*Supplementary Material for*

# Direct Hydrogenation of $CO_2$ to Ethanol at Ambient Conditions using Cu(I)-MOF in a Dielectric Barrier Discharge Plasma Reactor

Nan Zou[a,b,c], Jie Chen[a,c], Ting Qiu[a,c 1], Ying Zheng[b 2]

[a] *College of Chemical Engineering, Fuzhou University, Fuzhou 350108, Fujian, P.R. China.*

[b] *Department of Chemical and Biochemical Engineering, Western University, London, ON N6A 3K7, Canada*

[c] *Engineering Research Center of Reactive Distillation, Fujian Province Higher Education Institutes.*

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[1] Corresponding authors. E-mail addresses: tingqiu@fzu.edu.cn

[2] Corresponding authors. E-mail addresses: ying.zheng@uwo.ca

## SECTION S1 SUPPLEMENTARY METHODS

### Catalyst Characterization

The optical microscope images were photographed via the Nikon FASTCAM SA1.1. The $N_2$ adsorption-desorption isotherms and the heat of $CO_2$ adsorption was analyzed using ASAP2020 Plus physisorption. The thermal stability of Cu(I)-HKUST-n were evaluated through the thermogravimetry (TG) detection of the Netzsch STA449C. The surface morphology (SEM) was detected using the Hitachi S-4800 model device. X-ray diffraction (XRD) patterns of catalysts were obtained via the Bruker D8 Advance diffractometer equipped with CuKa radiation in the 2θ range from 3° to 60°.

#### Parameter Definition

The carbon (in mol) of all the gaseous products (including unreacted $CO_2$) was quantified using a flow meter and a fully calibrated GC for 2 hours. The carbon (in mol) of liquid products collected in the same 2-hour period were determined using GC analysis. The sum of the carbon (in mol) of the liquid products and gaseous products is then compared to the carbon of the $CO_2$ fed to the reactor. A sample calculation of carbon balance is shown in **Table S1**. The experimental errors mainly include the analysis of the product by GC and the collection of the liquid product by the cold trap.

The conversion of $CO_2$ is defined as

$$X_{CO_2}(\%) = \frac{Carbon\ of\ CO_2 converted\ \ (mol\,)}{Carbon\ of\ initial\ CO_2\ \ (mol\,)} \times 100 \quad (1)$$

The selectivity of products can be calculated as

$$S_{CO}(\%) = \frac{Carbon\ of\ CO\ produced\ \ (mol\,)}{Carbon\ of\ CO_2 converted\ \ (mol\,)} \times 100 \quad (2)$$

$$S_{CH_4}(\%) = \frac{Carbon\ of\ CH_4\ produced\ \ (mol\,)}{Carbon\ of\ CO_2 converted\ \ (mol\,)} \times 100 \quad (3)$$

The selectivity of one liquid product ($C_xH_yO_z$) can be calculated as

$$S_{C_xH_yO_z}(\%) = \frac{Canbon\ \ of\ C_aH_bO_c\ \ (mol\,)}{Carbon\ of\ CO_2 converted\ \ (mol\,)} \times 100 \quad (4)$$

The yield of $C_xH_yO_z$ can be calculated as

$$Y_{C_xH_yO_z}(\%) = \frac{Canbon\ \ of\ C_xH_yO_z\ \ (mol\,)}{Carbon\ of\ initial\ CO_2\ \ (mol\,)} \times 100 \quad (5)$$

The space-time yield of ethanol (EtOH) can be calculated as

$$STY_{EtOH}\left(g_{EtOH}\ h^{-1}\ g_{cat.}^{-1}\right) = \frac{Ethanol\ production\ (g)}{Reaction\ time\ (h)\ \times\ amount\ of\ catalyst\ (g)} \quad (6)$$

The energy efficiency for $CO_2$ conversion can be calculated as

$$EE_{CO2}\left(mmol\ kJ^{-1}\right) = \frac{CO_2\ consumed\ (mmol)}{Power\ (kJ)} \quad (7)$$

