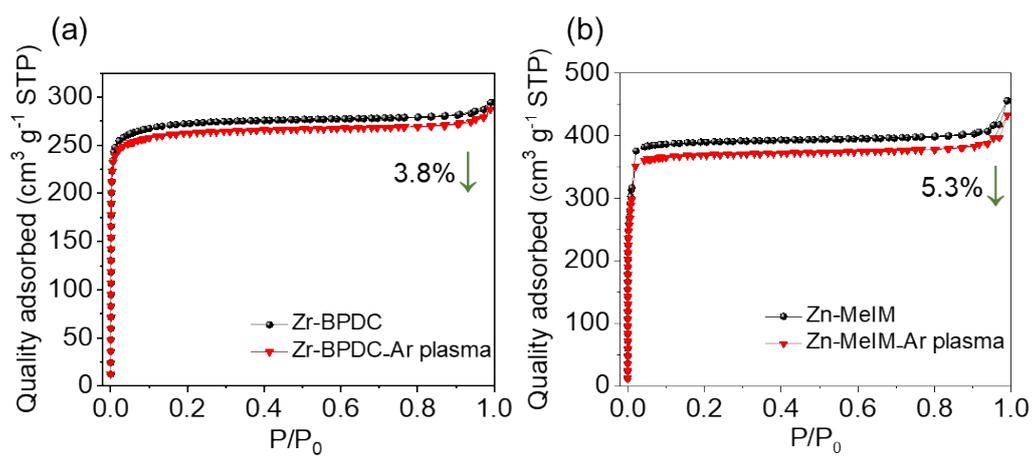


Fig. S5. N₂ adsorption-desorption isotherms at 77 K of Zr-BPDC (a) and Zn-MeIM (b) after the Ar plasma treatment (at 12 W for 2 h).

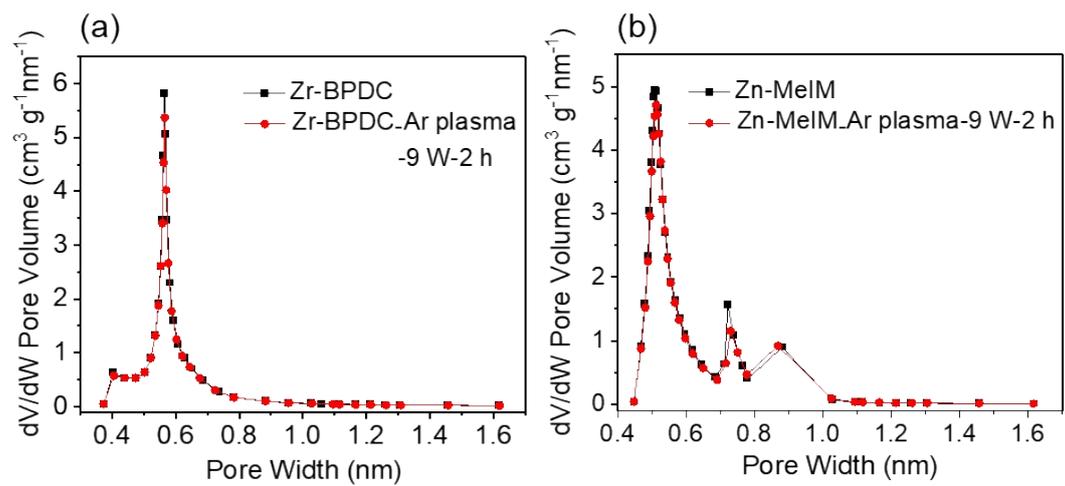


Fig. S6. Pore-size distribution of (a) Zr-BPDC and (b) Zn-MeIM after the Ar plasma treatment with different input power and time.

