# **Electronic Supporting Information**

for

Inception of Molybdate as "Pore Forming Additive" to Enhance the Bifunctional Electrocatalytic Activity of Nickel and Cobalt based Mixed Hydroxides for Overall Water

# Splitting

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Materials: Nickel nitrate hexahydrate [Ni(NO<sub>3</sub>)<sub>3</sub>.6H<sub>2</sub>O], cobalt nitrate hexahydrate [Co(NO<sub>3</sub>)<sub>3</sub>.6H<sub>2</sub>O], ammonium heptamolybdate tetrahydrate [(NH<sub>4</sub>)<sub>6</sub>Mo<sub>7</sub>O<sub>24</sub>.4H<sub>2</sub>O], urea [CO(NH<sub>2</sub>)<sub>2</sub>], potassium hydroxide [KOH], nitric acid [HNO<sub>3</sub>], ammonium carbonate [(NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub>] and acetonitrile were purchased from Merck. Potassium hexafluorophosphate  $[KPF_6]$  was purchased from Aldrich chemicals. All chemicals were used without any further purification. Cu gauze (100 mesh woven from 0.11mm diameter wire) and hydrophilic carbon fibre cloth (Product Code: 1591002-1) were purchased from Alfa-Aesar and ELAT, respectively. 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 Cu mesh and an Ag/AgCl (3.5 M KCl) were used as working and reference electrodes, respectively. Further, a Pt wire and a graphite rod were employed as counter electrodes during evaluating the activity of materials towards OER and HER, respectively. All measurements were conducted in 1 M KOH solution. During HER, the electrolyte was purged with hydrogen gas to minimize the effect of dissolved oxygen. Prior to data collection, all catalysts were subjected to precondition by performing 20 cycles of CV in the desired potential window. The uncompensated solution resistance ( $R_{\mu}$ ) of the electrochemical cell was determined by choosing "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. Chronopotentiometry was performed for 20 minutes at the current density of 10 mA/cm<sup>2</sup><sub>geo</sub>. Electrochemical impedance spectroscopy (EIS) was performed in the same setup at 1.55 V vs RHE for OER and -0.10 V vs RHE for HER. For evaluating the prospect of the materials in an overall water-splitting system, a two electrode cell comprising the material coated

Cu meshes as both anode and cathode was constructed. The electrochemical cell was purged with Ar prior to data collection. Chronoamperometry was performed for 7 days in a similar setup to assess the stability of electrocatalytic performance of the materials under continuous usage. 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.<sup>[1]</sup> A 0.15 M KPF<sub>6</sub> solution in acetonitrile was used as the electrolyte and an Ag/Ag<sup>+</sup> 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  $\pm 30$ mV potential window with respect to OCP. For Faradaic efficiency calculation, the catalysts were inserted in water filled inverted burets and chronocoulometry was performed for different time intervals. The evolved gases accumulate on top of the burets causing lowering of water level and this provides accurate measurement of the volume of generated gases. This was then compared with the theoretical output value (from chronocoulometry) to figure out the Faradaic efficiency of the electrocatalyst.

**Characterization:** PXRD measurements were carried out in a Rigaku-Smartlab diffractometer attached with a D/tex ultradetector and Cu Kα source operating at 35 mA and 70 kV. Field emission SEM images and EDAX were acquired on a SUPRA 55-VP instrument with patented GEMINI column technology. The samples were coated with a thin layer of gold-palladium in order to avoid charging effects. 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 a ThermoFisher Scientific XPS system.

Electrochemical measurements were carried out in CHI604D and 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.



