Electronic Supplementary Material (ESI) for CrystEngComm.

Polymorphs of copper coordination compound: Interlinking active sites enhanced electrocatalytic activity of coordination polymer compared to coordination complex

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Experimental section:

Copper nitrate trihydrate ($Cu(NO_3)_2.3H_2O$), 2,6-pyridinedicarboxylic acid (2,6-PDA), triethylenediamine (DABCO) and nafion 117 solution were obtained from Sigma-Aldrich and used as received.

Cu PDA-C and **Cu PDA-P synthesis**: Copper nitrate ($Cu(NO_3)_2.3H_2O$, 0.074 g), 2,6-dicarboxylic acid (2,6-PDA, 0.068 g) and DABCO (0.048 g) were dissolved in 15 ml water and sonicated for 10 min to form a clear solution. The final mixture was kept in a beaker at room temperature without disturbing. After several days two different coloured (blue, cyan) crystals were formed. The crystals were collected and washed with water several times and dried under vacuum.

Characterization

PXRD (Bruker, Cu-Kα: $\lambda = 0.1540598$ nm) and TGA (SDT Q600, TA Instruments, USA, Q-600-0947). Single crystals were coated with paratone-N oil and the diffraction data measured at 100K with synchrotron radiation ($\lambda = 0.62998$ Å) on a ADSC Quantum-210 detector at 2D SMC with a silicon (111) double crystal monochromator (DCM) at the Pohang Accelerator Laboratory, Korea. CCDC Nos. – 1936561 contain the supplementary crystallographic data for this paper.

Electrochemical measurements

Electrochemical measurements were performed in a three electrode system at an electrochemical work station (CHI660E, Austin, Texas, USA). The three-electrode configuration using a saturated calomel electrode(SCE) as the reference electrode, a graphite rod as the counter electrode, and a modified glassy carbon electrode as the working electrode (GCE, 3 mm diameter). Prior to the surface coating, the GCE was polished using 1 mm, 0.3 mm and 0.05 mm alumina powder, followed by sonication in ethanol and allowed to dry. The working electrode was fabricated as follow: 4mg of the catalysts were dispersed in 400 µl ethanol, 100 µl water and 40 µl of 5 wt% nafion and then the mixture was sonicated for 30 min to form a homogenous ink. Then

0.3±0.02 mg catalyst was loaded onto glassy carbon electrode. Cyclic voltammetry and linear sweep voltammetry with scan rate of 50 mV s^{-1} was conducted in 1.0 M KOH and 1.0 M PBS respectively. For a Tafel plot, the linear portion is fit to the Tafel equation. In 1.0 M KOH (pH 14) and 1.0 M PBS (pH 7), $E_{(RHE)} = E_{(SCE)} + E^{o}_{(SCE)} + 0.059pH$. All the potentials were reported in our manuscript were calibrated to a reversible hydrogen electrode (RHE). Electrochemical impedance spectroscopy data were carried out in 1.0 M KOH and 1.0 M PBS aqueous solution with frequencies from 0.1 to 100000 Hz and an amplitude of 10 mV.

