

Electronic Supporting Information

**Paradoxical Observance of “Intrinsic” and “Geometric” Oxygen Evolution Electrocatalysis
in Phase Tuned Cobalt Oxide/hydroxide Nanoparticles**

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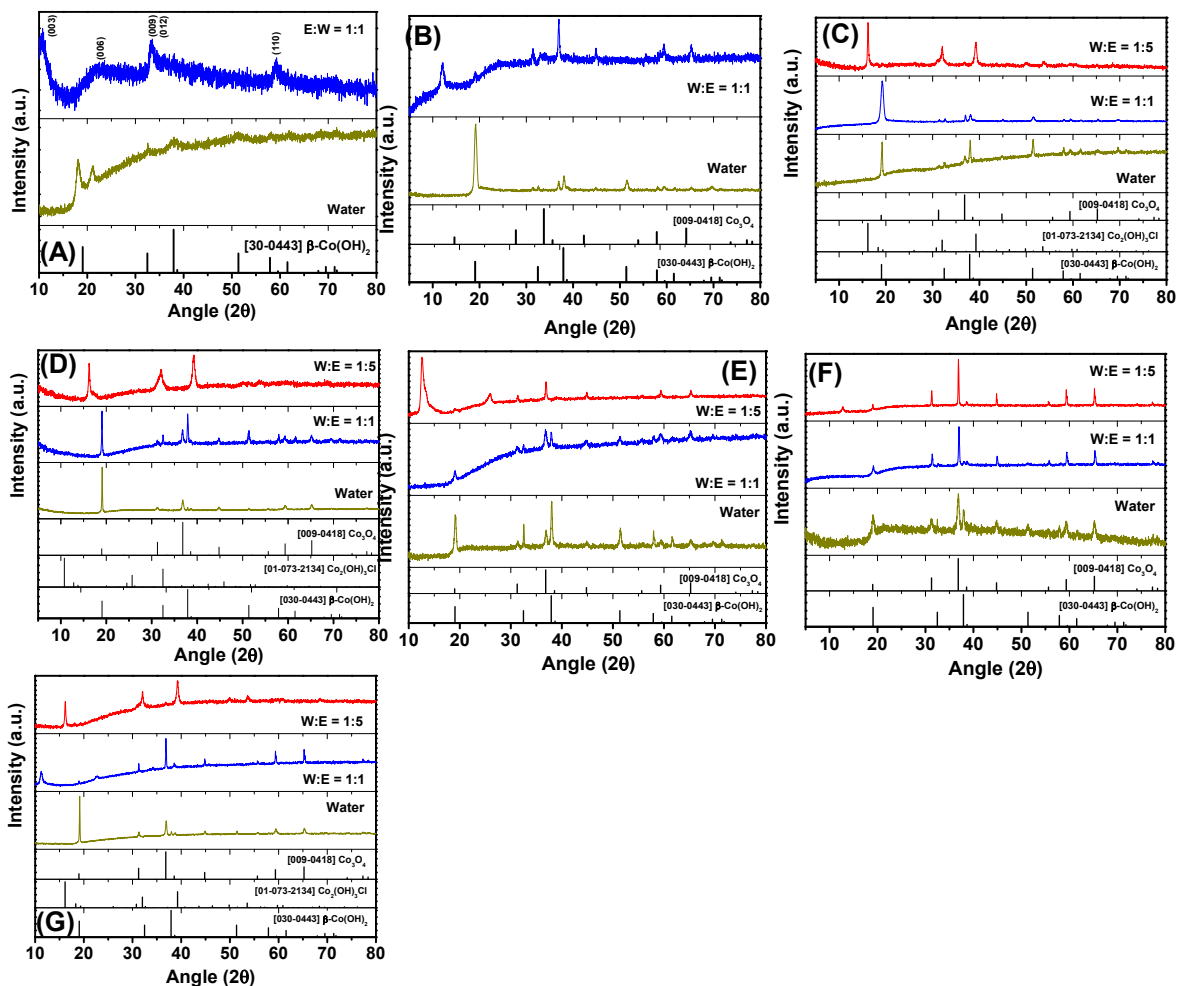


Figure S1: PXRD pattern of materials synthesized in different solvent systems with (A) triethanolamine, (B) methyldiethanolamine, (C) dimethylethanolamine, (D) ethanolamine, (E) triethylamine, (F) diethylamine and (G) ammonia.

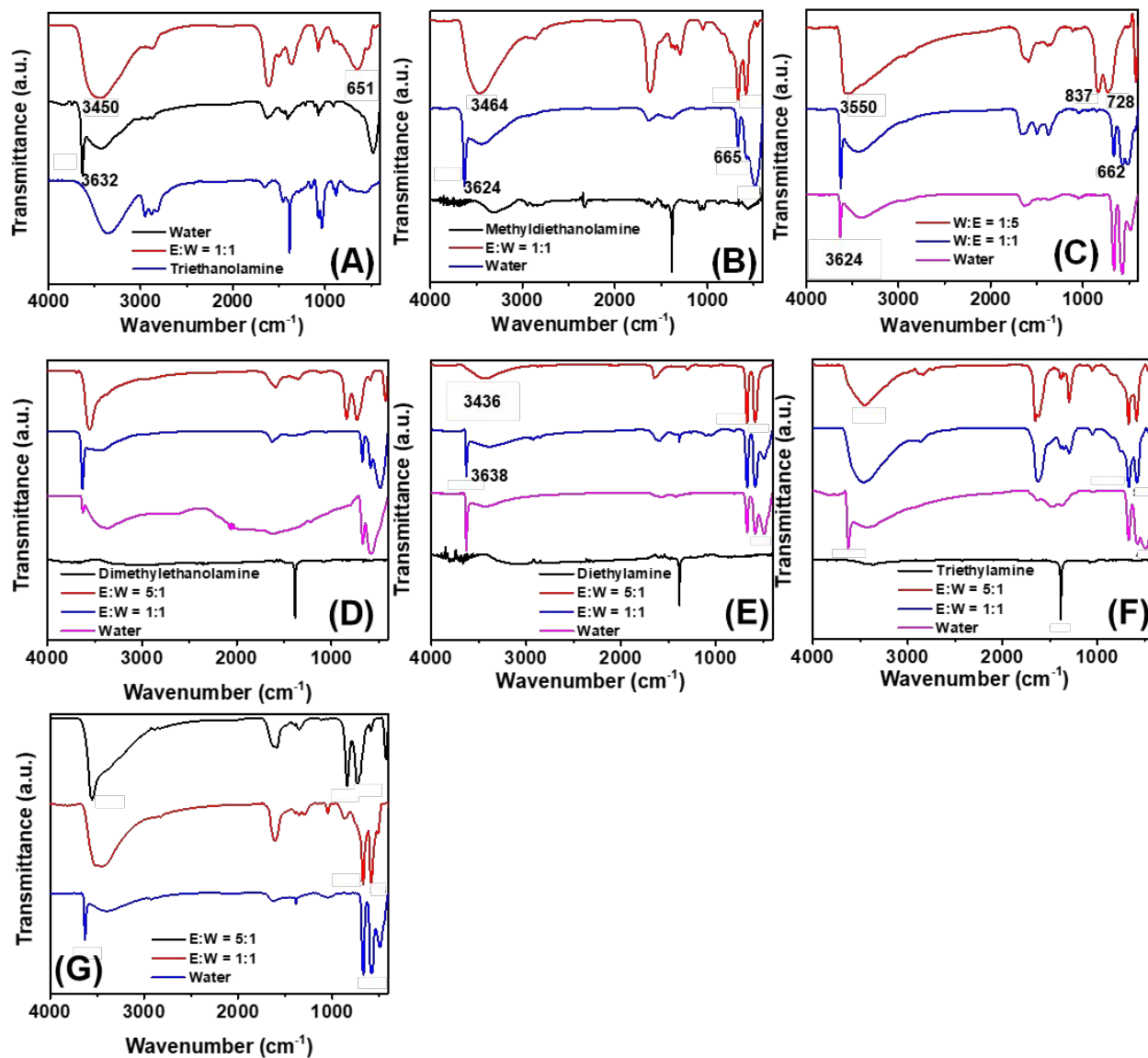


Figure S2: FT-IR spectra of materials synthesized in different solvent systems with (A) triethanolamine, (B) methylidiethanolamine, (C) ammonia, (D) dimethylethanolamine, (E) ethanolamine, (F) triethylamine and (G) diethylamine.

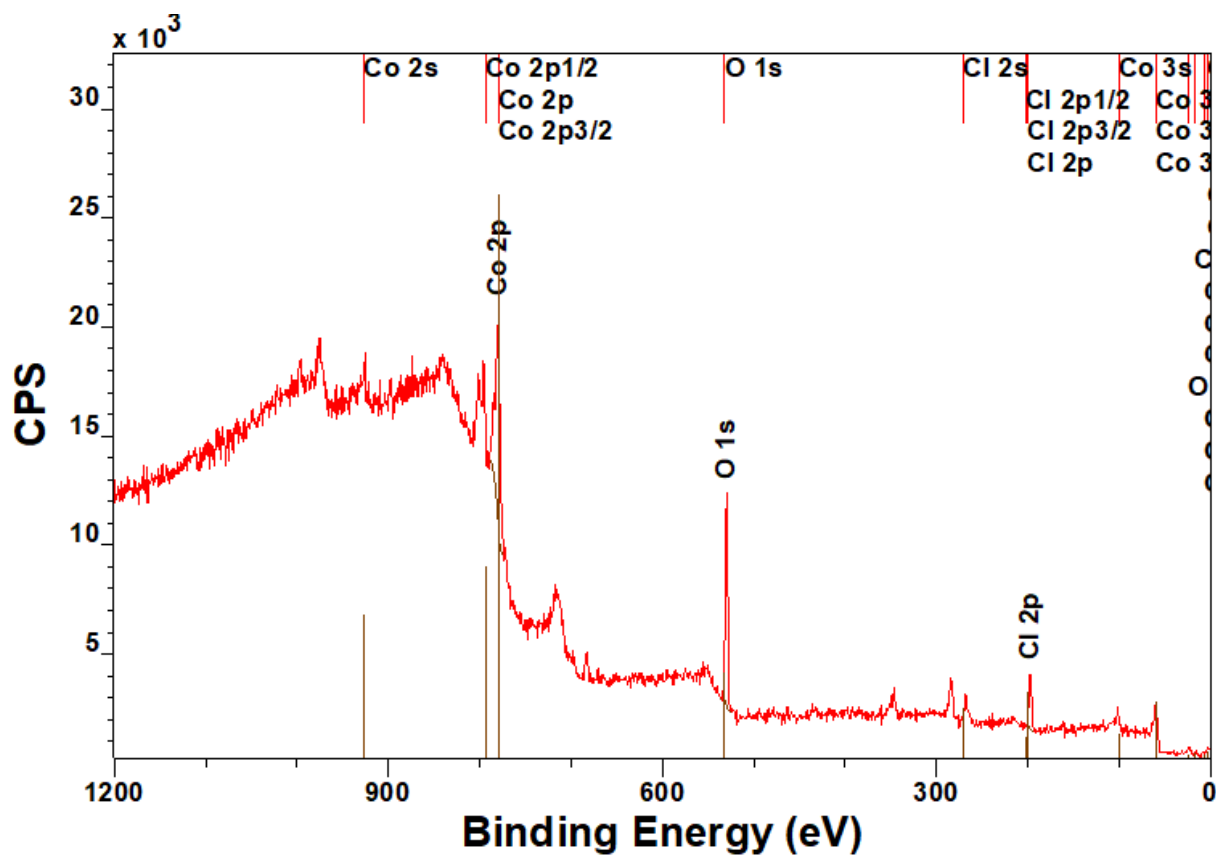


Figure S3: Survey scan of XPS for HT(II,III) phase synthesized with triethanolamine in water: ethanol (1:1) solvent.

