Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Probing into the effect of heterojunctions between $Cu/Mo_2C/Mo_2N$ on HER performance

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S1. Detailed procedure for catalysts synthesis

1. Synthesis of precursors

a. Synthesis of RGO

Graphite flakes have been used to synthesize GO by the modified Hummer method. The obtained GO was further thermally exfoliated at 900 °C for 15 minutes in Argon environment with a flow rate of 30 mL/min. This thermally exfoliated RGO was further used as a carbon source in the synthesis of catalysts.

b. Synthesis of Mo precursor

The Mo precursors has been synthesized with 0.025 mol (1.5 gm) of Urea $(NH_2)_2CO$ and 1 mmol (12.358 gm) of ammonium molybdate tetrahydrate $((NH_4)_6Mo_7O_{24}.4H_2O)$ dissolved into 20 mL ammonia solution (25%) and stirred till it become transparent. The pH of the solution has been optimised to 1-2 by addition of acetic acid. This solution mixture (Mo-X) was further used for synthesis of CuMoCat1, CuMoCat2 and CuMoCat3.

While for synthesis Mo_2C and Mo_2N this solution mixture has been hydrothermally heated at 180 °C for 24 hr and dried (Mo-Y).

c. Synthesis of Mo-Cu-rGO precursor

A Mo-Cu-rGO was prepared by mixing of as obtained Mo-X solution precursor with 50 ml ethanolic solution of copper nitrate and 200 mg of rGO. Here, 0.05 mmol for CuMoCat1, 0.3 mmol for CuMoCat2 and 0.5 mmol for CuMoCat3 copper nitrate have been used to prepare Mo-Cu-rGO precursor of different copper concentration followed by the sonication for 2 h. The obtained dispersion transferred into a hydrothermal bomb and heated at 180 °C for 24 h and dried.

2. Synthesis of catalyst

a. Synthesis of Mo_2C

The 200 mg of Mo precursor (Mo-Y) with 300 mg of rGO was mixed with mortar pestle and kept in the quartz tube of the tubular furnace. The precursor was heated for 2 h at 720 ºC temperature in an argon atmosphere with a flow rate of 30 mL/min.

b. Synthesis of Mo_2N

The Mo_2N is obtained by annealing the mixture of 200 mg of Mo precursor (Mo-Y) and 100 mg of rGO by crushing it in mortar pestle and kept it in furnace tube in ammonia atmosphere for 2 h at 600 ºC with a flow rate of 20 mL/min.

c. Synthesis of MoCat-CN

The 200 mg of Mo precursor (Mo-Y) with 300 mg of rGO was mixed with mortar pestle and kept in the sealed quartz tube of the tubular furnace. The precursor was heated for 1 h at 600 ºC temperature in ammonia environment with a flow rate of 20 mL/min and 2 h at 720 ºC temperatures in argon atmosphere with a flow rate of 30 mL/min.

d. Synthesis of CuMoCat1, CuMoCat2, and CuMoCat3

The CuMoCat1, CuMoCat2 and CuMoCat3 catalyst has been synthesized by mixing of 200 mg of respective Mo-Cu-rGO precursor as mentioned in section 1c above with 500 mg of rGO in mortar pestle and kept in quartz tube of tubular furnace. The precursor was heated for 1 h at 600 ºC temperature in ammonia environment with a flow rate of 20 mL/min and 2 h at 720 ºC temperatures in argon atmosphere with a flow rate of 30 mL/min.

