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#### -Electronic Supplementary Information (ESI)-

# Unveiling the bifunctional role of morphological differences of self-supported Cu(OH)<sub>2</sub> in electrocatalysis

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# Materials

Copper foil -99% with the thickness of 5  $\mu$ m (Jagruti Metal Industries), urea, 99% (Fisher Scientific), acetic acid, 99% (Fisher Scientific), ascorbic acid, 99.7 % (SRL chemicals), and potassium hydroxide, 85% (Avra chemicals) was purchased and used as such without any pre-treatment. Distilled water with 18.2 M $\Omega$  was used for all the synthesis.

# **Characterization studies**

The X-ray diffraction (XRD) was used to investigate the crystalline nature and phase purity of Cu (OH)<sub>2</sub>/Cu<sub>2</sub>O using Malvern panalytical with Cu-Ka radiation ( $\lambda$ =0.15406 nm) at 45 kV (tension) and 40 mA (current) with a 0.02° per step scan and 1° per min speed. The Cu (OH)<sub>2</sub>/CuO and CuO/Cu percentage are calculated using Raman spectroscopy. The Raman

scattering measurements were carried out in a quasi-backscattering geometry with 5 mW of the excitation line  $\lambda = 514.5$  nm of an Ar +laser. The spectra were analysed using a DILOR-XY spectrometer and a back-illuminated CCD detector. The morphology of the prepared material was asserted using Field emission scanning electron microscopy (FE-SEM) images and Transmission electron microscopy (TEM) JEOL JEM-2100microscope operated at 200 kV. The oxidation state and binding energy of the material are identifies using X-ray photoelectron spectroscopy (XPS) by employing Kratos Axis HSi spectrometer equipped with a monochromated Al Ka X-ray source running at 90 W with normal emission, with the aid of magnetic focusing and a charge neutralizer. Surface compositions were determined by using suitable instrumental response factors and fitting the spectra with CasaXPS version 2.3.16, with energy reference to adventitious carbon at 284.6 eV. Cu K-edge XANES and EXAFS spectra for the reference samples (Cu foil, CuO and Cu<sub>2</sub>O) synthesized catalysts were recorded using the BL15 beamline of the Kyushu Synchrotron Light Research Center, Japan. The photon energies of the X-ray beam were adjusted from 8.9 to 9.2 keV using a Si (111) double-crystal monochromator. The samples were diluted with a high purity hexagonal boron nitride powder and mounted onto a sample holder using Kapton tape. The spectra for the samples were measured at room temperature in Auger mode. The storage ring was operated at a beam current of 287.1 mA and energy of 1.40 GeV. Linear combination (LC) fitting was performed to process the obtained data by utilizing the Athena programme suite (Demeter ver. 0.9.26) within the IFEFFIT software package.

#### **Electrochemical studies**

The oxygen evolution reaction was demonstrated by using cyclic voltammetry (CV), linear sweep voltammetry (LSV) and chronoamperometry (CA) studies in CHI 760E electrochemical workstation. The charge transfer resistance and overpotential are evaluated by Nyquist and

Tafel plot. The electrochemical analysis was performed by adopting three-electrode configuration with working electrode as copper foil, counter and reference electrode as Pt and Ag/AgCl, respectively.

# **Determination of Turn Over Frequency (TOF)**

The turnover frequency of the material is calculated by surface concentration of the material (**Eqn. S1**).

$$TOF = \frac{I \times N_A}{A \times F \times n \times \Gamma}$$
(S1)

Where, "I" is current,  $N_A$ - Avogadro Number, A- Geometrical surface area, F- Faraday constant, n- Number of electrons,  $\Gamma$ - Surface concentration.

#### Number of electrons transferred during OER based on Tafel slope

The slope of the Tafel plot was calculated using eqn. S2.

$$Slope = \frac{(1-\alpha)nF}{2.303 RT}$$
(S2)

Where, "n" is the number of electrons transferred, "F"- Faraday constant and " $\alpha$ " is the charge transfer coefficient.

If n=4, for OER activity.

#### Determination of electrochemically active surface area (ECSA)

There are numerous ways for determination of ECSA of an electro-material, in this study we have chosen the double layer capacitance method with reference to the reported literature studies.<sup>1, 2</sup> First, scan rate was varied from 10-200 mV/s and we acquired the current density that used for the ESCA calculation (**eqn. S3**).

$$\mathbf{ESCA} = \frac{C_s}{C_{dl}}$$
(S3)

Where, "Cs" is specific capacitance and value denoted as 0.035 mF cm<sup>-2</sup> and C<sub>dl</sub>- double-layer capacitance

# Determination of roughness factor (RF)

The roughness factors (RF) were computed by eqn. S4.

$$R_f = \frac{Electrochemical surface area(ESCA)}{Geometric surface area}$$
(S4)



Fig. S1. The i-t curves for CuK, CuKU and CuKAA materials in 1M KOH, 1M KOH+ 55 mM Urea and 1 M KOH+ 5 mL acetic acid at the potential of -0.06 V respectively.



Fig. S2. FE-SEM images of Bare, CuK, CuKU and CuKAA material with various magnifications (10X, 30X and 70X).



Fig. S3. HR-TEM images of CuK material with different magnification.