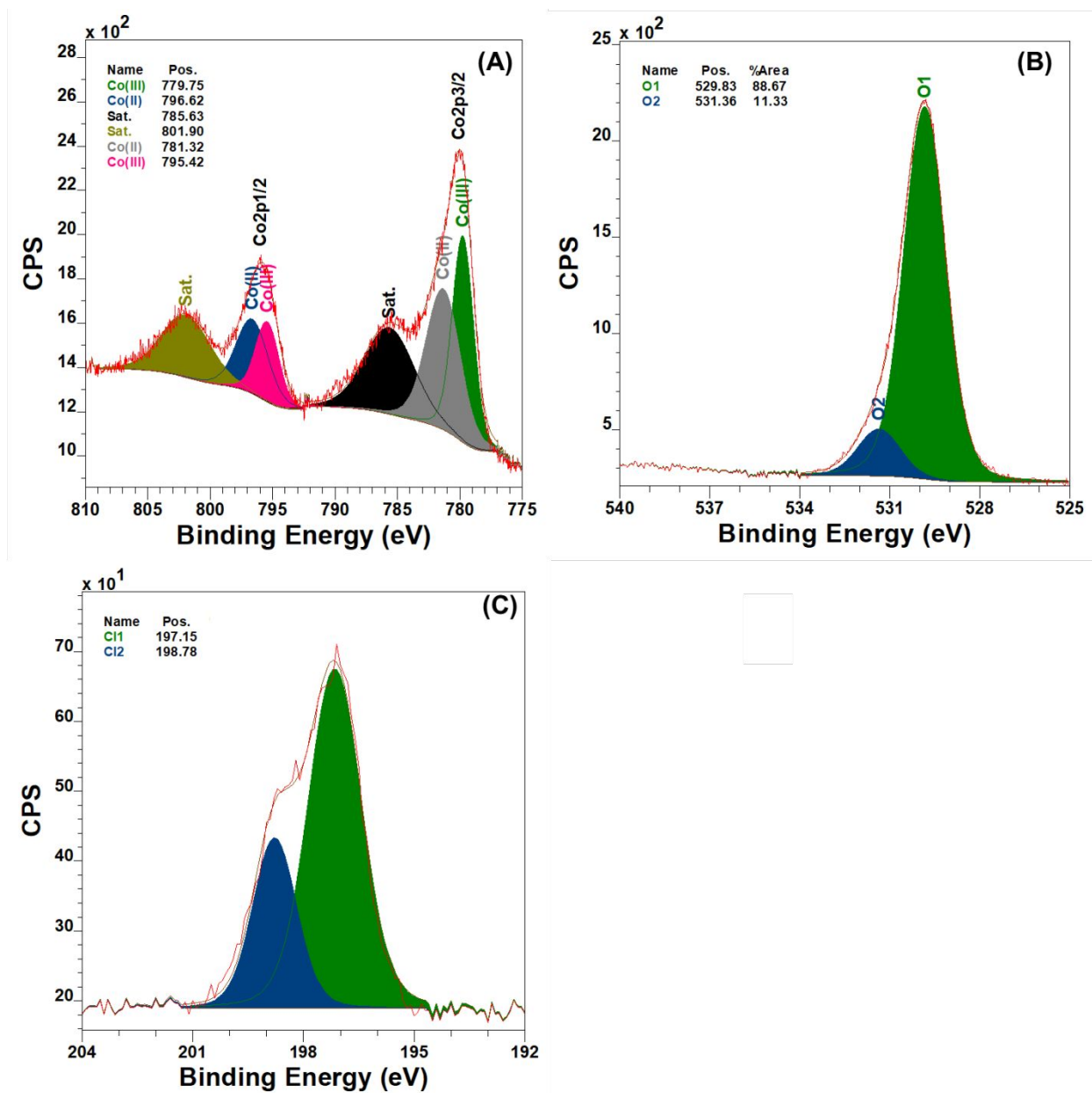


Figure S4: Narrow scan XPS of XPS of HT(II,III) phase synthesized with triethanolamine in water: ethanol (1:1) solvent. (A) Co 2p, (B) O 1s and (C) Cl 2p. In (A), Co was found to exist in both (II) and (III) oxidation state.

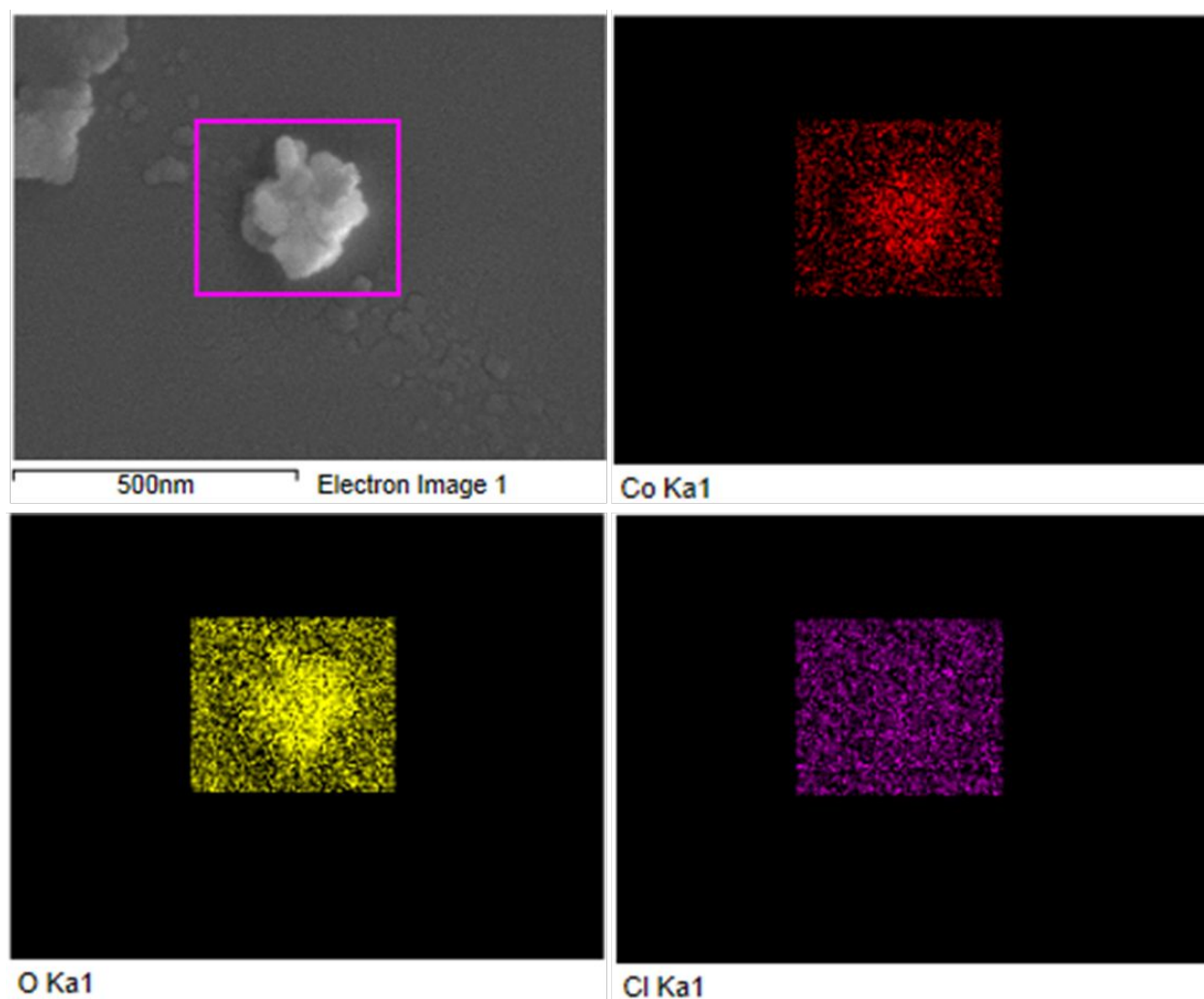


Figure S5: Elemental mapping of HT(II,III) shows the presence of Co, O and Cl in the material.

Table S1: Summary of materials synthesized in different solvent systems with different amines.

Base	Ethanol (50 ml) + Water (10 ml)	Ethanol (30 ml) + Water (30 ml)	Water (60 ml)
Ammonia	$\text{Co}_2(\text{OH})_3\text{Cl}$	$\text{HT(II)} + \text{Co}_3\text{O}_4$	$\text{Co}_3\text{O}_4 + \beta\text{-Co(OH)}_2$
Ethylamine	$\text{Co}_2(\text{OH})_3\text{Cl} + \text{Co}_3\text{O}_4$	Co_3O_4	Co_3O_4
Diethylamine	$\text{Co}_3\text{O}_4 + \text{HT(II)}$	$\text{Co}_3\text{O}_4 + \beta\text{-Co(OH)}_2$	$\beta\text{-Co(OH)}_2 + \text{Co}_3\text{O}_4$
Triethylamine	$\text{HT(II)} + \text{Co}_3\text{O}_4$	$\beta\text{-Co(OH)}_2 + \text{Co}_3\text{O}_4$	$\beta\text{-Co(OH)}_2 + \text{Co}_3\text{O}_4$
Ethanolamine	$\text{Co}_2(\text{OH})_3\text{Cl}$	$\beta\text{-Co(OH)}_2 + \text{Co}_3\text{O}_4$	$\beta\text{-Co(OH)}_2 + \text{Co}_3\text{O}_4$
Dimethylethanolamine	$\text{Co}_2(\text{OH})_3\text{Cl}$	$\text{Co}_3\text{O}_4 + \beta\text{-Co(OH)}_2$	$\beta\text{-Co(OH)}_2 + \text{Co}_3\text{O}_4$
Methyldiethanolamine	No Product	$\text{HT(II)} + \text{Co}_3\text{O}_4$	$\beta\text{-Co(OH)}_2 + \text{Co}_3\text{O}_4$
Triethanolamine	No Product	HT(II, III)	$\beta\text{-Co(OH)}_2 + \text{HT}$