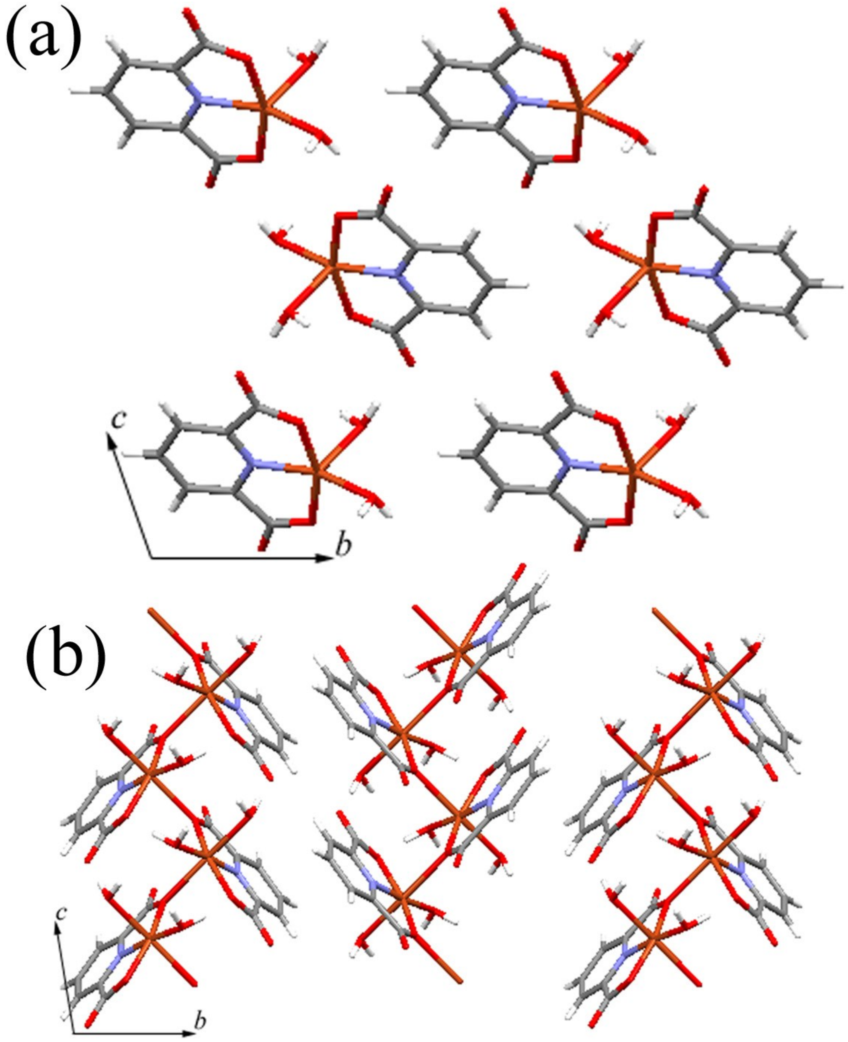

Figure S1. Molecular packing in the crystal lattice (a) Cu-C and (b) Cu-P. C (grey), N (blue), O (red), H (white) and Cu (orange).

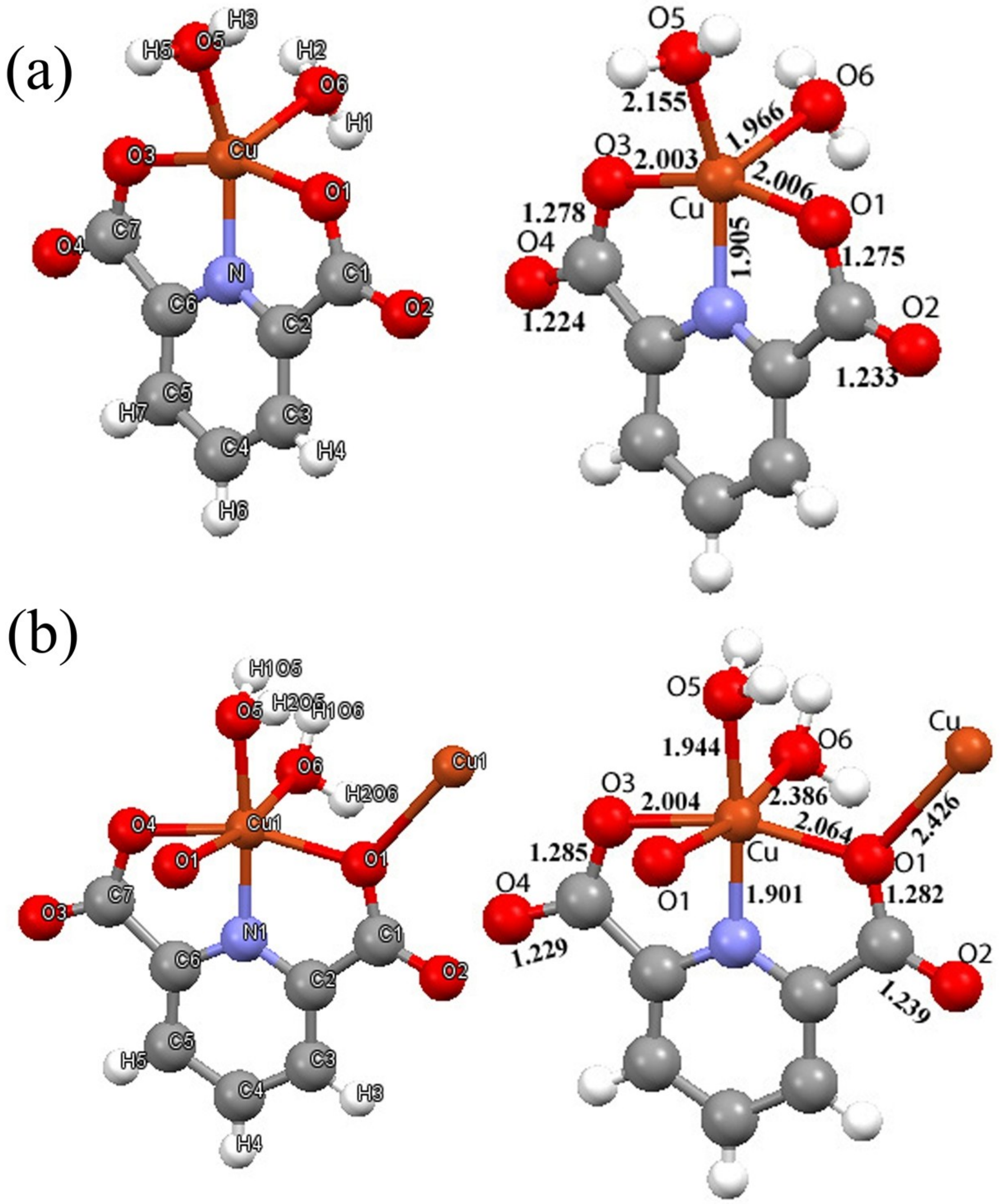

Figure S2. (a) The coordination geometry of Cu with PDA in (a) Cu-C and (b) Cu-P crystal lattice with elemental labelling. C (grey), N (blue), O (red), H (white) and Cu (orange). The coordination bond distances around Cu metal centre are marked (Å)