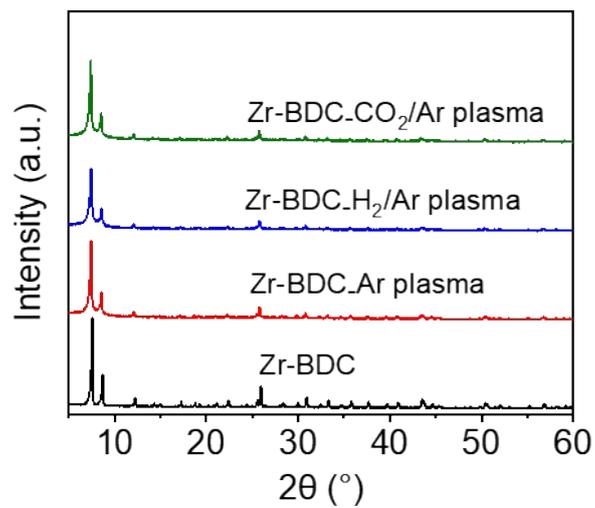


Fig. S7. XRD patterns of Zr-BDC after 2 h plasma treatment under various gases at the input power of 12 W.

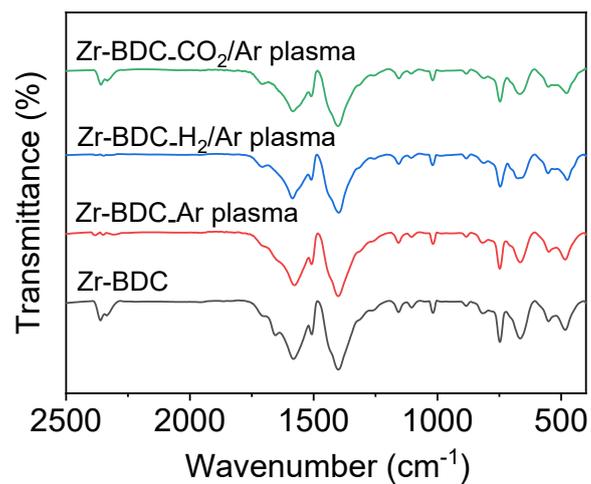


Fig. S8. FT-IR spectra of Zr-BDC after 2 h plasma treatment under various gases at the input power of 12 W.

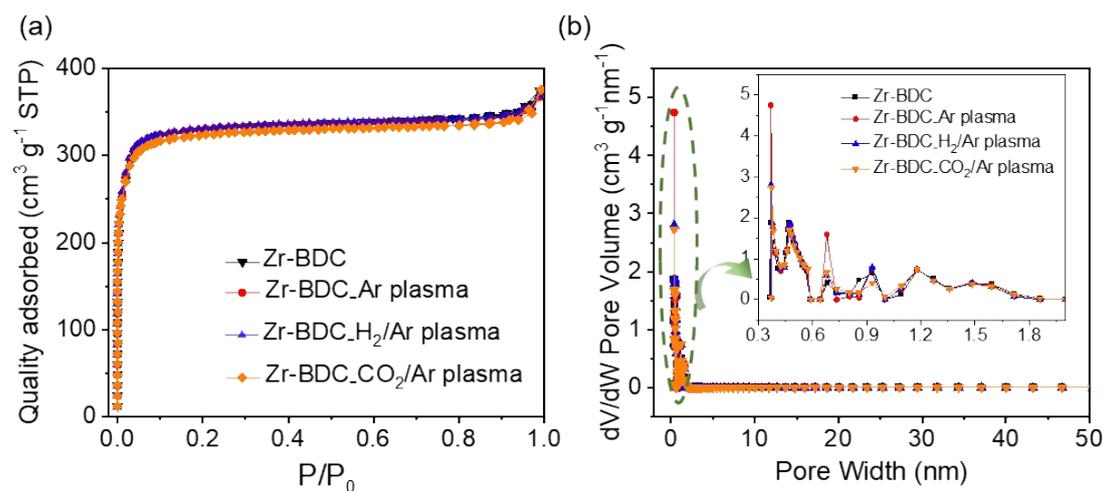


Fig. S9. N_2 adsorption-desorption isotherms at 77 K (a), and Pore-size distribution (b) of Zr-BDC after 2 h plasma treatment under various gases at the input power of 12 W.

