New Journal of Chemistry

Electronic Supplementary Information

Electrocatalytic Oxidation of Water using Self-assembled Copper(II) Tetraaza Macrocyclic Complexes on a 4-(Pyridine-4′-amido)benzene Grafted Gold Electrode

Abhinandan Mahanta, [a] Koushik Barman, [a,b] Umme Solaem Akond, [a] and Sk. Jasimuddin [a]*

[a] Department of Chemistry, School of Physical Sciences, Assam University, Silchar,Assam-788011, India

[b]Department of Chemistry, Queens College-CUNY, Flushing, NY, 11367, USA

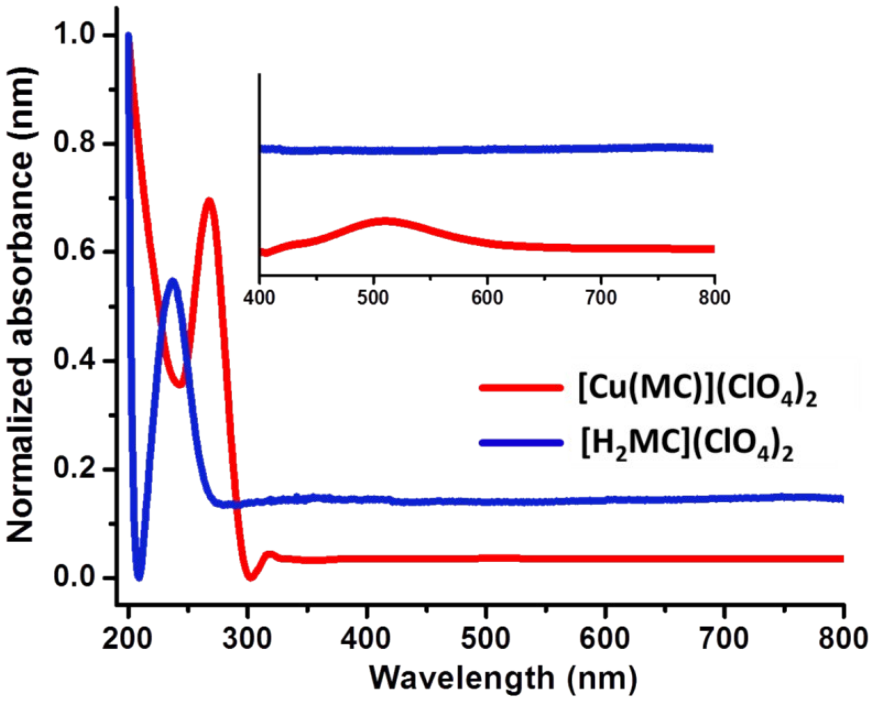


Fig. S1 UV-Vis spectra of $[H_2MC](ClO_4)_2$and $[Cu(MC)](ClO_4)_2$ in MeOH.

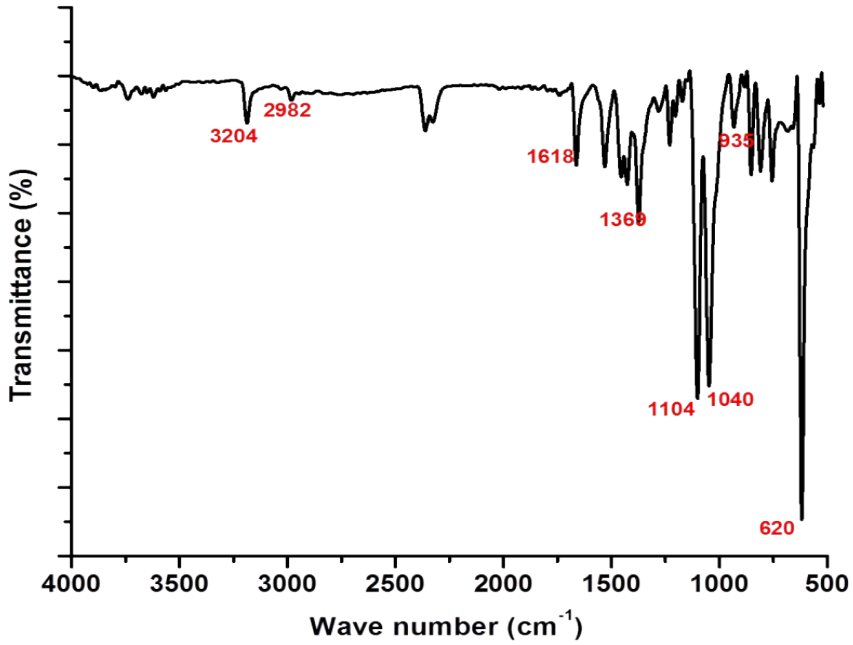


Fig.S2a FTIR spectra of $[H_2MC](ClO_4)_2$.

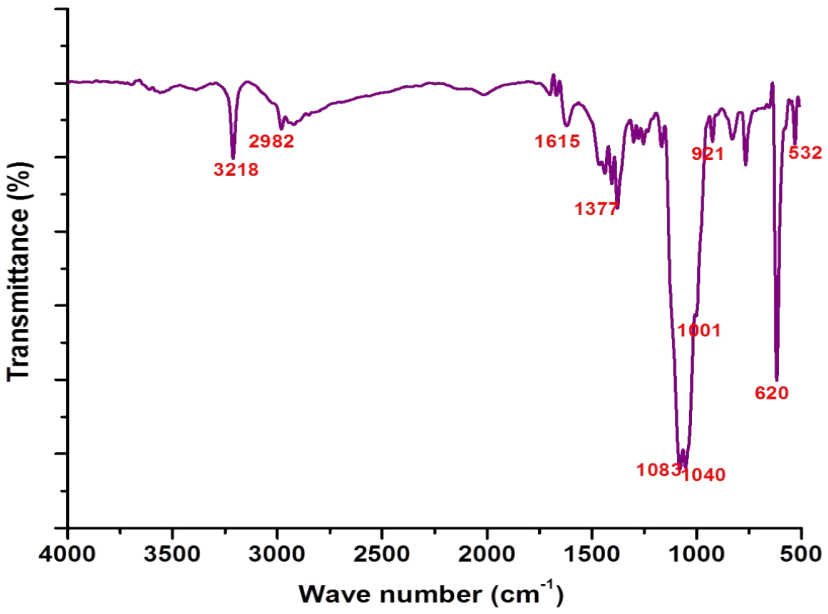


Fig S2b FTIR spectra of $[Cu(MC)](ClO_4)_2$.