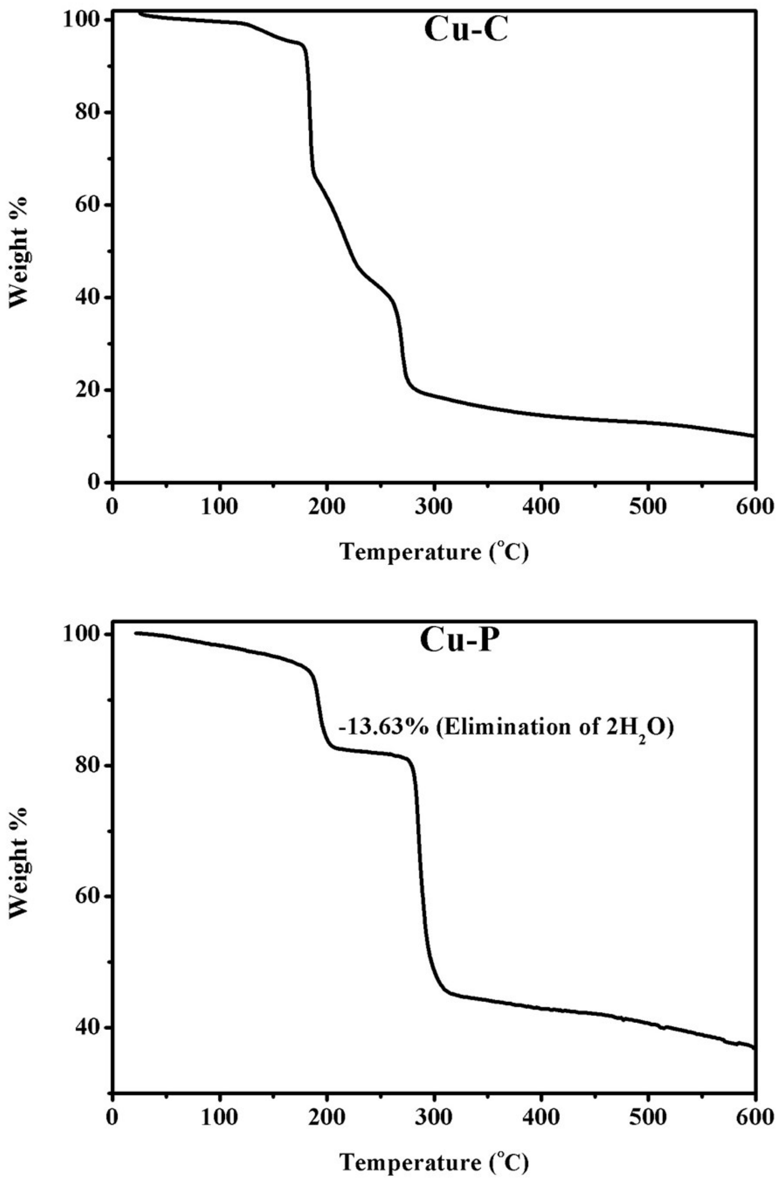

Figure S3. TGA analysis of Cu-C and Cu-P.