Note: The heating rate during the annealing was kept at 5 °C/min in all the reactions

S2. PXRD of MoCat-CN, Mo_2C, Mo_2N and RGO

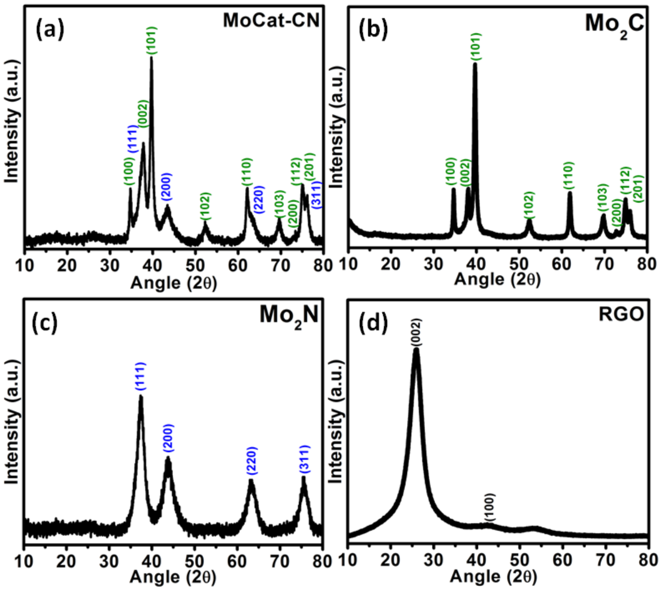

Figure S1. **PXRD of (a) MoCat-CN consist of Mo_2C and Mo_2N phases (b) Mo_2C (c) Mo_2N and (d) RGO**

S3. Rietveld Refinement

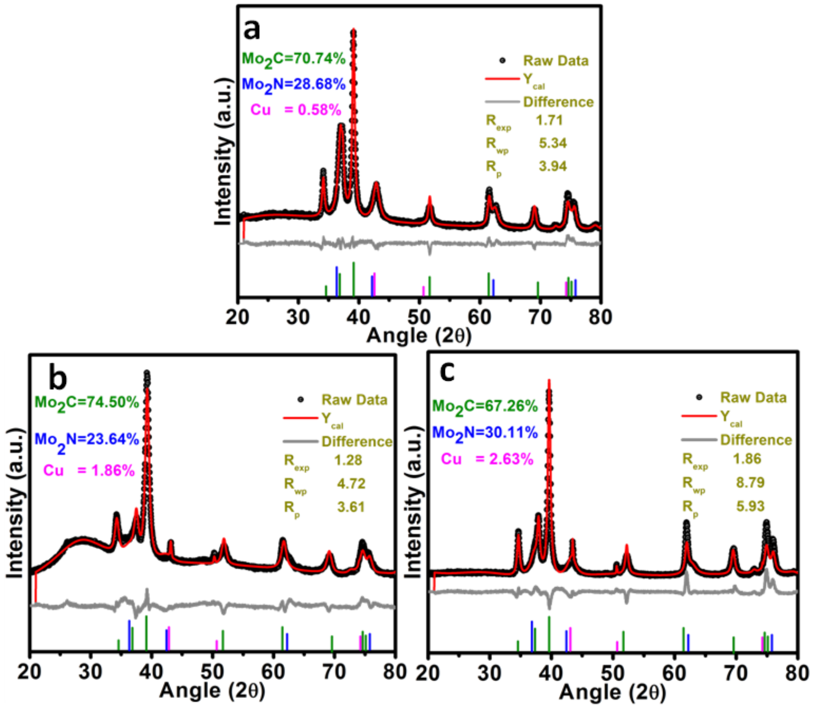

Figure S2. Rietveld refinement of (a) CuMoCat1, (b) CuMoCat2 and (c) CuMoCat3 catalyst. Rietveld analysis of catalyst shows a composition 0.58 %, 1.86 % and 2.63 % of Cu in the CuMoCat1, CuMoCat2 and CuMoCat3 catalyst respectively. The figure typically shows existence of all three Mo_2C, Mo_2N, and Cu phases.