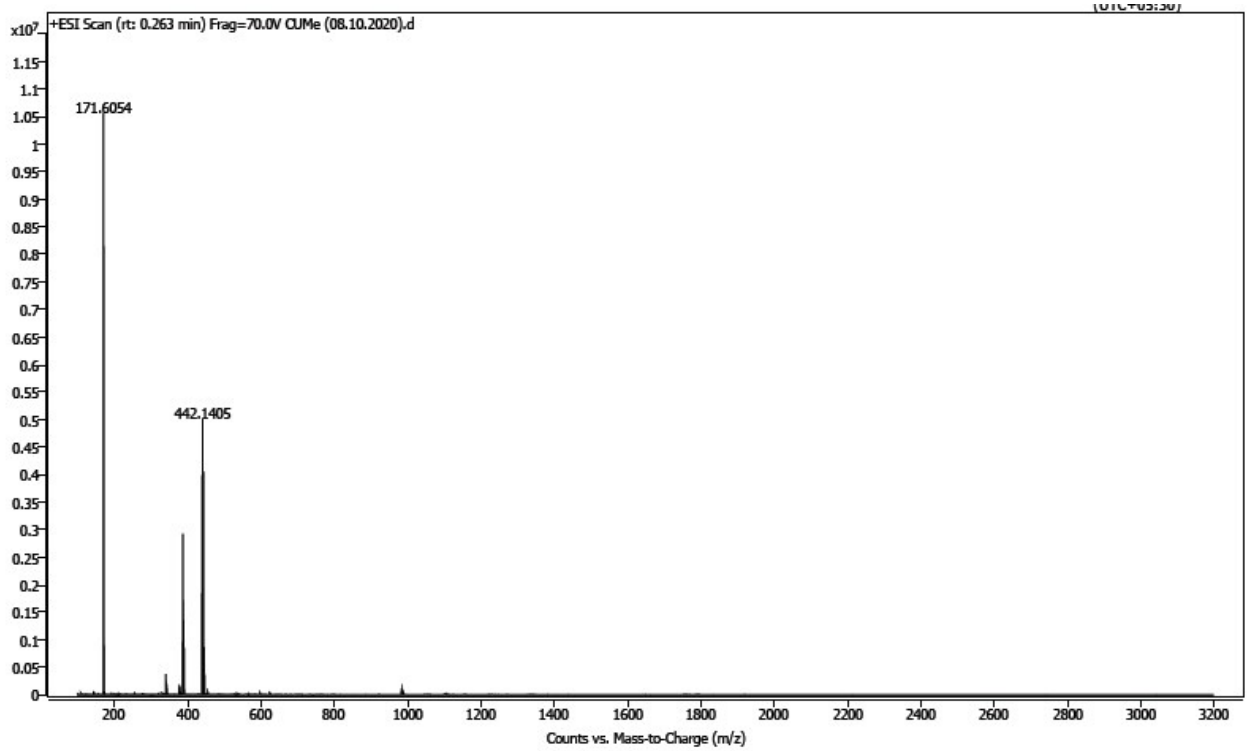


Fig. S3 ESI-MS spectra of $[Cu(MC)](ClO_4)_2$

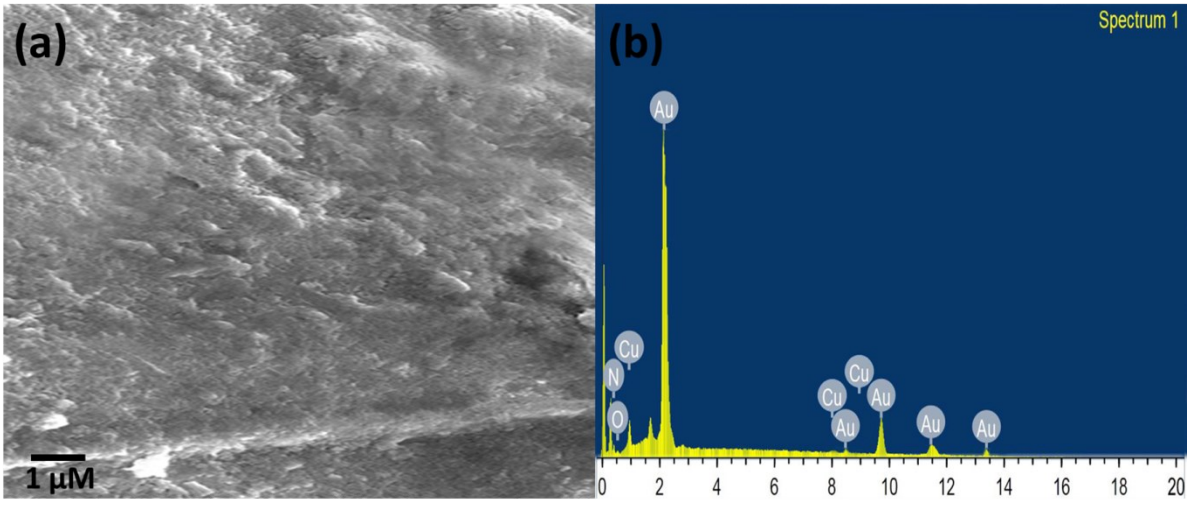


Fig. S4 FE-SEM image and EDX spectra of [Cu(MC)]-L-Au electrode.

