

Amorphous Cobalt-Copper Oxide for Upgrading Anodic Electro-oxidation of Glycerol to Formate Production in Basic Medium

Biplab Kumar Manna^{a,b}, Rajib Samanta^{a,b}, Manjunatha Kempasiddaiah^{a,b} and Sudip Barman*^{a,b}

^a School of Chemical Sciences, National Institute of Science Education and Research (NISER), Bhubaneswar, Orissa-752050, India, Tel.: +91 6742494183.

^b Homi Bhabha National Institute, Training School Complex, Anushakti Nagar, Mumbai – 400094.

*S.B.: E-mail, sbarman@niser.ac.in; Tel: +91(674)2494183.

Materials:

All chemicals were purchased and used without further purification. Formamide (HCONH₂, HPLC grade), Cobalt nitrate hexahydrate (Co(NO₃)₂·6H₂O, 98.5%) was purchased from Sigma-Aldrich. Copper nitrate hexahydrate (Cu(NO₃)₂·6H₂O, ≥ 98%), hydrochloric acid (HCl), and potassium hydroxide (KOH, ≥ 85%) were acquired from Alfa-Aesar. Sodium borohydride was obtained from Spectrochem. Glycerol (C₃H₈O₃, ≥ 99.5%), glycolic acid (C₂H₄O₃, ≥ 99%), formic acid (CH₂O₂, ≥ 98%), and deuterium oxide (D₂O, 99.9%), were all obtained from Sigma-Aldrich. Mili-Q water was obtained from ultra-filtration system (Mili-Q, Milipore) with the measured conductivity 35 mho/cm at 25 °C.

Instrumentation and Analyses:

Surface morphology analysis was performed by utilizing a field-emission scanning electron microscope (Carl Zeiss, Germany, Model Sigma). To conduct FE-SEM analysis, samples were prepared by depositing 0.05 mL of a solution (1 mg/mL) on a silicon wafer through drop-casting, followed by drying at 45 °C. X-ray diffraction patterns (p-XRD) were acquired using a Bruker instrument DAVINCI D8 ADVANCE diffractometer furnished with Cu K α radiation ($\lambda = 0.15406$ nm). For detail investigation the surface morphology of the prepared materials, high-resolution transmission electron microscopy (HRTEM, JEOL F200) operating at 200 kV was employed. For TEM analysis, 10 μ L of ethanolic solution (1 mg/mL) was drop casting on TEM gride and dried in air around 45 °C. X-ray photoelectron spectroscopy (XPS) measurements were conducted using VG Microtech by drop-casting the samples on a silicon wafer. The monochromatic source employed that was Mg K α X-ray. The textural property of the sample measured by physical

adsorption desorption of N₂ gas molecules, BET (Brunauer–Emmett–Teller) surface areas were acquired using Quantachrome Instruments (AutosorbiQ-XR-XR (2 Stat.)) Vinton. ThermoScientific iCAP 7000 series inductively coupled plasma–optical emission spectroscopy was used to quantify the total metal percentage of metal present in the sample. Electrochemical measurements were carried out exclusively with the use of an electrochemical workstation (Autolab, Metrohm, PGSTAT 320N). The working electrolyte's pH was measured using a Hanna (HI 2209) pH meter. The ¹H NMR spectrum was acquired utilizing the water suppression method with a Bruker 400 MHz instrument. An ultrasound bath sonication was performed by Genei Laboratories Private Limited., Bangalore, India.

Electrochemical Performance Test:

Electrochemical measurements were conducted using a three-electrode system coupled with an electrochemical workstation (Autolab) to evaluate the electrochemical performances. Here, the Ag/AgCl electrode, Pt electrode, and catalyst-coated carbon cloth are used as reference, counter, and working electrode, respectively. The catalytic performance of Co₃O₄-CuO/CN_x-300, along with other catalysts, was assessed for Oxygen Evolution Reaction (OER) and Glycerol Oxidation Reaction (GOR) in a 1M KOH solution. A 15 mL solution of 1 M KOH and 0.1M glycerol electrolyte was introduced into anodic chambers, on the other hand cathodic chamber filled with 15 mL of 1M KOH solution. A Nafion 117 proton exchange membrane separated these chambers. The anodic compartment was fixed with Ag/AgCl (saturated KCl, +197 mV vs SHE) and working electrodes respectively, with a distance of 0.5 cm, and another cathodic compartment connected with a Pt counter electrode. The measured potentials versus Ag/AgCl were adjusted to the reversible hydrogen electrode (RHE) scale using the following equation

$$V_{\text{RHE}} = V_{\text{Ag/AgCl}} + 0.1976 + 0.0592\text{pH} \dots\dots\dots(\text{S1})$$

Linear sweep voltammetry (LSV), EIS, and chronoamperometric measurements were conducted to show how well it works towards OER and GOR.

Electrochemically active surface area (ECSA) calculation:

The electrochemical surface area of the Co₃O₄-CuO/CN_x-300 composite, with different ratio was measured from the double layer capacitance (C_{dl}). The quantity of the electrical capacitance between the double layers can be measured from the CV curves at different scan rates by the equation

$$v \times C_{dl} = J_c \dots\dots\dots(S2)$$

Where *v* is the scan rate, and *J_c* is the double layer charging current. The slope obtained from the plot between the double layers charging current and scan rate is directly considered as the double layer capacitance (C_{dl}) of the catalyst. The ECSA value is directly proportional to double layer capacitance by the following equation

$$ECSA = C_{dl} / C_{sp} \dots\dots\dots(S3)$$

Where *C_{sp}* is the specific capacitance.

Tafel plot:

The linear region of the Tafel plots is fitted using the Tafel formula:

$$\eta = b \log (J) + a \dots\dots\dots(S4)$$

Where ‘*η*’, ‘*J*’, ‘*b*’, and ‘*a*’ are overpotential, current density, Tafel slope, and constant respectively.

And *b* = 2.3RT/*α*F (*R* - gas constant, *α* - symmetry coefficient, *T* - absolute temperature, *F* - faraday constant). The lower value of the Tafel slope (*b*) indicates the faster electron transfer during the electrochemical process.

Turn Over frequency (TOF) calculation:

Assumptions: (a) Every metal atom present on the carbon cloth electrode are involved in GOR. The TOF per active site for GOR was calculated by following equation:

(b) It is the lower limit of the TOF value.

The TOF per active site for GOR was calculated by following equation:

$$\text{TOF (GOR/s)} = x = (J * S) / (z * F * n) \dots\dots\dots(\text{S5})$$

J = current density (mA/cm²) at particular overpotential, S = Geometrical surface area of the working electrode, F = Faraday's constant (96485.3 coulomb/mol), z = the no. of electron involved in the OER or GOR process, where $z = 4$ for OER and $z = 8$ for GOR, n = Number of moles of active site on the electrode.

