Supplimentary Information

Cu/Fe embedded N-doped carbon as highly durable oxygen reduction electrocatalyst

Banafsha Habib[a, b], Shaowei Chen[b], Forrest Nichols[b], Shamraiz Talib[c], Nasima Arshad[d], Anham Zafar[a], Arshad Mahmood[e], Shahid Zaman[f], Naveed Janjua*[a]*

[a]Department of Chemistry Quaid-i-Azam University, Islamabad, 45320, Pakistan

[b]Department of Chemistry and Biochemistry, University of California, 1156 High Street, Santa Cruz, California 95064, USA

[c]Department of Chemistry and Key Laboratory of Organic Optoelectronics & Molecular Engineering of Ministry of Education, Tsinghua University, Beijing 100084, China

[d]Department of Chemistry, Allama Iqbal Open University Islamabad Pakistan

[e]Material Science and Engineering Division, National Institute of Laser and Optronics/PIEAS, Islamabad, 45650, Pakistan

[f]Institut d'Innovations en Écomatériaux, Écoproduits et Écoénergies, Université du Québec à Trois-Rivières, 3351 boul. des forges, Trois-Rivières, Québec G8Z 4M3, Canada

Correspondence: shahid.zaman@uqtr.ca (S. Zaman), nkjanjua@qau.edu.pk (N. K. Janjua)

Materials and methods

Chemicals

All the chemicals, Pt/C (20wt %), copper (II) chloride dihydrate ($CuCl_2 \cdot 2H_2O$), zinc nitrate hexahydrate ($ZnNO_3 \cdot 6H_2O$), potassium hydroxide (KOH), 2-methylimidazole ($CH_3C_3H_2N_2H$), ferric chloride anhydrous ($FeCl_3$), tannic acid ($C_{76}H_{52}O_{46}$), potassium thiocyanate (KSCN) and H_2O (18.3 MΩ·cm) were purchased from certified ACS fisher chemicals and were used as received without further purification.

Preparation of ZIF-8

For the synthesis of ZIF-8, $ZnNO_3 \cdot 6H_2O$ (1.116 g), 30 mL of methanol was dissolved in one flask (solution 1), and in another flask, 2-methylimidazole (1.232 g) was dissolved in 30 mL of methanol (solution 2). Mix both solutions under sonication for 10 min until the solution mixture turns from transparent to milky white. Transfer this solution into a Teflon-lined stainless-steel autoclave (100 mL) at 120 °C for 3.5 h. Then collected the milky white precipitates with methanol by centrifugation for 10 min at 6000 rpm, and dried in the vacuum oven for 24 h at 50 °C. These dried precipitates were called ZIF-8 crystals.

Preparation of hollow ZIF-8

To prepare hollow ZIF-8, 80 mg of ZIF-8 crystals were taken and dispersed in deionized H_2O (3 mL) and sonicated for 20 min. Tannic acid solution (5 mg mL^{-1} in water) was added under constant stirring until the solution changed color from milky white to orange. Finally, the solution was washed with deionized water and dried completely under the vacuum for 24 h at 50 °C.

Preparation of HNC

To synthesize HNC, the pyrolysis of hollow ZIF-8 was done and moved into the ceramic boats. These ceramic boats were placed in the middle of the tube furnace. The tube furnace was heated at 900 °C with an increasing and decreasing rate of 5 °C min^{-1} under the vacuum for 3 h. The obtained product was cooled to room temperature.

Preparation of Cu/Fe(x:y)-HNC

The HNC (20 mg) was dispersed in methanol (30 mL) and varying ratios of $CuCl_2 \cdot 2H_2O$ and anhydrous $FeCl_3$ *i.e.,* Cu/Fe (1:1), (2:1), (3:1), were added and sonicated for 30 min. These solutions were heated to reflux in an oil bath for 12 h. The synthesized precipitates were separated

and dried in vacuum for 24 h. The final products were sintered at 900 °C with an increasing rate of 5 °C and decreasing rate of 10 °C for 3 h. These final samples were labelled as Cu-HNC, Fe-HNC, and Cu/Fe (1:1)-HNC, Cu/Fe (2:1)-HNC, and Cu/Fe (3:1)-HNC, respectively. [40]
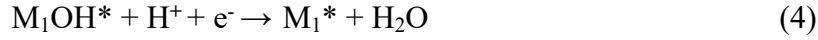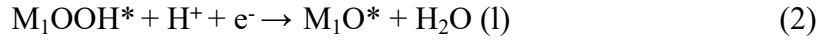
Electrode modification