**Figure S1:** PXRD pattern of different materials formed during chemical bath deposition. (A) The diffraction patterns for Ni and Co match with the standard patterns of  $3Ni(OH)_2.2H_2O$  (ICDD 022-0444) and Co(CO<sub>3</sub>)<sub>0.5</sub>OH.0.11H2O (ICDD 048-0083), respectively. The diffraction

for Mo has resemblance with several ammonium copper molybdenum compounds, such as (NH<sub>3</sub>)<sub>4</sub>CuMoO<sub>4</sub>, (Cu(NH<sub>3</sub>)<sub>4</sub>)MoO<sub>4</sub>, etc. (B) Diffraction pattern of bimetallic materials consisting of both nickel and cobalt hydroxides. (C) Diffraction pattern of bimetallic materials consisting either nickel and molybdenum or cobalt and molybdenum. (D) Diffraction pattern of NiCo<sub>2</sub>Mo synthesized in presence and absence of Cu mesh and (E) Diffraction pattern of other nickel, cobalt and molybdenum containing materials.



**Figure S2:** FT-IR spectrum of as synthesized products. (A) The IR band in the region of 1330-1570 cm<sup>-1</sup> (green box) that signifies nitrate and carbonate groups were present in molybdate free samples. (B-C) For materials synthesized in presence of molybdate, the absence of this band with concurrent presence of molybdate peaks indicate preferential incorporation of molybdate over nitrates and carbonates in the materials.



**Figure S3:** Diffraction pattern of NiCo<sub>2</sub>Mo annealed at 800 °C. This has close resemblance with the standard patterns of CoMoO<sub>4</sub> (ICDD 021-0868) and NiMoO<sub>4</sub> (ICDD 045-0142) thereby suggesting the form of molybdenum in NiCo<sub>2</sub>Mo to be molybdate.



**Figure S4:** Nitrogen adsorption-desorption isotherm of (A) NiMo and (B) NiCo<sub>2</sub>Mo. (C) Pore size distribution of Co, NiCo<sub>2</sub> and NiCo<sub>2</sub>Mo.

**Table S1**: Surface area and porosity features of different materials as obtained from nitrogen

 adsorption-desorption measurement.

Sample Name	Surface Area (m²/g)	Pore Volume (cc/g)	Pore Diameter (nm)
NiCo <sub>2</sub> Mo	58	0.096	9.01
NiCo <sub>2</sub>	37	0.009	6.4
NiMo	49	0.014	6
Со	16	0.005	7.3



**Figure S5:** SEM images of as-prepared catalyst materials on Cu mesh: (a-b) Co, (c-d) NiCo<sub>2</sub> and (e-f) NiCo<sub>2</sub>Mo. (g-i) cross-sectional image of catalyst (NiCo<sub>2</sub>Mo) coated Cu mesh.



**Figure S6:** TEM images of NiCo<sub>2</sub>Mo: (a and b) HR-TEM images show the presence of lattice fringes having interplanar distance of  $d_{hkl}$ = 0.215 nm, 0.233nm and 0.222 nm. These corresponds to very closely situated peaks near 2 $\Theta$ = 42° in the PXRD pattern (as shown in (c)).



**Figure S7:** (a-b) SEM images of NiCo<sub>2</sub>Mo after 6 hours of reaction shows the presence of micro-spheres on the Cu mesh; (c) PXRD pattern and (d) SEM images of NiCo<sub>2</sub>Mo prepared using ammonium bicarbonate instead of urea under similar reaction conditions. The inset in the SEM image reveals the presence of material with irregular morphology.



**Figure S8:** TEM images of NiCo<sub>2</sub>: (a-c) show the evolution of rod like morphology; (c) HR-TEM image shows the presence of lattice fringes having interplanar distance of  $d_{hkl}$ = 0.262 nm.



**Figure S9:** TEM images of NiMo: (a, b and c) show sheet like morphology with the presence of deep foldings; (d) HR-TEM image shows the presence of lattice fringes having interplanar distance of  $d_{hkl}$ = 0.215 nm. This corresponds to the peak at 2 $\Theta$ = 42° in the PXRD pattern (as shown in (e)).



**Figure S10:** TEM images of Co<sub>2</sub>Mo: (a, b and c) show the presence of lamellae like structure; (d) HR-TEM image shows the presence of lattice fringes having interplanar distance of  $d_{hkl}$ = 0.268 nm. This corresponds to the peak at 2 $\Theta$ = 33.68° in the PXRD pattern (as shown in (e)).