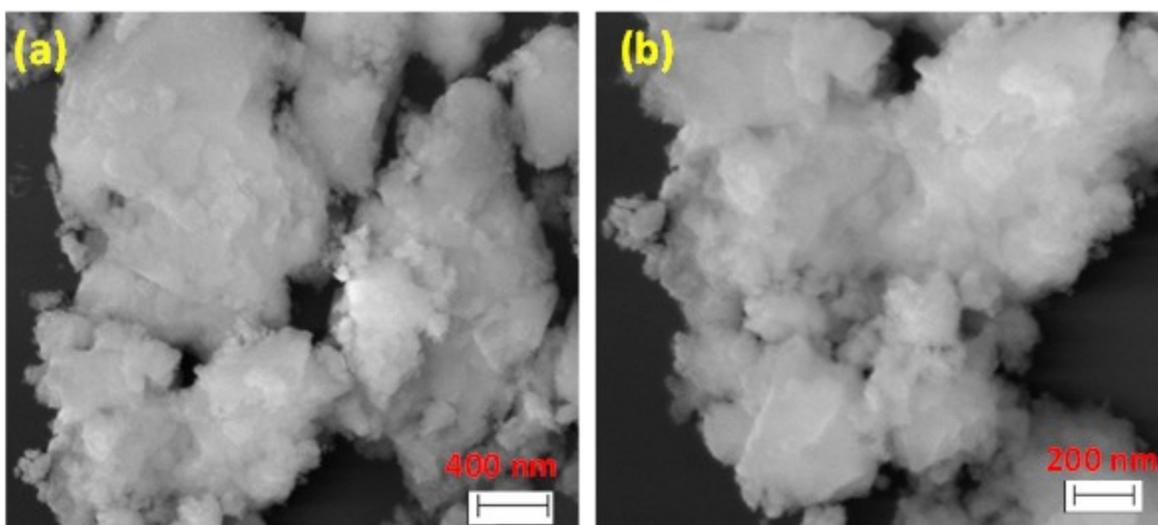


Figure S1. (a, b) FE-SEM images of CoCu/CN_x-RT.

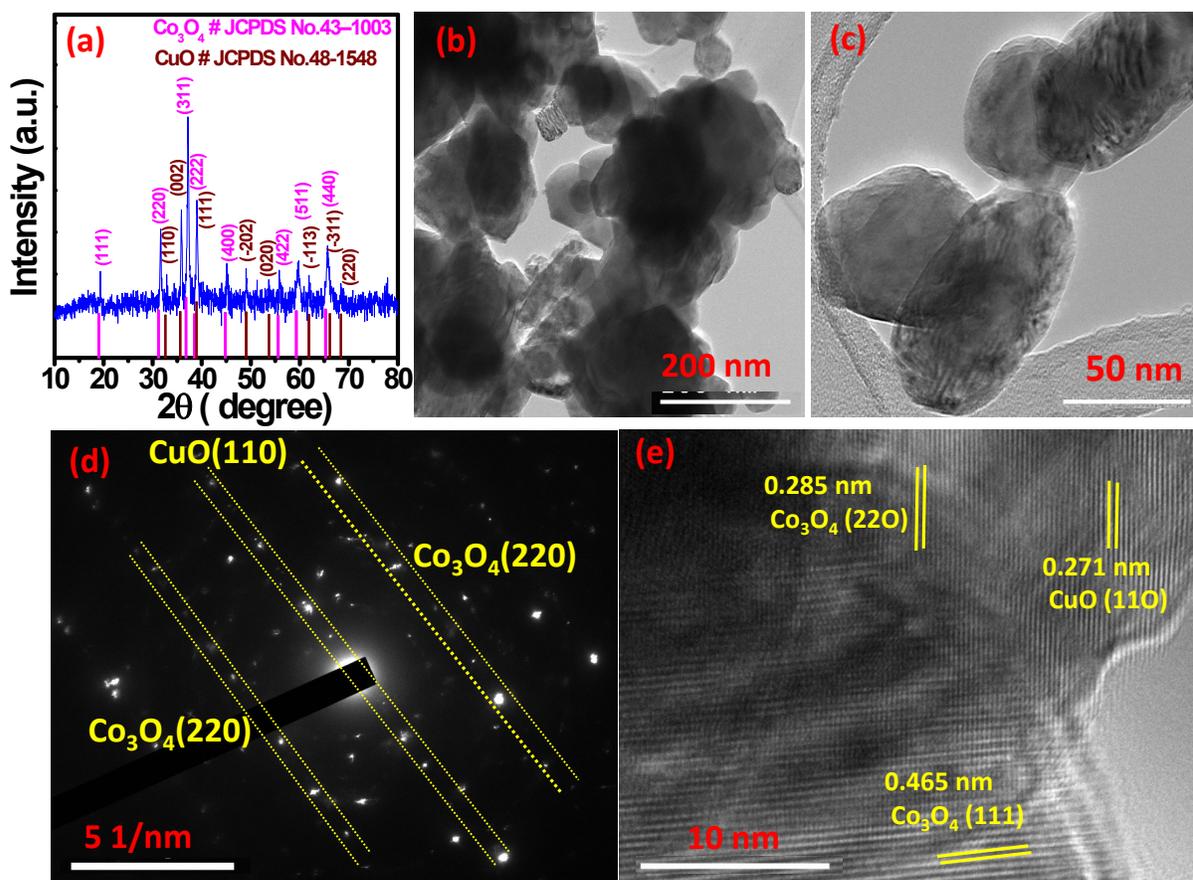


Figure S2. (a) p-XRD pattern, (b,c) TEM images, (d) SEAD pattern, (e) HRTEM image of Co_3O_4 - $\text{CuO}(\text{Crys})$.

