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

Electronic Supporting Information

Atomically Precise Copper Nanoclusters as Potential Catalyst for Electrochemical Oxygen Evolution Reaction (OER)

Vishal Saini,‡[a] Krishankant‡,[b] Shweta Choudhary,[a] Ashish Gaur,[b] Swastika Banerjee,[a]* Vivek Bagchi[b]* and V. Venkatesh[a]*

[a]Department of Chemistry, Indian Institute of Technology Roorkee, Roorkee-247667, Uttarakhand, India. E-mail: venkatesh.v@cy.iitr.ac.in, sbanerjee@cy.iitr.ac.in

[b]Institute of Nano Science and Technology, Sector-81, Knowledge City, SAS Nagar, Mohali, Punjab 140306, India. E-mail: vivekbagchi@gmail.com

***Corresponding Authors**

Table of Content

ATR-FTIR Spectra of 4-Mercaptopyridine and CuNCs@4MP

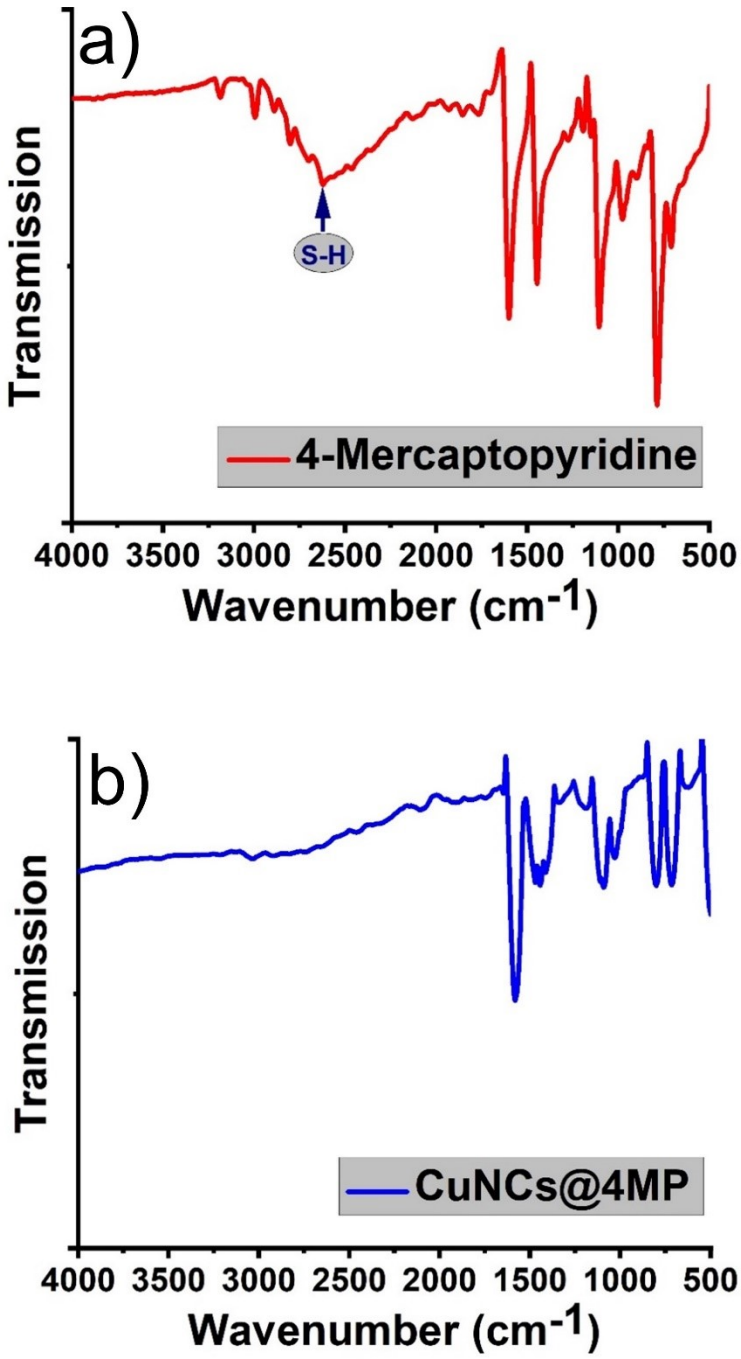

Fig. S1: ATR-FTIR spectra of a) 4-Mercaptopyridine (4MP); b) CuNCs@4MP, absence of S–H stretching at 2622 cm^{-1} after CuNCs formation.