#### **Structural Evolution: PXRD and TEM analysis**

To investigate the role of molybdenum on morphological evolution process, microscopy of materials on Cu mesh were performed. For NiCo<sub>2</sub>, a hierarchical micro chrysanthemum-like architecture (5-8  $\mu$ m) along with protruding nano-rod of 30-50 nm diameter from the core to surface was observed (Figure S3 c&d). In absence of molybdenum, primary particles grew as 1D nanorods through crystallographic facets with the coverage of {110} plane. It further refers the contribution of molybdenum in growth mechanism for the formation of porous sheet like network. We believe that absence of molybdenum actually inhibits the interconnection of nanorods throughout grain boundary regime thereby leading to 3D micro chrysanthemum-like architecture. Control experiment of Co sample was further conducted to understand the function of nickel behind microstructure (Figure S5a&b). SEM analysis reveal that architecture for Co sample is wire-like.

Influence of individual cobalt and nickel was revealed from microstructural analysis of NiMo (Figure S9) and  $Co_2Mo$  (Figure S10) respectively. NiMo sample allows the formation of nano-flake like architecture with thickness of 5-10 nm. Interestingly, the absence of cobalt actually causes lattice strains, which leads to formation of corrugated nano-sheets. In contrast, micro brush-like textural features is obtained for  $Co_2Mo$ . This clearly indicate that both nickel and molybdenum favour formation of sheet like structure.



**Figure S11:** (A) Survey scan in XPS of NiCo<sub>2</sub>Mo showing the presence of Ni, Co, Mo, O, C and Cu. (B-G) Narrow scan of (B) Co 2p, (C) Ni 2p, (D) Mo 3d, (E) Cu 2p, (F) O 1s, (G) C 1s and further deconvolution.

# **ICP-AES** Analysis

*Sample Preparation*: To gain information regarding the atomic percentage of different elements in NiCo<sub>2</sub>Mo, post- HER NiCo<sub>2</sub>Mo and post- OER NiCo<sub>2</sub>Mo, the Cu meshes containing these materials were digested in concentrated suprapur nitric acid and then diluted with milli Q water.

Atomic Percentage Calculation:

Element	ppm	mg/l	Atomic Mass	mM/l
Nickel	9.348	9.348	58.693	0.159
Cobalt	15.117	15.117	58.933	0.257
Molybdenum	1.130	1.130	95.95	0.012

 Table S2: Elemental composition of NiCo2Mo

Nickel : Cobalt : Molybdenum = 13.25 : 21.42 : 1

**Table S3:** Elemental composition of post- HER NiCo<sub>2</sub>Mo

Element	ррт	mg/l	Atomic Mass	mM/l
Nickel	10.464	10.464	58.693	0.178
Cobalt	20.770	20.770	58.933	0.352
Molybdenum	0.011	0.011	95.95	0.000115

Nickel : Cobalt : Molybdenum = 1548 : 3060 : 1

Table S4: Elemental composition of post- OER NiCo<sub>2</sub>Mo

Element	ppm	mg/l	Atomic Mass	mM/l
Nickel	11.172	11.172	58.693	0.190
Cobalt	21.407	21.407	58.933	0.363
Molybdenum	0.078	0.078	95.95	0.000813

Nickel : Cobalt : Molybdenum = 233 : 446 : 1



**Figure S12:** Elemental mapping of as-prepared NiCo<sub>2</sub>Mo on Cu mesh. The images clearly show the ubiquitous presence of Ni, Co, Mo and O on the catalyst materials.



Figure S13: OER CV data for different electrocatalysts on Cu mesh.



**Figure S14**: Chronopotentiometry @  $10 \text{ mA/cm}_{geo}^2$  current density for NiCo<sub>2</sub>Mo on Cu mesh in 1 M KOH. Inset shows the backward LSV scan for the same material. The overpotential values obtained to reach the benchmark current density from both techniques were found to be in good agreement.