Table S1. The weight percentage of Cu and Co determined from ICP-OES measurements.

Compounds	Weight % of Co	Weight % of Cu	Ratio
Co_3O_4 - CuO / CN_x -300	42	21	1:0.5
$\text{CoCu} / \text{CN}_x$ -RT	39	19	1:0.48
$\text{Co}_3\text{O}_4 / \text{CN}_x$ -300	65		
CuO / CN_x -300		41	

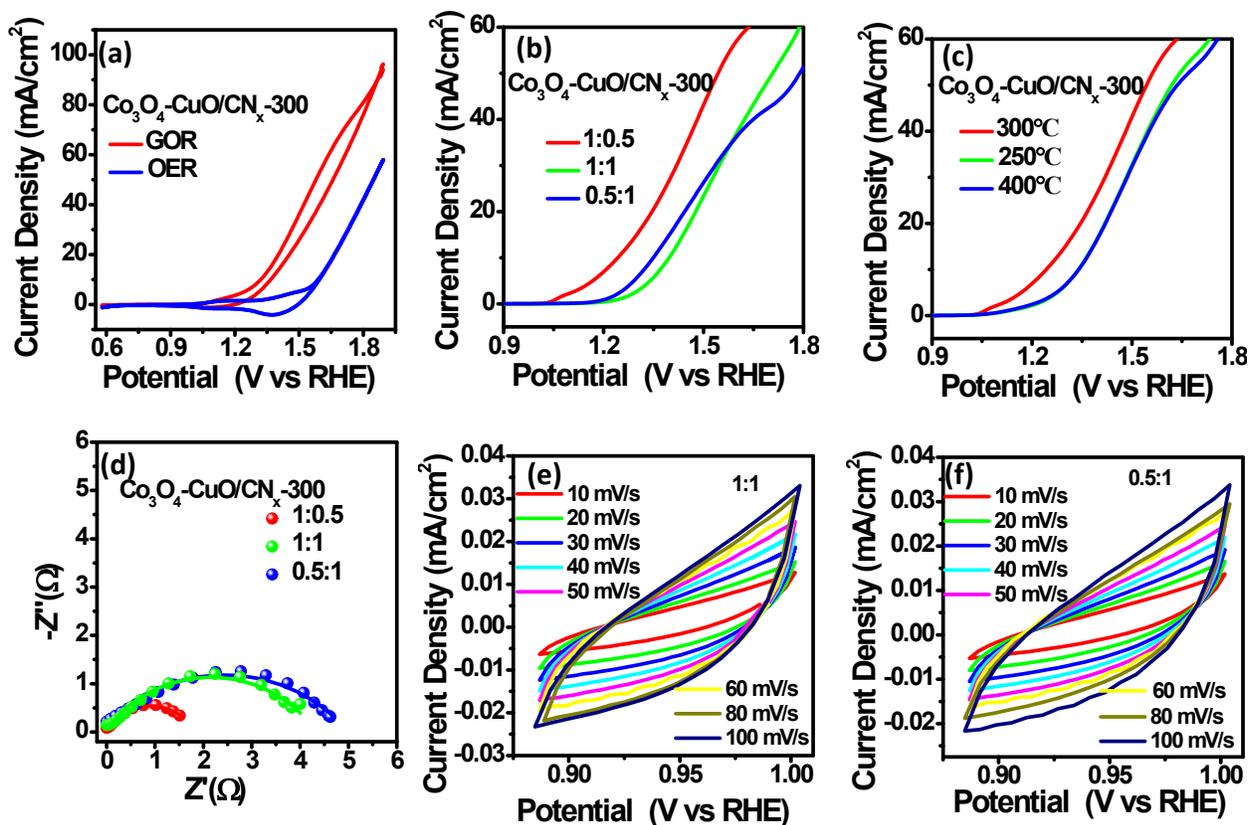


Figure S3. (a) Cyclic voltammetry plots of $\text{Co}_3\text{O}_4\text{-CuO/CN}_x\text{-300}$, for