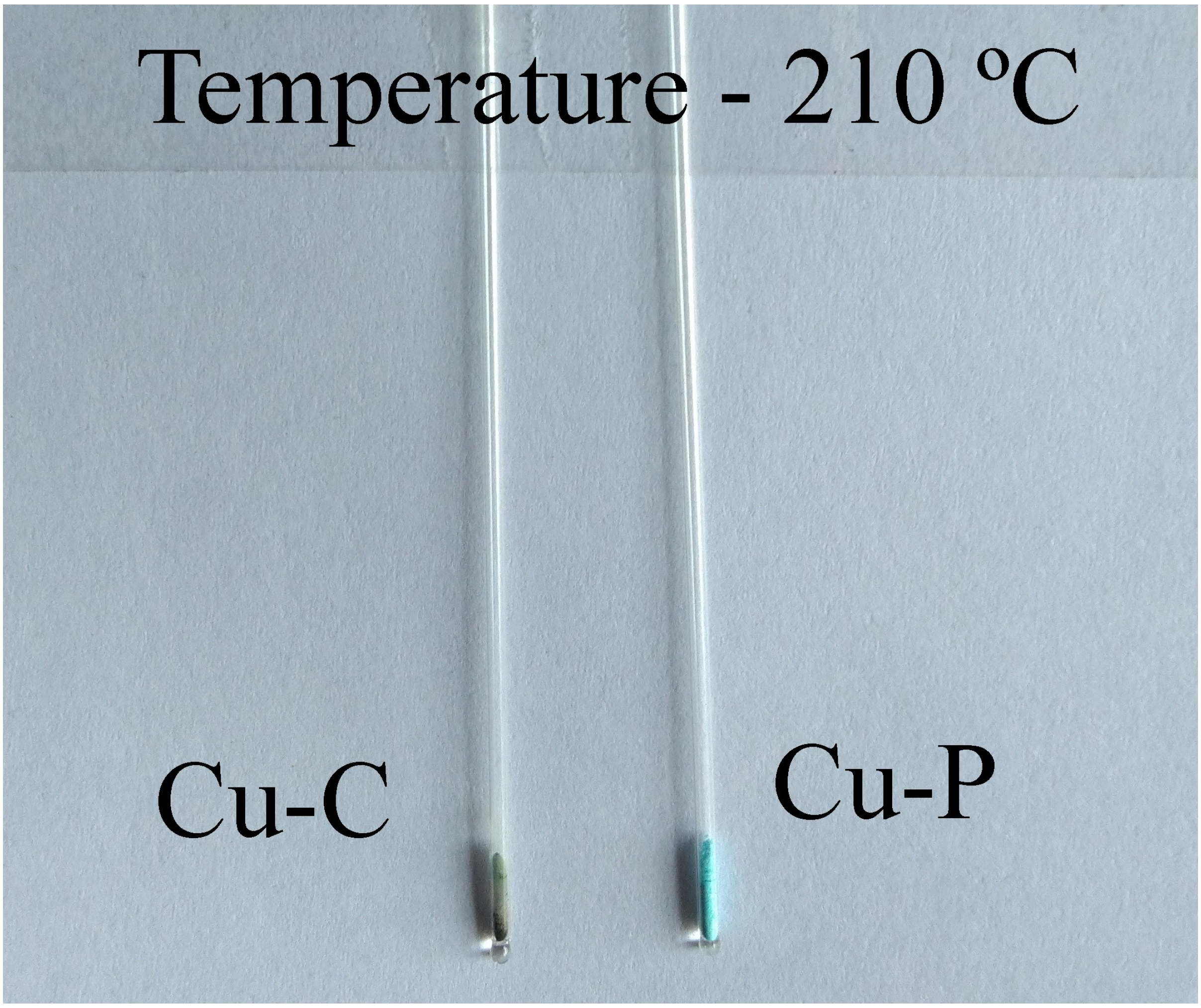

Figure S4. Digital images of Cu-C and Cu-P powder after heating over 200 °C.