Figure S15: Backward LSV data (iR corrected) for different electrocatalysts on Cu mesh.

<b>Table S5:</b> Potentials at which different electrocatalysts on Cu mesh reach $10 \text{ mA/cm}_{geo}^2$ and $100$
mA/cm <sup>2</sup> <sub>geo</sub> during OER backward LSV.

Sl. No.	Abbreviation	Potential (V) at 10 mA/cm <sup>2</sup> geo	Potential (V) at 100 mA/cm <sup>2</sup> geo
1	Ni	1.59	1.68
2	Co	1.56	1.62
3	Мо	1.7	1.79
4	NiCo	1.58	1.69
5	NiCo <sub>2</sub>	1.56	1.68
6	Ni <sub>2</sub> Co	1.57	1.68
7	NiMo	1.59	1.67
8	Ni <sub>2</sub> Mo	1.7	Not able to reach
9	СоМо	1.55	1.69
10	Co <sub>2</sub> Mo	1.56	1.69
11	NiCoMo	1.54	1.60
12	NiCo <sub>1.5</sub> Mo	1.54	1.62
13	NiCo <sub>2</sub> Mo	1.52	1.57
14	Ni <sub>2</sub> CoMo	1.55	1.67
15	Ni <sub>2</sub> Co <sub>2</sub> Mo	1.54	1.69
16	Blank	1.64	1.75

No.	Material	OER overpotential (mV) for 10mA/cm <sup>2</sup> current density	OER overpotential (mV) for 10mA/cm <sup>2</sup> current density	Reference
		(only iR corrected)	(capacitance, redox current and iR corrected)	
1	Cu@CoS <sub>x</sub> /CF	270		Adv. Mater. 2017, 29, 1606200
2	MoO <sub>2</sub> /Ni foam	300		Adv. Mater. 2016, 28, 3785
3	NiFeO <sub>x</sub> /CFP	280		Nat Commun.2015, 6, 7261.
4	CoO <sub>x</sub> @CN	370		J. Am. Chem. Soc. 2015, 137, 2688
5	NiFe LDH/NF	470		Science 2014, 345, 1593
6	NiFe/NiCo <sub>2</sub> O <sub>4</sub> /NF	440		Adv. Funct. Mater. 2016, 26, 3515.
7	Ni-Co based nanowires	485		Adv. Energy Mater. 2015, 5, 1402031
8	(Pr <sub>0.5</sub> Ba <sub>0.5</sub> )CoO <sub>3-x</sub> (0.1M KOH)		310	Nat. Commun. 2013, 4, 2439
9	Ba <sub>0.5</sub> Sr <sub>0.5</sub> Co <sub>0.8</sub> Fe <sub>0.2</sub> O <sub>3-</sub> <sub>x</sub> /AC black (0.1M KOH)		320	Adv. Energy Mater. 2015, 5, 1402033
10	$Ni_{0.7}Co_{0.1}Fe_{0.3}O_xH_y$	237		ACS Catal. 2018, 8, 5621
11	CS-NiFeCu		224	Nat. Commun., 2018, 9, 381
12	$Ni_xFe_{1-x}Se_2$ -DO		195	Nat. Commun. 2016, 7, 12324

**Table S6:** Comparison of NiCo<sub>2</sub>Mo on Cu mesh with reported highly active electrocatalysts towards OER under alkaline conditions.