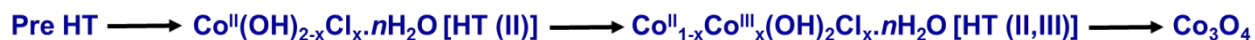
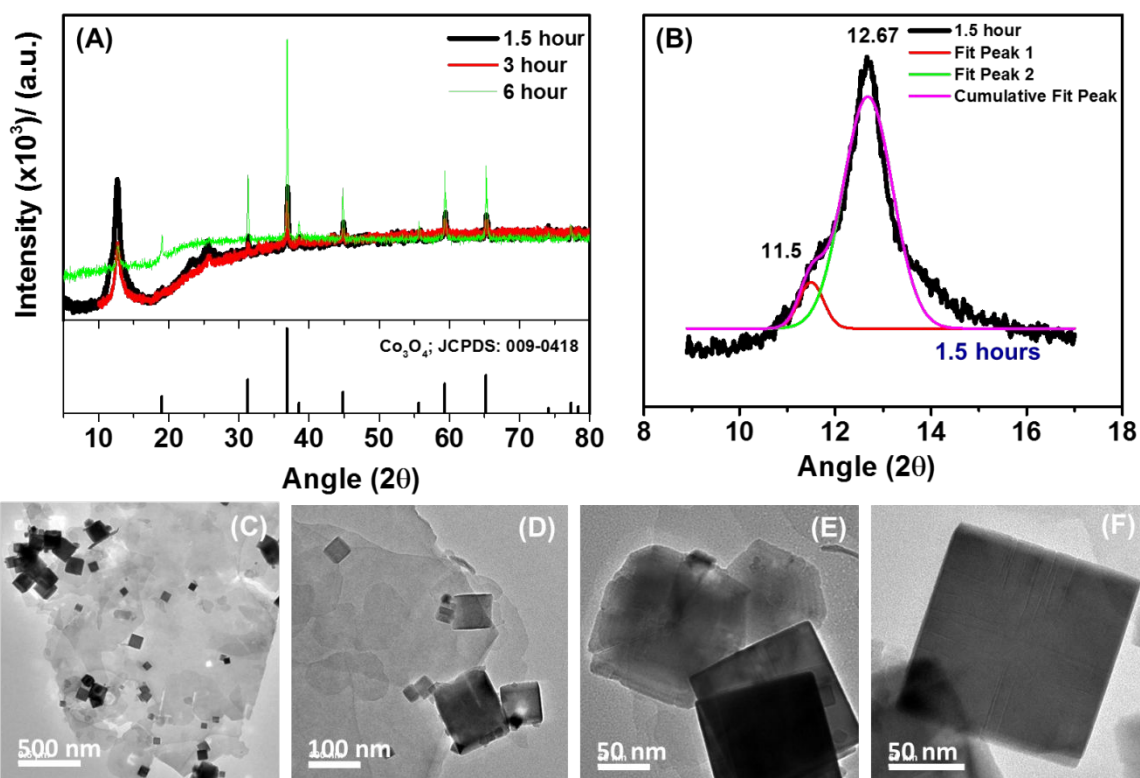


Figure S6: (A) Time-dependent PXRD of material synthesized in ethanol: water (5:1) solvent ratio with diethylamine. A continuous decrease of the peak around 12° belonging to HT phases with concurrent intensification of characteristic peaks of Co_3O_4 with increase in reaction time was observed. (B) The peak around 12° was found to arise due to a convolution of two different peaks at 11.5° and 12.67° . As per reports, the peak at lower 2θ belong to HT(II,III) phase. (C-F) TEM images show the coexistence of both flakes and cubes belonging to Co-hydroxides and Co_3O_4 , respectively in the material obtained after 6 hours.

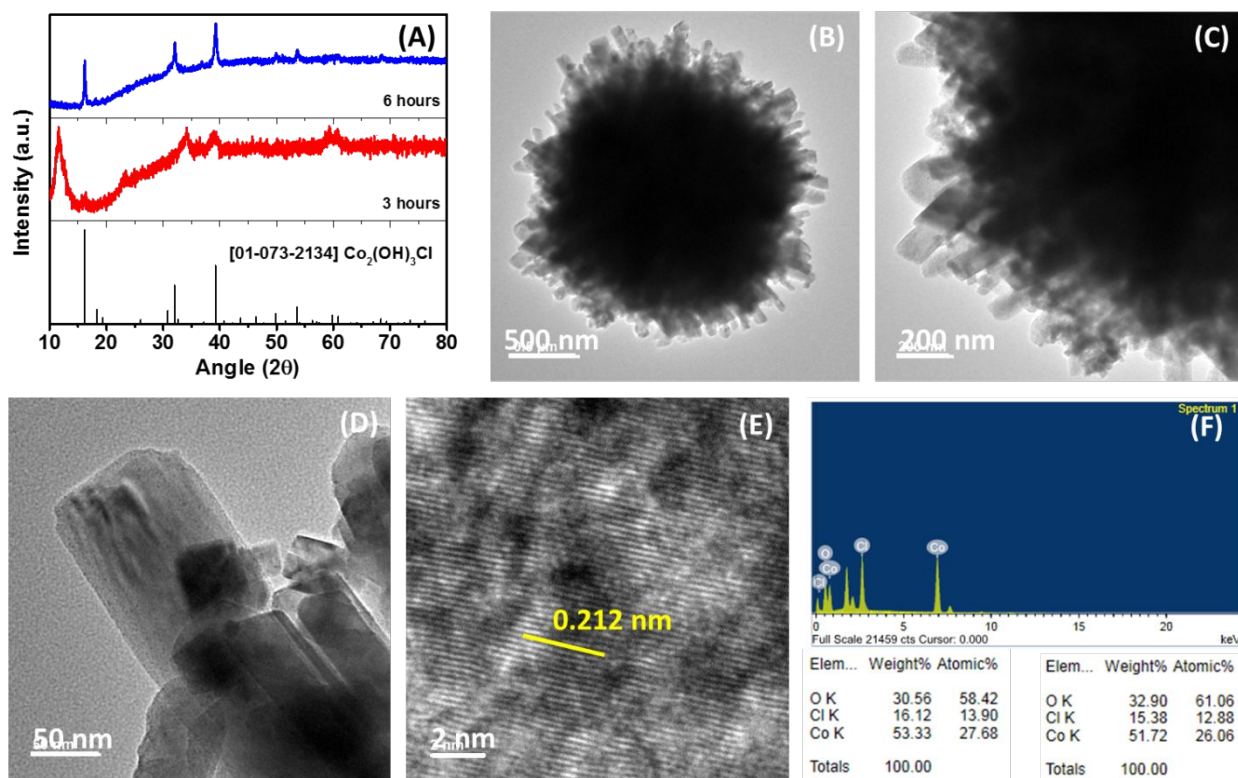


Figure S7: (A) Time-dependent PXRD of material synthesized in ethanol: water = 5:1 solvent ratio with ammonia. While peak around 12° indicates the presence of HT(II) phase after 30 minutes of reaction, peaks from the material synthesized for six hours belong to pure $\text{Co}_2(\text{OH})_3\text{Cl}$ thereby indicating that the HT(II) phase acts as the precursor for the formation of the final product. (B-E) TEM and HR-TEM images suggest the presence of pom-pom type microballs composed of rod like structures. (F) EDS analysis suggests the presence of cobalt and chlorine in the ratio of 2:1.

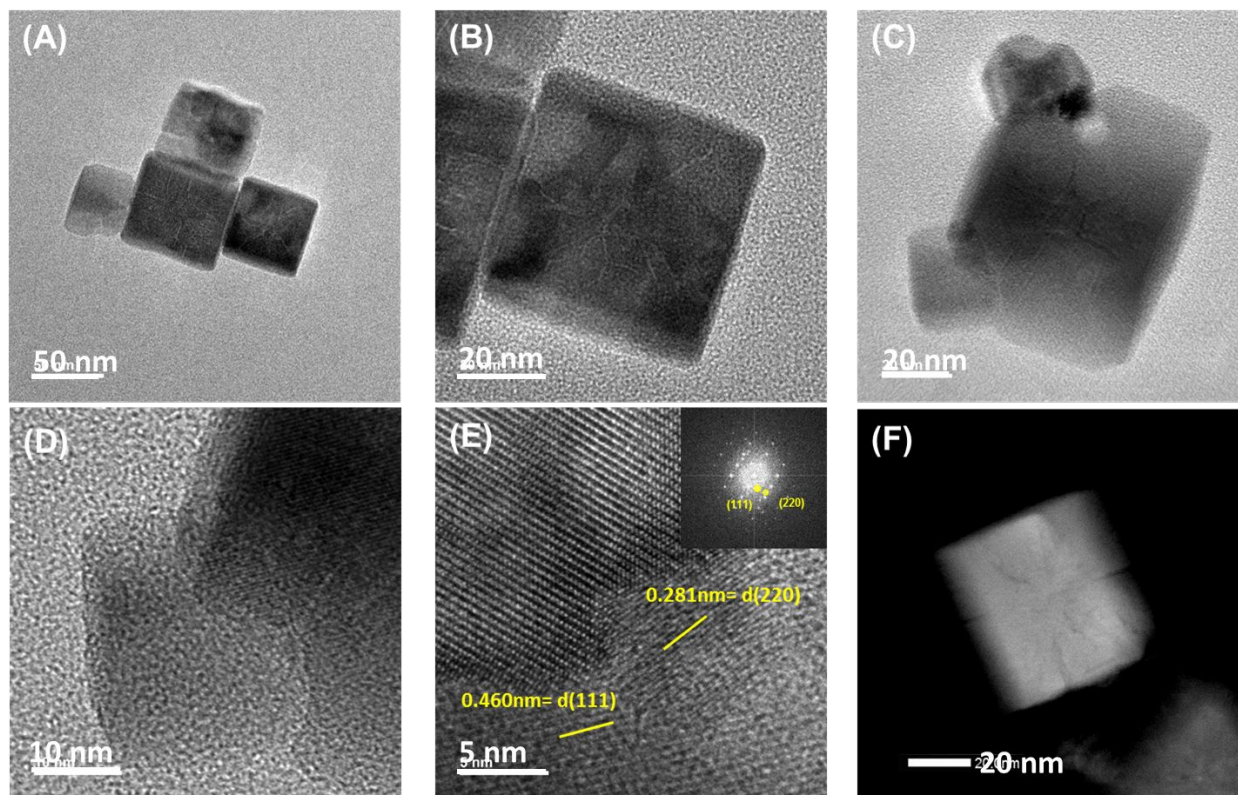


Figure S8: (A-B) TEM images of the material (Co_3O_4) synthesized in ethanol: water (1:1) solvent ratio with ethylamine. Presence of cracks is clearly visible in the cubic structures. (C-E) Imperfect attachment of smaller particles to form a relatively larger material is evident from the TEM images. (F) STEM shows the presence of cracks in the as-synthesized material.