Field emission scanning electron microscope (FESEM) images of solid sample of CuNCs@4MP

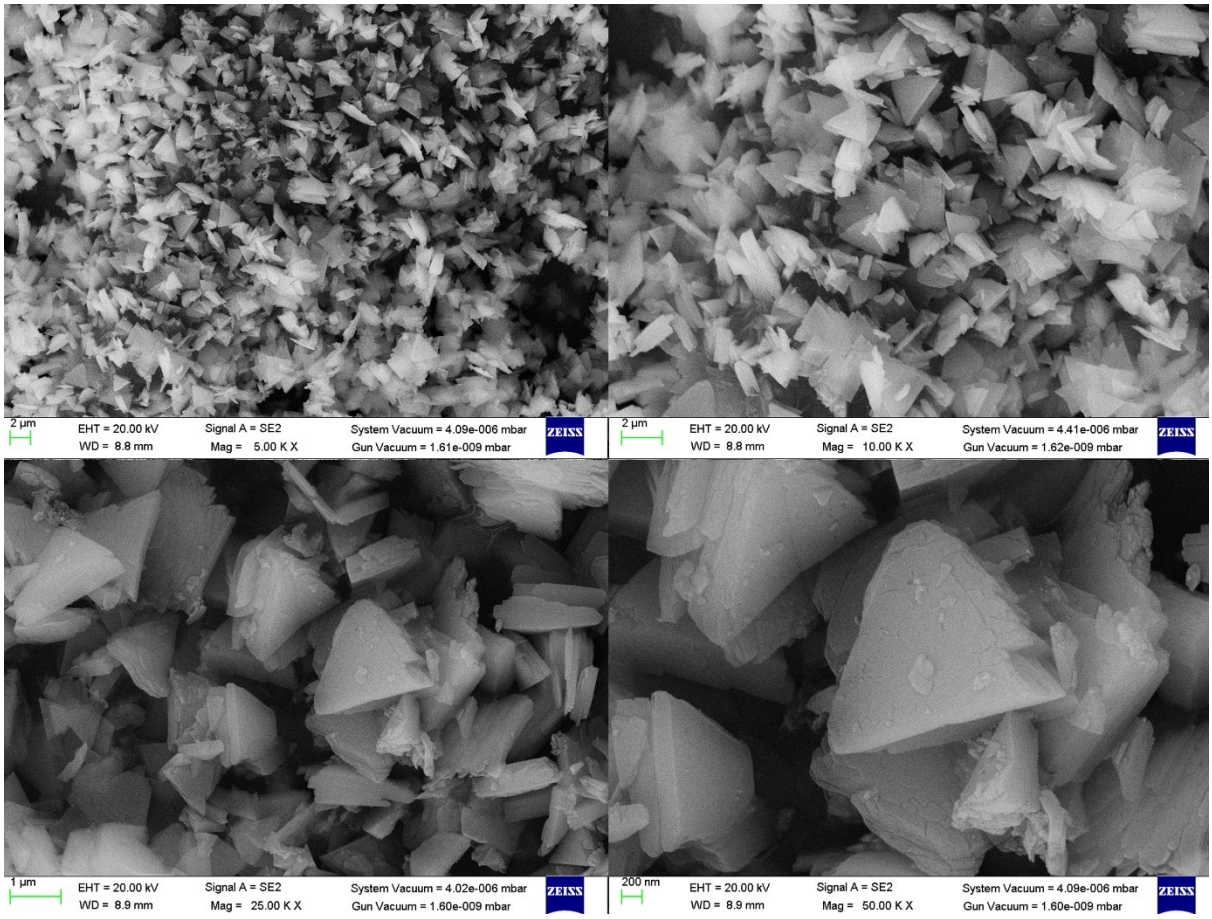

Fig. S2: The FESEM images of solid samples of CuNCs@4MP showing the chips like morphology.