13	NiCo <sub>2</sub> S <sub>4</sub> @NiFe LDH/NF	201 (60 mA/cm <sup>2</sup> )		ACS Appl. Mater. Interfaces, 2017, 9, 15364
14	EG/Co <sub>0.85</sub> Se/NiFe- LDH	270 (150 mA/cm <sup>2</sup> )		Energy Environ. Sci., 2016,9, 478
15	NiFe-LDH NP	280 (300 mA/cm <sup>2</sup> )		Chem. Commun., 2014, 50, 6479
16	FeNi-GO LDH	210		Angew. Chem. Int. Ed., 2014, 53, 7584
17	Ni <sub>2/3</sub> Fe <sub>1/3</sub> -NS/rGO	210		ACS Nano, 2015, 9, 1977
18	TiN@Ni <sub>3</sub> N nanowire	350		J. Mater. Chem. A, 2016, 4, 5713
19	Ni <sup>2+</sup> /Birnessite	400		Angew. Chem. Int. Ed. 2016, 55, 10381
20	Ni-Al LDH	236 (20 mA/cm <sup>2</sup> )		Adv. Mater. 2017, 1604765
21	Defect rich ultrathin Co(OH) <sub>2</sub>		236	ACS Energy Lett. 2019, 4, 328
22	Ni <sub>0.82</sub> Co <sub>0.18</sub> O@C/NF	320 (50 mA/cm <sup>2</sup> )		Appl. Catal. B, 2019, 252, 214
23	Ni–Co LDH@CoS	170		ACS Sustainable Chem. Eng. 2019, 7, 8255
20	Molybdate incorporated NiCo <sub>2</sub> hydroxide on Cu mesh		290	This Work

Sl. No.	Abbreviation	Mass Loading (mg/cm <sup>2</sup> )
1	Ni	10.57
2	Co	11.92
3	Mo	12
4	NiCo	13.10
5	NiCo <sub>2</sub>	12.74
6	Ni <sub>2</sub> Co	12.72
7	NiMo	10.86
8	Ni <sub>2</sub> Mo	13.99
9	СоМо	2.51
10	Co <sub>2</sub> Mo	2.1
11	NiCoMo	16.72
12	NiCo <sub>1.5</sub> Mo	10.73
13	NiCo <sub>2</sub> Mo	16.86
14	Ni <sub>2</sub> CoMo	15.79
15	Ni <sub>2</sub> Co <sub>2</sub> Mo	11.44

 Table S7: Mass loading of different materials on Cu mesh.



Figure S16: OER Tafel slope analysis of all materials.

Sl. No.	Abbreviation	Tafel slope	<b>Overpotential region</b>
1	Ni	99	360-460
2	Со	62	330-370
3	Мо	86	450-550
4	NiCo	114	360-460
5	NiCo <sub>2</sub>	110	330-400
6	Ni <sub>2</sub> Co	101	340-400
7	NiMo	85	350-420
8	Ni <sub>2</sub> Mo	164	520-620
9	СоМо	40	290-320
10	Co <sub>2</sub> Mo	37	300-320
11	Ni <sub>2</sub> CoMo	111	320-400
12	NiCo <sub>2</sub> Mo	43	290-320
13	Ni <sub>2</sub> Co <sub>2</sub> Mo	100	320-360
14	NiCoMo	58	320-360
15	NiCo <sub>1.5</sub> Mo	64	310-350

**Table S8:** OER Tafel slope values for all materials.



**Figure S17:** Overpotential requirement by different electrocatalysts to reach the mass activity of 2.5mA/mg<sub>mass</sub>.



**Figure S18:** PXRD pattern (red) of NiCo<sub>2</sub>Mo after OER on Cu mesh substrate. The sharp peaks at 43°, 50° and 74° correspond to metallic Cu (JCPDS: 00-004-0836) and is coming from the substrate. Interestingly, the intensity of the peak at 36° that is arising from Cu<sub>2</sub>O (JCPDS: 00-005-0667) has increased by ~87%. The high oxidative potential applied during OER has resulted in further oxidation of the Cu mesh leading to increased formation of Cu<sub>2</sub>O species. As the material became very thin during OER, no other significant peak from the material was observed in PXRD.



**Figure S19:** Post-catalysis microscopic images of NiCo<sub>2</sub>Mo: (a) SEM after 3 hours OER, (b) SEM after 24 hours OER, (c) TEM after 3 hours OER and (d) HR-TEM after 24 hours OER.