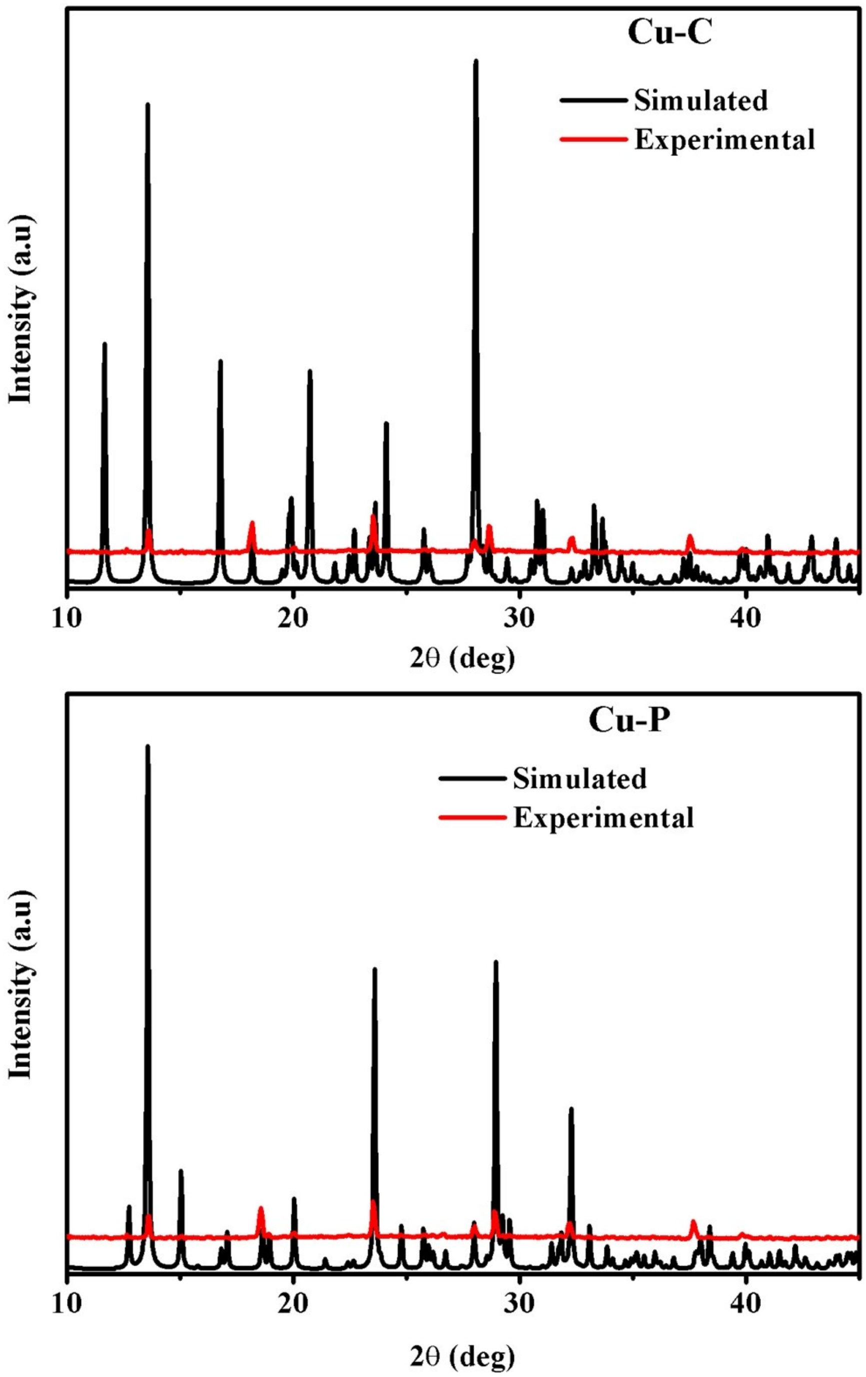

Figure S5. Comparison of experimental and simulated PXRD pattern of Cu-C and Cu-P.

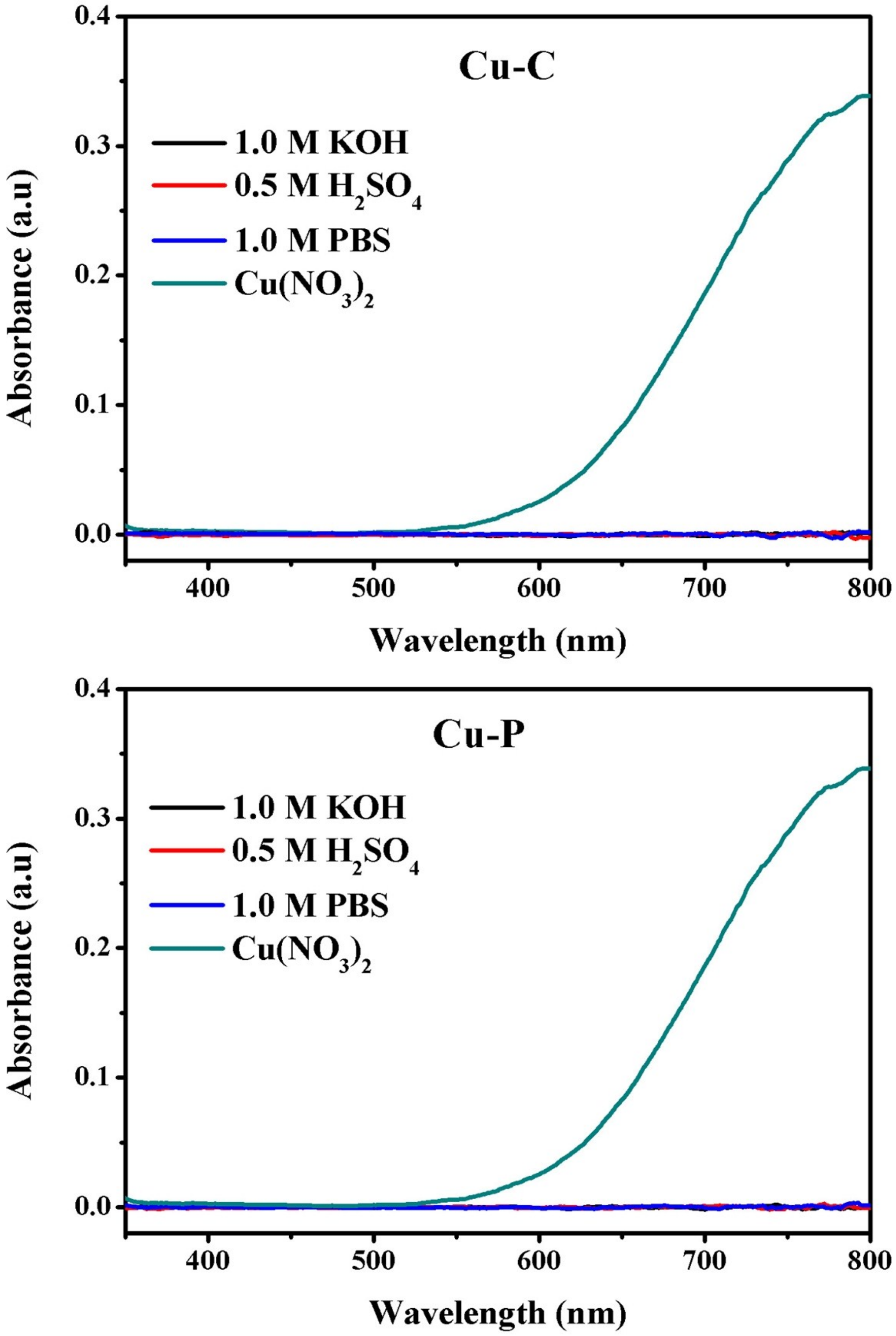

Figure S6. Absorption spectra of Cu-C and Cu-P in different medium.