A CHI-710 electrochemical workstation was used to evaluate the ORR activity of samples by means of a standard three-electrode cell, and Ag/AgCl (1M KCl), graphite rod and rotating gold ring disk electrode (RRDE) were used as reference, counter and working electrodes, respectively. The area for RRDE was estimated to be 0.246 cm^2. The reference electrode was calibrated against a reversible hydrogen electrode (RHE) and the ring potential was set at +1.5 V *vs.* RHE for ORR test. 2 mg of each sample were sonicated into 1 mL of isopropanol for 15 min to prepare the catalyst inks and 100 wt % of Nafion solution (10 μL) was subsequently added and sonicated for 25 min to form a homogeneous ink. 20 μL of the ink were drop-casted onto the glassy carbon disk electrode which was dried at room temperature. Finally, 5 μL of a 20 wt% Nafion solution were drop casted onto it. The loaded amount of the catalyst was 0.162 mg cm^{-2}.

DFT calculations

Code of Vienna Ab-initio Simulation Package (VASP) was used to determine DFT calculations. At the same time, generalized gradient approximation (GGA) of Perdew-Burke-Ernzerhof (PBE) was employed to determine exchange- correlation term. Projector-augmented wave, pseudopotentials were used to model the interactions between outer and core electrons. [35] The cutoff energy for the plane-wave expansion was set to 450 eV. For geometry optimization total energy and residual forces to be employed are 2 eV/A^{-1} and 0.02 eV/A^{-1}, respectively. To avoid the interlayer interactions, a model consisting of 2×2×1 supercell has been optimized in a periodically repeated slab with a vacuum layer of 20 Å. The reciprocal space was sampled by the gamma points in the Brillouin zones with a grid of 3×3×1. Gibbs free energy change (ΔG) was computed for each elemental step via a standard hydrogen electrode (SHE).

The number of electrons involved in the oxygen reduction process on Cu/Fe (2:1)-HNC interface using Figure 4, was calculated to be closer to 4, suggesting that ORR on Cu/Fe (2:1)-HNC platforms predominantly follows 4-electron reduction pathways as detailed in the following steps:

$$M_1* + O_2 \text{ (g)} + H^+ + e^- \rightarrow M_1OOH* \qquad (1)$$

$$M_1OOH^* + H^+ + e^- \rightarrow M_1O^* + H_2O \text{ (l)} \qquad (2)$$

$$M_1O^* + H^+ + e^- \rightarrow M_1OH^* \qquad (3)$$

$$M_1OH^* + H^+ + e^- \rightarrow M_1^* + H_2O \qquad (4)$$

The difference of Gibbs free energies (ΔG_{OOH^*}, ΔG_{O^*}, ΔG_{OH^*}) involving electron transfers for all the elementary steps were calculated by using the following equation:

$$\Delta G = \Delta E + \Delta ZPE - T\Delta S + \Delta G_U + \Delta G_{pH} \qquad (5)$$

where ΔE corresponds to the energy difference among the free-standing and adsorption states of reaction intermediates, ΔZPE is the change in zero-point energies, ΔS is the entropy change, and T is the temperature (T=298.15 K), respectively. DFT calculations were attained from the vibrational frequency which intern directly provided the adsorption energies of ΔE. ΔG_U = -eU, where "e" and "U" are the number of electrons transferred and "U" denotes the optimal potential established on the SHE. ΔG_{pH} directs the Gibbs free energy correction of the pH, which can be calculated by: ΔG_{pH} = -k_BT In10^*pH, where k_B is the Boltzmann constant (1.380649×10^{-23} JK^{-1}) and T indicates 298.15 K. The vibrational frequencies and entropies of the molecules in gas phase were taken from the NIST database. The ΔG of four elementary steps for ORR processes can be defined as: $\Delta G_1 = \Delta G_{OOH^*} - 4.92$ eV, $\Delta G_2 = \Delta G_{O^*} - \Delta G_{OOH^*}$, $\Delta G_3 = \Delta G_{OH^*} - \Delta G_{O^*}$, $\Delta G_4 = \Delta G_{OH^*}$. The overpotential ($\eta$) is a primary parameter used to further justify the catalytic activity of ORR, (η^{ORR}) was calculated by using the following equation, [41]