S4. BET analysis of CuMoCat

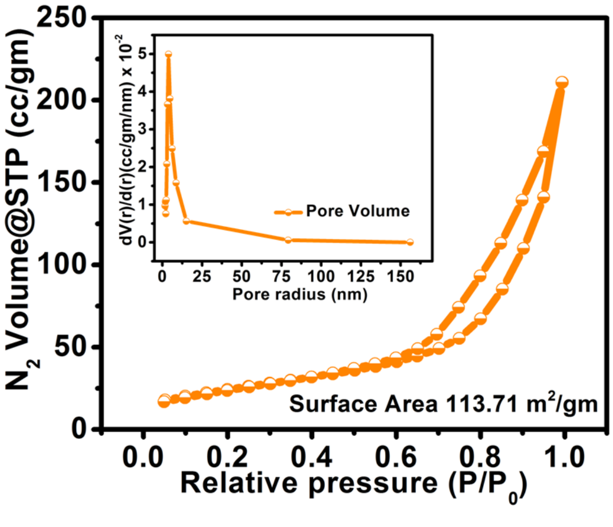

Figure S3. Nitrogen adsorption-desorption BET isotherms and inset showing BJH pore size distribution. The curve represents the mesoporous structure of the catalyst.

S5. XPS Survey spectrum of CuMoCat

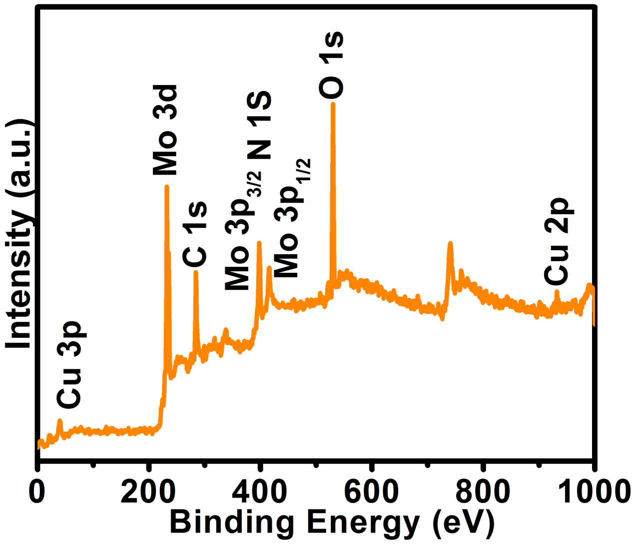

Figure S4. XPS wide angle spectrum of CuMoCat catalyst. The spectrum consists of peaks at binding energy corresponds to Mo, C, N and Cu elements present in the CuMoCat catalyst.

S6. Deconvoluted peak parameters of the XPS analysis

Element	Peak	BE (eV)	FWHM	Area (%)
Mo 3d	Mo^{2+}	228.5 and 231.6	1.613 and 1.613	6.82 and 16.43
	Mo^{6+}	232.4 and 235.5	1.734 and 1.734	37.68 and 39.05
C 1s	Mo_2C	284.2	1.671	61.55
	C-N	285.3	3.317	38.44
N 1s	Mo_2N	395.4	2.674	23.65
	N-C	398.1	2.638	51.32
	N-Q	401.2	2.312	25.03
Cu 2p	Cu^{+}	932.6	2.391	56.26
	Cu^{2+}	933.7	3.034	43.73

Table S1. Table showing the existing elements with corresponding deconvoluted peaks positions and FWHM values.

S7.1. Electrochemical Study of CuMoCat1, CuMoCat2 and CuMoCat3

From the polarisation curve, the measured overpotential value of CuMoCat1, CuMoCat2 and CuMoCat3 are 112, 147 and 163 mV respectively.