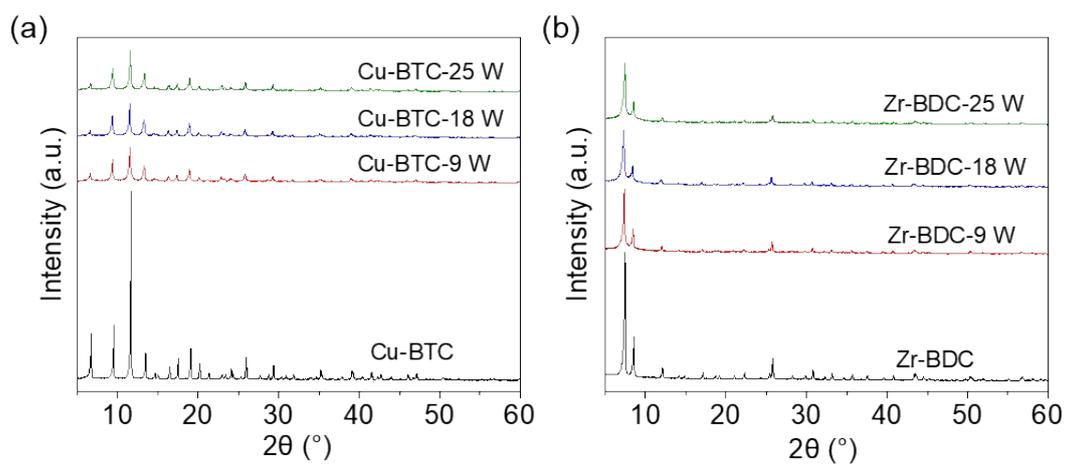


Fig. S10. XRD patterns of the (a) Cu-BTC and (b) Zr-BDC after the plasma-assisted CO₂ hydrogenation

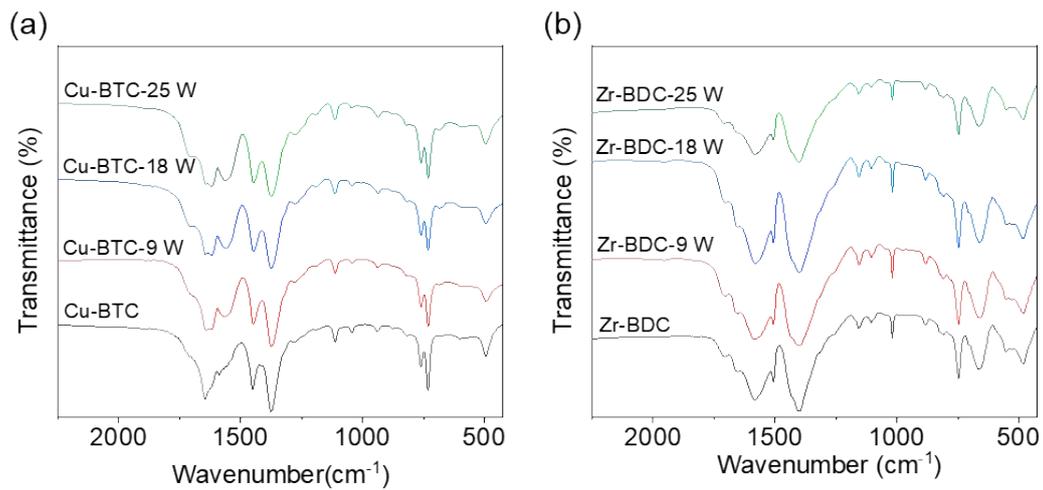


Fig. S11. FT-IR spectra of the (a) Cu-BTC and (b) Zr-BDC after the plasma-assisted CO_2 hydrogenation.