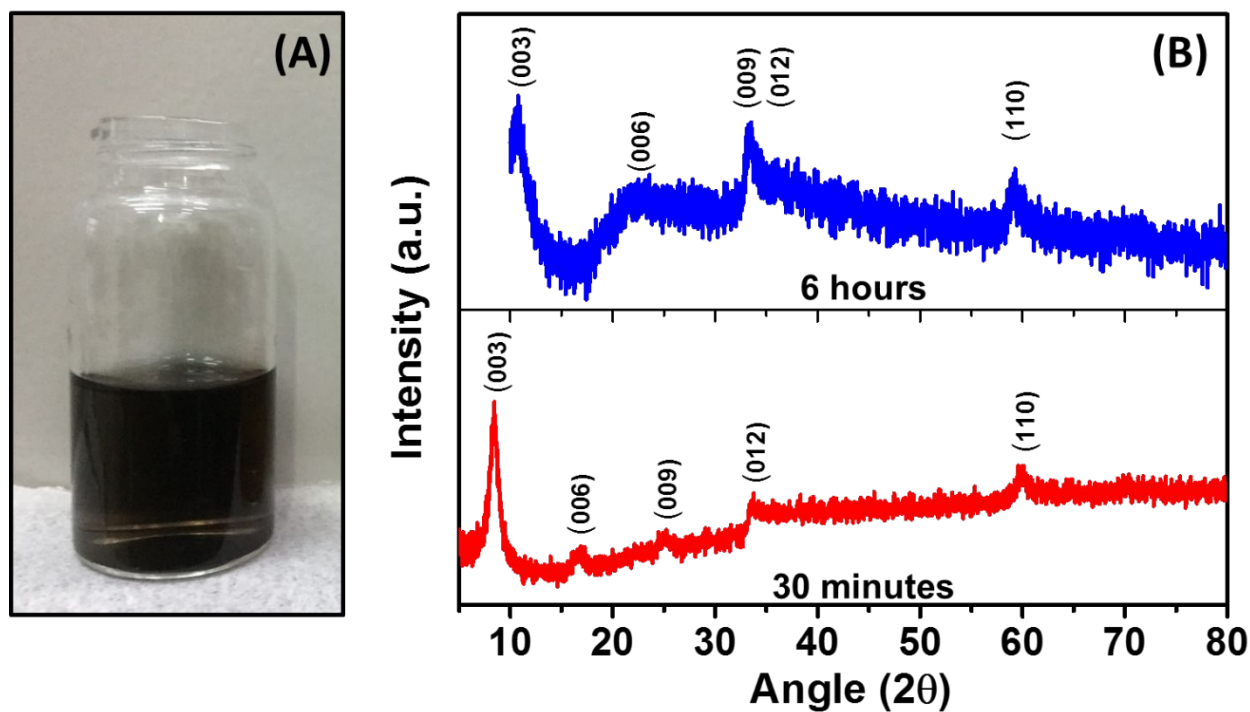


Figure S9: (A) The deep brown coloured solution formed after the addition of triethanolamine in an aqueous solution of cobalt nitrate. (B) Time-dependent PXRD of materials formed with triethanolamine in ethanol: water (1:1) solvent mixture.

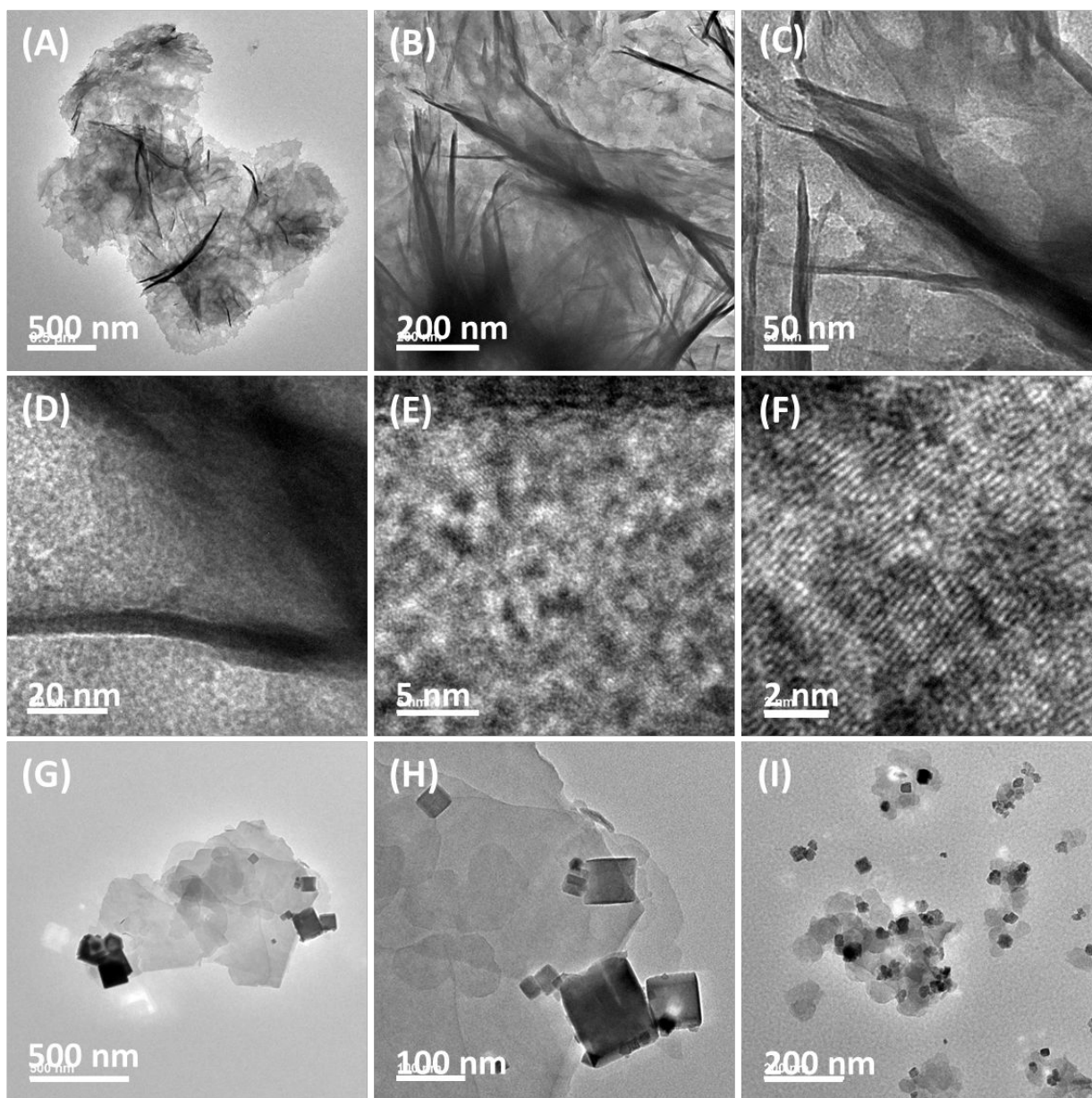


Figure S10: TEM images of (A-F) HT(II,III) synthesized using triethanolamine in ethanol:water (1:1) solvent, (G-H) end product obtained using diethylamine in ethanol:water (5:1) solvent and (I) end product from methyldiethanolamine in ethanol:water (1:1) solvent. The hydroxides generated using triethanolamine has a relatively uneven surface compared to those (flake like entities in the TEM images (G-I) obtained using more hydrophobic amines.

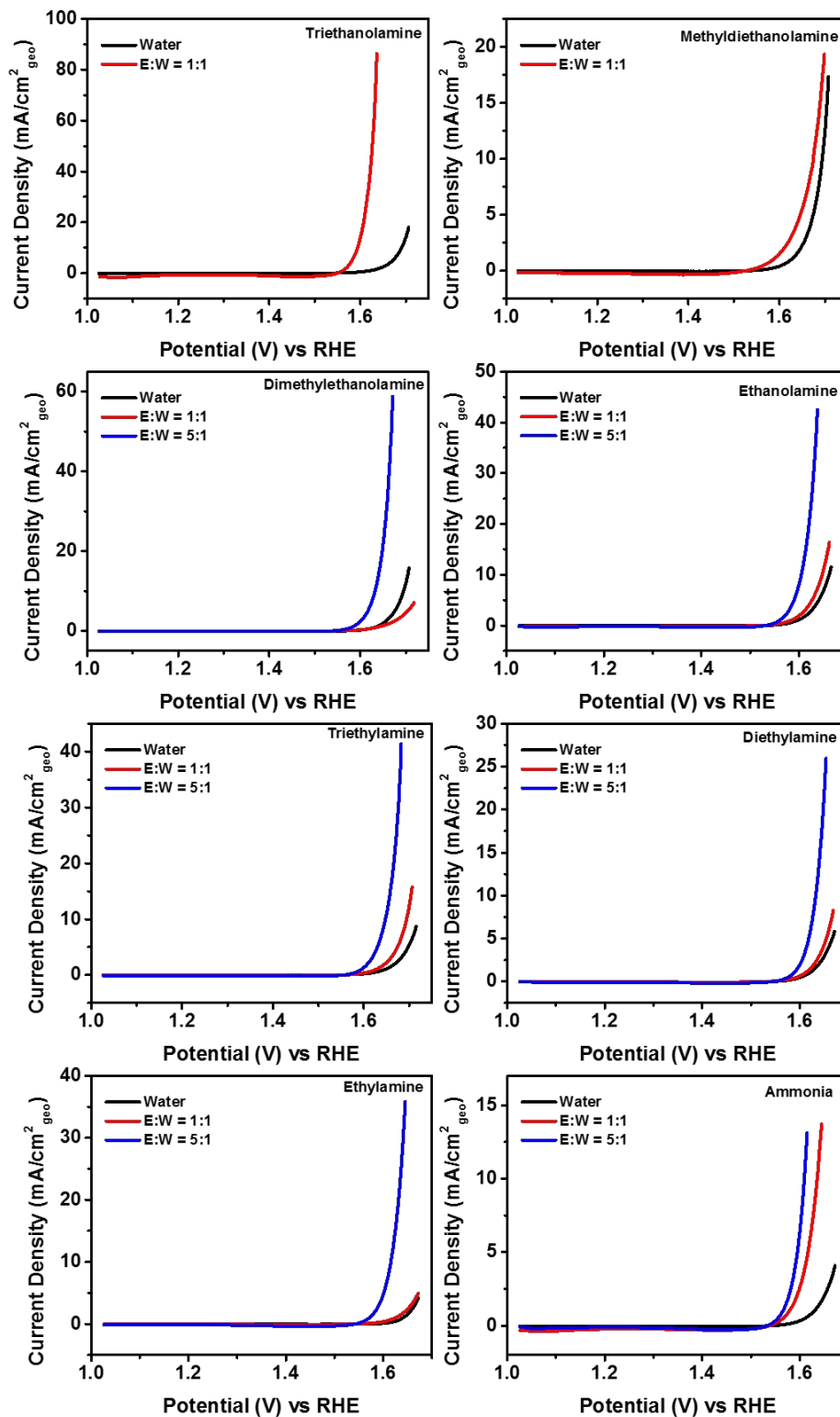


Figure S11: Backward LSV scans (iR corrected) in the potential region of 1.73-1 V vs. RHE for different materials in 1M KOH.

Table S2: Comparison of geometric OER electrocatalytic activity with recently reported Co-based OER electrocatalysts in the alkaline electrolyte.