$$\eta^{ORR} \text{ (V)} = \max [\Delta G_1, \Delta G_2 \, \Delta G_3, \Delta G_4] / e + 1.23 \qquad (6)$$
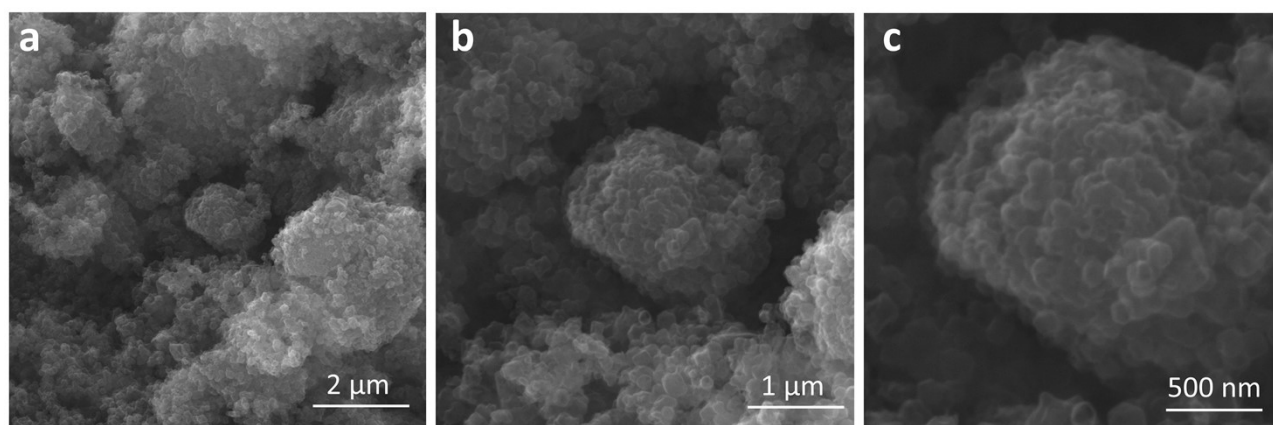
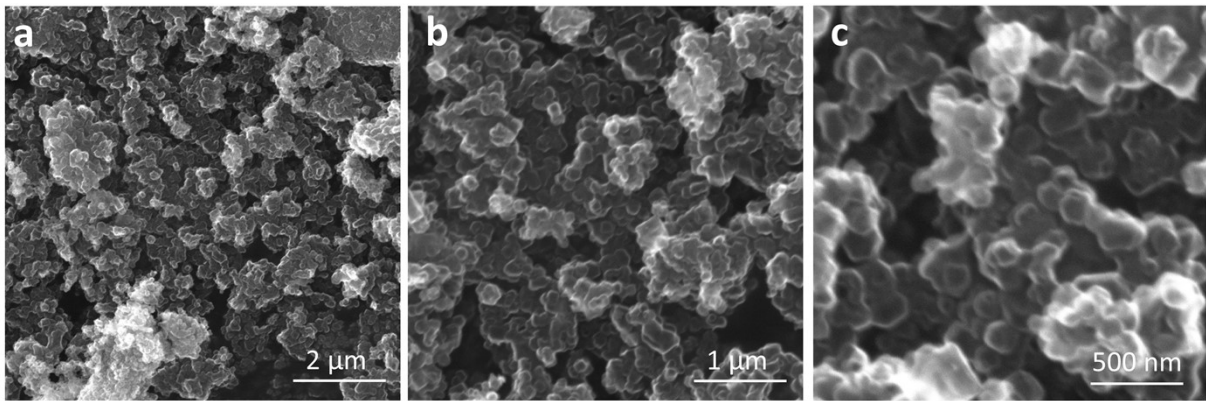**Figure S1.** SEM images of Cu/Fe (1:1)-HNC.
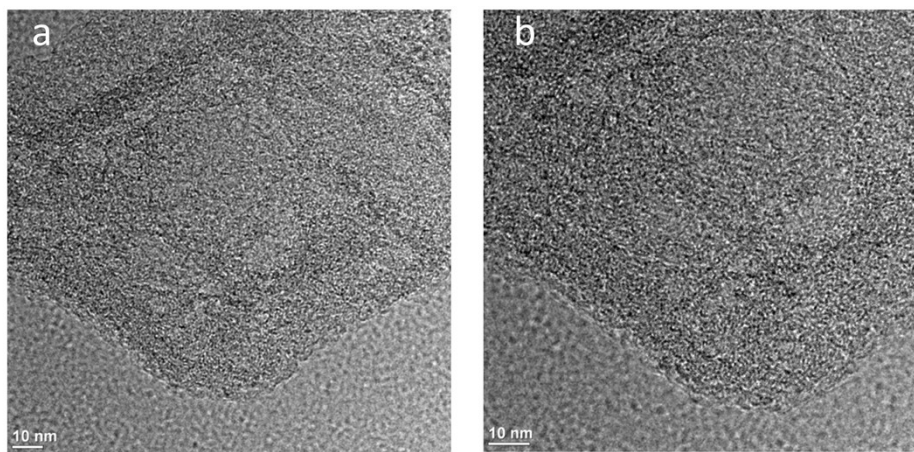
Figure S2. SEM images of Cu/Fe (3:1)-HNC.

