Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Supporting Information

Highly oriented MOF thin film-based electrocatalytic device for the reduction of CO_2 to CO exhibiting high faradic efficiency

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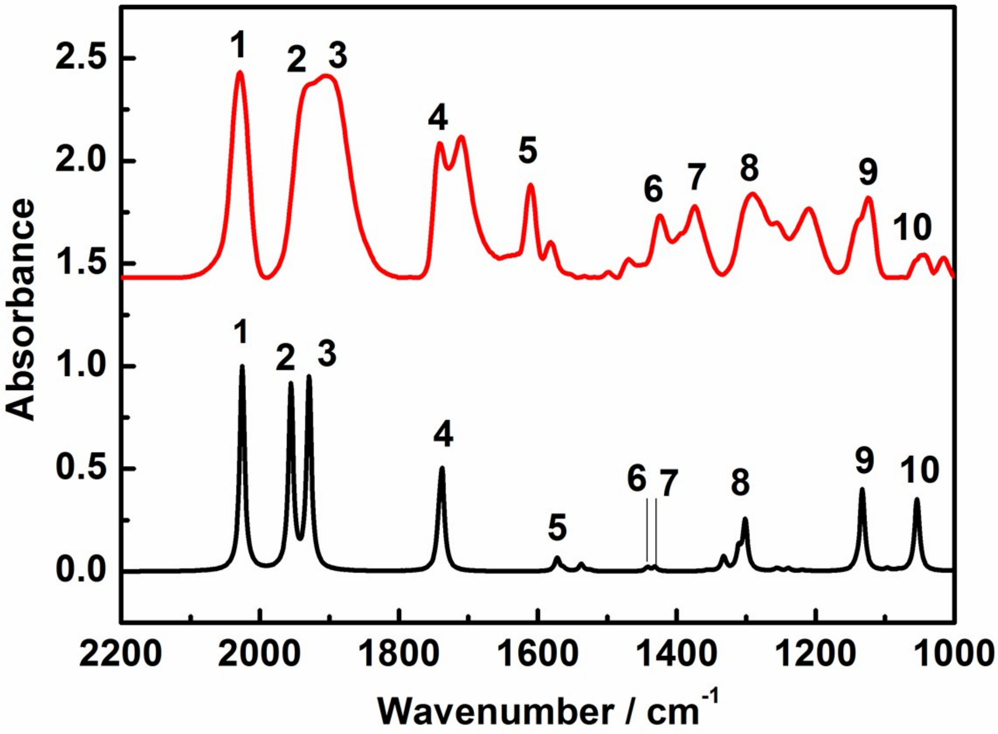

Figure S1**.** Infrared spectra of bulk Re-linkers in KBr pellet (in red) and calculated free Re-linker (in black).

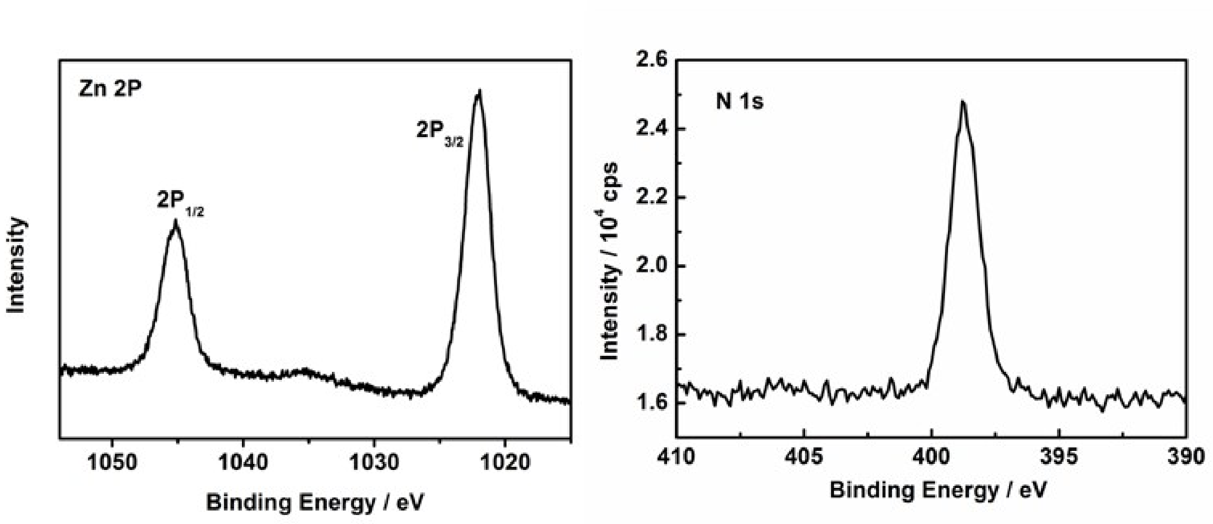

Figure S2. N 1s and Zn 2p X-ray photoelectron spectra of Re-SURMOF grown on FTO substrate.