Material	Overpotential (mV) value at $10\text{mA}/\text{cm}^2_{\text{geo}}$ (forward scan)	Overpotential (mV) value at $10\text{mA}/\text{cm}^2_{\text{geo}}$ (backward scan)	Reference
$\alpha\text{-Co}(\text{OH})_2\text{-Cl}$	320		J. Mater. Chem. A, 2016, 4, 9578
reduced Co_3O_4	410		Adv. Energy Mater., 2014, 4, 1400696
$\alpha\text{-Co}(\text{OH})_2\text{-Cl}$	380		Dalton Trans., 2017, 46, 10545
$\text{Co}(\text{OH})_2$	290		Applied Surface Science, 2018, 427, 253
crumpled graphene- CoO	340		Energy Environ. Sci., 2014, 7, 609
$\alpha\text{-Co}(\text{OH})_2$ hollow nanoflowers	310		Journal of Materials Research, 2018, 33, 568
$\alpha\text{-Co}_4\text{Fe}(\text{OH})_x$	295		J. Mater. Chem. A, 2017, 5, 1078-1084
$\text{CoO}_x@\text{CN}$	260		J. Am. Chem. Soc. 2015, 137, 2688-2694
This work		360	

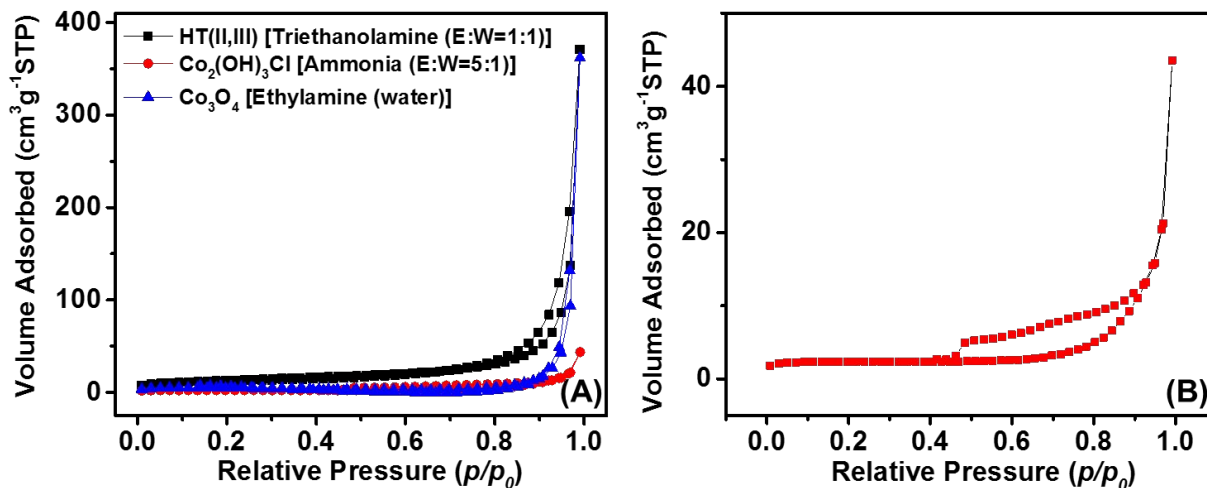


Figure S12: (A) Nitrogen adsorption-desorption isotherms of HT(II,III), Co_3O_4 [ethylamine in water] and $\text{Co}_2(\text{OH})_3\text{Cl}$ [ammonia in ethanol:water (5:1)]. (B) Nitrogen adsorption-desorption isotherm of $\text{Co}_2(\text{OH})_3\text{Cl}$ [ammonia in ethanol:water (5:1)] showing a H2 hysteresis through a quick stair around $p/p_0 = 0.45$. The large H2 hysteresis loop at high relative pressure suggests the abundance of ink-bottle like mesoporosity within the material.

Table S3: Surface area, average pore diameter and total pore volume as obtained from nitrogen adsorption-desorption studies for pure phase materials.

Sample Name	S_{BET} (m^2gm^{-1}) ^a	$V_{\text{p-Total}}$ ($\text{cm}^3\text{gm}^{-1}$) ^b	Pore diameter (nm) ^c
HT(II,III)	44	0.101	9.89
$\text{Co}_2(\text{OH})_3\text{Cl}$	7	0.018	5.26
Co_3O_4	12	0.023	13.05

^a BET surface area; ^b Total pore volume; ^c Average pore diameter

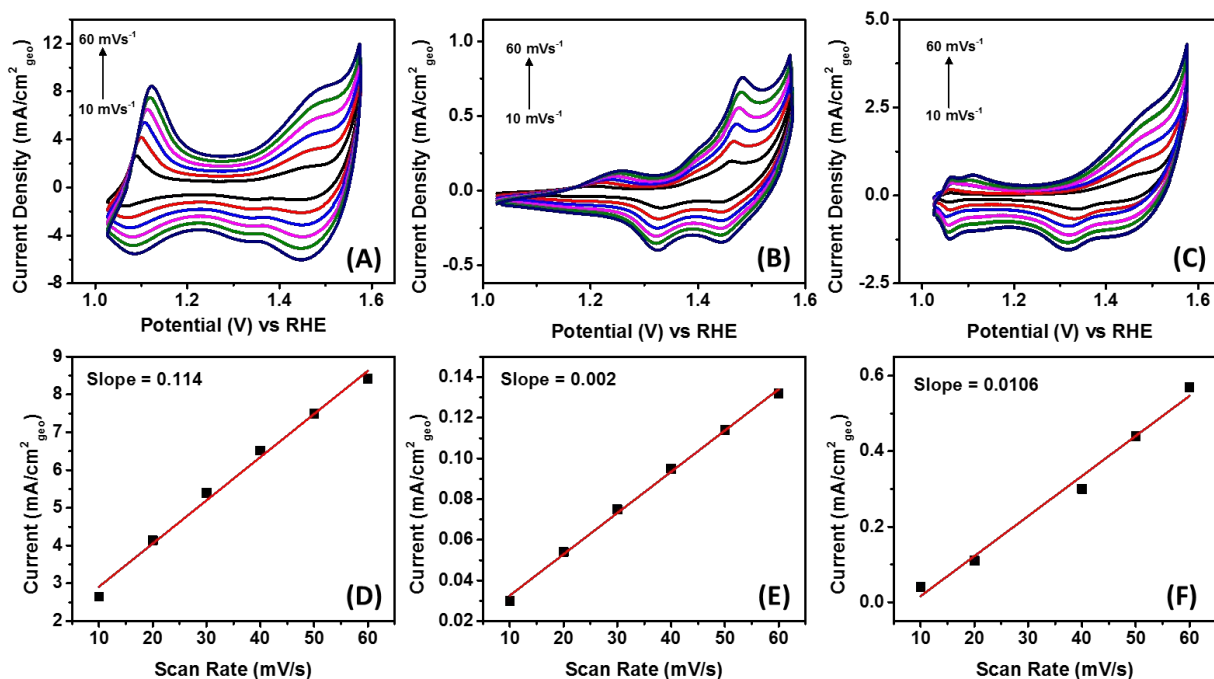


Figure S13: Cyclic voltammetry of pure phase materials at different scan rates: (A) HT(II,III), (B) Co₃O₄ [ethylamine in water] and (C) Co₂(OH)₃Cl [ammonia in ethanol:water (5:1)]. Plot of Co³⁺/Co²⁺ peak current vs. scan rate for (D) HT(II,III), (E) Co₃O₄ [ethylamine in water] and (F) Co₂(OH)₃Cl [ammonia in ethanol:water (5:1)].

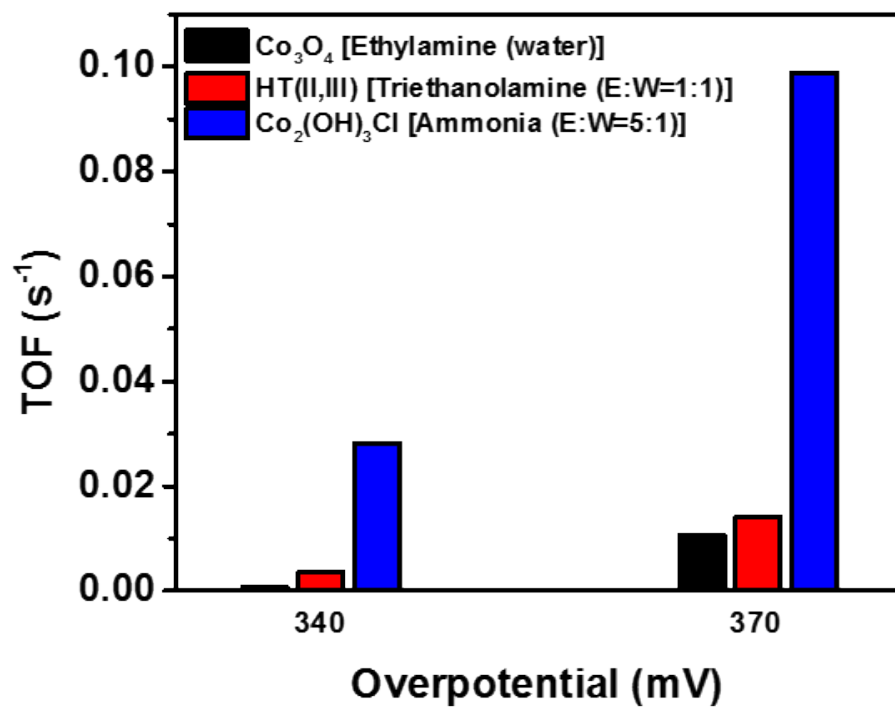


Figure S14: Turn over frequency of different pure phase materials during OER at different overpotentials.

Table S4: Comparison of geometric OER electrocatalytic activity with recently reported Co-based OER electrocatalysts in the alkaline electrolyte.

Material	TOF (mol O ₂ s ⁻¹)	Overpotential (mV)	Method of Calculation	Reference
NiCo sulfide (200)	0.080	360 (FS)	A	R. Soc. open sci. 5, 180927
La _{0.4} Sr _{0.6} Ni _{0.5} Fe _{0.5} O ₃	0.038	400 (FS)	-	Frontiers in Chemistry, 2019, 7, 224
SSU-Co-900	0.034	420 (FS)	A	Journal of Materials Research, 2018, 33, 568
Co ₃ O ₄ @CoOSC	0.049	400 (FS)	A	Nat. Commun. 2015, 6, 8106
Ni-Co-Bi/CC	0.33	500 (FS)	C	Small 2017, 13, 1700394
CuCo ₂ S ₄	0.143	310 (FS)	B	ACS Catal. 2017, 7, 9, 5871
HT (II,III)	0.004 0.012	340 (BS) 370 (BS)	C	This work
Co₂(OH)₃Cl	0.029 0.090	340 (BS) 370 (BS)	C	This work
Co₃O₄	0.001 0.010	340 (BS) 370 (BS)	C	This work

A: active site determined from ICP-MS data or quantitative XPS, considered every metal site to be active for electrocatalysis.

B: using BET surface area and lattice parameter to determine atoms per surface area

C: active site determined electrochemically, only those participating in redox process have been considered for the calculation (method adopted in this work).

FS: Forward Scan has been considered for TOF calculation.

BS: Backward Scan has been considered for TOF calculation.