EDX spectra of CuNC@4MP

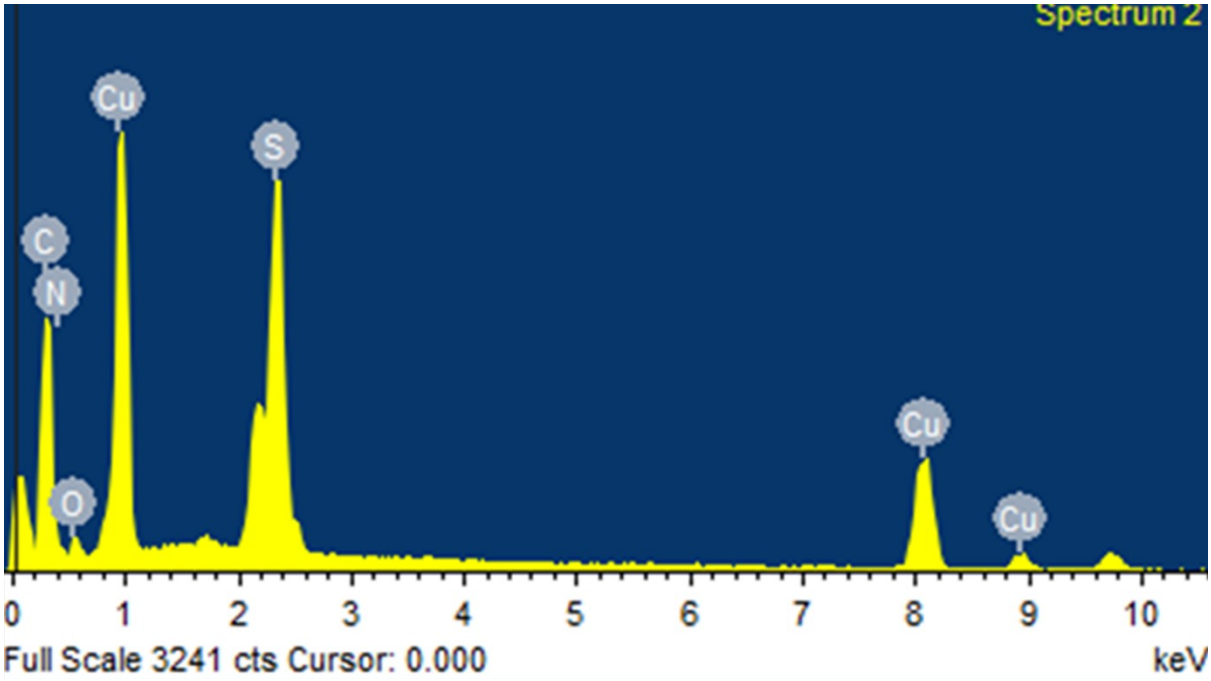

Fig. S3: Energy-dispersive X-ray (EDX) analysis confirmed the existence of Cu, C, N, and S in CuNCs@4MP.