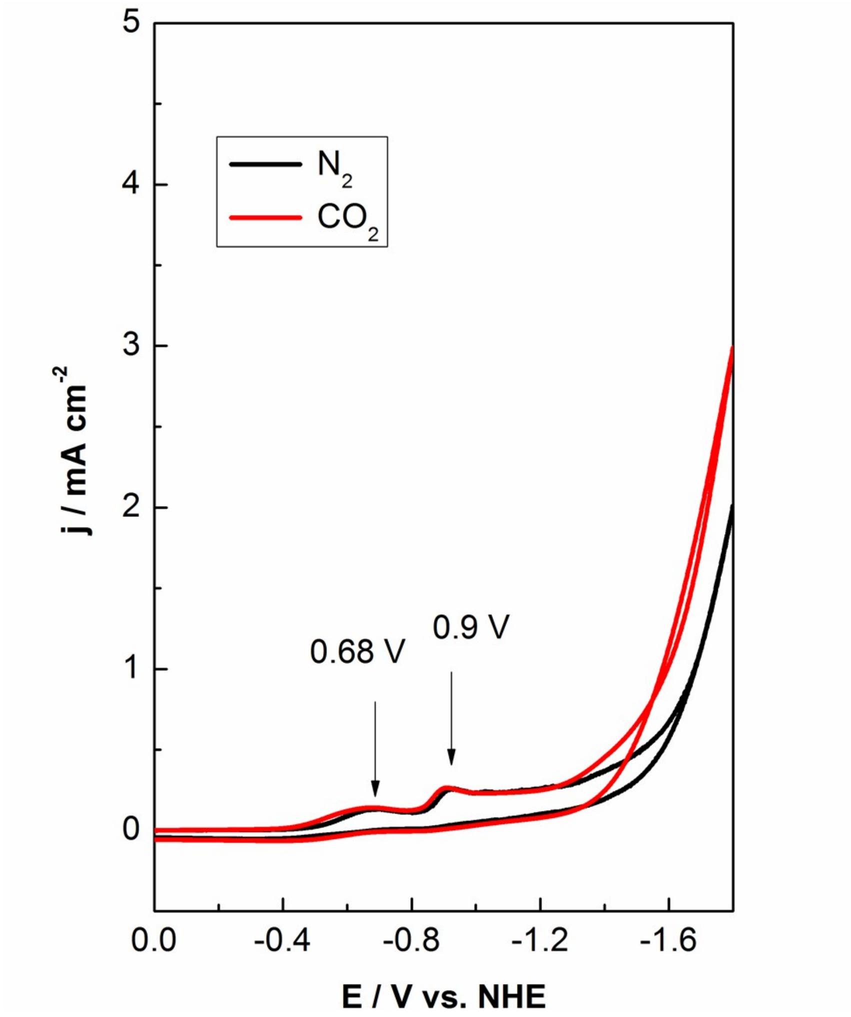

Figure S3. Cyclic voltammogram of the Re-linkers (0.5 M) in N_2- and CO_2-saturated electrolyte at scan rate of 100 mV/s. Bare FTO substrate is used as working electrode, and Ag/$AgNO_3$ as reference electrode, Pt wire as counter electrode.

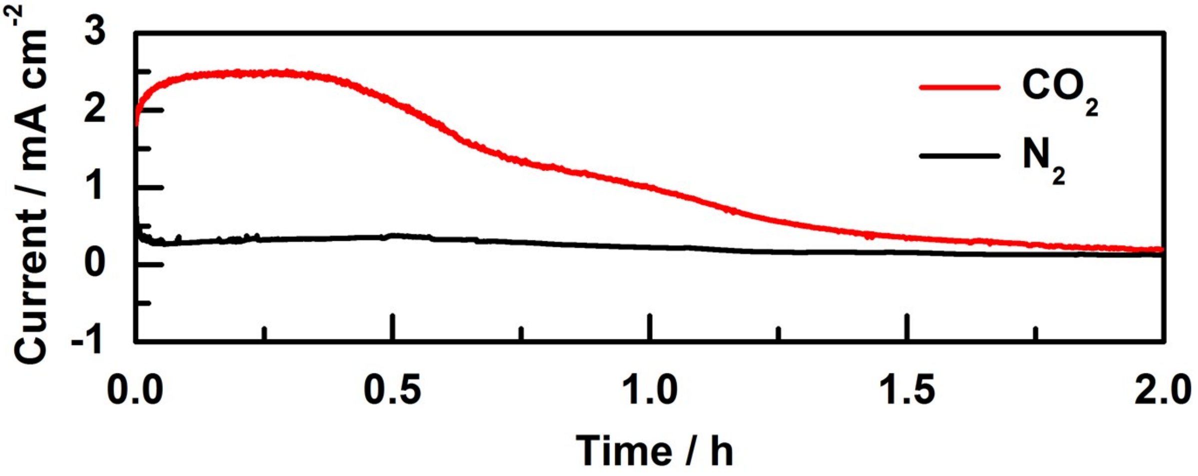

Figure S4. Current density of Re-SURMOF catalyzed CO_2 reduction in CO_2- and N_2-saturated electrolyte at the potential of -1.6 V vs. NHE in 2 hours.