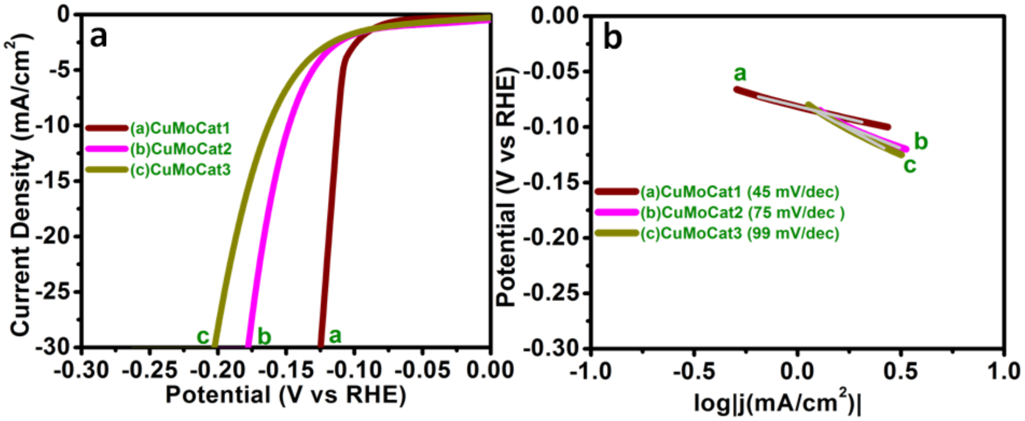

Figure S5. (a) Polarization curves and corresponding (b) Tafel slope of CuMoCat1, CuMoCat2 and CuMoCat3 catalysts in 0.5 M H_2SO_4 solution.

S7.2. Table for electrochemically measured kinetic parameters

Catalyst	Onset (vs RHE)	η_{10} (vs RHE)	η_{20} (vs RHE)	η_{30} (vs RHE)	Tafel Slope (mV/dec)	Exchange Current Density (mA/cm^2)
CuMoCat	40 mV	82 mV	101 mV	112 mV	33	3.12×10^{-2}
CuMoCat1	77 mV	112 mV	119 mV	125 mV	45	2.97×10^{-2}
MoCat-CN	26 mV	127 mV	182 mV	217 mV	111	2.43×10^{-3}
CuMoCat2	78 mV	147 mV	166 mV	178 mV	75	1.96×10^{-3}
CuMoCat3	75 mV	163 mV	186 mV	202 mV	99	1.09×10^{-3}
Mo_2C	233 mV	294 mV	320 mV	340 mV	64	1.17×10^{-4}

Table S2. Table showing all electrochemical kinetic parameters of all the electrocatalysts

S7.3 Durability test

The long term stability of CuMoCat is performed and shown below.

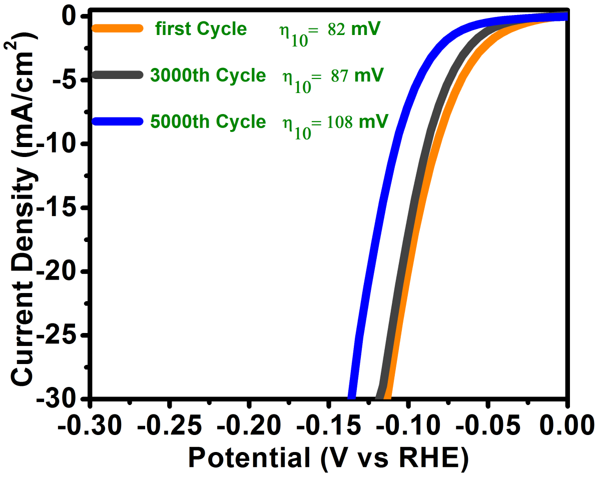

Figure S6: LSV stability curve of CuMoCat catalyst

The stability of the catalyst after 5000 cycles are shown in the above figure and was found to shift from 87 mV to 108 mV.

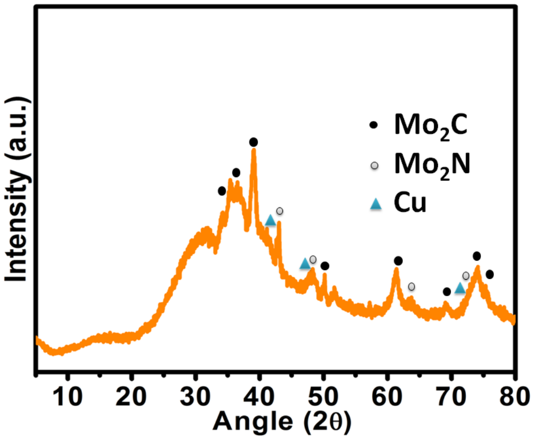

Figure S7: XRD pattern of CuMoCat catalyst after stability performing 5000 LSV Cycles in 0.5 M H_2SO_4