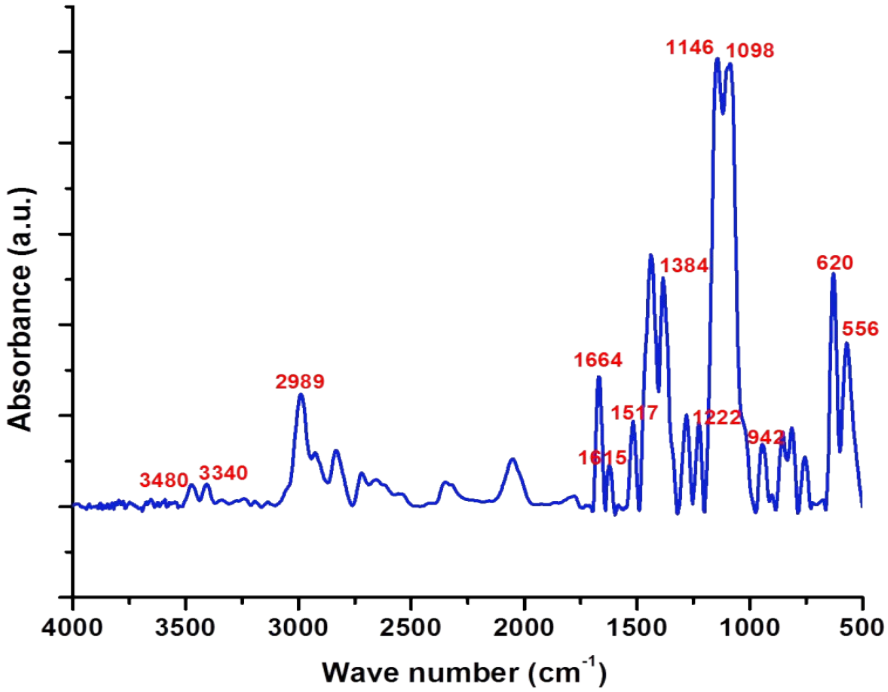


Fig. S5 ATR-FTIR spectra of [Cu(MC)]-L-Au electrode surface

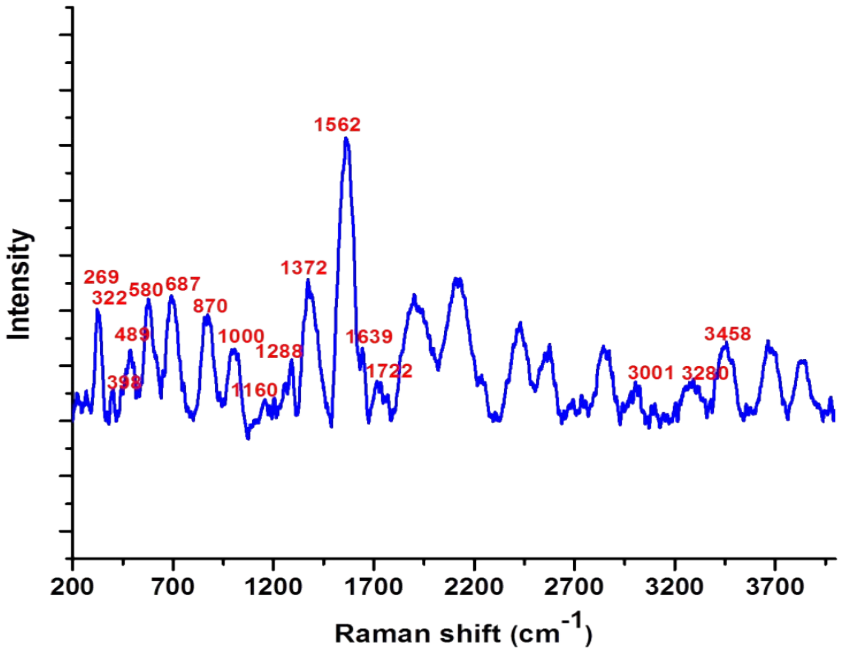


Fig. S6 SERS spectra of [Cu(MC)]-L-Au electrode surface

Table S1: Comparison of FTIR, ATR-FTIR and SERS spectral data

	FTIR (ν, cm^{-1})	FTIR (ν, cm^{-1})	ATR-FTIR (ν, cm^{-1})	SERS (ν, cm^{-1})
	$[H_2MC](ClO_4)_2$	$[Cu(MC)](ClO_4)_2$	[Cu(MC)]-L-Au	[Cu(MC)]-L-Au
CH_3	2982	2982,	2989	3001
	1369	1377	1384	1372
C=N(of MC)	1618	1615	1615	1639
C-N(of MC)	935	921	942	870
NH (of MC)	3204	3218	3340	3280
ClO_4	1040	1040	1098	1000
	1104	1083	1146	1160
	620	1001	620	687
		620	556	580
		532	-	-
NH (of L)	-	-	3480	3458
CO (of L)	-	-	1664	1722
CN (of L)	-	-	1517	1562
			1222	1288
Cu-N(MC)	-	-	-	489
Cu-N(Py)	-	-	-	269
Cu-O (ClO_4)	-	-	-	322
Au-C	-	-	-	398

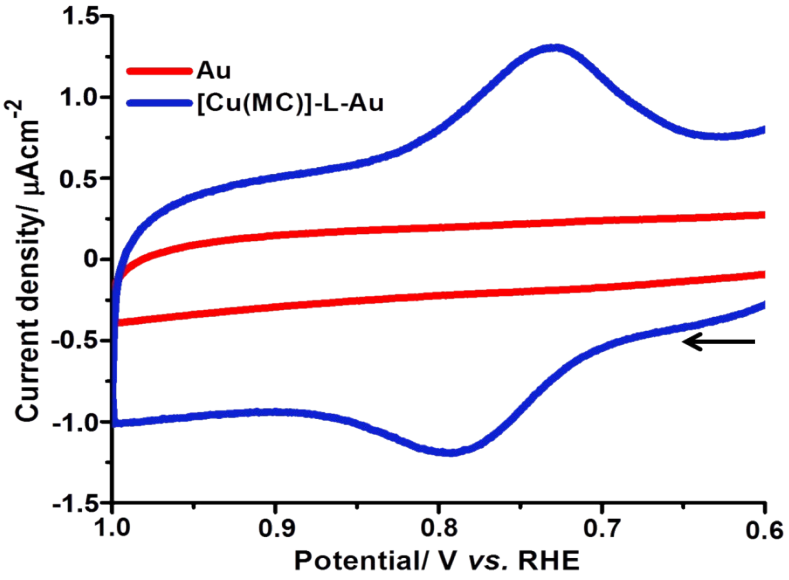


Fig. S7 Overlaid CV in neutral 0.1 M PBS obtained at bare and [Cu(MC)]-L-Au electrode

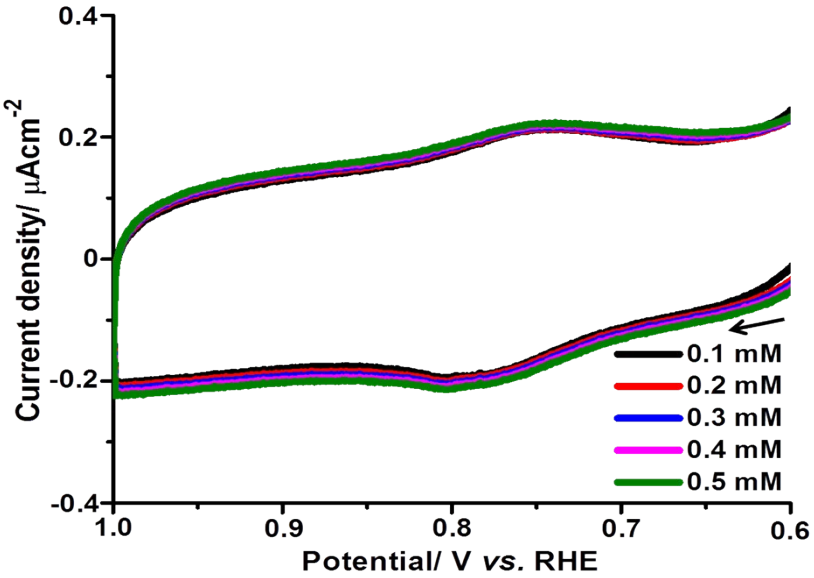


Fig. S8 Overlaid CV in neutral 0.1 M PBS obtained with increasing concentration of $[Cu(MC)](ClO_4)_2$ on L-Au electrode