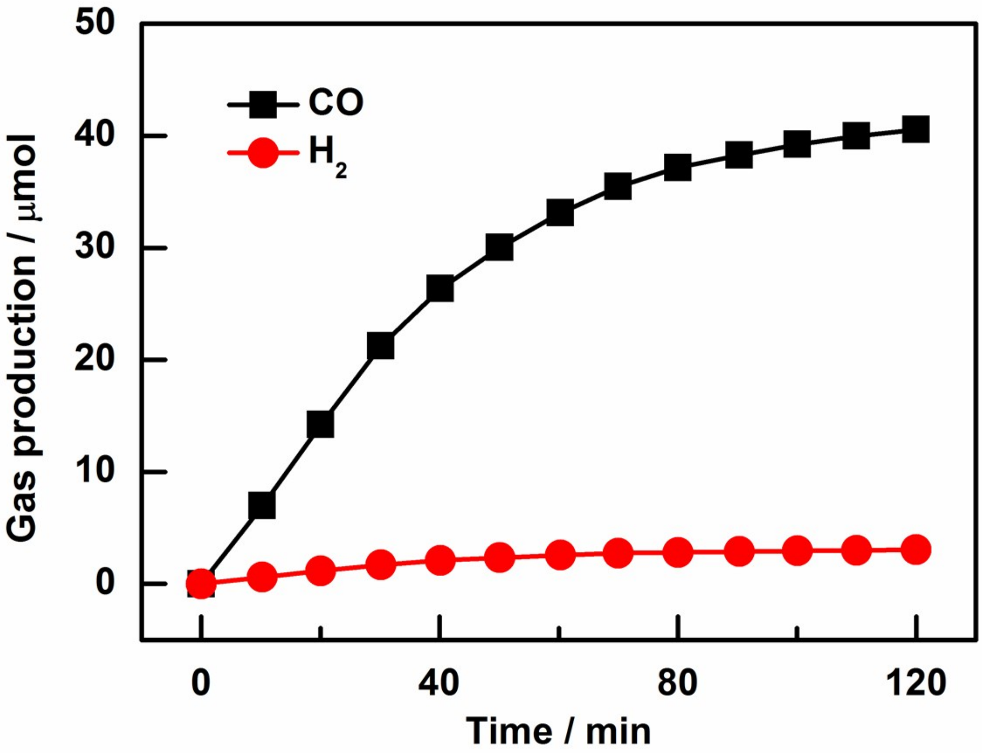

Figure S5. Generated gas amounts of Re-SURMOF catalyzed CO_2 reduction in saturated electrolyte at -1.6 V.

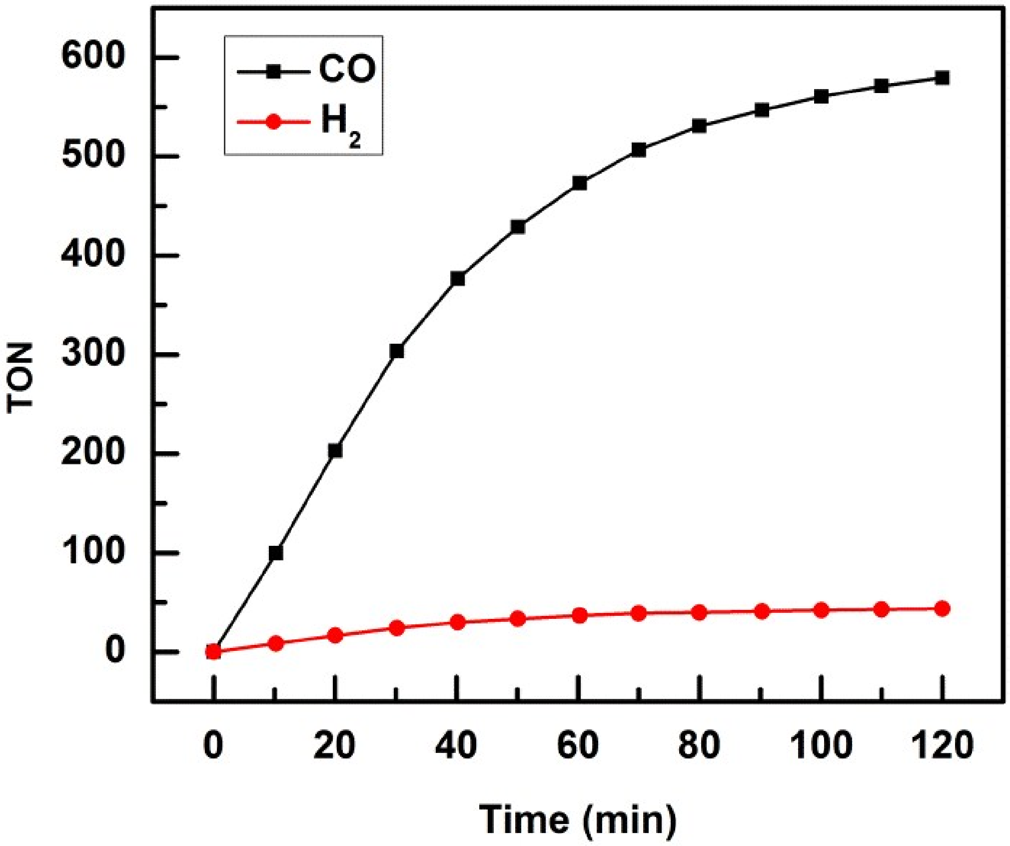

Figure S6. TON of Re-SURMOF catalyzed CO_2 reduction.