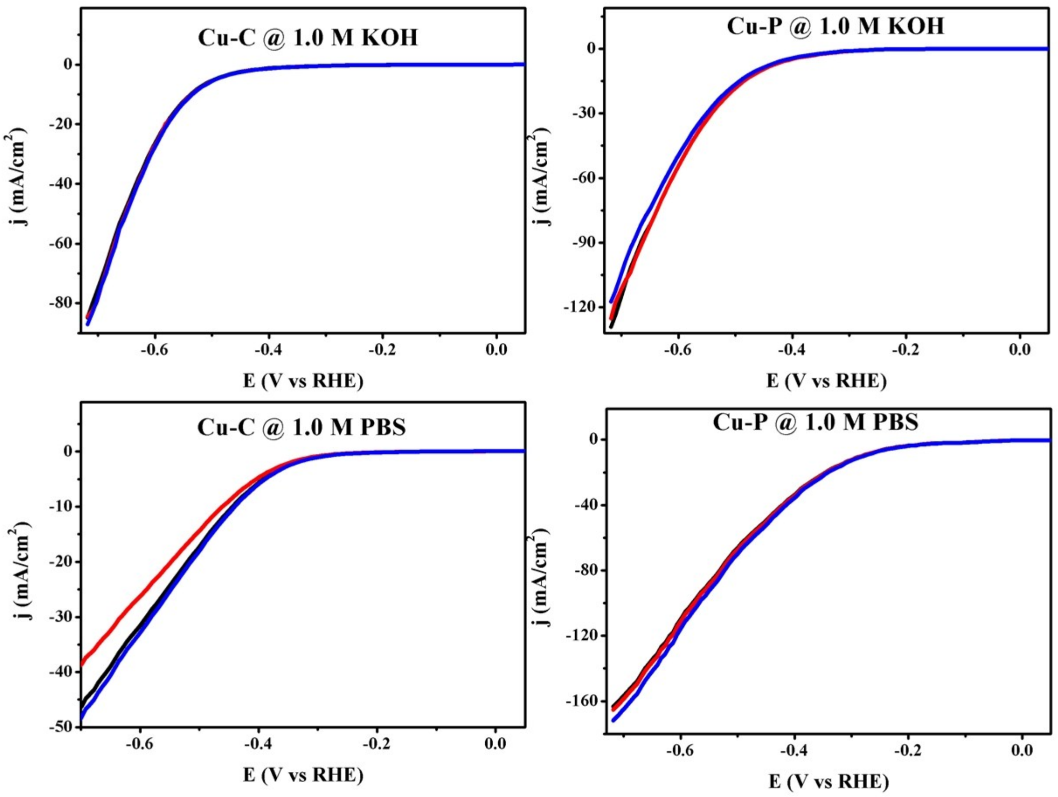

Figure S7. Reproducibility studies of Cu-C and Cu-P in alkaline and neutral medium.