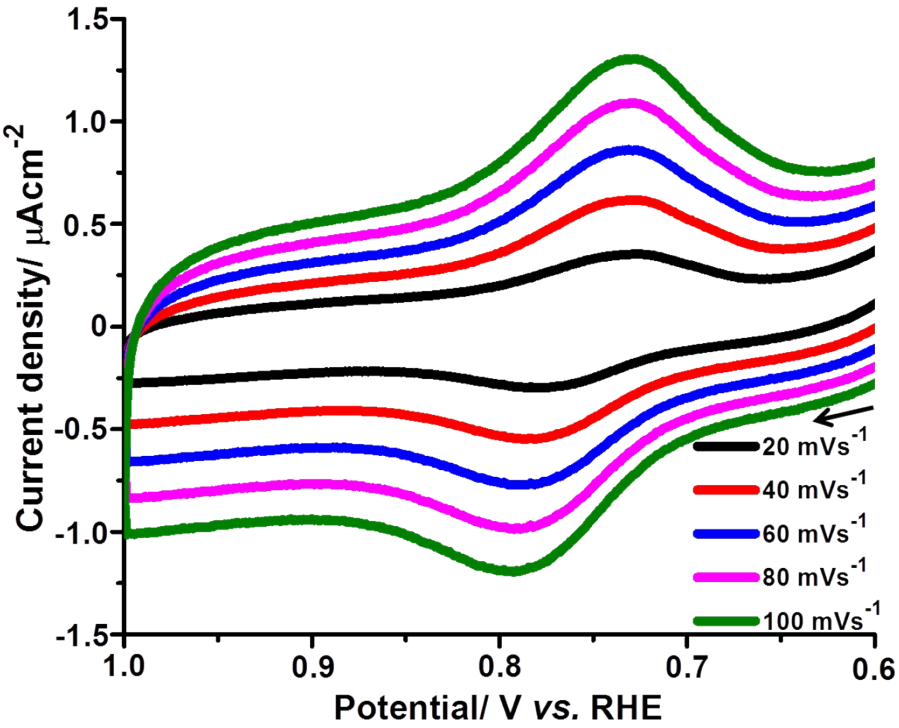


Fig. S9a.Overlaid CV in neutral 0.1 M PBS obtained with increasing scan rate at [Cu(MC)]-L-Au electrode

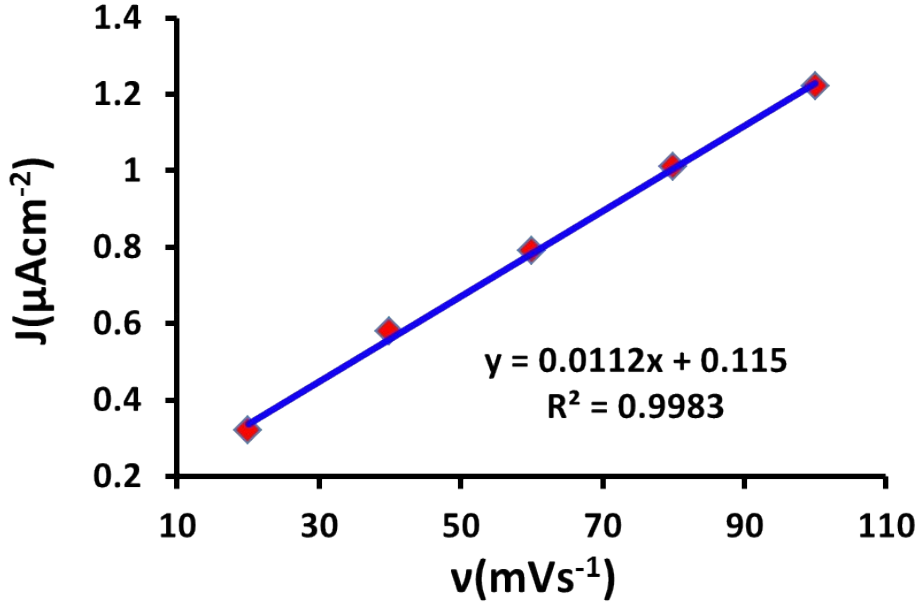


Fig. S9b. Plot of current density *versus* scan rate

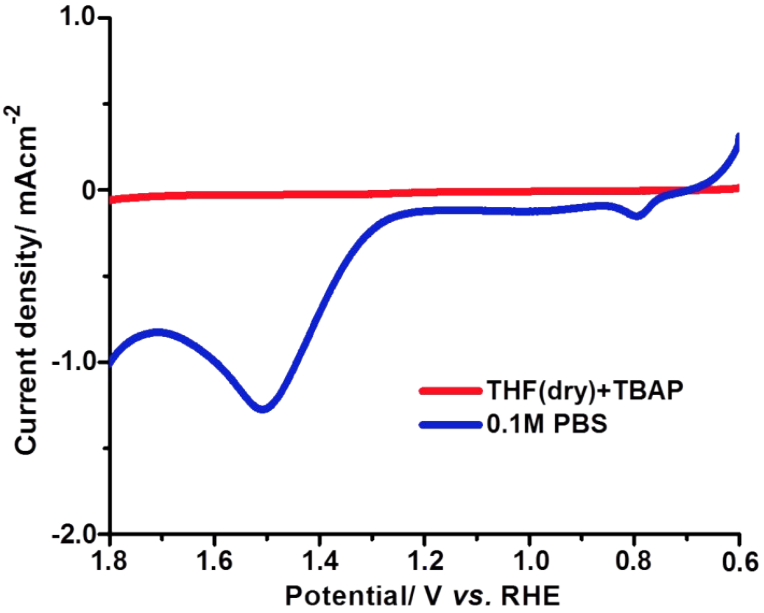


Fig.S10 Overlaid LSV taken in aqueous (blue curve) and non-aqueous solvent (red line) at [Cu(MC)]-L-Au electrode

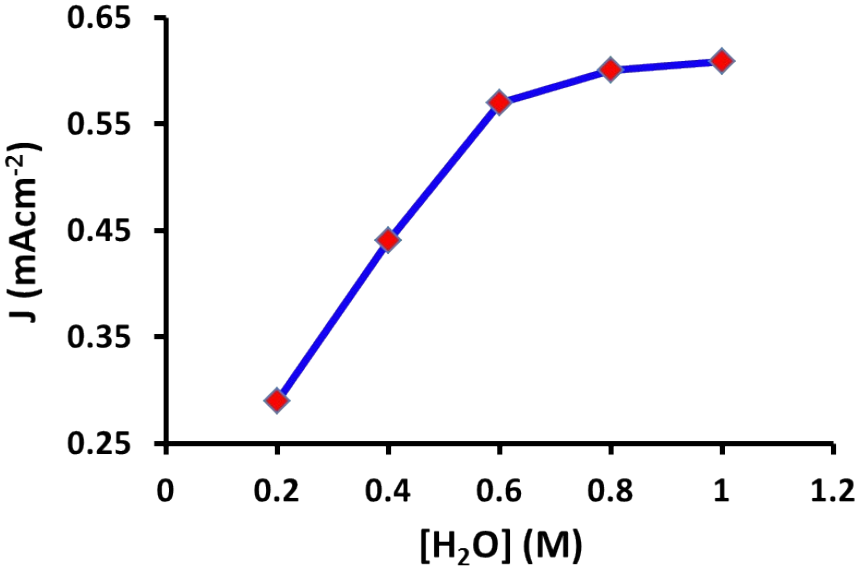


Fig. S11 Plot of current density versus concentration of water (0.2-1.0 M)