OER, GOR (b,c) GOR polarization curves at different temperatures and different ratios of $\text{Co}_3\text{O}_4\text{-CuO/CN}_x\text{-300}$; (d) corresponding Nyquist plots of $\text{Co}_3\text{O}_4\text{-CuO/CN}_x\text{-300}$ (e,f) CVs $\text{Co}_3\text{O}_4\text{-CuO/CN}_x\text{-300}$ at different scan rate.

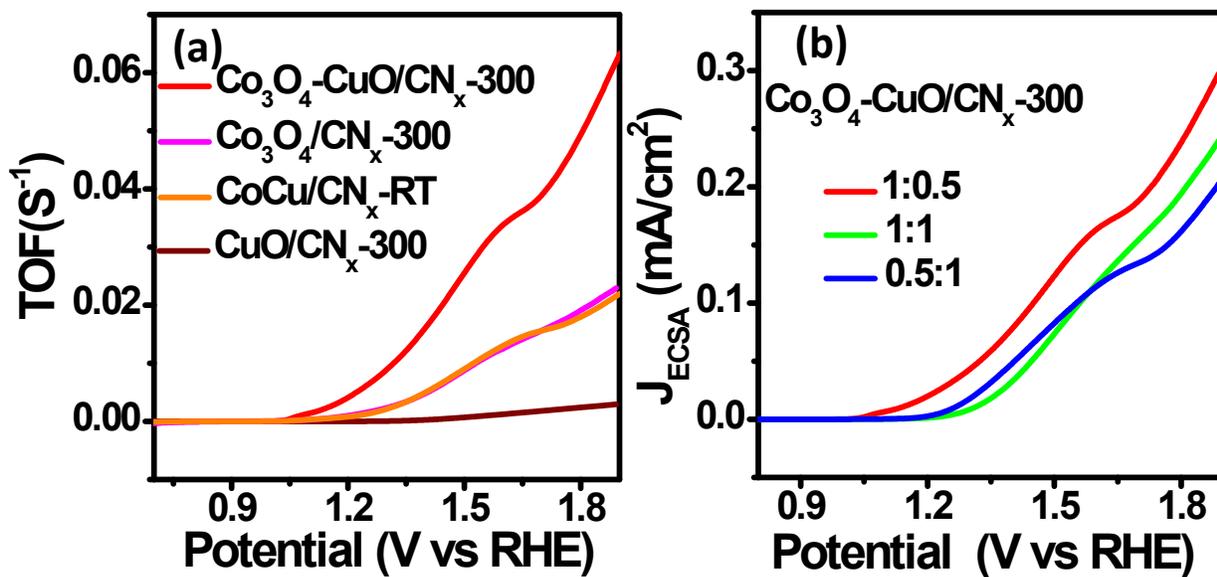
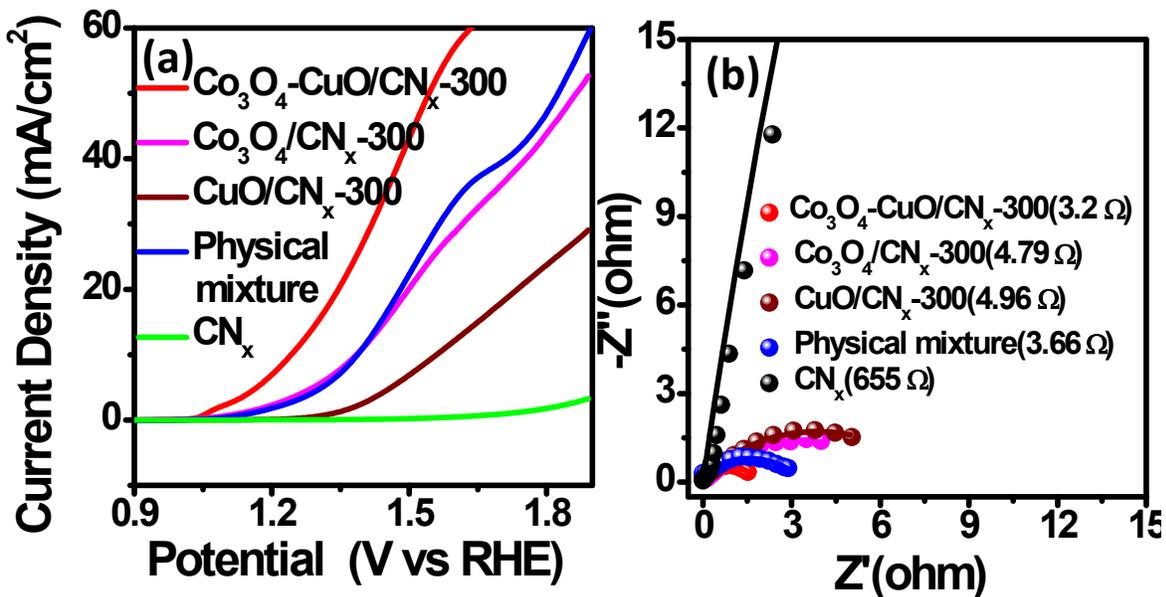