The volume power density can be calculated as

$$VPD\ \left(W\ cm^{-3}\right) = \frac{Output\ Power\ (W)}{Discharge\ zone\ volume\ (cm^3)} \quad (8)$$

The volume space velocity can be calculated as

$$SV\ \left(min^{-1}\right) = \frac{The\ volumetric\ flow\ rate\ of\ the\ reactants\ (cm^3\ min^{-1})}{The\ volume\ of\ the\ reactor\ (cm^3)} \quad (9)$$

The carbon balance can be calculated as

$$C_B(\%) = \frac{Canbon\ \ of\ unreacted\ \ CO_2\ and\ production\ \ (mol)}{Carbon\ of\ initial\ CO_2\ (mol)} \times 100 \quad (10)$$

**Table S1.** Carbon balance data of Cu(I)-HKUST-17.5 applied in plasma-assisted $CO_2$ hydrogenation

| **Input carbon (mmol)** | **Output carbon** | | | |
|---|---|---|---|---|
| | **Gaseous phase (mmol)** | | **Liquid phase (mmol)** | |
| 40.0 | Unreacted $CO_2$ | 23.5 | Produced MeOH* | 2.02 |
| | Produced $CH_4$ | 0.54 | Produced EtOH* | 9.33 |
| | Produced CO | 2.85 | Produced IPA* | 0.41 |

Carbon Balance (%) = Output carbon/ Input carbon × 100 = 96.6%

* MeOH, EtOH and IPA are abbreviations for methanol, ethanol and isopropanol, respectively.