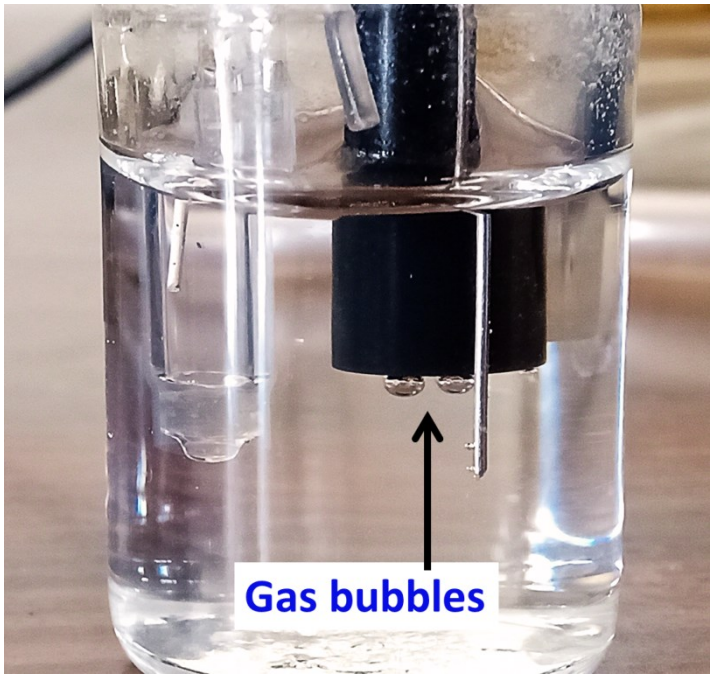


Fig. S12 Formation of oxygen gas bubbles on the [Cu(MC)]-L-Au electrode after ten repetitive scans

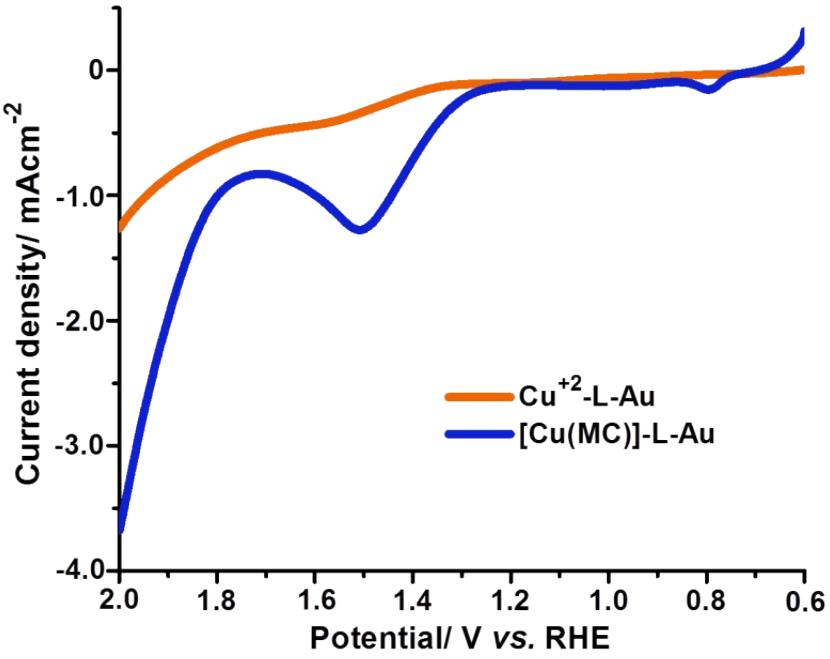
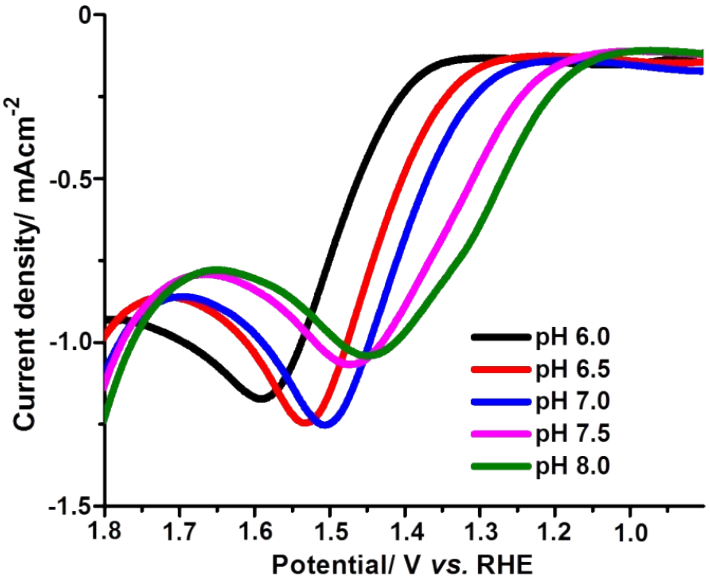
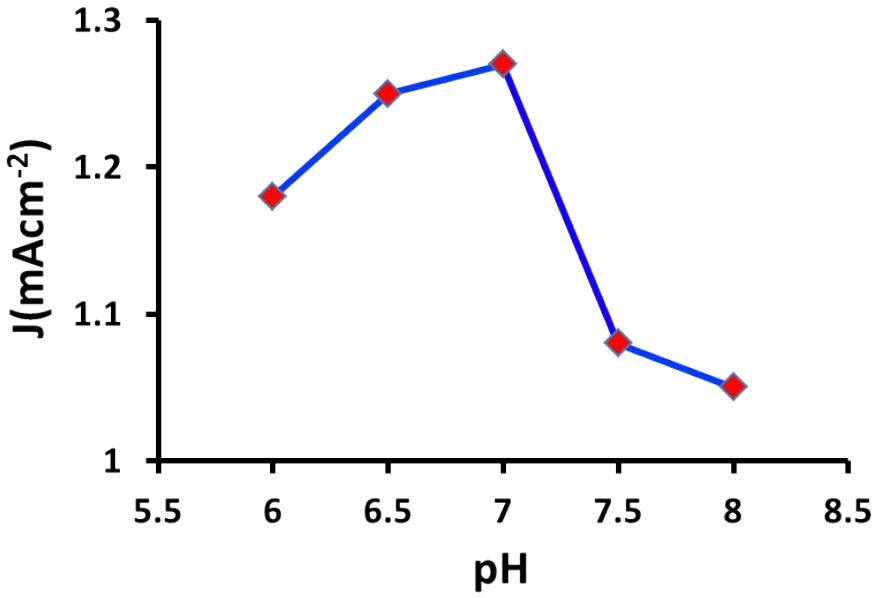


Fig. S13 Overlaid LSV obtained in 0.1 M PBS solution using [Cu(MC)]-L-Au and Cu^{2+}-L-Au electrodes



(a)



(b)

Fig. S14 Overlaid LSV obtained at [Cu(MC)]-L-Au electrode by varying pH of the solution (a). The plot of current density *versus* pH of the medium (b).