S.8. Theoretical Studies

Vienna Ab-initio Simulation Package (VASP) with projector-augmented wave (PAW) method and the Perdew, Burke, and Ernzerhof (PBE) exchange-correlation functional version of the generalized gradient approximation (GGA) is used for the relaxed ground states and adsorption energy calculation. Supercell of the heterostructure has 128 atoms and dimensions a=8.50 Å, b=24.58 Å and c=16.17 Å. Heterostructure is shown in Fig. S6.

Separate calculation is performed for the Mo_2C and Mo_2N slab with 24 atoms and 28 atoms respectively. The dimension of Mo_2C is a=9.50 Å, b=18.22 Å and c=5.24 Å and Mo_2N is a=8.52 Å, b=4.26 Å and c=24.26Å. Structure relaxation is performed using PAW method and PBE exchange-correlation functional as implemented in VASP with k-point mesh 5×5×1. The obtained bond length and adsorption energy for the Mo_2C and Mo_2N individual slab is listed in Table. S3 and S4. Individual Mo_2C or Mo_2N slab has comparatively higher absorption energy compare to heterostructure at Mo/C/N sites.

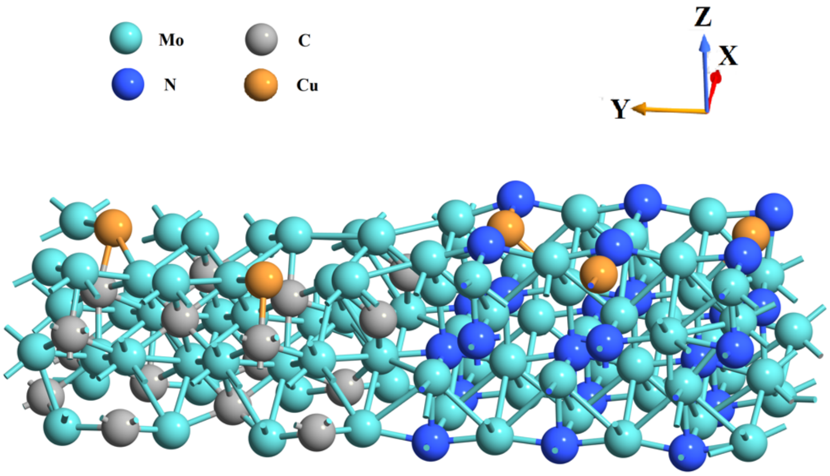

Figure S8. Structure figure showing Cu is dopped both in Mo_2N and Mo_2C site.

Table S3.

Adsorption site on Mo_2N (doped/undoped)	**Bond length (Å)**		**ΔE_{ads} (eV)**		**ΔG (eV)**	
	doped	**undoped**	**doped**	**undoped**	**doped**	**undoped**
Mo	**1.78**	**1.753**	**-0.268**	**-0.572**	**-0.028**	**-0.332**
N	**1.031**	**1.039**	**0.274**	**0.5914**	**0.514**	**0.8314**
Cu	**1.478**	**-**	**0.817**	**-**	**1.057**	**-**

Table S4.

Adsorption site on Mo_2C (doped/undoped)	**Bond length (Å)**		**ΔE_{ads} (eV)**		**ΔG (eV)**	
	doped	**undoped**	**doped**	**undoped**	**doped**	**undoped**
Mo	**1.761**	**1.755**	**-0.2219**	**0.0829**	**0.018**	**0.3229**
C	**1.123**	**1.121**	**-0.803**	**-0.645**	**-0.563**	**-0.405**
Cu	**1.527**	**-**	**0.5020**	**-**	**0.7420**	**-**