## SECTION S2 SUPPLEMENTARY FIGURES

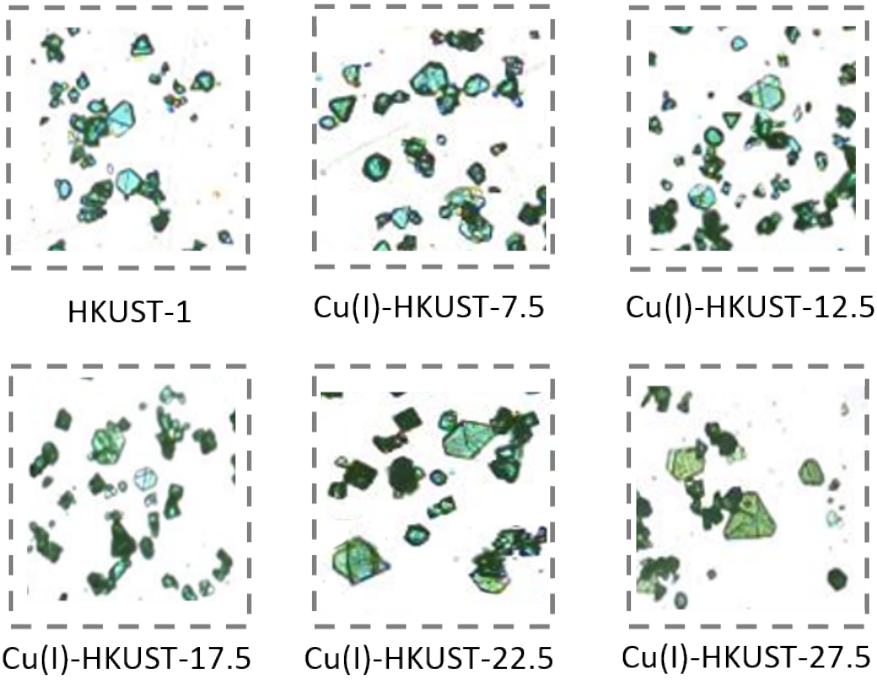


**Figure S1.** Optical microscope image of HKUST-1 and Cu(I)-HKUST-n

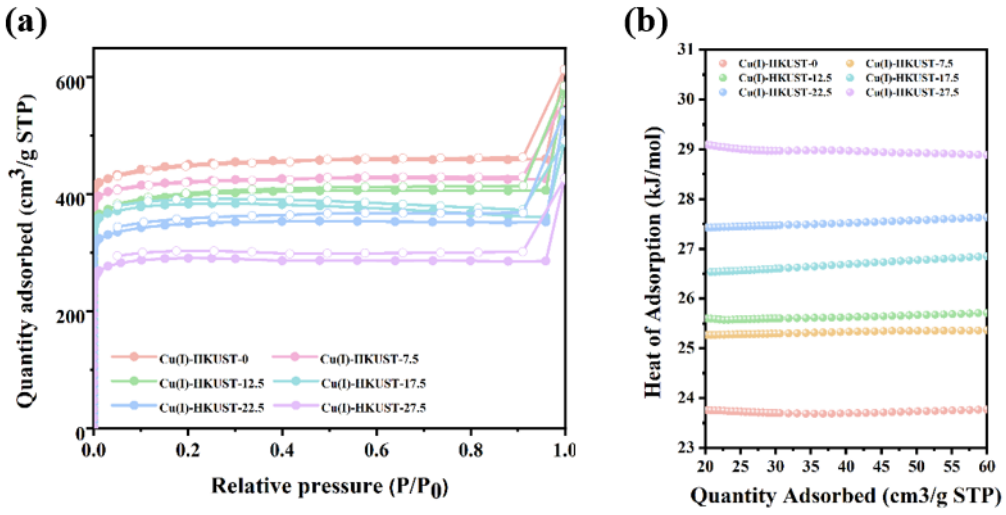

**Figure S2**. (a) $N_2$ adsorption-desorption isotherms and (b) $CO_2$ heat of adsorption of HKUST-1 and Cu(I)-HKUST-n

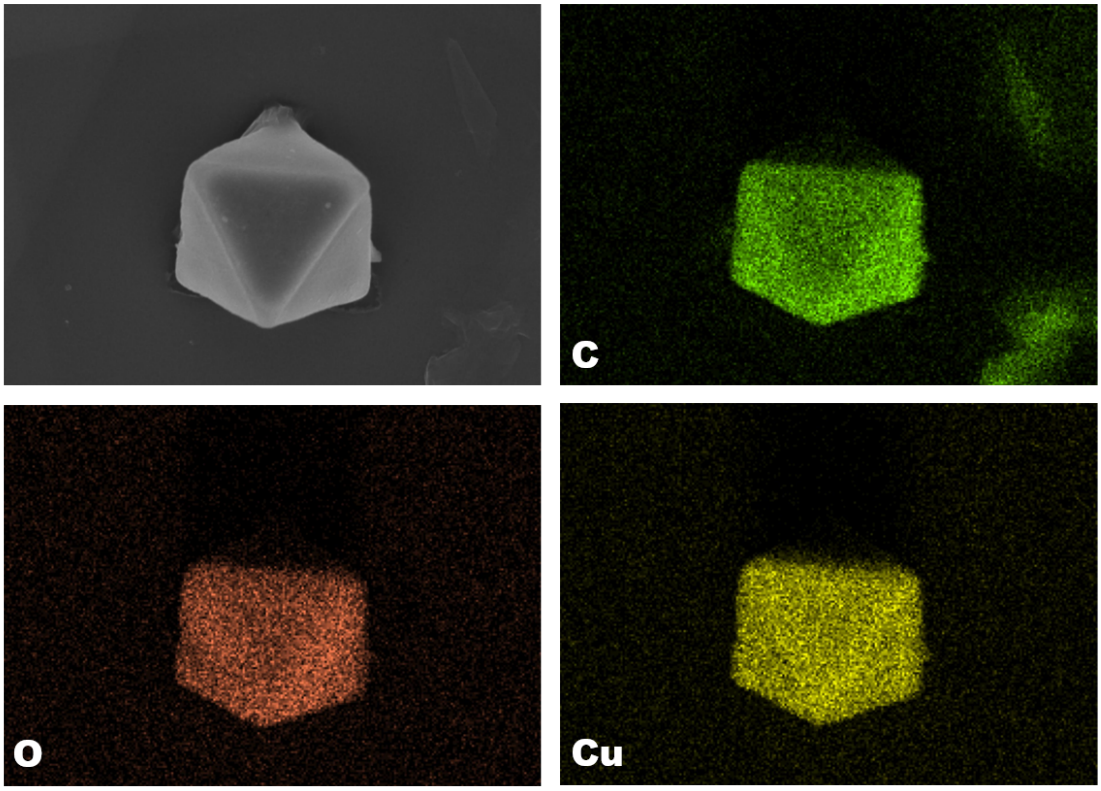


**Figure S3.** EDS mappings of C, O and Cu elements of Cu(I)-HKUST-17.5.

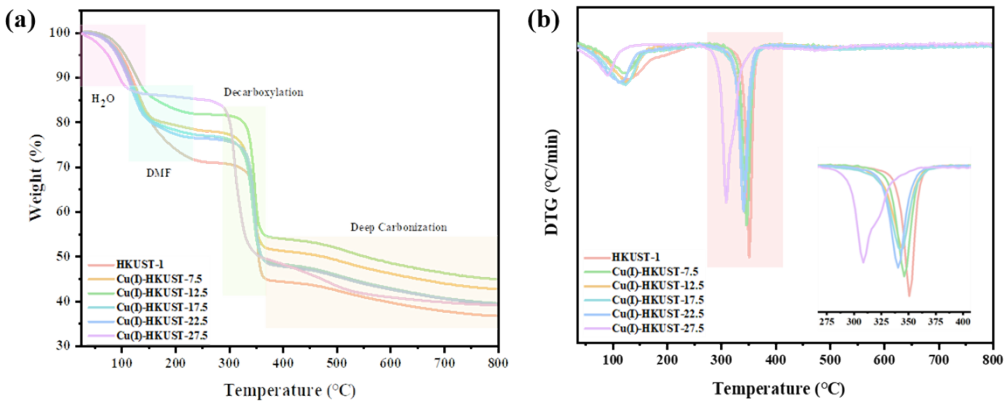