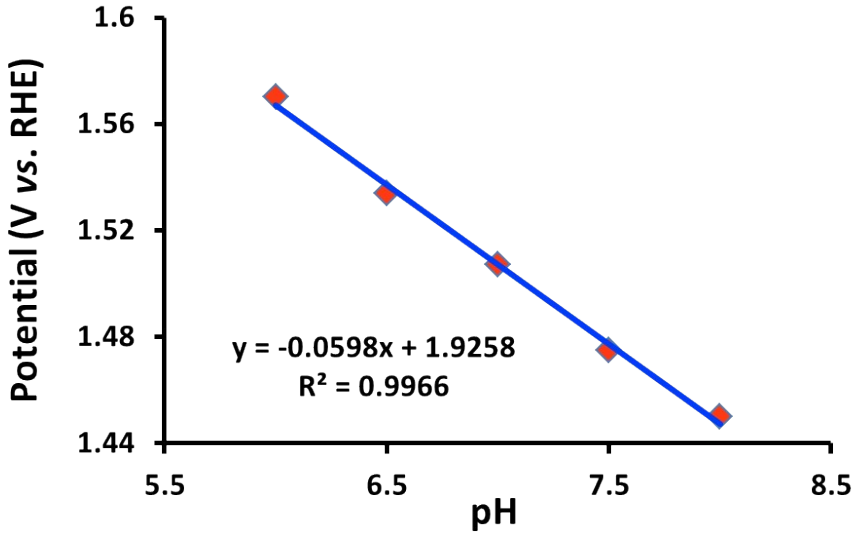


Fig. S15 Plot of potential versus pH of the medium (water oxidation).

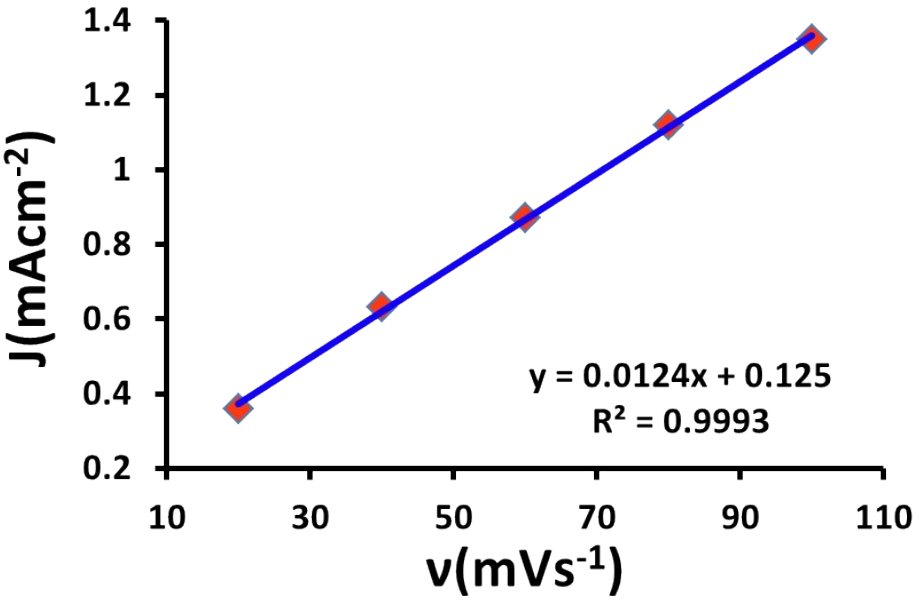


Fig. S16a Plot of current density *versus* scan rate (20-100 mVs^{-1})

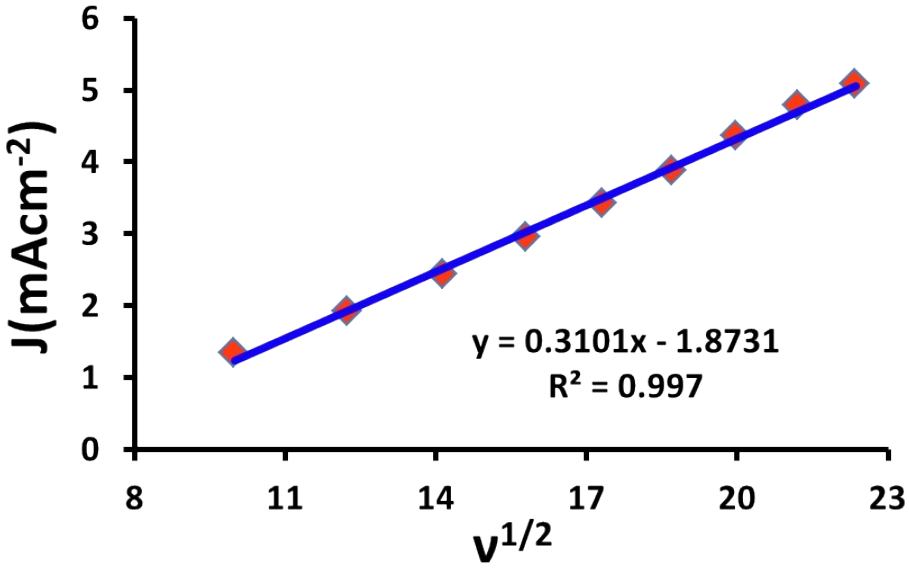


Fig. S16b Plot of current density *versus* square root of scan rate (100-500 mVs^{-1})