Zeta potential of CuNCs@4MP

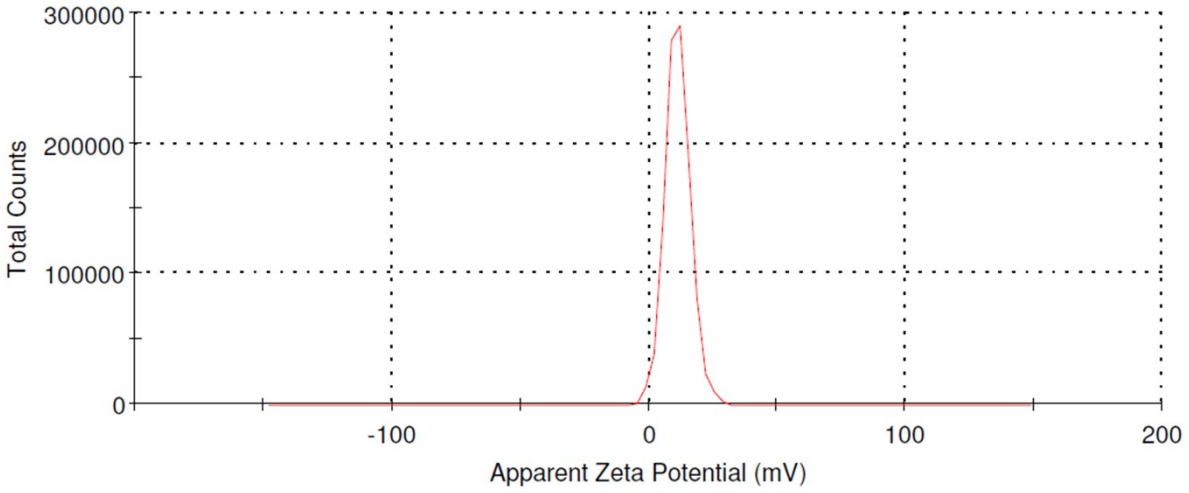

Fig. S4: The surface charge (i.e., zeta potential, ζ) of CuNCs@4MP was observed to be +11.5 ± 4.9 mV.

Stability of CuNCs@4MP at different pH

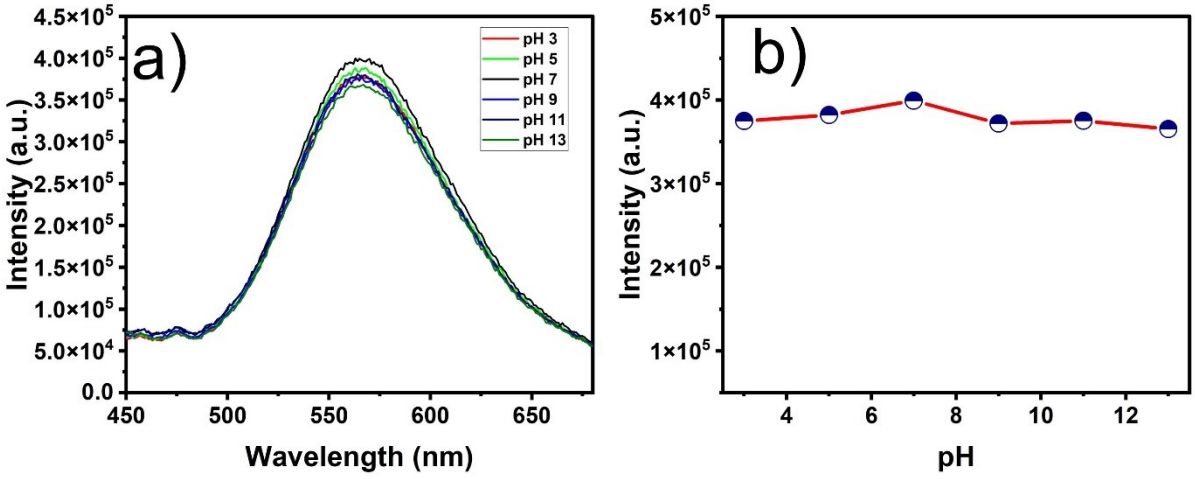

Fig. S5: a) Fluorescence emission spectra of CuNCs@4MP at different pH range (from pH 3 to 13); b) represents no significant changes in the emission intensity of CuNCs@4MP at different pH ranges.

Fluorescence intensity comparison of old and fresh sample of CuNCs@4MP

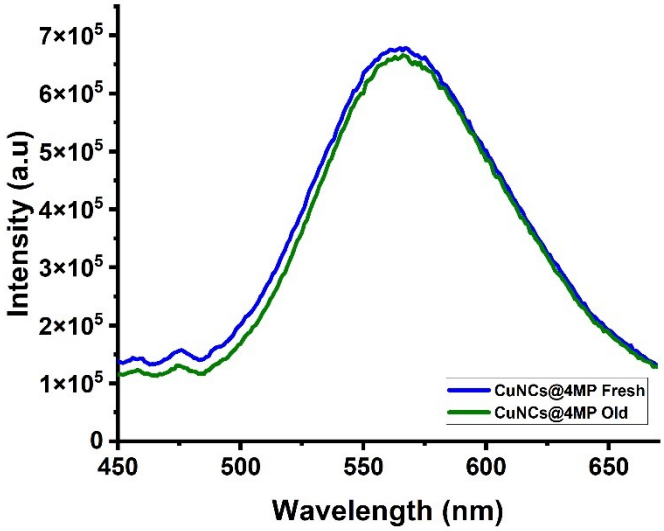

Fig. S6: Comparison of fluorescence emission intensities of freshly prepared and nine months old CuNCs@4MP.