**Figure S4.** TG (a) and DTG (b) curve of HKUST-1 and Cu(I)-HKUST-n

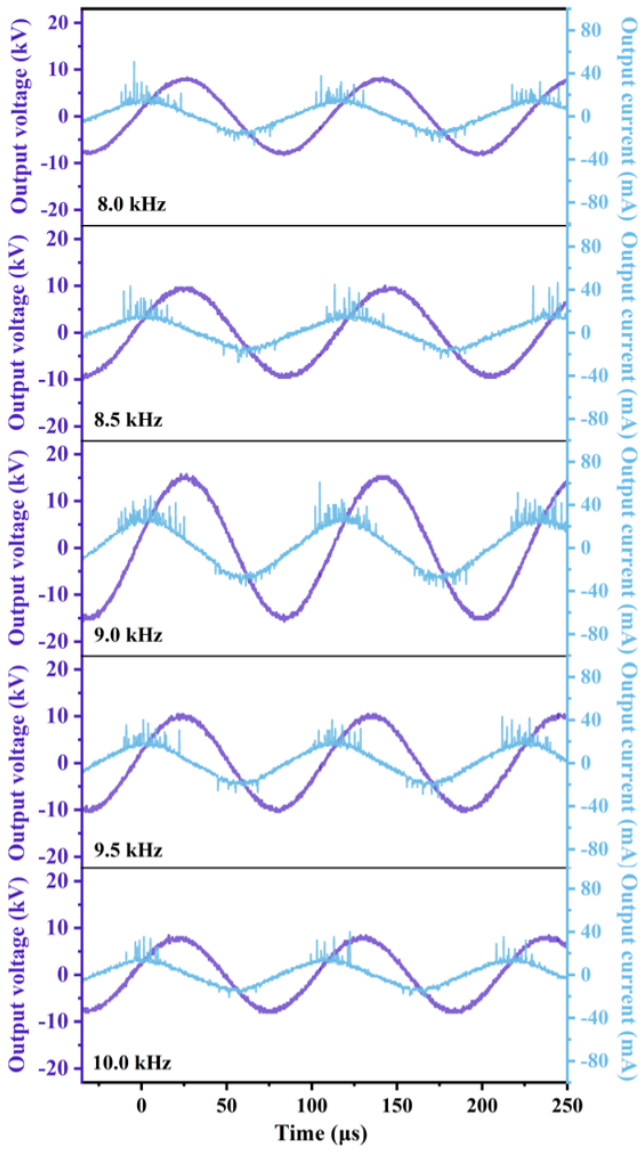


**Figure S5.** Output voltage and discharge current at different frequencies

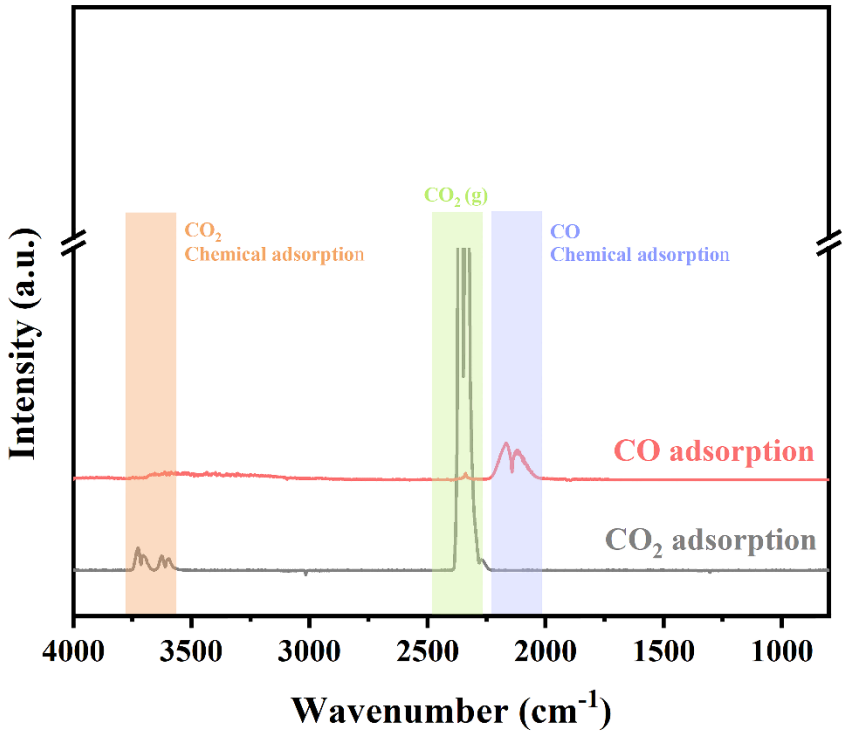


**Figure S6**. DRIFTS spectra of $CO_2$ and CO adsorption on Cu(I)-HKUST-17.5

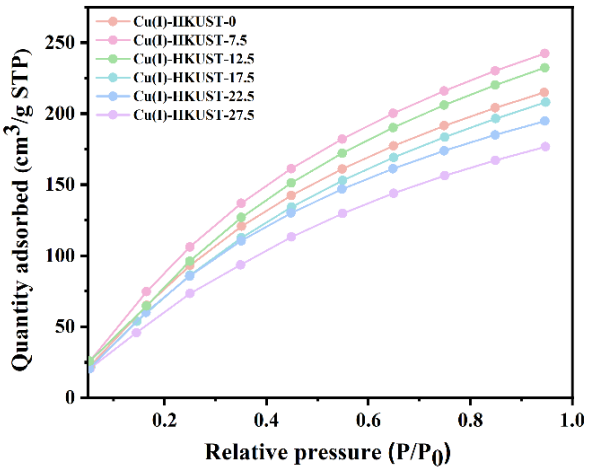


**Figure S7**. $CO_2$ adsorption-desorption isotherms of HKUST-1 and Cu(I)-HKUST-n

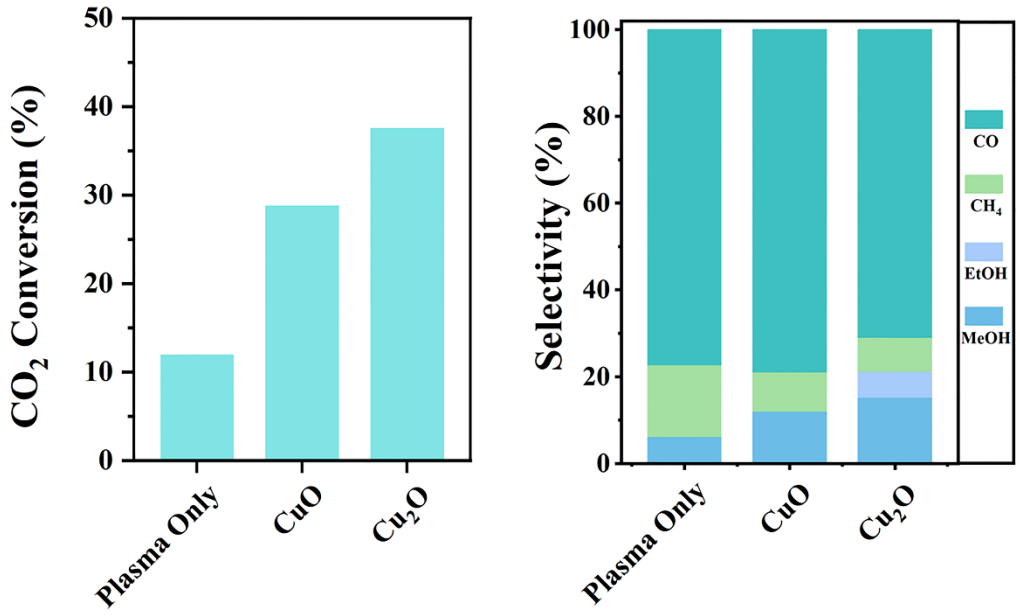


**Figure S8**. (a) $CO_2$ conversion and (b) selectivity of NTP-assisted $CO_2$ hydrogenation