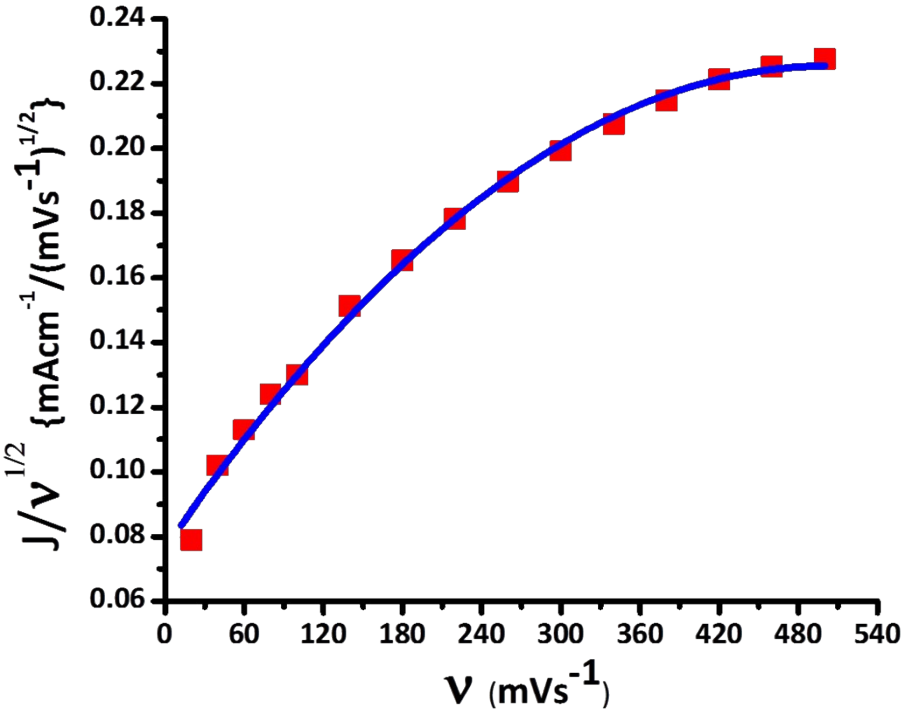


Fig. S17 Plot of scan rate normalized current density *versus* scan rate

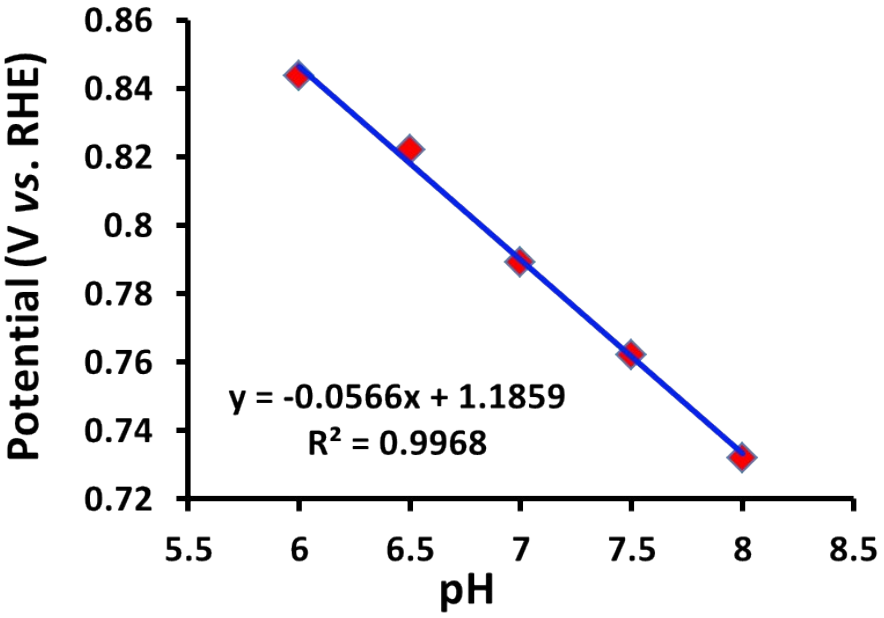


Fig. S18 Plot of potential versus pH for $Cu^{II/III}$ couple

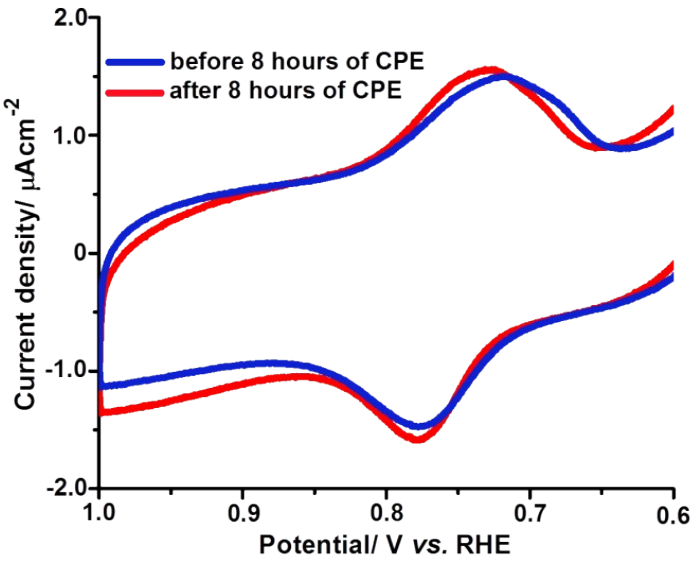


Fig. S19 Overlaid CV in 0.1 M PBS (pH 7.0) obtained by using [Cu(MC)]-L-Au electrode before and after electrolysis.

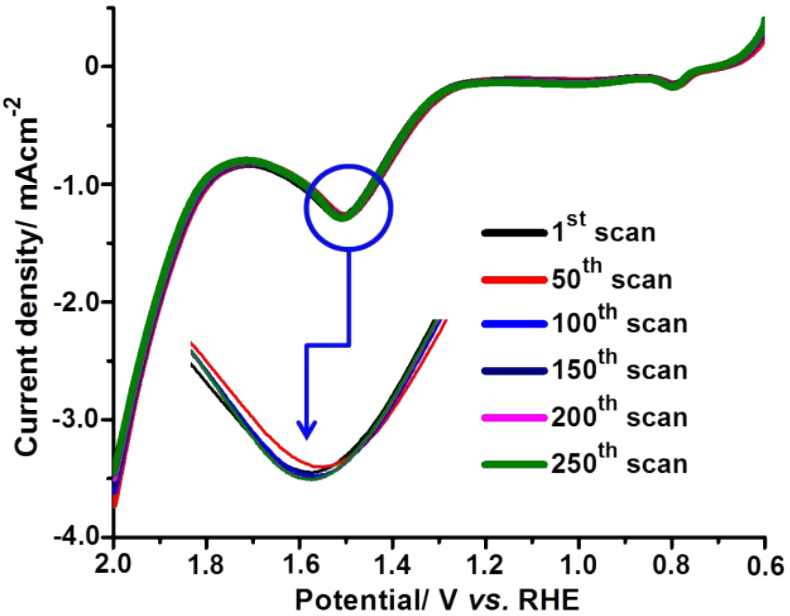


Fig. S20 Repetitive LSV at [Cu(MC)]-L-Au electrode in 0.1 M PBS (pH 7.0)

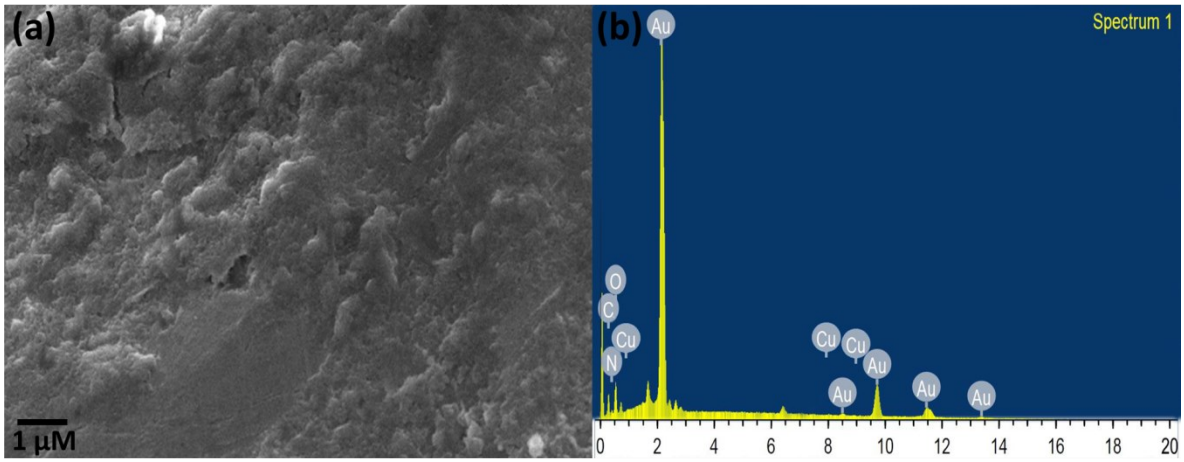


Fig. S21 FE-SEM (a) and EDX spectra (b) after 8 h controlled potential electrolysis using [Cu(MC)]-L-Au electrode in 0.1 M PBS (pH 7.0)