ECSA normalized LSV and apparent TOF for CuNCs.

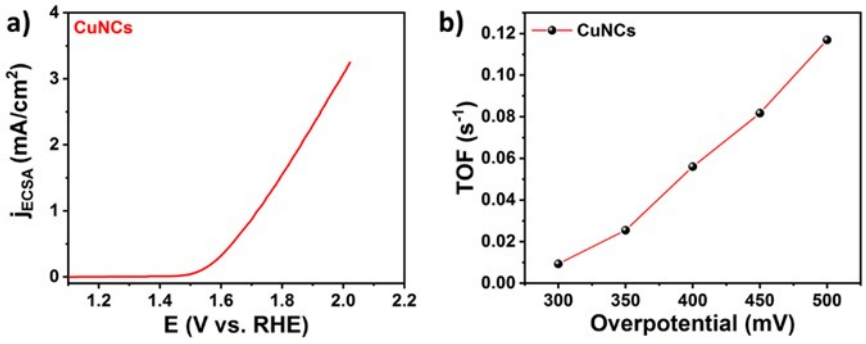

Fig. S7: a) ECSA normalized LSV and b) apparent TOF for CuNCs.

High resolution XPS of Cu 2p pre and post-OER CuNCs, and O1s

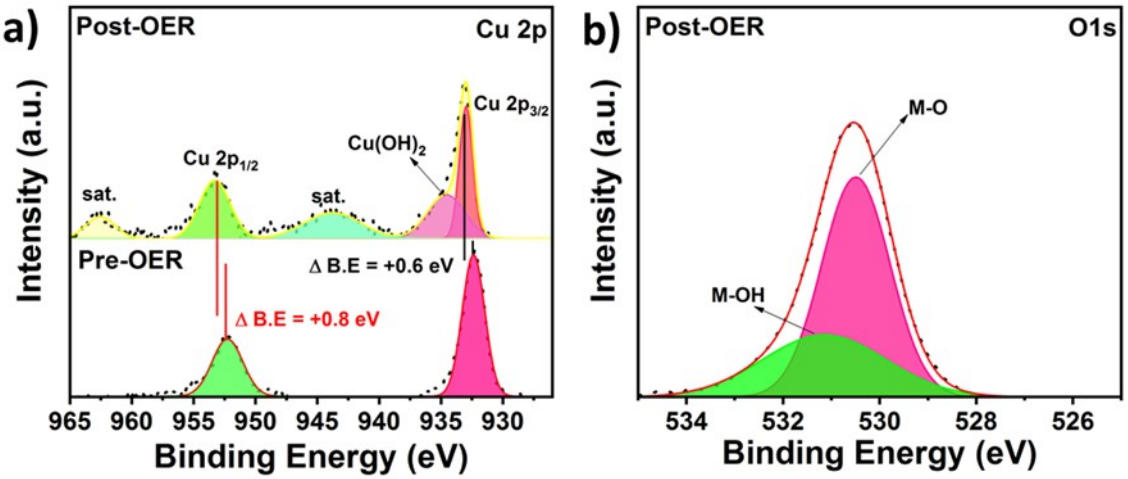