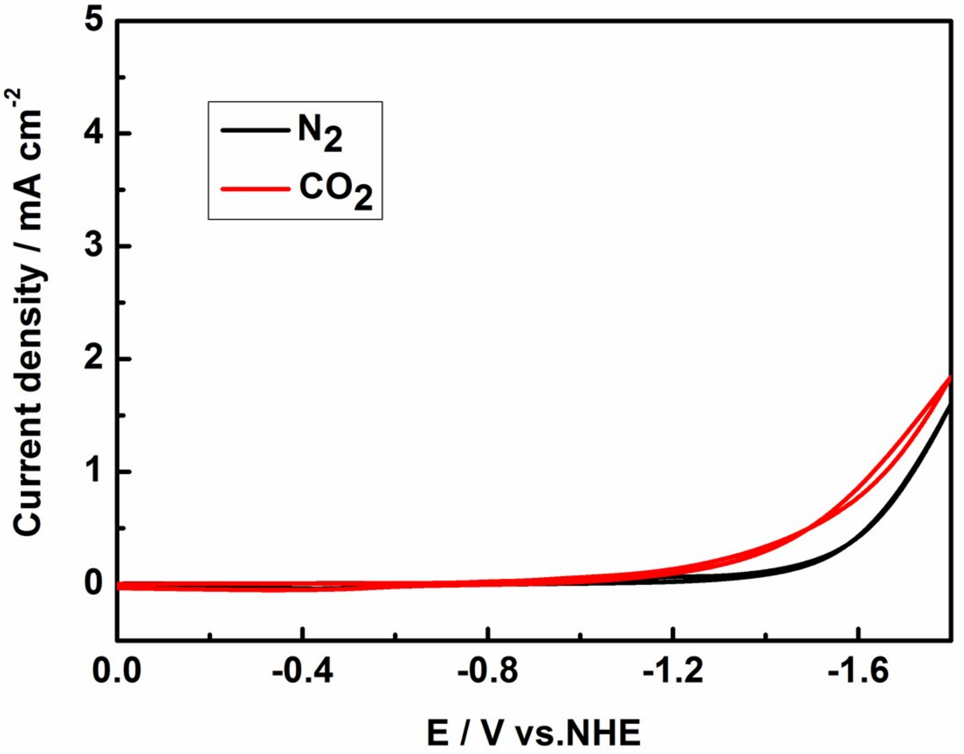

Figure S7. Cyclic voltammogram of bare FTO substrate in N_2- and -CO_2-saturated electrolyte at scan rate of 100 mV/s; FTO is used as working electrode. The electrolyte solution is 0.1 M tetrabutylammonium hydroxide (TBAH) acetonitrile solution with 5% trifluoroethanol (in volume).

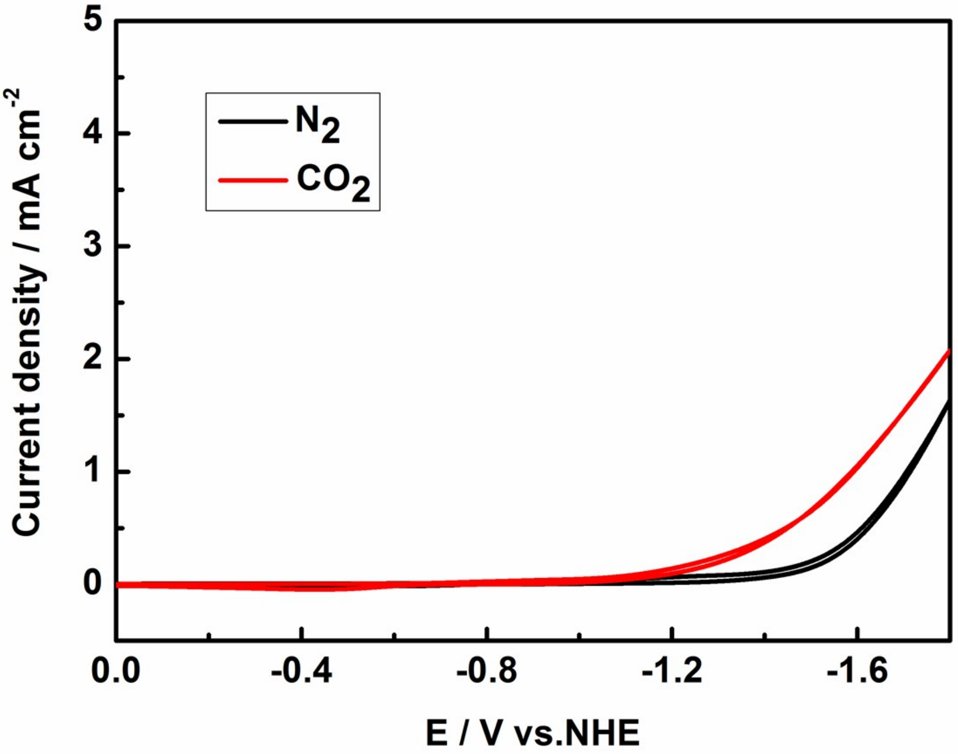

Figure S8. Cyclic voltammogram of Zn acetate in N_2- and -CO_2-saturated electrolyte at scan rate of 100 mV/s; FTO is used as working electrode. The electrolyte solution is 0.1 M tetrabutylammonium hydroxide (TBAH) acetonitrile solution with 5% trifluoroethanol (in volume).