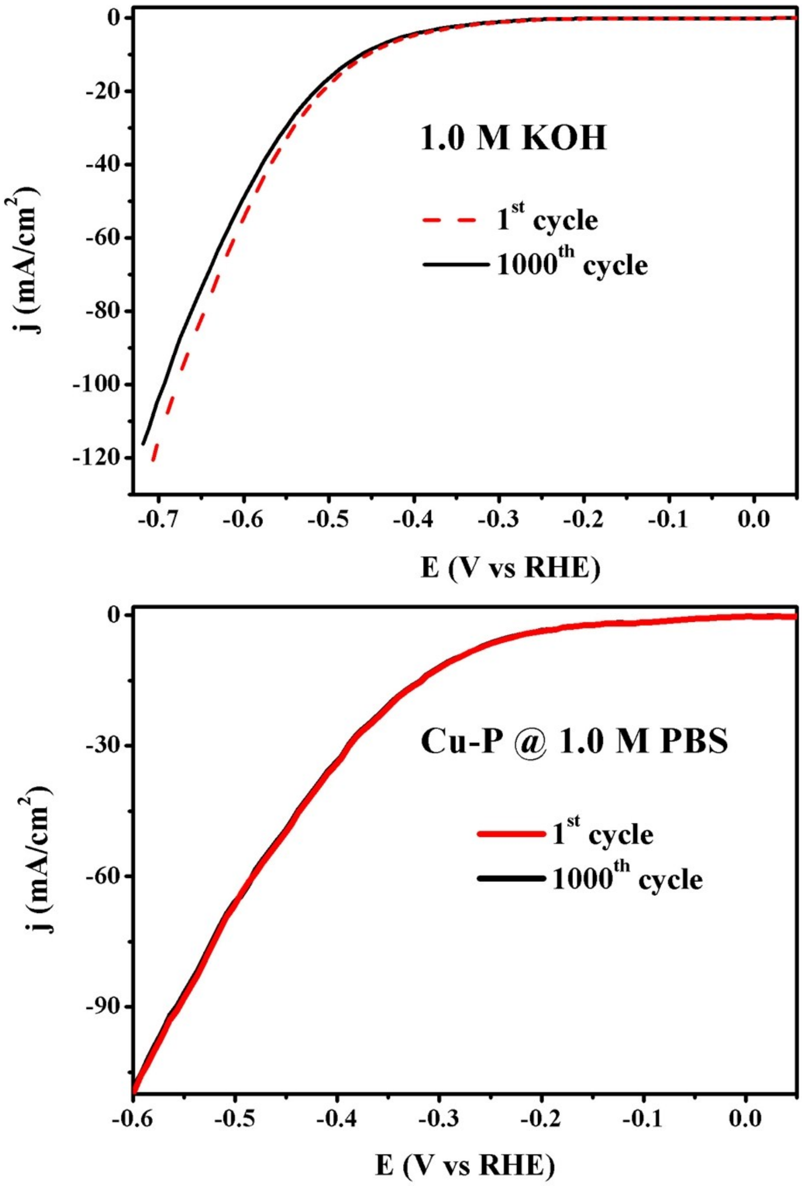

Figure S8. HER stability of Cu-P in alkaline and neutral medium.

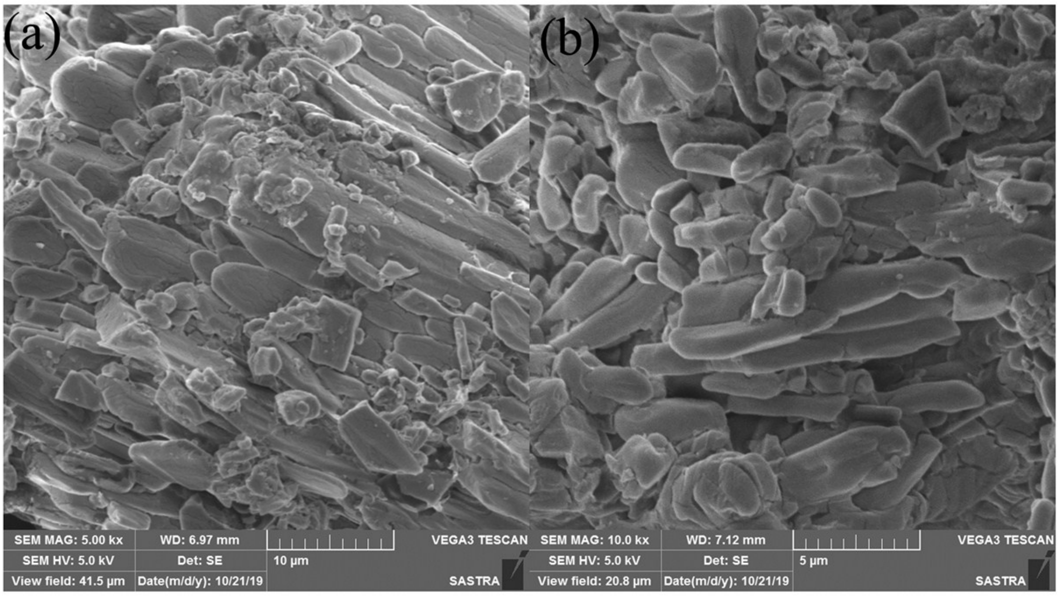

Figure S9. FE-SEM images of (a) Cu-C and (b) Cu-P crushed microcrystals.