Fig. S8: High resolution XPS of a) Cu 2p pre and post-OER of CuNCs, and b) O1s

Morphological studies of pre and post OER treated CuNCs

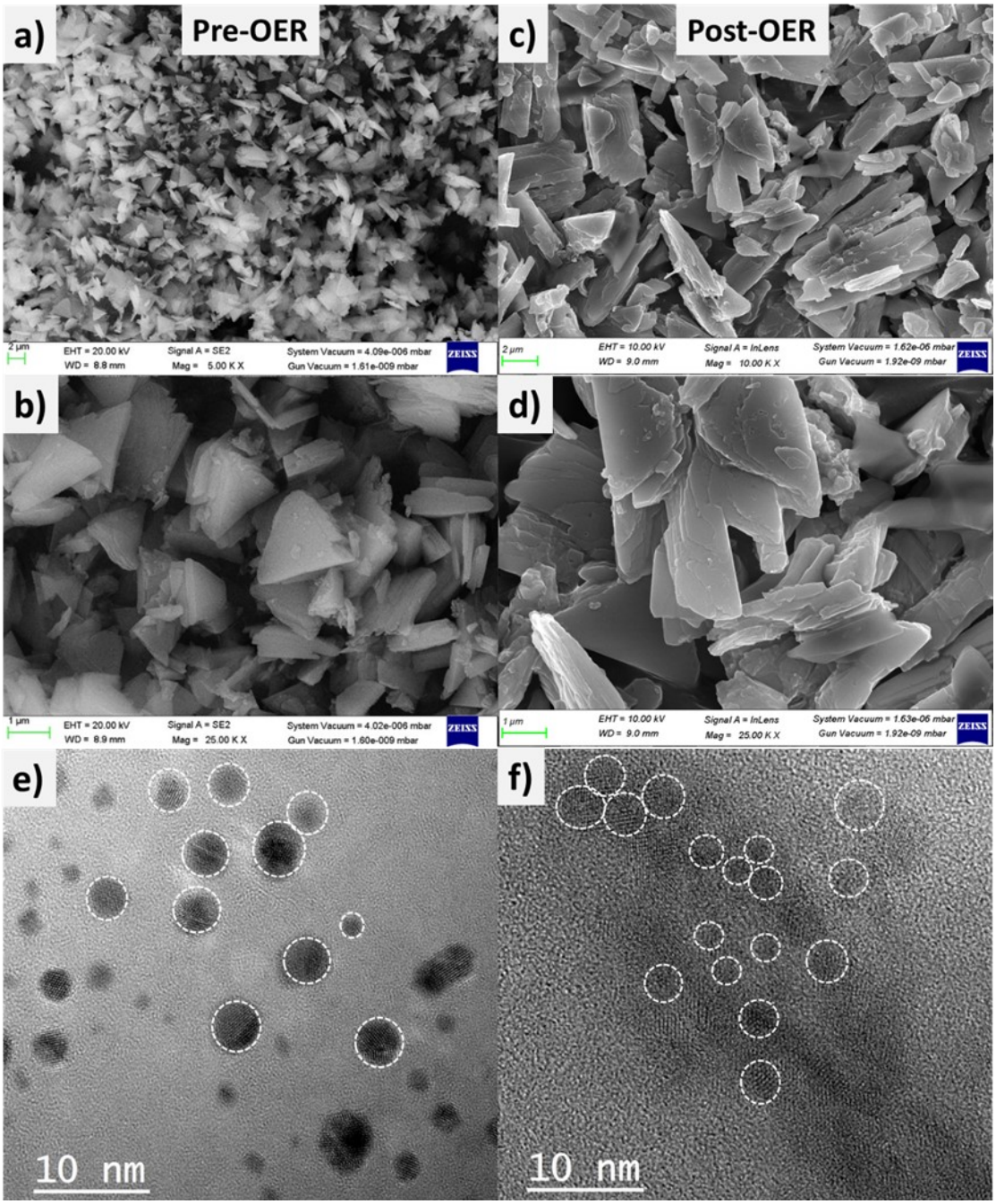

Fig. S9: FESEM micrographs of CuNCs a-b) pre-OER and c-d) post-OER at 2 and 1 µm respectively and TEM images of e) pre-OER and f) post-OER