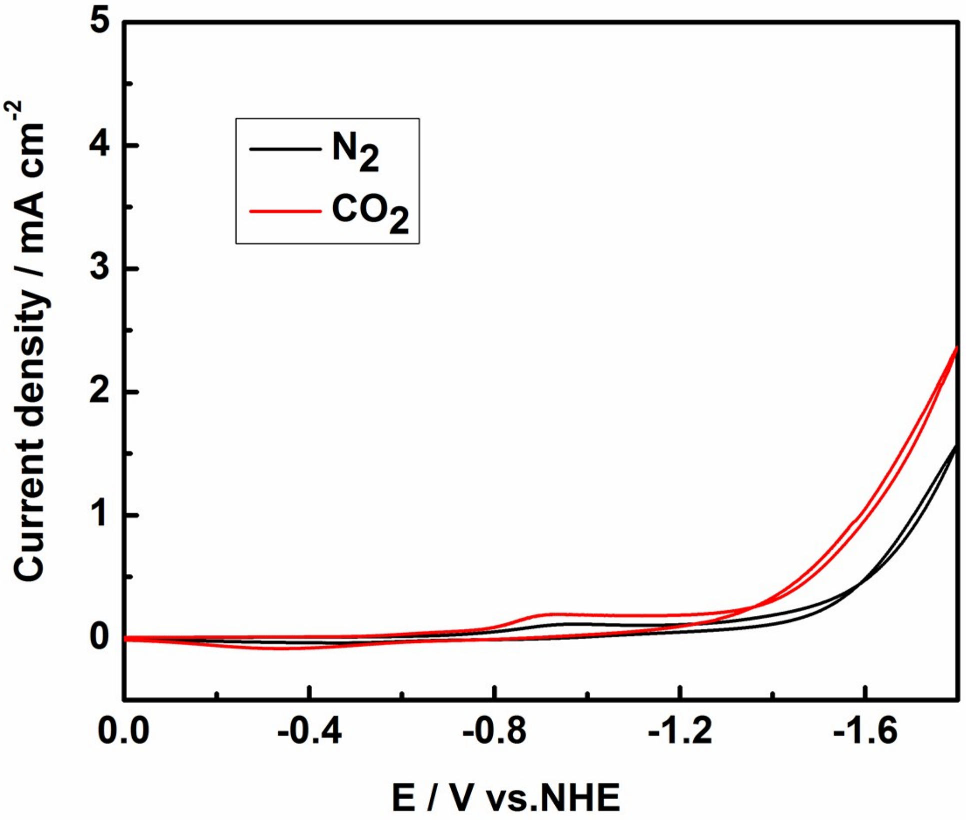

Figure S9. Cyclic voltammogram of Re(CO)$_3$Cl linkers (7 × 10^{-8} mol) and Zn acetates (7 × 10^{-8} mol) fixed onto FTO substrate using Nafion in N$_2$- and -CO$_2$-saturated electrolyte at scan rate of 100 mV/s. The electrolyte solution is 0.1 M tetrabutylammonium hydroxide (TBAH) acetonitrile solution with 5% trifluoroethanol (in volume).

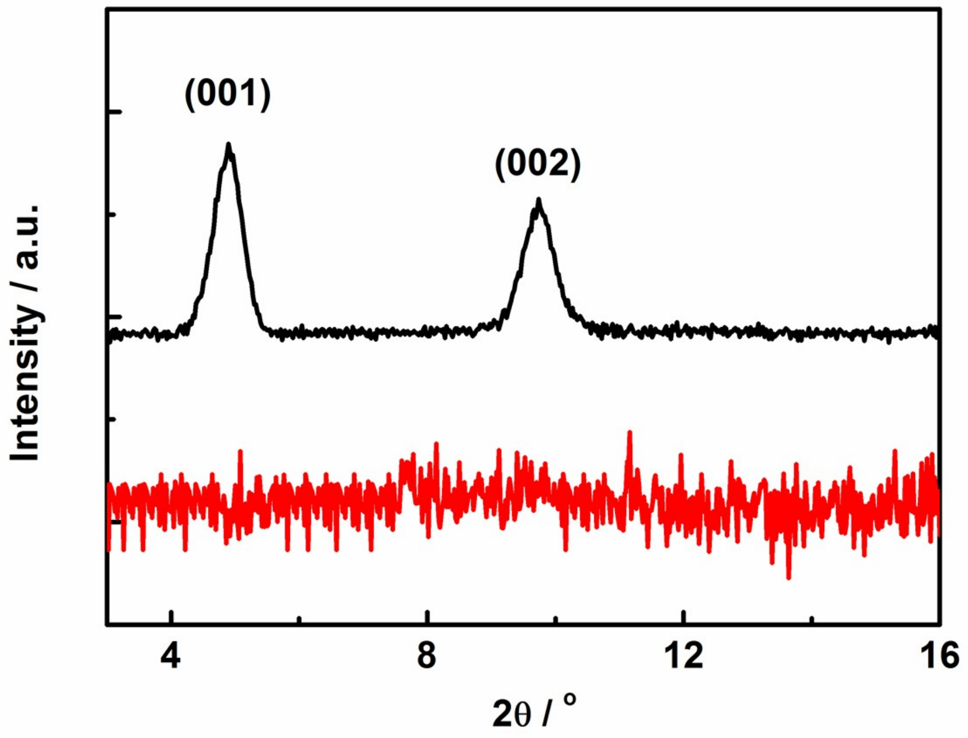

Figure S10. XRD data of Re-SURMOF samples after two hours electrolysis (in red) and pristine Re-SURMOF (in black).

The XRD data show that the Re-SURMOF gradually degrades during the electrolysis process, and lose the crystalline structure after 2 hours electrolysis.