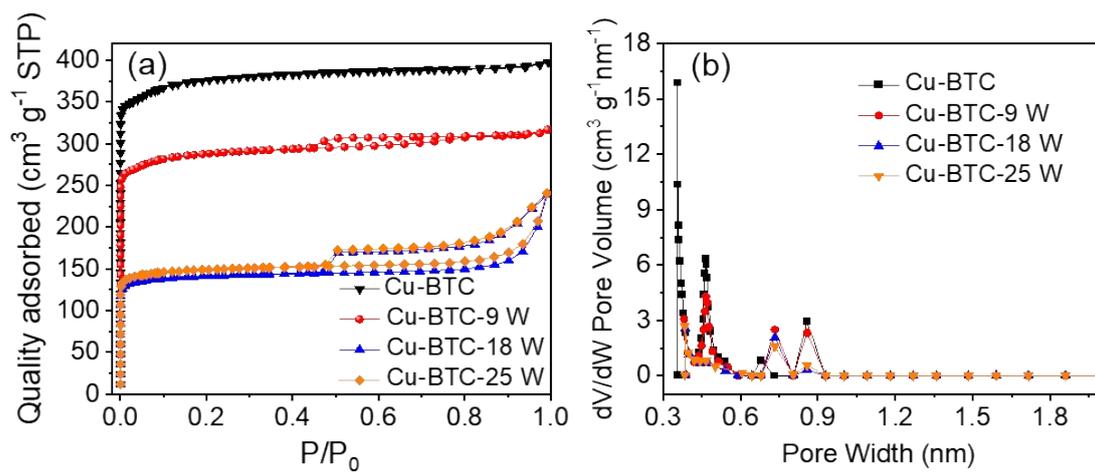


Fig. S12. N_2 adsorption-desorption isotherms (a) and Pore size distribution (b) of Cu-BTC after the plasma-assisted CO_2 hydrogenation.

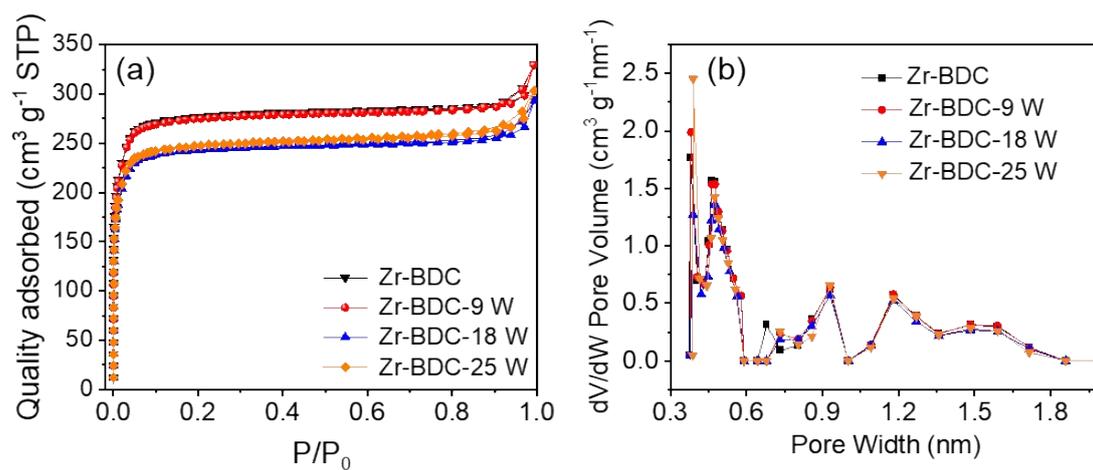


Fig. S13. N_2 adsorption-desorption isotherms (a) and Pore size distribution (b) of Zr-BDC after the plasma-assisted CO_2 hydrogenation.

References:

1. N. Al-Janabi, P. Hill, L. Torrente-Murciano, A. Garforth, P. Gorgojo, F. Siperstein and X. Fan, *Chem. Eng. J.*, 2015, **281**, 669-677.
2. S. Zhuang, R. Cheng and J. Wang, *Chem. Eng. J.*, 2019, **359**, 354-362.
3. Y. Liu, Y. Huo, X. Wang, S. Yu, Y. Ai, Z. Chen, P. Zhang, L. Chen, G. Song, N. S. Alharbi, S. O. Rabah and X. Wang, *J. Clean. Prod.*, 2021, **278**, 123216.
4. S. Shang, Z. Tao, C. Yang, A. Hanif, L. Li, D. C.W. Tsang, Q. Gu and J. Shang, *Chem. Eng. J.*, 2020, **393**, 124666.
5. L. Valenzano, B. Civalleri, S. Chavan, S. Bordiga, M. H. Nilsen, S. Jakobsen, K. P. Lillerud and C. Lamberti, *Chem. Mater.*, 2011, **23**, 1700-1718.
6. X. Min, X. Wu, P. Shao, Z. Ren, L. Ding and X. Luo, *Chem. Eng. J.*, 2019, **358**, 321-330.
7. N. Li, L. Zhou, X. Jin, G. Owens and Z. Chen, *J. Hazard. Mater.*, 2019, **366**, 563-572.