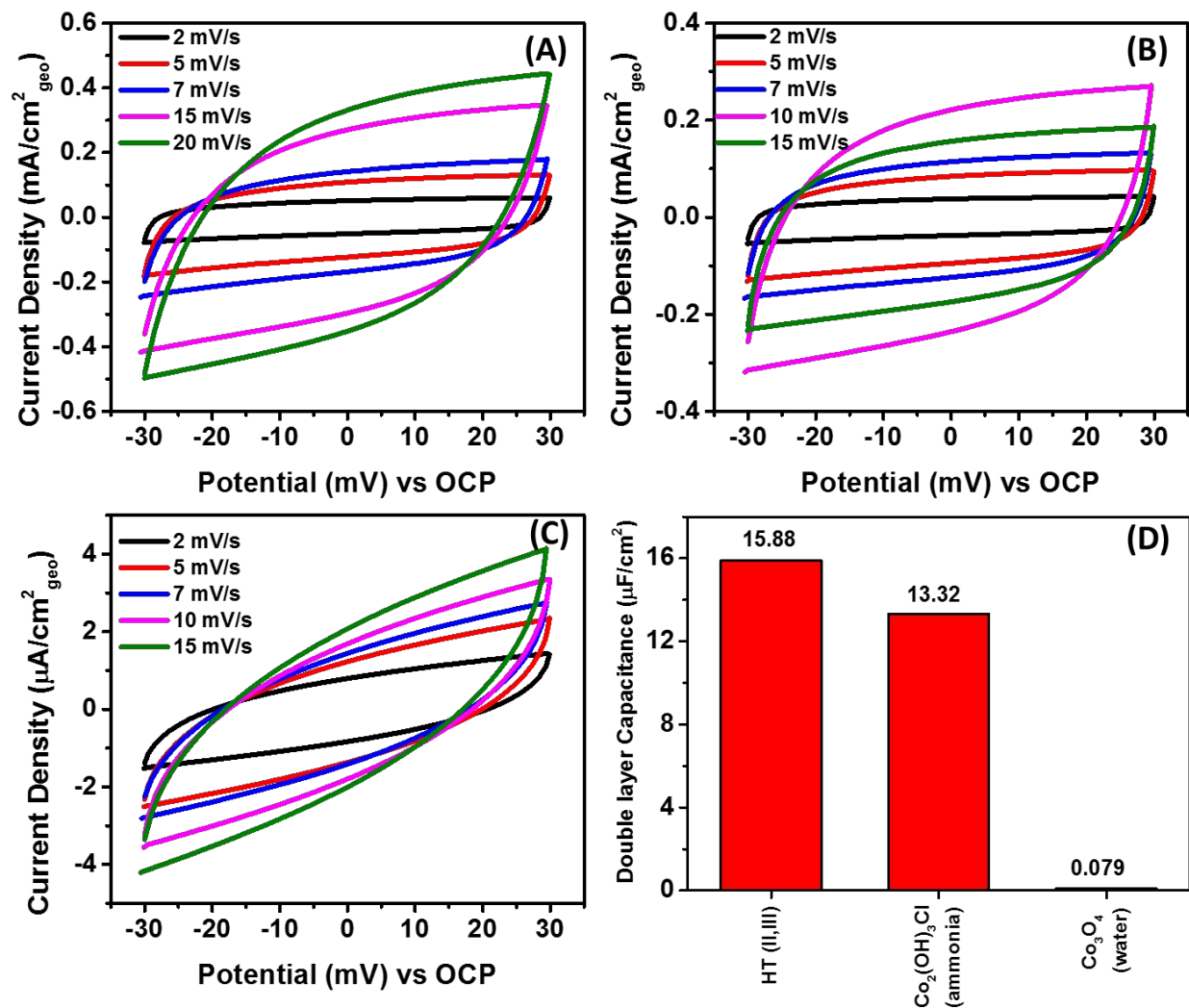


Figure S15: CV scans at different scan rates in CH₃CN/KPF₆ of (A) HT(II,III), (B) Co₂(OH)₃Cl [ammonia in ethanol:water (5:1)] and (C) Co₃O₄ [ethylamine in water]. (D) The double layer capacitance of the materials.

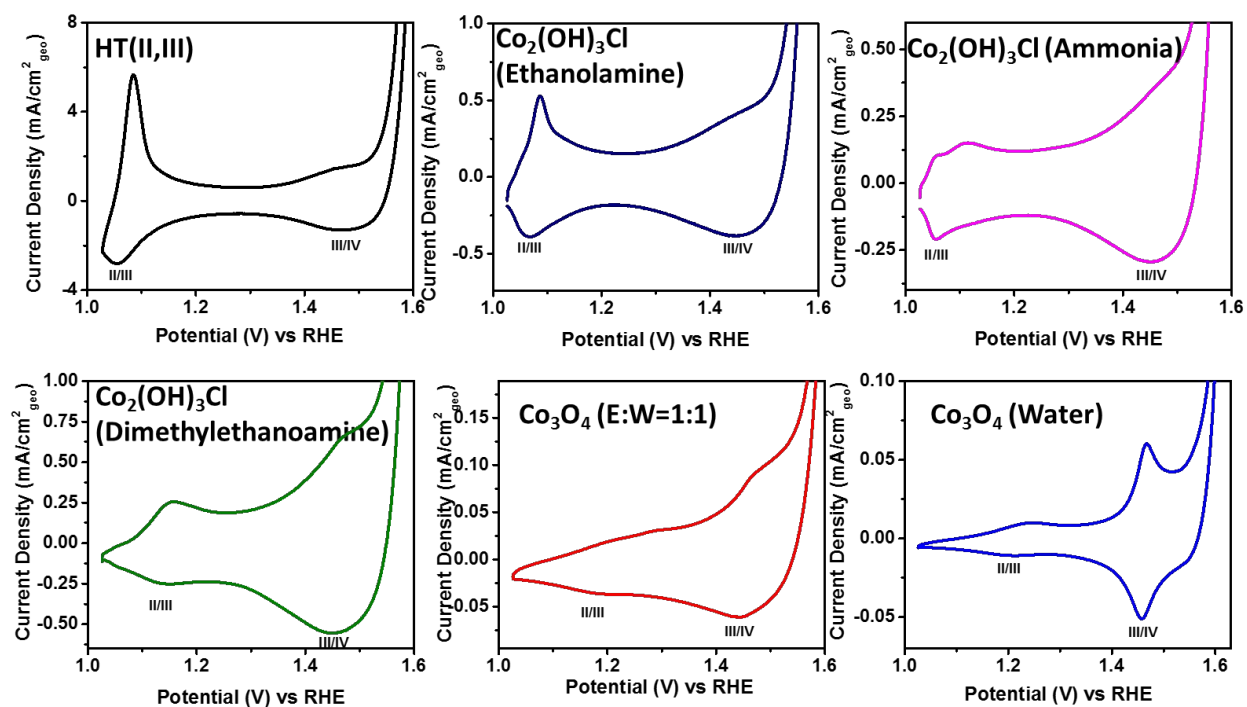


Figure S16: Cyclic voltammetry of pure phase materials showing the Co(II/III) and Co(III/IV) redox peaks with different current density.

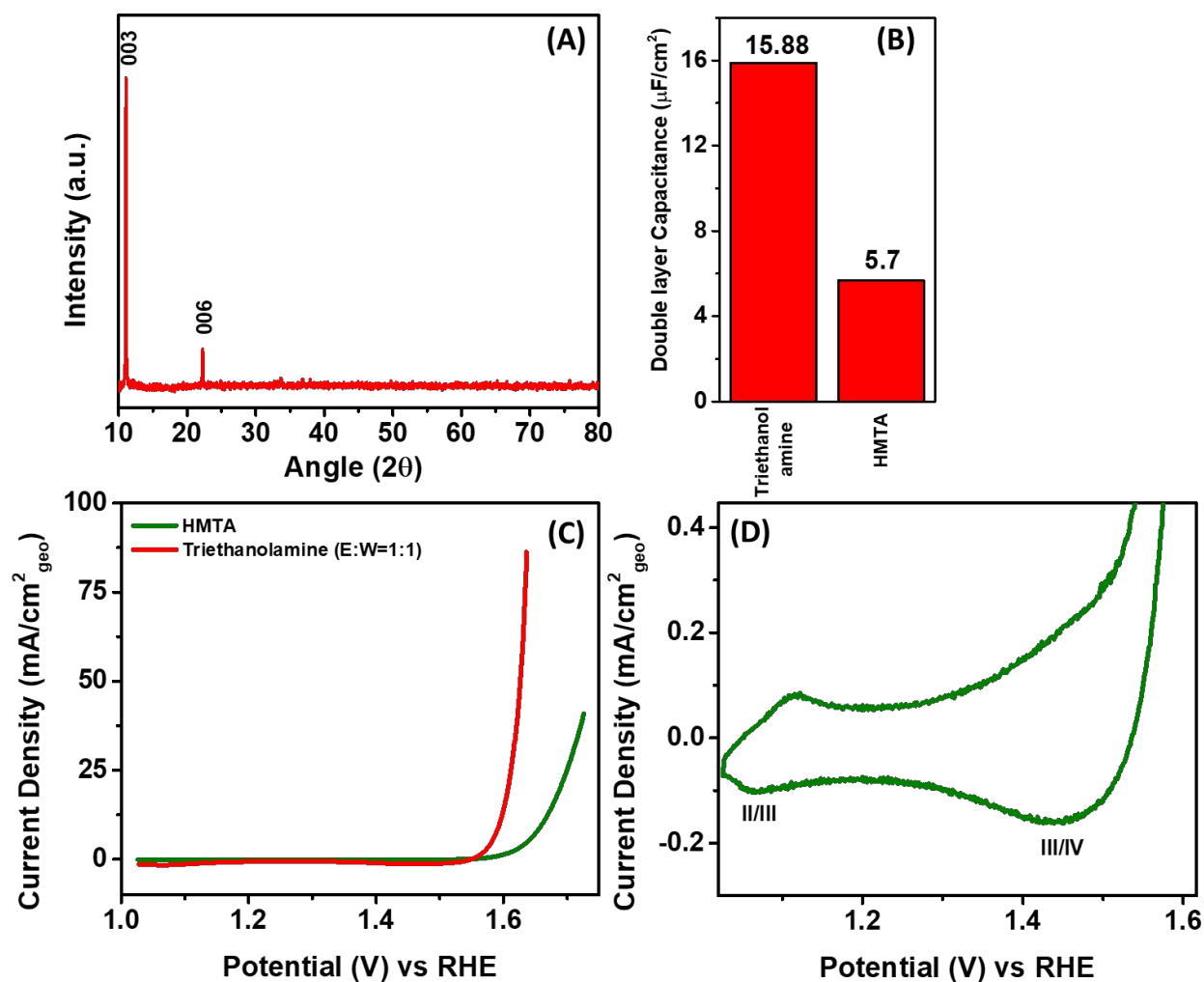


Figure S17: (A) PXRD pattern of α -Co(OH)₂ suggests high crystallinity of the as-synthesized material. (B) Double layer capacitance data shows that the materials synthesized using HMTA has a much lower ECSA compared to that synthesized using triethanolamine. (C) Backward LSV scans (iR corrected) comparing the geometric OER electrocatalytic activity of α -Co(OH)₂ synthesized using HMTA and triethanolamine. (D) The redox feature of α -Co(OH)₂ synthesized with HMTA shows a significantly lower Co(II/III) redox current compared to that synthesized with triethanolamine implies relatively lower OER site density.