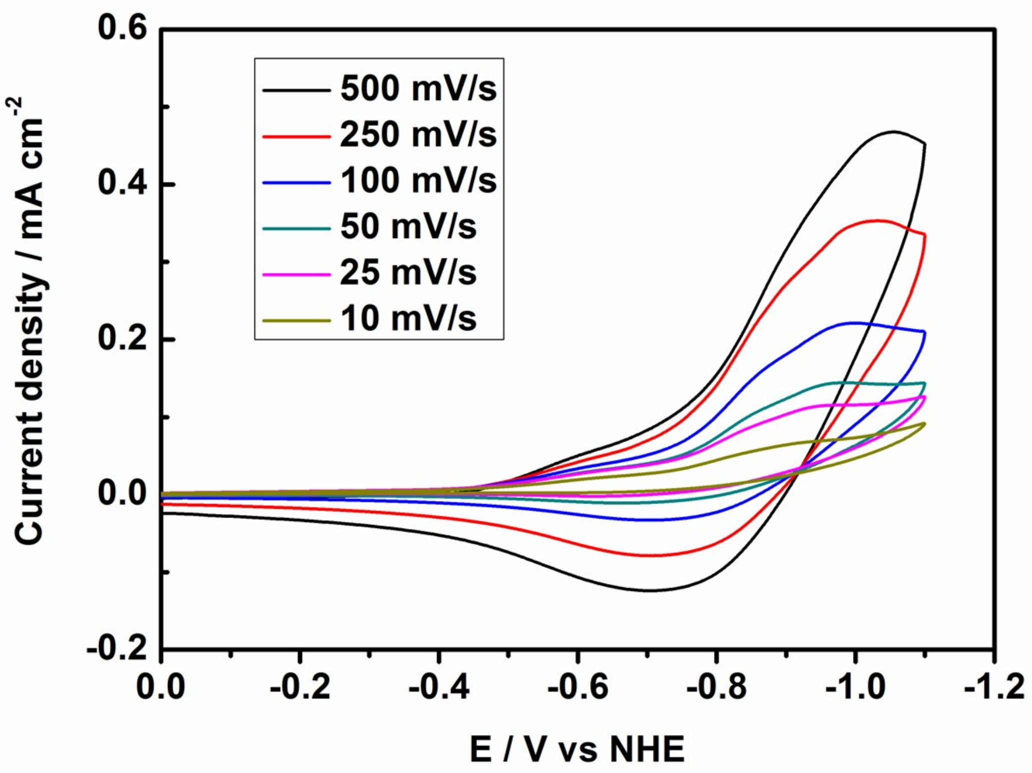

Figure S11. Scan rate dependent CV of Re-SURMOF thin film.

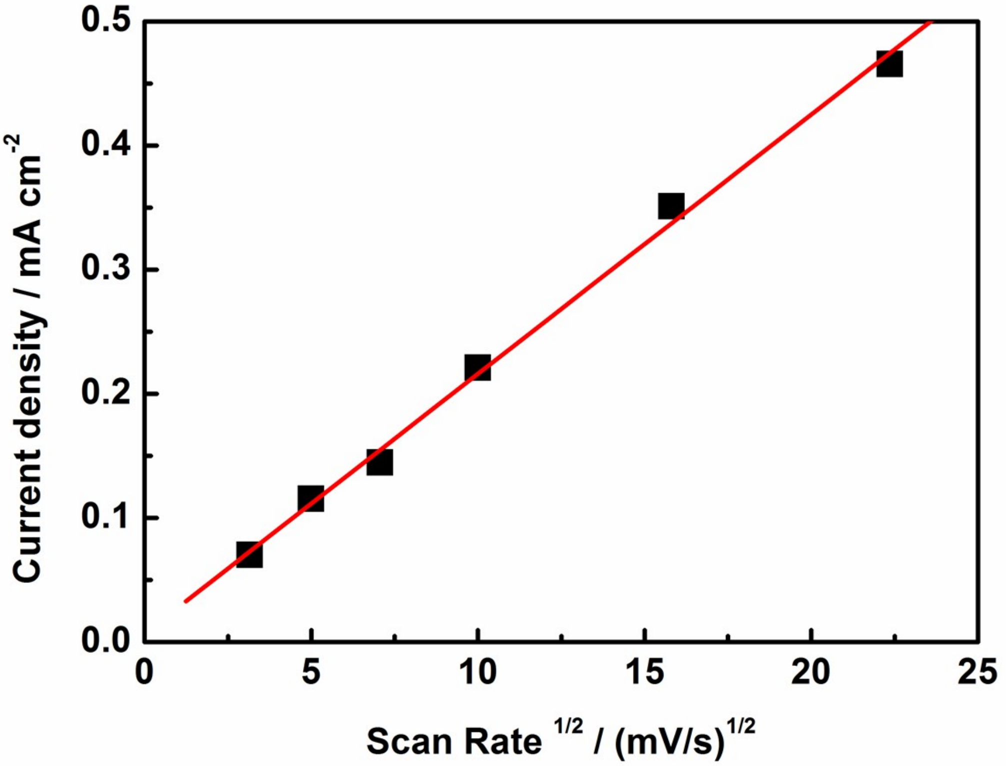

Figure S12. Re(I/0) peak current as a function of square root of scan rate. The linear relation indicates the occurrence of diffusion-limited electron transfer reaction towards CO_2 reduction to CO.