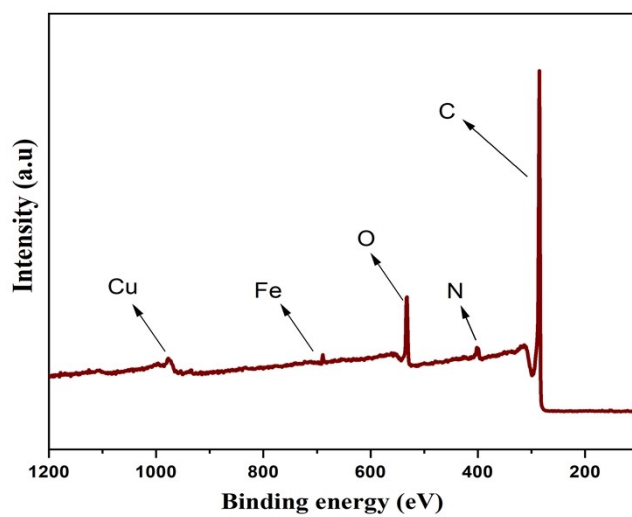**Figure S3.** TEM images of Cu/Fe (2:1)-HNC at 10 nm.

Figure S4. survey spectra demonstrate the presence of Cu at 934, Fe at 710 and N at 400 and O at 531, and C at 285 eV respectively in the Cu/Fe (2:1)-HNC.
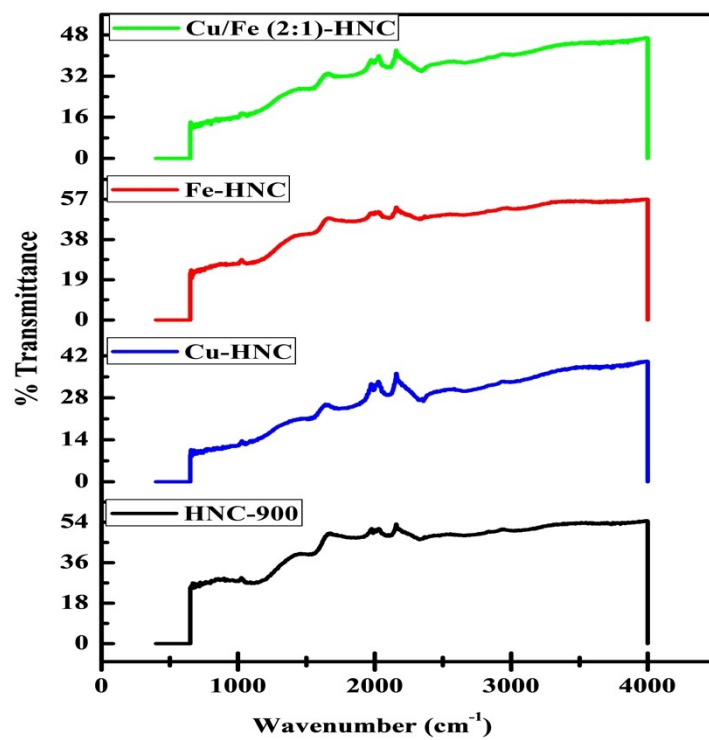
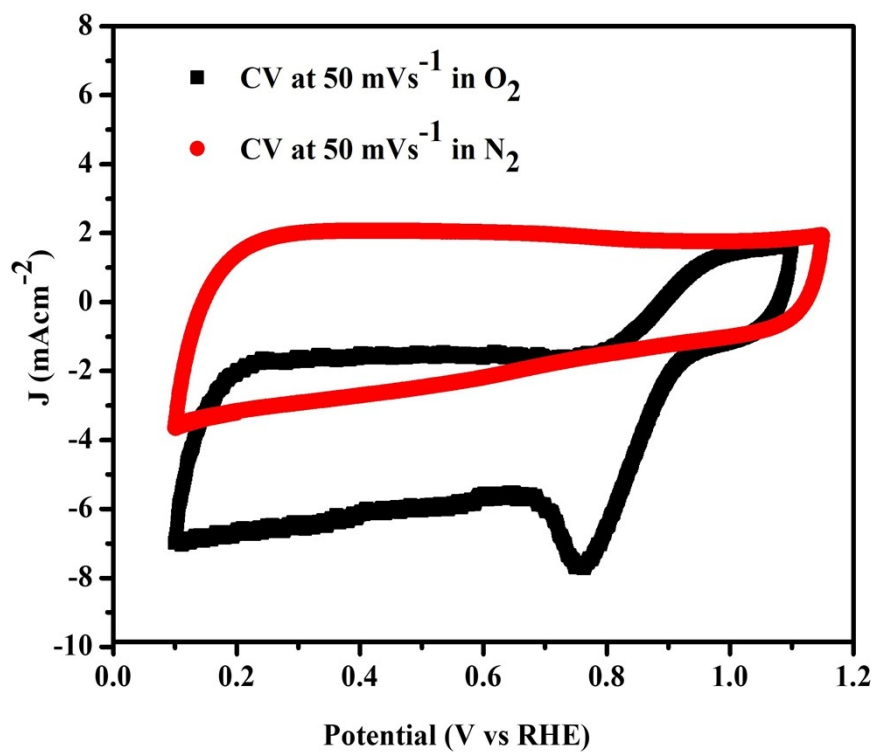**Figure S5.** FTIR spectra for HNC, Cu-HNC, Fe-HNC, and Cu/Fe (2:1)-HNC