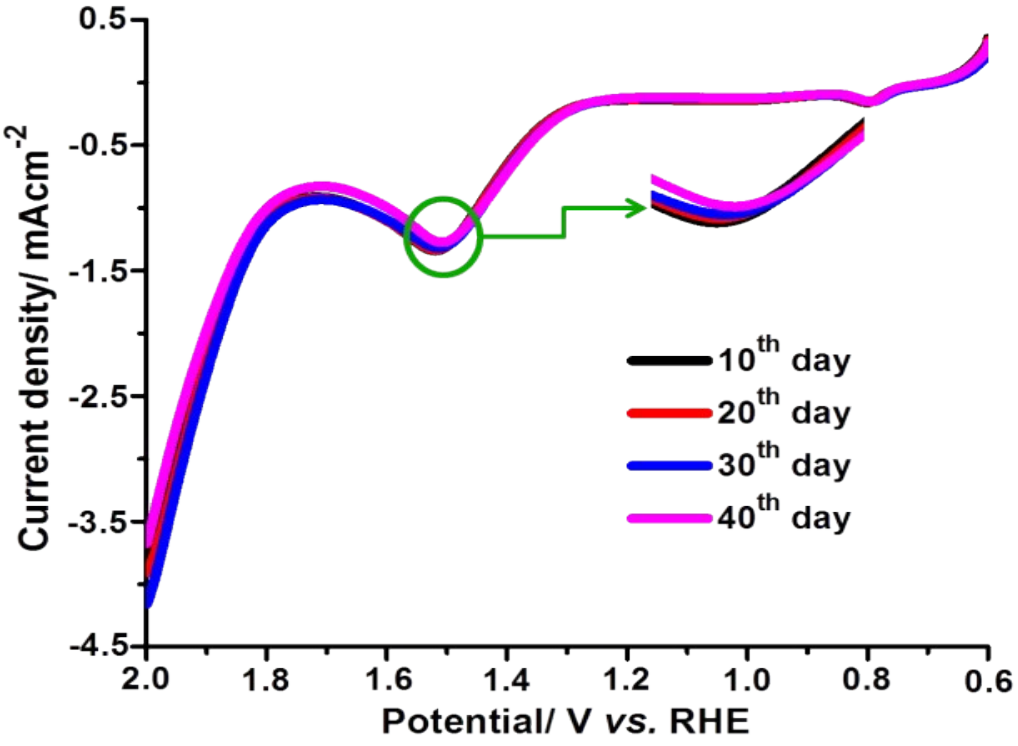


Fig. S22 Overlaid LSV obtained in 0.1 M PBS at [Cu(MC)]-L-Au electrode at an scan rate 100 mVs^{-1} in 10 days interval for 40 days.

Table S2. Comparison table of various homogeneous and heterogeneous copper based electro –catalysts for the oxidation of water

Catalysts	Electrolyte	pH	Onset overpotential	Tafel Slope ($mVdecade^{-1}$)	Stability Study (CPE) t (h)	Reference
Cu^{2+}-ion	0.1 M Borate buffer	9.0	440	89	10	[1]
Cu^{II}-Gly	0.2 M PBS	12	380	64	10	[2]
Cu^{II}-Py	0.2 M PBS	9.2	600	56	-	[3]
Cu^{II}-en	0.2 M PBS	12	540	62	10	[4]
CuO	1M KOH	13.6	430	61	24	[5]
$Cu(OH)_2$	0.1 M KPi	9.2	450	78	10	[6]
CuO_x-NLs	0.2 M CBS	11	450	44	20	[7]
Cu_2O-Cu	1M KOH	13.6	250	67	50	[8]
$[(bpy)Cu(OH)_2]$	0.1 M Acetate buffer	12.5	540	-	0.5	[9]
$[Cu(dhbpy)(OH)_2]$	0.1 M Acetate buffer	12.4	330	-	2.5	[10]
$[Cu(pyalk)_2]$	0.1M KNO_3/0.1M KOH	13.3	560	-	10	[11]
$[Cu(TMC)(H_2O)]^{2+}$	0.1 M PBS	7.0	600	-	1	[12]
$[Cu_2(bpman)(\mu\text{-}OH)]^{3+}$	0.1 M PBS	7.0	800	-	2	[13]
$[Cu\text{-}L_1(OAc)]^{-}$	0.1M CBS	8.0	530	-	10	[14]
$[Cu(TPA)(OH_2)]^{2+}$	0.1 M PBS	8.5	780	-	5	[15]
[Cu(MC)L]	0.1 M PBS	7.0	227	48	8	Present work

dhbpy = 6,6′-dihydroxy-2,2′-bipyridine , Pyalk = 2-pyridyl-2-propanol, bpman = 2,7-(bis(2-pyridylmethyl)aminomethyl)-1,8-naphthyridine, L_1 = N, N′-2,6-dimethylphenyl-2,6-pyridinedicarboxamide, TPA = tris(pyridylmethyl)amine, TMC = Me_4cyclam.

References

[1] F. Yu, F. Li, B. Zhang, H. Li, L. Sun, *ACS Catal.* **2015**, 5, 627–630.

[2] C. Lu, J. Wang, Z. Chen, *ChemCatChem*, **2016**, 8, 2165-2170.

[3] X. Liu, H. Jia, Z. Sun, H. Chen, P. Xu, P. Du, *Electrochem. Commun.* **2014**, 46, 1–4.

[4] C. Lu, J. Du, X.-J. Su, M.-T. Zhang, X. Xu, T. J. Meyer, Z. Chen, *ACS Catal.* **2016**, 6, 77–83.

[5] X. Liu, S. Cui, Z. Sun, Y. Ren, X. Zhang, P. Du, *J. Phys. Chem. C* **2016**, 120, 831–840.

[6] S. Cui, X. Liu, Z. Sun, P. Du, *ACS Sustainable Chem. Eng.* **2016**, 4, 2593–2600.

[7] K. S. Joya, H. J. M. de Groot, *ACS Catal.* **2016**, 6, 1768–1771.

[8] H. Xu, J. –X. Feng, Y. –X. Tong, G. R. Li, *ACS Catal*., **2017**, 7, 986-991.

[9] S. M. Barnett, K. I. Goldberg, J. M. Mayer. *Nat. Chem.* **2012**, 4, 498–502.

[10] T. Zhang, C. Wang, S. Liu, J.-L. Wang, W. Lin, *J. Am. Chem. Soc.* **2014**, 136, 273–281.

[11] K. J. Fisher, K. L. Materna, B. Q. Mercado, R. H. Crabtree, G. W. Brudvig, *ACS Catal.* **2017**, **7**, 3384–3387.

[12] F. Yu, F. Li, J. Hu, L. Bai, Y. Zhu, L. Sun, *Chem. Comm*. **2016**, 52, 10377-10380.

[13] X.-J. Su, M. Gao, L. Jiao, R.-Z. Liao, P. E. M. Siegbahn, J.-P. Cheng, M.-T. Zhang, *Angew. Chem. Int. Ed.* **2015**, 54, 4909–4914.

[14] Y. Liu, Y. Han, Z. Zhang, W. Zhang, W. Lai, Y. Wang, R. Cao, *Chem. Sci.* **2019**, 10, 2613–2622.

[15] X. –J. Su, C. Zheng, Q. –Q. Hu, H. –Y. Du, R. –Z. Liao, M. –T. Zhang, *Dalton Trans*, **2018**, 47, 8670-8675.