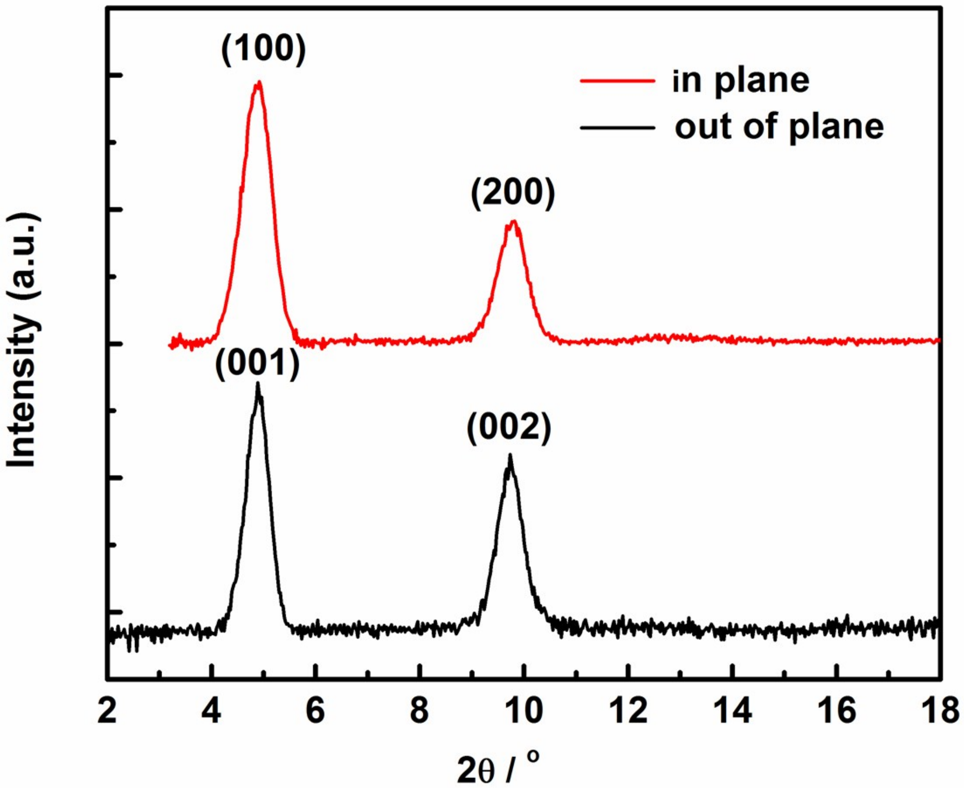

Figure S13. In plane (in red) and out of plane (in black) XRD data of Re-SURMOF grown on FTO substrate.

As discussed in the main manuscript, the XRD pattern of Re-SURMOF is in excellent agreement with the simulated XRD pattern, suggesting the presence of a SURMOF-2 structure, which was reported in our previous work (J. X. Liu, et al., *Sci. Rep.*, 2012, 2, 1-5.) with P4-geometry, i.e. a=b≠c. The out-of-plane and in-plane XRD measure the order of the MOF thin materials in the direction perpendicular and parallel to the substrate, respectively, which gives the lattice parameters a and b, therefore (100) and (001) have the same 2θ position in PXRD of in-plane and out-of plane.

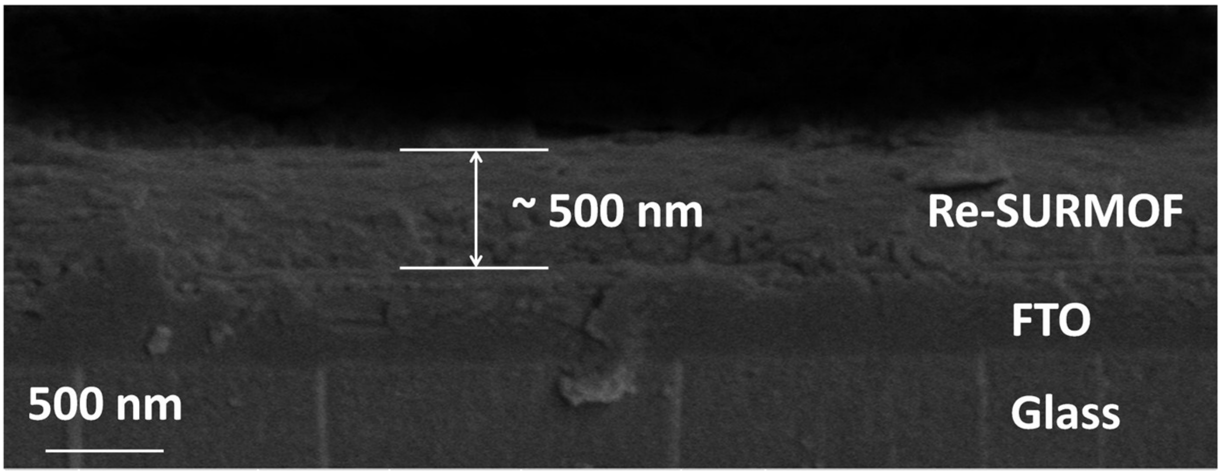

Figure S14. SEM cross-section image of Re-SURMOF grown on FTO substrate. The thickness of compact Re-SURMOF thin film amounts to be ~ 500 nm.