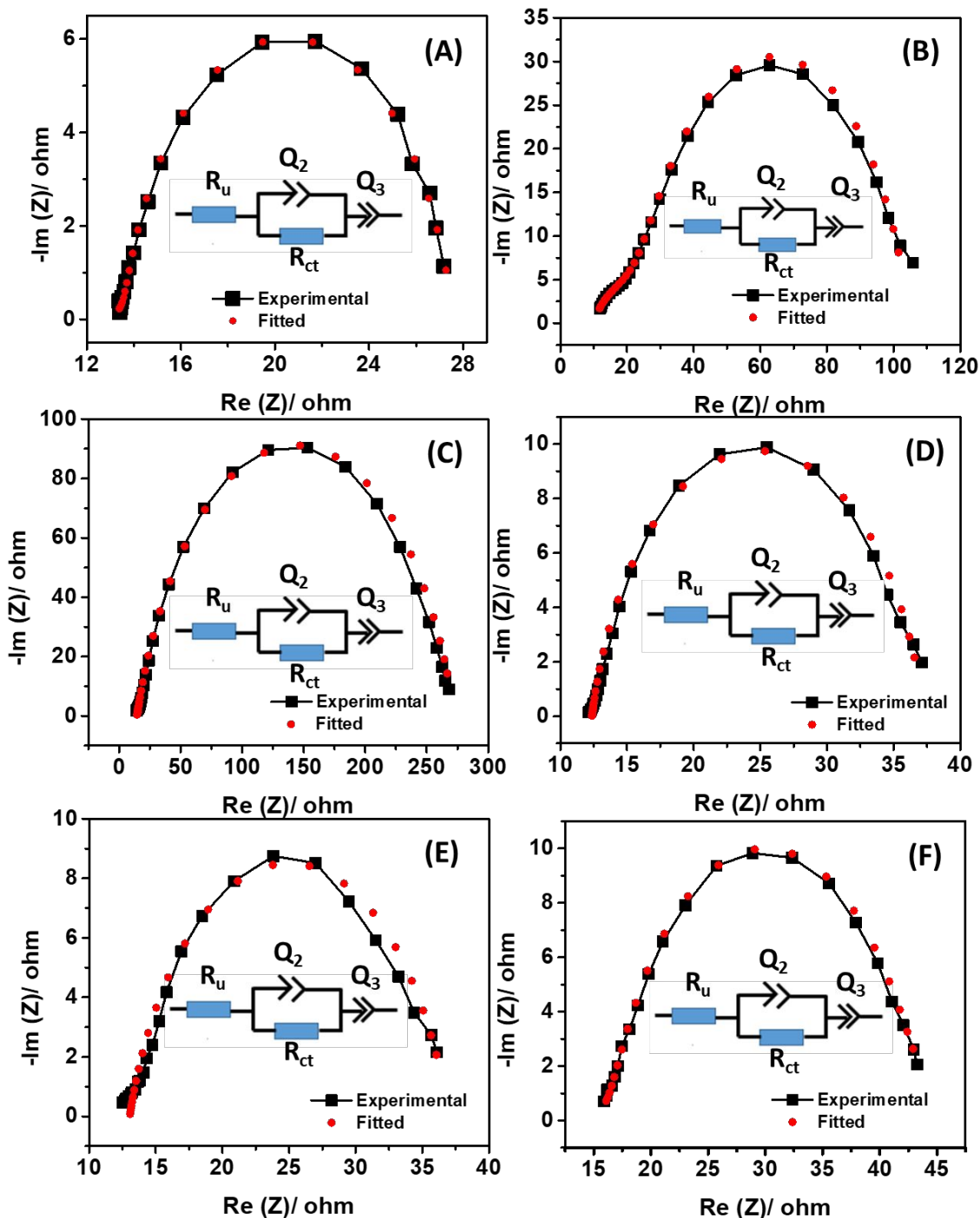


Figure S18: EIS (conducted at 1.63 V vs. RHE in 1M KOH) and corresponding fitting parameters for (A) HT(II,III), (B) Co_3O_4 [ethylamine in ethanol:water = 1:1], (C) Co_3O_4 [ethylamine in water], (D), $\text{Co}_2(\text{OH})_3\text{Cl}$ [ethanolamine in ethanol:water = 5:1] (E) $\text{Co}_2(\text{OH})_3\text{Cl}$ [dimethylethanolamine in ethanol:water = 5:1] and (F) $\text{Co}_2(\text{OH})_3\text{Cl}$ [ammonia in ethanol:water = 5:1].

R1+Q2/R2+Q3 (A)	
R1	13.7 Ohm
Q2	$8.039 \times 10^{-3} \text{ F.s}^{(a-1)}$
A2	0.923 3
R2	13.21 Ohm
Q3	$0.074 16 \text{ F.s}^{(a-1)}$
a3	7.743×10^{-3}

R1+Q2/R2+Q3 (B)	
R1	9.70 Ohm
Q2	$0.5559 \times 10^{-3} \text{ F.s}^{(a-1)}$
A2	0.8231
R2	95.2 Ohm
Q3	$0.0.843 \times 10^{-3} \text{ F.s}^{(a-1)}$
a3	0.4954

R1+Q2/R2+Q3 (C)	
R1	14.55 Ohm
Q2	$0.450 1 \times 10^{-3} \text{ F.s}^{(a-1)}$
A2	0.782 5
R2	258.3 Ohm
Q3	$8.737 \times 10^{12} \text{ F.s}^{(a-1)}$
a3	0.641 2

R1+Q2/R2+Q3 (D)	
R1	12.38 Ohm
Q2	$2.782 \times 10^{-3} \text{ F.s}^{(a-1)}$
A2	0.845 1
R2	24.92 Ohm
Q3	$32.63 \times 10^{12} \text{ F.s}^{(a-1)}$
a3	0.889 3

R1+Q2/R2+Q3 (E)	
R1	13.04 Ohm
Q2	$3.083 \times 10^{-3} \text{ F.s}^{(a-1)}$
A2	0.786 6
R2	23.95 Ohm
Q3	$32.58 \times 10^{12} \text{ F.s}^{(a-1)}$
a3	1

R1+Q2/R2+Q3 (F)	
R1	13.02 Ohm
Q2	$3.385 \times 10^{-3} \text{ F.s}^{(a-1)}$
A2	0.8306
R2	24.54 Ohm
Q3	$0.1654 \text{ F.s}^{(a-1)}$
a3	0.08518

Figure S19: Fitting parameters of EIS (conducted at 1.63 V vs. RHE in 1M KOH) for (A) HT(II,III), (B) Co_3O_4 [ethylamine in ethanol:water = 1:1], (C) Co_3O_4 [ethylamine in water]., (D), $\text{Co}_2(\text{OH})_3\text{Cl}$ [ethanolamine in ethanol:water = 5:1] (E) $\text{Co}_2(\text{OH})_3\text{Cl}$ [dimethylethanolamine in ethanol:water = 5:1] and (F) $\text{Co}_2(\text{OH})_3\text{Cl}$ [ammonia in ethanol:water = 5:1].

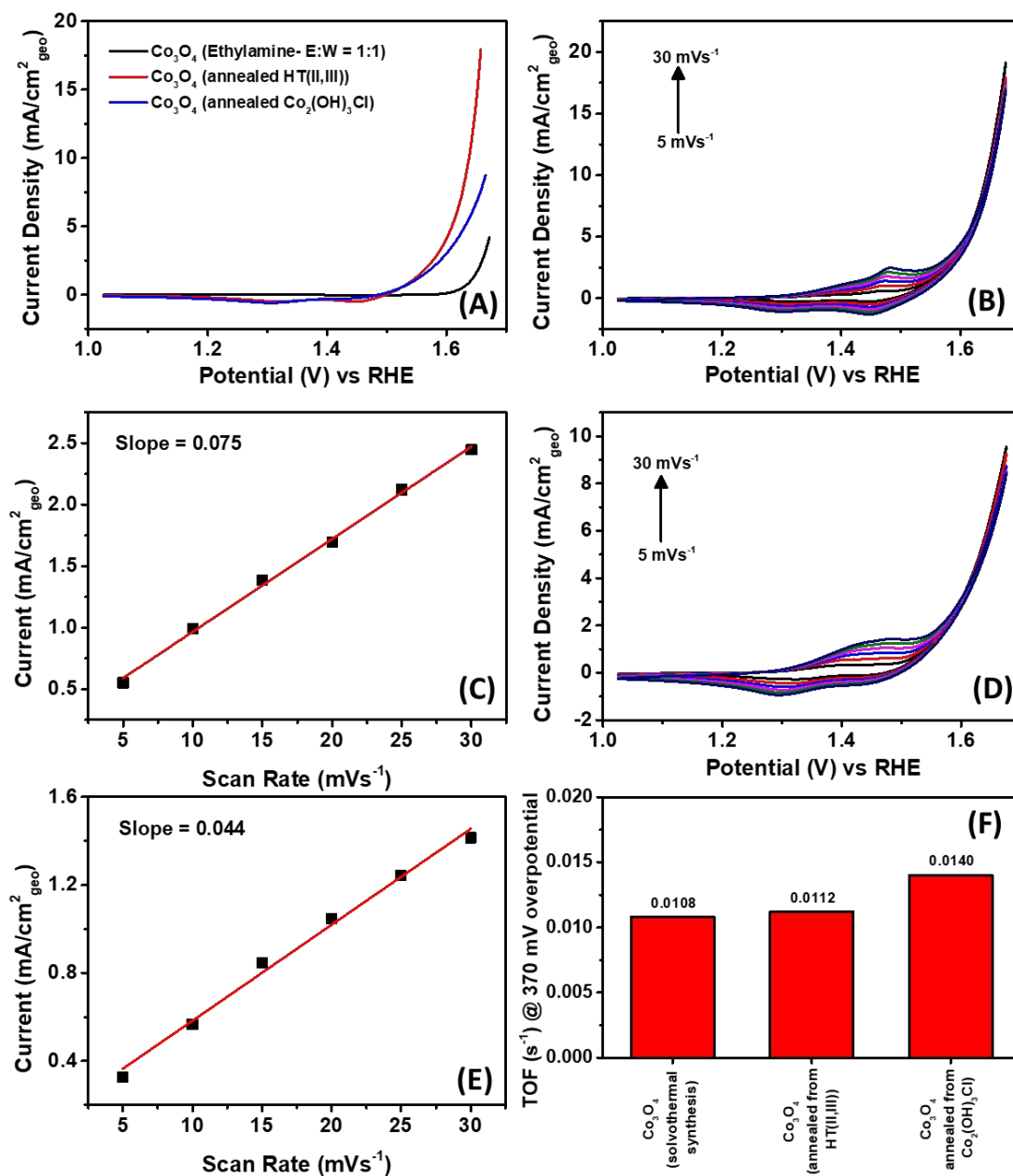


Figure S20: (A) Backward LSV scans using Co_3O_4 synthesized by various methods. Cyclic voltammetry of (B-C) Co_3O_4 HT(II,III)annealed and (D-E) Co_3O_4 $\text{Co}_2(\text{OH})_3\text{Cl}$ annealed materials at different scan rates to determine number of electrochemical active site. (F) TOF of Co_3O_4 synthesized by different routes at 370 mV overpotential.