Controlled comparative electrochemical tests

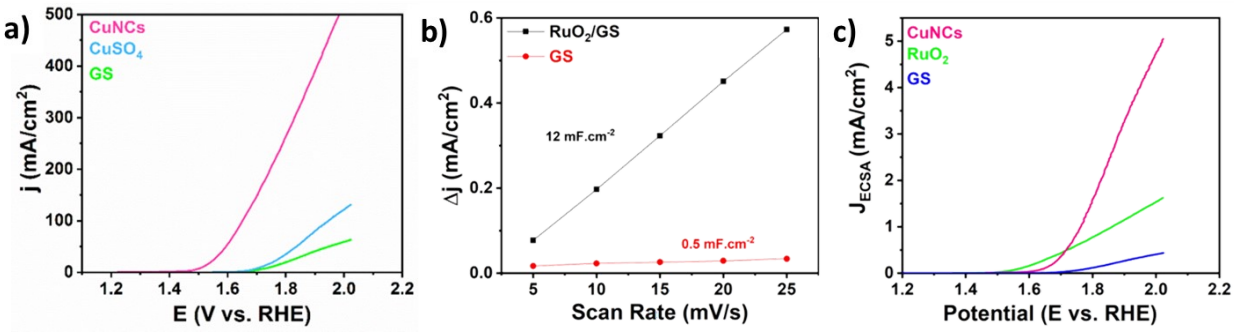

Fig. S10: a) Comparative plot of LSV, b) C_{dl} plot for RuO_2/GS and bare GS, c) ECSA normalized LSV plot.

DFT Calculations

For each of four OER elementary steps, ΔE at any applied potential U is expressed as:

$$\Delta E_1 = E(*OH) - E(*) + \tfrac{1}{2} E(H_2) - E(H_2O) - eU$$

$$\Delta E_2 = E(*O) - E(*OH) + \tfrac{1}{2} E(H_2) - eU$$

$$\Delta E_3 = E(*OOH) - E(*O) + \tfrac{1}{2} E(H_2) - E(H_2O) - eU$$

$$\Delta E_4 = E(O_2) + E(*) + \tfrac{1}{2} E(H_2) - E(*OOH) - eU$$

with total energy given as $E_n = \sum_{k=1}^{n} \Delta E_k$

and the theoretical overpotential (η) at U = 1.23 V is given by:

$$\eta = \left(\frac{1}{e} \max_{n = 1, 2, 3, 4} \Delta E_n\right) - U_o$$

where U_o is equilibrium potential, 1.23 V.