Figure S6. Cyclic Voltammetry profile of the best catalyst Cu/Fe (2:1)-HNC in N_2 and O_2 saturated 0.1 M KOH solution.
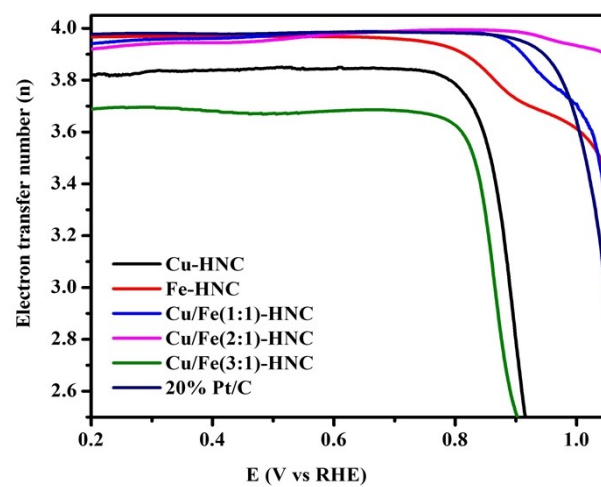
Figure S7. Variation of the electron transfer number (n) with electrode potential for all the catalysts along with benchmark 20% Pt/C.
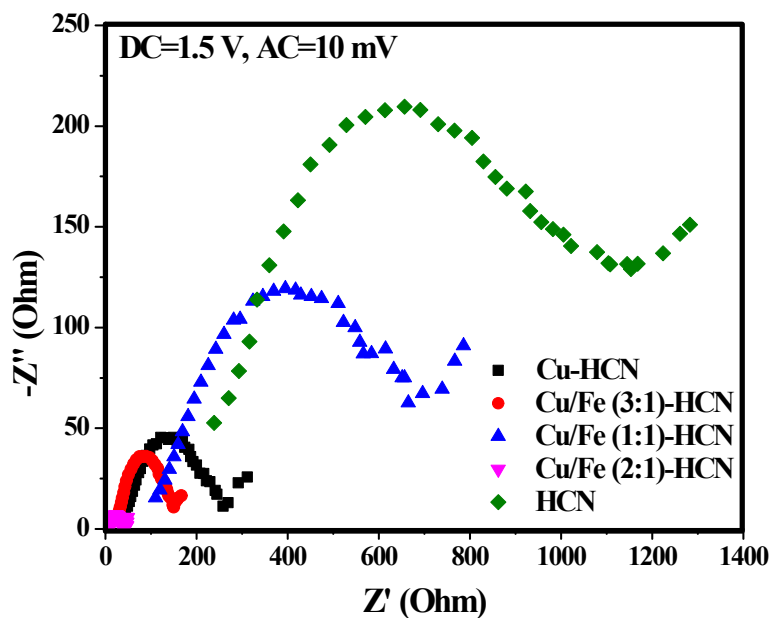
Figure S8. EIS performance of HNC, Cu-HNC, Fe-HNC, Cu/Fe(1:1)-HNC, Cu/Fe(2:1)-HNC and Cu/Fe(3:1)-HNC in 1M KOH.