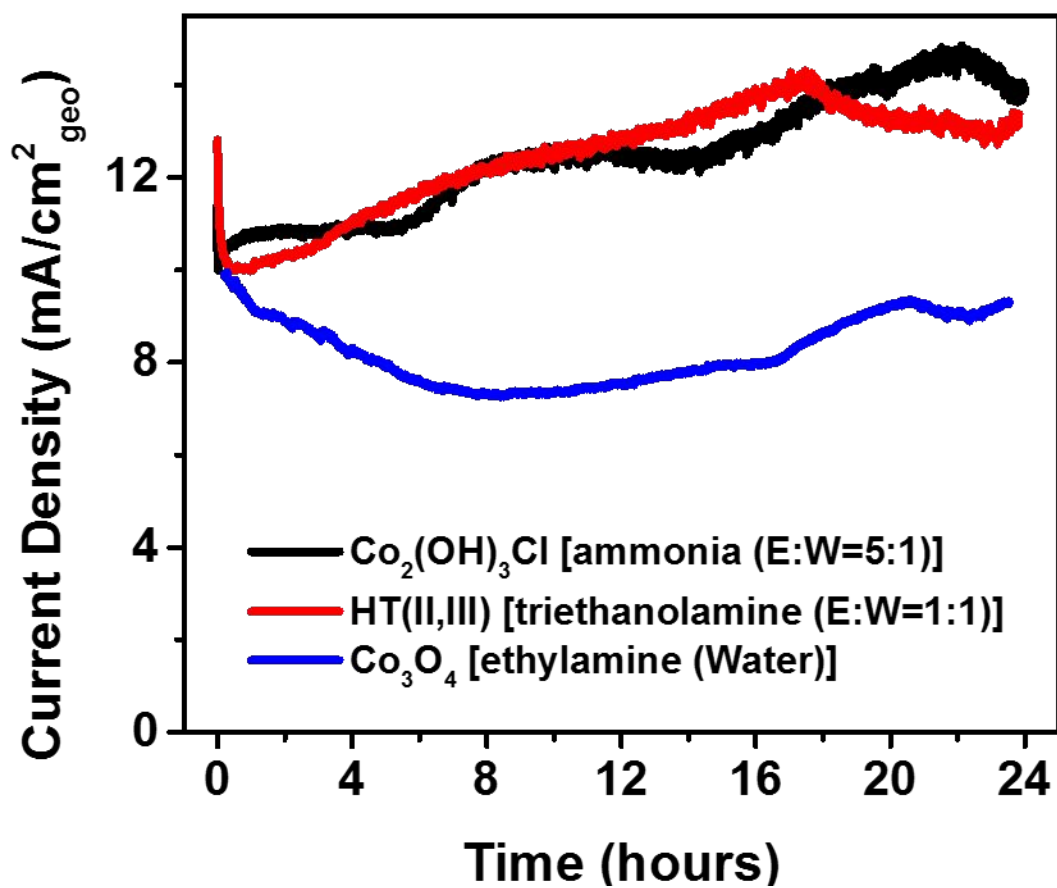


Figure S21: Chronoamperometry experiment of pure phase materials dropcasted on conductive carbon paper substrate for 24 hours at potentials corresponding to 10 mA/cm²_{geo}.

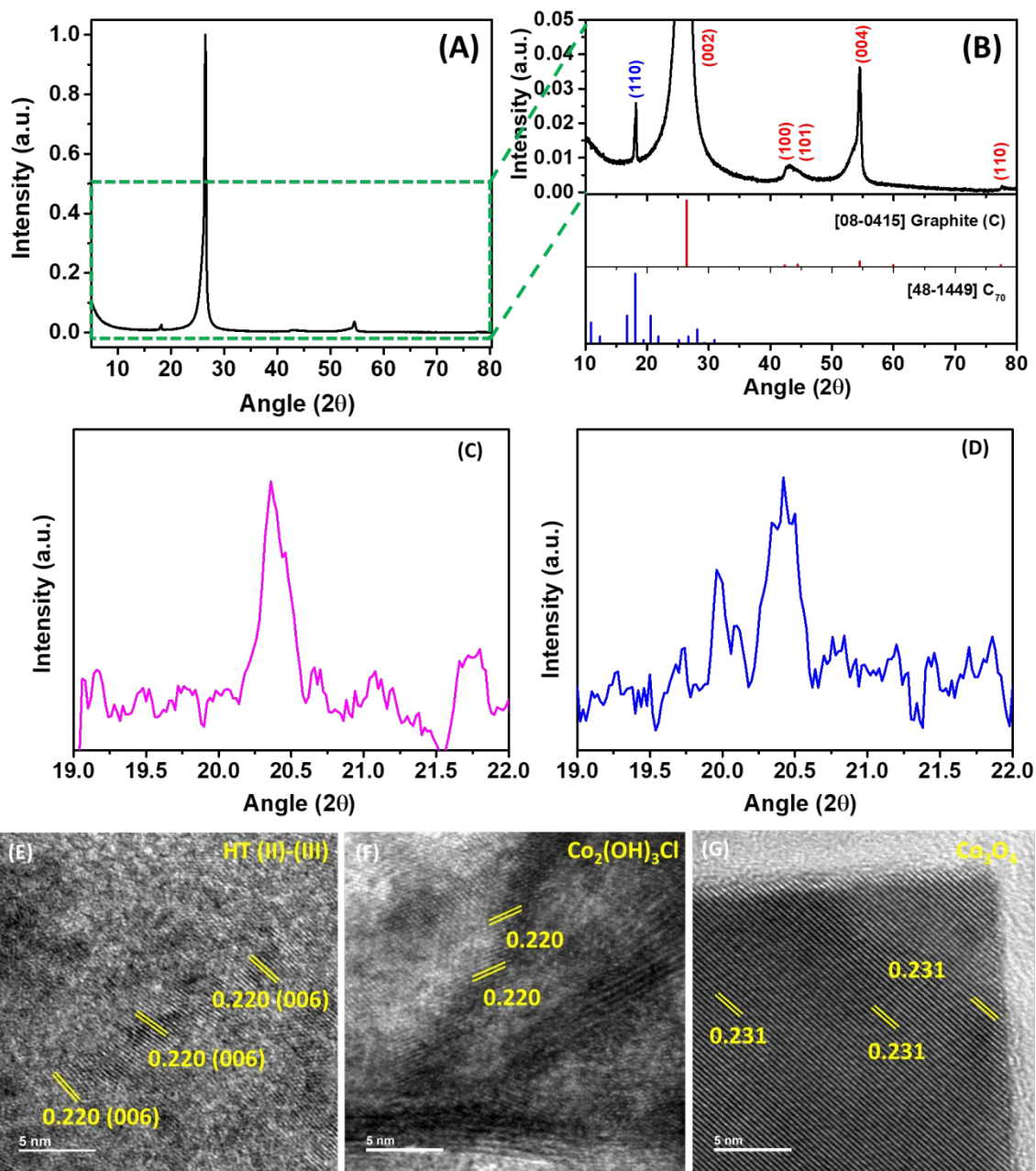


Figure S22: (A-B) PXRD of carbon paper substrate shows the presence of graphitic C and C70 in the material. (C-D) A peak at $2\theta = \sim 20.5^\circ$ was found to be present for $\text{Co}_2(\text{OH})_3\text{Cl}$ and Co_3O_4 after electrocatalysis suggesting the formation of CoOOH . (E-F) HR-TEM images of the materials after electrocatalysis.

Materials: Cobalt chloride hexahydrate [CoCl₂.6H₂O], ethanol, potassium hydroxide and ammonia were purchased from Merck. Triethanolamine (TEthA), methyldiethanolamine (MeDEthA), dimethylethanolamine (DMeEthA), ethanolamine (EthA), diethylamine (DEtA) and ethylamine- methanolic solution (EtA) were purchased from Sigma Aldrich. Glassy carbon electrode and conductive carbon paper were procured from CH Instruments and Toray, respectively.

Synthesis Apparatus: The solvothermal reactions were carried out in Berghof DAB-3 pressure vessels. A Berghof DAH heating block fitted with a Berghof BTC-1000 temperature controller was employed for heating purpose.

Electrochemical Techniques: The electrocatalytic activities of the materials were evaluated by linear sweep voltammetry (LSV) and cyclic voltammetry (CV) techniques in a three electrode cell setup. During electrochemical reactions, the material coated glassy carbon or carbon paper and an Ag/AgCl (3.5 M KCl) were used as working and reference electrodes, respectively. Further, a Pt wire was employed as counter electrode during evaluating the activity of materials towards OER, respectively. All measurements were conducted in 1 M KOH solution. Prior to data collection, all catalysts were subjected to precondition by performing 15 cycles of CV in the desired potential window. The uncompensated solution resistance (R_u) of the electrochemical cell was determined by choosing “PEIS iR compensation” method provided with the potentiostat and the obtained data were subsequently corrected by using the equation: $(V - iR_u)$. Further, all data were calibrated to reversible hydrogen electrode (RHE) scale for ease of understanding. To probe the post-catalytic state of the pure phase materials, the materials were first dropcasted on conductive carbon papers and subjected to chronoamperometry for 24 hours at potentials corresponding to 10 mA/cm²_{geo} for each material. Electrochemical impedance spectroscopy (EIS) was performed in the same setup at 1.63 V vs. RHE. To estimate electrochemically active surface area (ECSA) of the catalysts, double layer capacitance (DLC) of each material was determined by the protocol developed by Surendranath *et al.* in the recent past.^[1] A 0.15 M KPF₆ solution in acetonitrile was used as the electrolyte and an Ag/Ag⁺ electrode was used as the reference electrode during the measurements. Initially, the open circuit voltage (OCP) of each catalyst (material coated Cu mesh) was determined with respect to the reference electrode and

thereafter, cyclic voltammetry at different scan rates was obtained at ± 30 mV potential window with respect to OCP.

Characterization: PXRD measurements were carried out in a Rigaku-Smartlab diffractometer attached with a D/tex ultradetector and Cu K α source operating at 35 mA and 70 kV. FT-IR measurements were carried out in a Perkin Elmer Spectrum Two instrument. EDS was acquired on a SUPRA 55-VP instrument with patented GEMINI column technology. TEM images were collected on a JEM 2100F field emission transmission electron microscope operating at 200 kV. ICP-AES analysis was carried out in ACROS, Simultaneous ICP Spectrometer manufactured by SPECTRO Analytical Instruments GmbH, Germany. XPS analysis was performed in PHI 5000 Versa Probe II, FEI Inc. XPS system. Electrochemical measurements were carried out in Biologic SP300 electrochemical workstations. Nitrogen adsorption-desorption measurements were conducted at 77 K with a Micromeritics Gemini VII-2390t instrument. The powders were outgassed in vacuum at 90 °C for 4 hours prior to measurements.

Details of electrode fabrication:

- *Preparation of catalyst ink:*

2 mg of NiCo₂Mo precipitate was mixed in 0.5 ml 1:1 water: ethanol solution by sonication. 25 μ l PVDF-NMP (8mg/ml) solution was then added and further sonicated to attain homogeneous mixing.

- *Preparation of electrode:* About 4 μ l of catalyst inks were dropcasted on a polished glassy carbon electrode (3 mm diameter). It was then carefully dried in an oven at ~ 55 °C and used as the working electrode during electrochemical measurements.

[1] Y. Yoon, B. Yan, Y. Surendranath, *J. Am. Chem. Soc.* **2018**, *140*, 2397.