over CuO and $Cu_2O$ catalyst. Reaction condition: 35°C, atmospheric pressure, a volume space velocity of 3.53 $min^{-1}$, a $H_2/CO_2$ flow ratio of 3:1, an input voltage of 30 V and reaction time of 2 hours. The amounts of CuO and $Cu_2O$ were determined based on the molar amounts of copper ions on HKUST-1, which were 18.3 and 16.5 mg, respectively. For maintaining the same packing volume, CuO and $Cu_2O$ were mixed with 6 μm glass beads, respectively.

**Table S2** The $CO_2$ conversion, the selectivity of gaseous products and liquid products for NTP-assisted $CO_2$ hydrogenation over different catalysts. Reaction condition: 35°C, atmospheric pressure, a volume space velocity of 3.53 $min^{-1}$, a $H_2/CO_2$ flow ratio of 3:1, an input voltage of 30 V and reaction time of 2 hours.

| | $X_{CO2}$ (%) | $S_{Gaseous\ products}$ (%) | $S_{Liquid\ products}$ (%) |
|---|---|---|---|
| **Plasma Only** | 11.9 | 93.3 | 6.10 |
| **HKUST-1** | 32.3 | 69.8 | 30.2 |
| **Zeolite-A** | 27.7 | 89.4 | 10.6 |
| **Cu(II)@zeolite-A** | 30.2 | 81.3 | 18.7 |