Figure S4. (a) TOF plot of $\text{Co}_3\text{O}_4\text{-CuO/CN}_x\text{-300}$, $\text{Co}_3\text{O}_4/\text{CN}_x\text{-300}$, and $\text{CuO/CN}_x\text{-300}$; and $\text{CoCu/CN}_x\text{-RT}$; (b) ECSA normalized LSV plot.



Figure

re S5. (a,b) GOR polarization curves and corresponding Nyquist plots of $\text{Co}_3\text{O}_4\text{-CuO/CN}_x\text{-300}$, $\text{Co}_3\text{O}_4/\text{CN}_x\text{-300}$, and $\text{CuO/CN}_x\text{-300}$; physical mixture and CN_x .

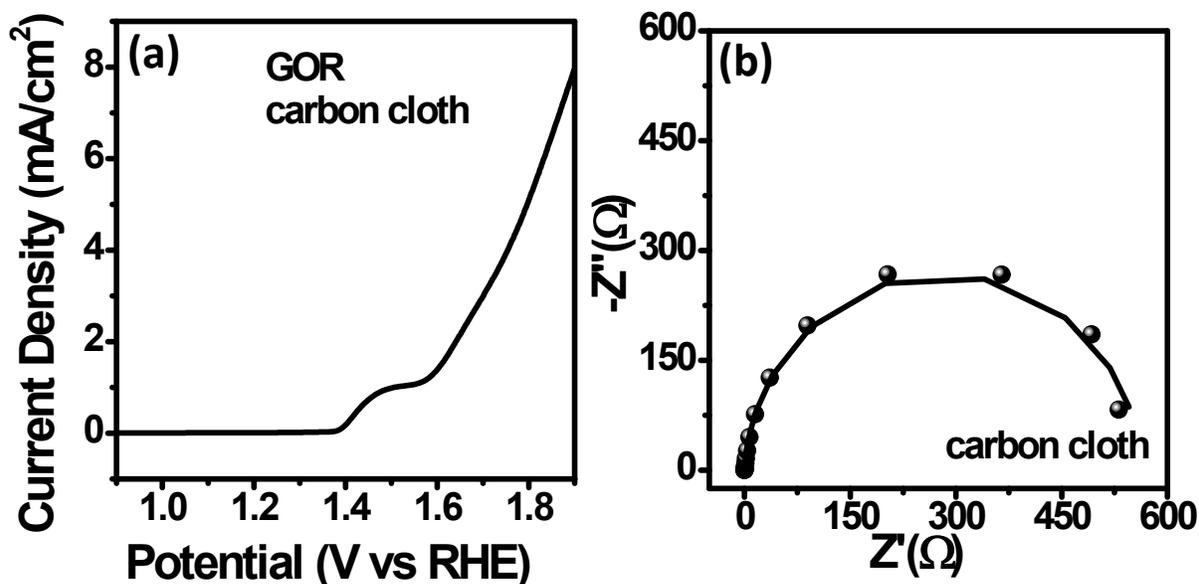
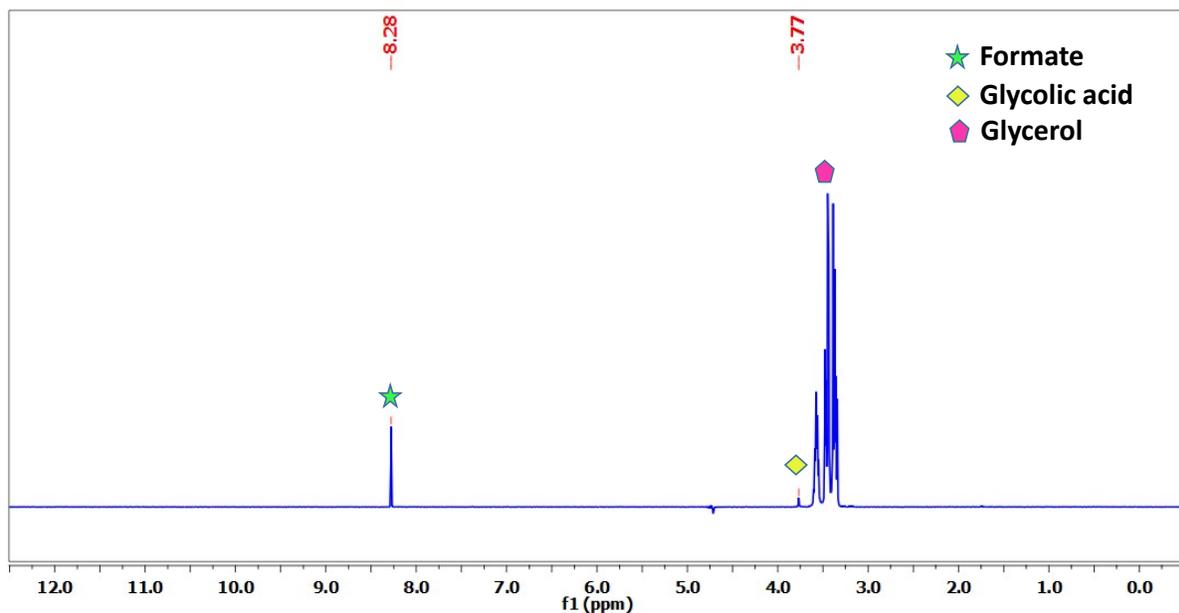


Figure S6. (a, b) GOR polarization curves and corresponding Nyquist plots of Carbon cloth.



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Figure S7. NMR spectrum of the reaction mixture after 0.5 h chronoamperometric experiment.

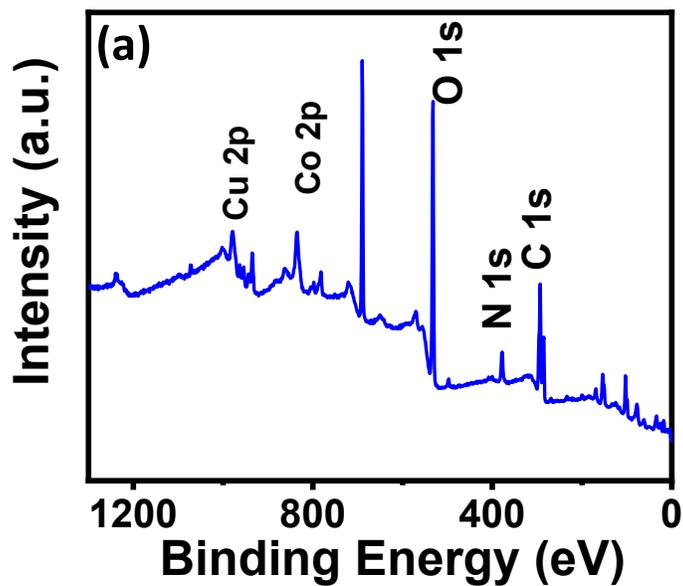


Figure S8. (a) XPS survey scan spectrum of $\text{Co}_3\text{O}_4\text{-CuO/CN}_x\text{-300}$ after stability.