Table S1. Summary of E_{onset} and $E_{1/2}$ of all the catalysts with Tafel slope values and "n" number

Catalysts	E_{On} (V *vs.* RHE)	$E_{1/2}$ (V *vs.* RHE)	n at +0.7 V	Tafel slope (mV/dec)
HNC-900	0.855	0.69	3.50	177
Cu-HNC	0.96	0.82	3.84	111
Fe-HNC	0.90	0.73	3.93	115
Cu/Fe(1:1)-HNC	0.95	0.78	3.98	110
Cu/Fe(2:1)-HNC	1.01	0.84	3.98	104
Cu/Fe(3:1)-HNC	0.90	0.76	3.68	96
20% Pt/C	1.00	0.82	3.98	115

Table S2. Summary of the kinetic current density of different catalysts at 0.8 V, 0.85 V,

and 0.9 V

Catalysts	J_k at +0.8 V (mAcm^{-2})	J_k at +0.85 V (mAcm^{-2})	J_k at +0.9 V (mAcm^{-2})
HNC-900	-0.25	-1.158	-0.130
Cu-HNC	-3.704	-1.678	-0.455
Fe-HNC	-1.029	-0.456	-0.255
Cu/Fe(1:1)-HNC	-1.803	-0.721	-0.174
Cu/Fe(2:1)-HNC	-4.674	-2.859	-1.174
Cu/Fe(3:1)-HNC	-1.298	-0.273	-0.077
20% Pt/C	-3.891	-2.243	-1.019

Table S3: Comparison of ORR active catalysts and activity parameters

Catalysts	E_{on} (V *vs.* RHE)	$E_{1/2}$ (V *vs.* RHE)	n	Electrolyte	References
Cu-HNC 900	0.96	0.81	3.97	0.1 M KOH	(This work)
Cu/Fe(2:1)-HNC	1.01	0.84	3.98	0.1 M KOH	(This work)
Ir-HNC 900	1.00	0.83	3.93	0.1 M KOH	(This work)
Cu-SAs/N-C	0.95	0.81	3.80	0.1 M KOH	Nat. Catal. 2018, 1, 781-786.
Co-ISAS/p-CN	0.97	0.83	3.87	0.1 M KOH	Adv. Mater. 2021, 1706508.
Co@Co3O4/NC-1	0.94	0.80	3.76	0.1 M KOH	Angew. Chem. Int. Ed. 2019, 55, 4087-4091.
Fe-N-SCCFs	1.00	0.88	3.98	0.1 M KOH	Nano Lett. 2017, 17, 2020-2021.
S,N-Fe/N/CCNT	0.95	0.82	3.86	0.1 M KOH	Angew. Chem. Int. Ed. 2017, 56, 610.
D-AC@2Mn-4Co	0.92	0.79	3.80	0.1 M KOH	Adv. Mater. 2020, 28, 8771.

Table S4. Summary of electrochemical parameters retrieved from EIS and CV for all the catalysts in 1 M KOH

Sample Code	Diffusion Coefficient D° $/\times10^{-9}$ $(cm^2.s^{-1})$	Mass Transport Coefficient, m_T $/\times10^{-4}$ $(cm.s^{-1})$	α	E_{On} (10 mAcm^{-2}) vs. RHE	Overpotential (V) at 10 mA.cm^{-2}
Cu-HCN	3.624	1.118	0.563	2.240	1.011
CuFe(1,1)-HCN	4.131	1.268	0.547	2.246	1.016
CuFe(2,1)-HCN	4.933	1.386	0.501	2.252	1.022
CuFe(3,1)-HCN	4.266	1.289	0.796	2.070	0.841