Fig. S4. Elemental mapping of CuK material.



Fig. S5. XRD patterns of bare, CuK, CuKU and CuKAA materials.



Fig. S6. SAED pattern of CuK material.



Fig. S7. Raman spectra of bare, CuK, CuKU and CuKAA materials.



Fig. S8. XPS survey spectra for CuK, CuKU and CuKAA materials.



Fig. S9. Cu 2p XPS spectra of CuK, CuKU and CuKAA materials.



Fig. S10. Cu  $(OH)_2$  and Cu composition present in the CuK, CuKU and CuKAA materials.



Fig. S11. Cyclic voltammogram of CuK material in 0.1M KOH at scan rate of 50 mV/s. [Reaction condition: at room temperature and pressure, as prepared catalyst in the given potential window of 0.65 to 2.0 V vs RHE.]



Fig. S12. Nyquist plot of CuK, CuKU and CuKAA material. [Reaction condition: at room temperature and pressure, as prepared catalyst at the open circuit potential.]



Fig. S13. Effect of scan rates responses of CuK, CuKU and CuKAA material for OER application. [Reaction condition: at room temperature and pressure, as prepared catalyst in the given potential window]

	Bare	CuK	CuKU	CuKAA
Roughness factor	4.416	9.66	9.55	5.51
TOF/ s	0.388	1.475	1.356	1.157
ESCA/ cm <sup>2</sup>	9.717	20.74	19.11	11.01

**Table S1.** The values of roughness factor, turnover frequency (TOF) and electrochemical active surface area (ESCA) of the prepared materials



Fig. S14. Stability study of CuK and bare Cu foil material in 0.1 M KOH for 72 hours at room temperature and pressure. [Reaction condition: At the overpotential value 0.4 V vs. RHE for CuK and Bare Cu]



Fig. S15. The polarisation curve of CuK material before and post stability (after 72 hours of chronoamperometry study at room temperature and pressure).



Fig. S16. The post stability (after 72 hours of chronoamperometry study at room temperature and pressure). FE-SEM images of CuK material with different magnification.



Fig. S17. EIS spectra of CuK material before and after stability (after 72 hours of chronoamperometry study at room temperature and pressure at the open circuit potential).



Fig. S18. Post stability (after 72 hours of chronoamperometry study at room temperature and pressure). XPS spectra of CuK material.

SI. No	Material	Onset potential/ mV	Overpotential/ mV	Tafel value/ mV dec <sup>-1</sup>	Substrate	References
1	CuO	600	470	90	FTO	3
2	Cu(OH) <sub>2</sub> -N WAs/Cu	NA	560	86	Cu foil	4
3	Cu2Se– Cu2O/TF	NA	465	144	Ti foil	5
4	CuO film	NA	810	130	ITO	6
5	Cu <sub>2</sub> Se	153	470	48.1	Si wafer	7
6	Cu(OH) <sub>2</sub> / CuO	114	400	59.33	Copper foil	This work

# Table S2. Comparison table of different materials for OER applications



Fig. S19. CVs of the CuK in 1M KOH with 0.25, 0.5, 1.0, and 1.5 M of methanol with a scan rate of 10 mV s<sup>-1</sup> solution. [Reaction condition: at room temperature and pressure, as prepared catalyst in the given potential window.]



Fig. S20. CVs of the CuK in 1M KOH with 0.25, 0.5, 1.0, and 1.5 M of methanol with a scan rate of 10 mV s<sup>-1</sup> solution (a) without nitrogen atmosphere and (b) with nitrogen atmosphere, The CVs of the bare, CuK, CuKU and CuKAA in 1 M KOH with and without 0.5 M methanol (c) without nitrogen atmosphere and (d) with nitrogen atmosphere. [Reaction condition: at room temperature and pressure, as prepared catalyst in the given potential window.]



Fig. S21. Effect of scan rates responses of CuK, CuKU and CuKAA material for MOR application. [Reaction condition: at room temperature and pressure, as prepared catalyst in the given potential window.]



Fig. S22.The CVs of the Pt/C in 1M KOH with 0.50 M of methanol with a scan rate of 10 mV s<sup>-1</sup> solution. [Reaction condition: at room temperature and pressure, as prepared catalyst in the given potential window.]



**Fig. S23.** Stability study of CuK, and bare material for MOR application at room temperature and pressure. [Reaction condition: At the overpotential value 0.6 V vs. RHE for CuK and Bare]

Sl. No	Material	Current density/ mAcm <sup>-2</sup>	Electrolyte	References
1	B/CuCo <sub>2</sub> O <sub>4</sub>	91	1 M KOH + 1 M MeOH	8
2	B/NiCu <sub>2</sub> O <sub>4</sub>	73	1 M KOH + 1 M MeOH	9
3	Cu(OH) <sub>2</sub> -CuO	120	1 M KOH + 0.5 M MeOH	10
4	Cu(OH) <sub>2</sub> -CuO	70	1 M KOH + 0.5 M MeOH	11
5	Cu/NiCu	35	1 M KOH + 1 M MeOH	12
6	Cu(OH) <sub>2</sub> / CuO	133	1 M KOH + 0.5 M MeOH	This work

**Table S3.** Comparison table of different materials for MOR applications

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