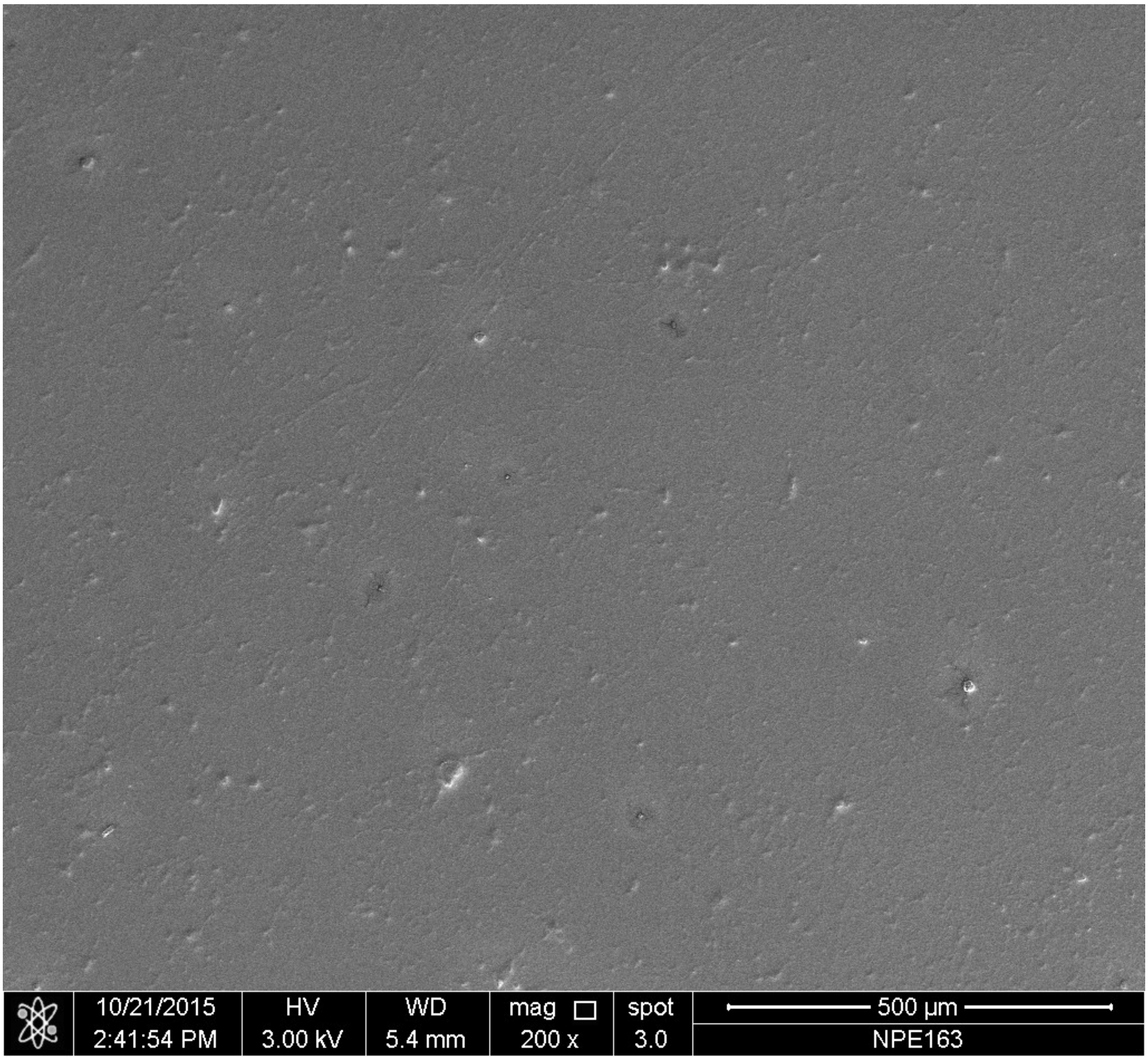

Figure S15. SEM image of Re-SURMOF grown on FTO substrate after two hours electrolysis.

Table S1. Vibrational frequencies of calculated and bulk Re-based molecular catalyst together with the assignments.

Band position / cm^{-1}			
No.	Assignment	Re-based molecular catalyst	
		Calc.	bulk
1	ν_s C=O (with Re)	2027	2028
2	ν_{as} C=O (with Re)	1956	1938
3	ν_{as} C=O (with Re)	1929	1890
4	ν C=O (-COOH)	1738	1740
5	ν CC Py	1575	1610
6	ν CC Py	1444	1425
7	ν CC Py	1430	1375
8	ν CH Py	1302	1290
9	ν CC Py	1133	1125
10	ν CH Py	1055	1055

Explanation of band assignments:

Py: band is attributed mainly to a vibration mode of the pyridine ring

ν: stretching mode

ν_{sym}: symmetric stretching mode

ν_{as}: asymmetric stretching mode

Table S2. Faradic efficiency of different catalysts towards CO_2 reduction at different potentials. A solution of 0.1 M tetrabutylammonium hydroxide (TBAH) in acetonitrile with 5% trifuoroethanol (in volume) was used as electrolyte. $Ag/AgNO_3$ was used as reference electrode and Pt as conter electrode.

No.	Sample	Faradic Efficiency
		-1.6 V vs. NHE
1	Re-SURMOF/FTO	93%
2 [a]	0.5 mM Re-linker /FTO	65%
3 [b]	Re-linker + $Zn(OAc)_2$/FTO	61%
4	FTO	12%
5	$Zn(OAc)_2$/FTO	17%
6 [c]	Re-SURMOF/FTO	Trace

[a] Bare FTO was used as working electrode, and the Re-linker was used as molecular catalysys.

[b] The Re-linker and $Zn(OAc)_2$ were mounted onto FTO substrate using Nafion .

[c] The Re-SURMOF/FTO was reused after two hours electrocatalysis.