Table S2. GOR activity of $\text{Co}_3\text{O}_4\text{-CuO/CN}_x\text{-300}$ which combines organic oxidation reactions recently reported in literature.

Compounds	Electrolyte	Product	Faradic efficiency/ Selectivity	Potential @ 10 mA/cm ² Three- electrode system	Potential (V) For Two- electrode system	References
N-CoO _x	1 M KOH + 1 M Glycerol	Formate	FE 96.2%	1.31	1.59	Z. J. Ke, N. Williams, X. X. Yan, S. Younan, D. He, X. Y. Song, X. Q. Pan, X. H. Xiao, J. Gu, J. <i>Mater. Chem. A</i> 2021, 9 , 19975.
Ni(OH) ₂	2 M LiOH + 0.1 M Glycerol	Formate	FE 81.3%	1.35	1.50	J. Wu, J. Li, Y. Li, X. Y. Ma, W. Y. Zhang, Y. Hao, W. B. Cai, Z. P. Liu, M. Gong, <i>Angew. Chem. Int. Ed.</i> 2022, 61 , e202113362.
CuCo ₂ O ₄	KOH+0.1 M glycerol	Formic acid	FE 89.1%	1.26		X. Han, H. Sheng, C. Yu, T. W. Walker, G. W. Huber, J. Qiu and S. Jin, <i>ACS Catal.</i> , 2020, 10 , 6741-6752.
HEA-NPs / CC	1 M KOH + 0.1 M Glycerol	Formate	FE 90%	1.25	1.34	L. Fan, Y. Ji, G. Wang, J. Chen, K. Chen, X. Liu, Z. Wen, <i>J. Am. Chem. Soc.</i> 2022, 144 , 7224.
CuO	0.1 M NaOH + 0.1 M Glycerol	Formate	Sel. 70%	2		C. Liu, M. Hirohara, T. Maekawa, R. Chang, T. Hayashi, C. Y. Chiang, <i>Appl. Catal. B</i> 2020, 265 , 118543.
Ni-Mo- N/CFC	1 M KOH+0. 1 M glycerol	Formic acid	FE 95%	1.30	1.36	Y. Li, X. Wei, L. Chen, J. Shi and M.

						He, <i>Nat. Commun.</i> , 2019, 10 , 1-12.
Ni _{0.33} Co _{0.67} (OH) ₂ @HOS/NF	1 mol L ⁻¹ KOH + 0.1 mol L ⁻¹ glycerol	formate	FE 95%	1.30	1.74	Y. Pei, Z. Pi, H. Zhong, J. Cheng and F. Jin. <i>J. Mater. Chem. A</i> , 2022, 10 , 1309-1319
CoNiPNIE	1 M KOH + 10 mM HMF	FDCA	FE 82%	1.29 @ 20 mA/cm ²	1.46	Y. K. Song, W. F. Xie, Y. J. Song, H. Li, S. J. Li, S. Jiang, J. Y. Lee, M. F. Shao, <i>Appl. Catal. B</i> 2022, 312 , 121400.
NiFeO _x NF	1 M KOH + 0.5 M Glucose	Glucaric acid	FE 87%	1.39@ 100 mA/cm ²	1.24	W. J. Liu, Z. Xu, D. Zhao, X. Q. Pan, H. C. Li, X. Hu, Z. Y. Fan, W. K. Wang, G. H. Zhao, S. Jin, G. W. Huber, H. Q. Yu, <i>Nat. Commun.</i> 2020, 11 , 265.
Co ₃ O ₄ -CuO/CN _x -300	1 M KOH + 0.1 M Glycerol	Formic acid + Glycolic acid	FE 91%	1.25	1.41	This work