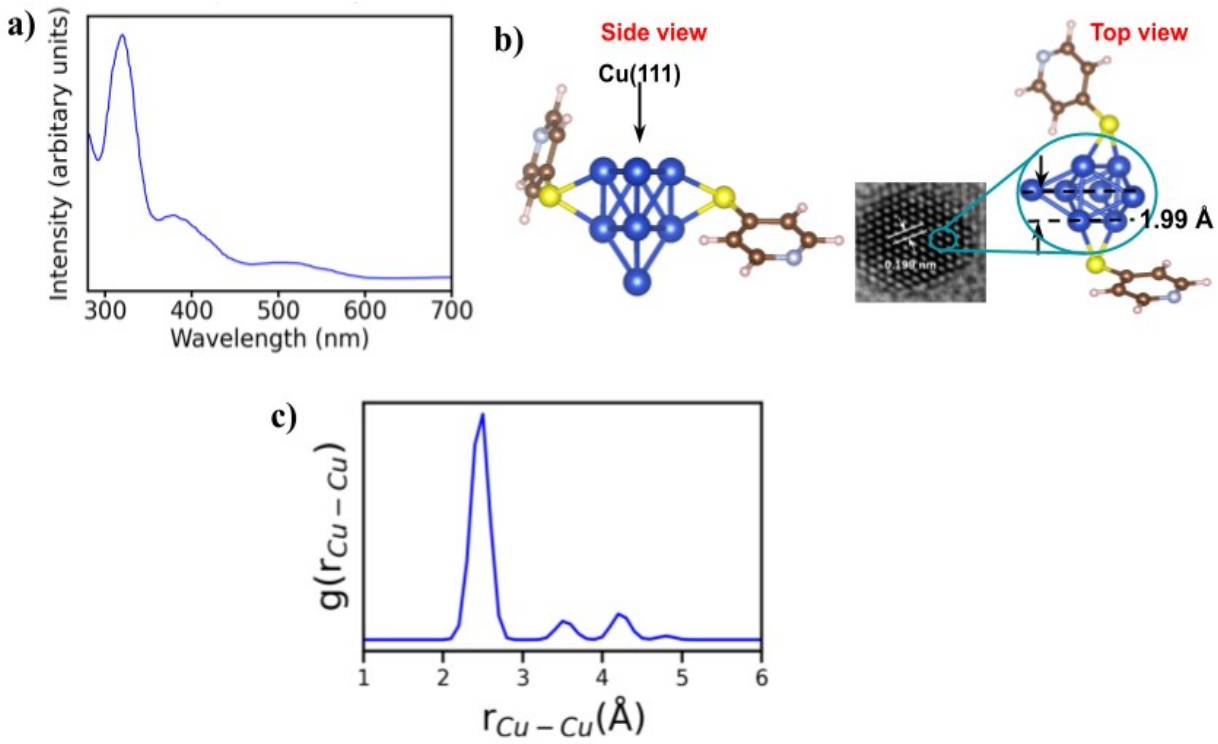

Fig. S11: a, b) Absorption spectra and the optimized structure of $Cu_8(4MP)_2$ nanocluster calculated using BSE@G_0W_0@B3LYP c) Radial distribution function (RDF) plot between Cu-Cu

Comparison of CuNCs@4MP stability with other reported nanoclusters

S.No.	Capping Ligand	Stability Time	Ref.
1.	ss DNA	30 minuets	1
2.	Egg white	48 hours	2
3.	PVP/Dihydrolipoic acid	3 days	3
4.	Cysteine	15 days	4
5.	BSA	18 days	5
6.	PVP	1 month	6
7.	Transferrin	1 month	7
8.	GSH	2 months	8
9.	BSA	2 months	9
10.	5-Methyl-2-thiouracil	3 months	10
11.	BSA	6 months	11
12.	**4-Mercaptopyridine**	**>9 months**	**This work**

Table S1: Stability of other reported CuNCs compared with our newly synthesized 4-Mercaptopyridine capped CuNCs.

References:

1. Z. Qing, X. He, D. He, K. Wang, F. Xu, T. Qing and X. Yang, *Angew. Chem., Int. Ed.*, 2013, **52**, 9719–9722.
2. D. Li, Y. Zhao, Z. Chen, X. Mei and X. Qiu, *Mater. Sci. Eng., C*, 2017, **78**, 653–657.
3. R. Ghosh, U. Goswami, S. S. Ghosh, A. Paul and A. Chattopadhyay, *ACS Appl. Mater. Interfaces*, 2014, **7**, 209–222.
4. K. Basu, S. Paul, R. Jana, A. Datta and A. Banerjee, *ACS Sustainable Chem. Eng.*, 2018, **7**, 1998–2007.
5. R. Rajamanikandan and M. Ilanchelian, *Anal. Methods*, 2018, **10**, 3666–3674.
6. Y.-e Shi, S. Luo, X. Ji, F. Liu, X. Chen, Y. Huang, L. Dong and L. Wang, *Dalton Trans.*, 2017, **46**, 14251–14255.
7. T. Zhao, X.-W. He, W.-Y. Li and Y.-K. Zhang, *J. Mater. Chem. B*, 2015, **3**, 2388–2394.
8. Q. Du, X. Hu, X. Zhang, H. Cao and Y. Huang, *Anal. Methods*, 2019, **11**, 3446–3451.
9. J. Xu and B. Han, *Nano*, 2016, **11**, 1650108.
10. N. Singh, K. P. Raul, A. Poulose, G. Mugesh and V. Venkatesh, *ACS Appl. Bio Mater.*, 2020, **3**, 7454–7461.
11. K. B. Busi, J. Kotha, S. Bandaru, J. P. Ghantasala, S. Haseena, K. Bhamidipati, N. Puvvada, M. K. Ravva, M. Thondamal and S. Chakrabortty, *RSC Adv.*, 2022, **12**, 17585–17595.