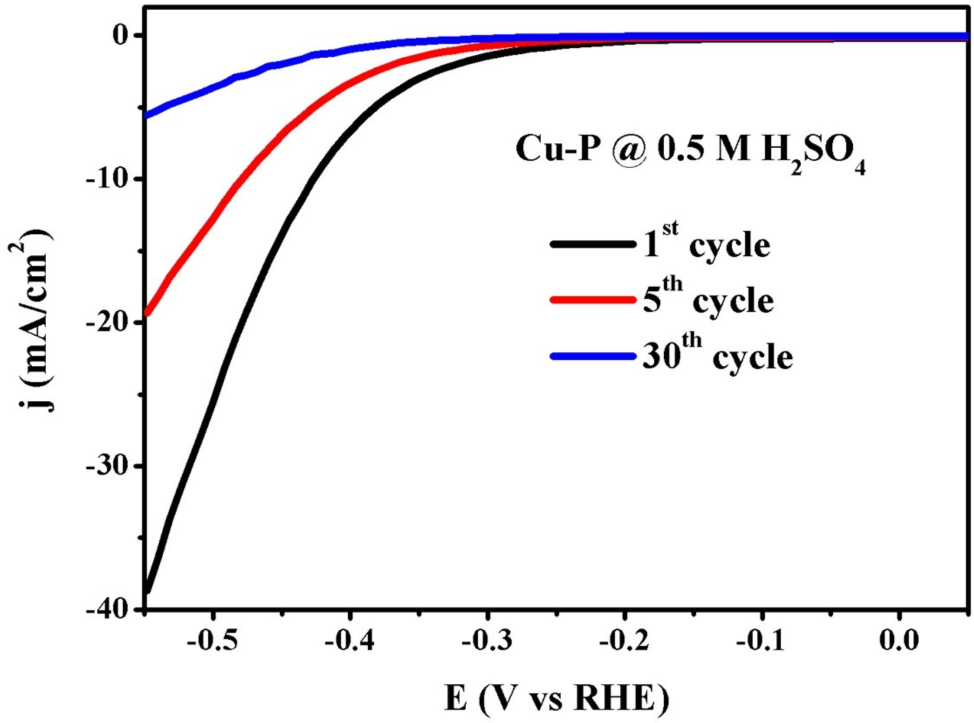

Figure S10. HER Polarization curves of Cu-P in 0.5 M H_2SO_4.

Table S1. Comparison of HER activities of different CPs/MOFs catalysts (*0.5M H_2SO_4 was used as electrolyte for all catalysts).

Catalyst$^{(*)}$	η@10 j (mV)	Tafel slope [mV/dec]	Ref
Cu PDA-3	290	83	1
Cu-MOF	369 (30 mA/cm^2)	135	2
Cu.BTC	577	147	3
CTGU-5 (Co)	388	125	4
CTGU-6 (Co)	425	176	5
CTGU-9 (Co)	424	137	6
Co-MOF	460	136	7
THTA -Co	295	71	8
THTA -Ni	315	76	9

Table S2. HER electrocatalytic activities of CPs/MOFs in presence of conducting composites.

Catalyst	**Overpotential [mV]**	**Tafel slope [mV/dec]**	**Stability tests**	**Electrolytes**	**Ref**
(GO 8 wt%) Cu-MOF	209 (30 mA/cm^2)	84	N/A	0.5M H_2SO_4	2
1.7 wt% AB &Cu.BTC	208	80	2000 cycles and 18h	0.5M H_2SO_4	3
AB&CTGU-5 (1:4) (Co)	44	45	96 h	0.5M H_2SO_4	4
AB&CTGU-9 (3:4) (Co)	128	87	2000 cycle and 21h	0.5M H_2SO_4	5
Gr(4wt%) &Co-MOF	125	91	1000 cycle	0.5M H_2SO_4	6
UiO-66-NH2-Mo-5 (Zr& Mo)	200	59	5000 cycles and 7h	0.5M H_2SO_4	8
MSZIF-900 (Co)	233	N/A	2.5 h	0.5M H_2SO_4	9

References:

1) P. Muthukumar, D. Moon and S. P. Anthony, *Catal. Sci & Tech.,* 2019, **9**, 4347–4354.
2) M. Jahan, Z. Liu and K. P. Loh, *Adv. Funct. Mat*., 2013, **23**, 5363–5372.
3) X. Wang, W. Zhou, Y.-P. Wu, J.-W. Tian, X.-K. Wang, D.-D. Huang, J. Zhao and D.-S. Li, *J. All. Comp*., 2018, **753**, 228–233.
4) Y.-P. Wu, W. Zhou, J. Zhao, W.-W. Dong, Y.-Q. Lan, D.-S. Li, C. Sun and X. Bu, *Angew. Chem. Int. Ed*., 2017, **56**, 13001–13005.
5) W. Zhou, Y.-P. Wu, X. Wang, J.-W. Tian, D.-D. Huang, J. Zhao, Y.-Q. Lan and D.-S. Li, *Cryst. Eng. Comm*., 2018, **20**, 4804–4809.
6) J.-W. Tian, M.-X. Fu, D.-D. Huang, X.-K. Wang, Y.-P. Wu, J. Y. Lu and D.-S. Li, *Inorg. Chem. Comm.,* 2018, **95**, 73-77.
7) R. Dong, Z. Zheng, D. C. Tranca, J. Zhang, N. Chandrasekhar, S. Liu, X. Zhuang, G. Seifert and X. Feng, *Chem.- Eur. J*., 2017, **23**, 2255–2260.
8) X. Dai,M. Liu,Z. Li,A. Jin,Y. Ma,X. Huang,H. Sun, H. Wang and X. Zhang, *J. Phys. Chem. C,* 2016, **120**, 12539−12548.
9) G. Jia, W. Zhang, G. Fan, Z. Li, D. Fu, W. Hao, C. Yuan and Z. Zou, *Angew. Chem. Int. Ed.,* 2017, **56**, 13781 –13785.