**Figure S20:** (A) Survey scan in XPS of NiCo<sub>2</sub>Mo after OER showing the presence of Ni, Co, Mo, O, C and Cu. (B-G) Narrow scan of (B) Co 2p, (C) Ni 2p, (D) Mo 3d, (E) Cu 2p, (F) O 1s, (G) C1s and (H) K 2p and further deconvolution.

### **Discussion on XPS:**

XPS has provided critical information about the catalyst material after OER. For example, the cobalt 2p main peaks have shifted to 779.7 and 794.7 eV with corresponding satellite peaks at 789.6 and 805 eV, which are characteristics of  $Co^{3+}$ . In addition, relatively weaker peaks were observed at 780.94 eV and 795.9 eV that signify the presence of  $Co^{2+}$ . Thus, the high potential applied during OER reaction oxidizes most  $Co^{2+}$  centers to  $Co^{3+}$ . Similarly, the

main peaks for nickel 2p shifts to 855.4 and 873 eV with corresponding satellite peaks at 862.4 and 882.1 eV. A relatively weaker peak was also present at 856.4 eV. These signify that during OER, most Ni<sup>2+</sup> centers oxidize to Ni<sup>3+</sup> under the high oxidation potential. For molybdenum, the peaks corresponding to Mo  $3d_{5/2}$  and Mo  $3d_{3/2}$  appeared at 231.60 and 234.82 eV, respectively indicating the presence of Mo<sup>6+</sup> state. For Cu, the main XPS peaks were observed at 934.2 and 954 eV along with corresponding satellite peaks at 942.2 and 962.7 eV. These values indicate the presence of Cu<sup>2+</sup> in the material after OER. Further, this observation is consistent with the report of Liu *et al.*<sup>2</sup> This is further confirmed by analyzing the O spectrum which shows peaks at 528.9 and 530.8 eV corresponding to O of CuO and Cu<sub>2</sub>O, respectively. Moreover, the peak due to – OH and adsorbed O appeared at 531.5 eV. The C 1s XPS shows peaks at 285 and 288.7 eV that are characteristic of C-C and C=O. Interestingly, two new peaks appeared at 292.3 and 295.1 eV. These signify K<sup>+</sup> ions that get adsorbed in the material during OER as KOH was used as the electrolyte.



**Figure S21:** The elemental ratio of nickel: cobalt: molybdenum was found to be 1.41: 1: 1.04 for NiCoMo (sheet like morphology) from EDS analysis. After 40 minutes of chronoamperometry at 1.6 V vs RHE, significant decrease of molybdenum content was observed.



Figure S22: Precondition data of CoMo,  $Co_2Mo$ ,  $NiCo_2Mo$ , NiCoMo and  $NiCo_{1.5}Mo$ . Emergence of capacitive behavior and rise in current density with increase in cycle number is evident in all five CV data.



Figure S23: Backward HER LSV data for different electrocatalysts on Cu mesh.

<b>Table S9:</b> potentials at which different electrocatalysts on Cu mesh reach $10 \text{ mA/cm}_{geo}^2$ during
HER from backward LSV.

Sl. No.	Abbreviation	Potential (V) at 10 mA/cm <sup>2</sup> geo
1	Ni	-0.360
2	Co	-0.216
3	Мо	-0.240
4	NiCo	-0.267
5	NiCo <sub>2</sub>	-0.261
6	Ni <sub>2</sub> Co	-0.306
7	NiMo	-0.303
8	Ni <sub>2</sub> Mo	-0.398
9	СоМо	-0.208
10	Co <sub>2</sub> Mo	-0.154
11	Ni <sub>2</sub> CoMo	-0.229
12	NiCo <sub>2</sub> Mo	-0.125
13	Ni <sub>2</sub> Co <sub>2</sub> Mo	-0.188
14	NiCoMo	-0.258
15	NiCo <sub>1.5</sub> Mo	-0.267
16	Blank	-0.201



Figure S24: HER Tafel slope analysis of all materials.

Sl. No.	Abbreviation	Tafel slope	<b>Overpotential region</b>
1	Ni	102	370-410
2	Со	110	230-340
3	Мо	188	250-450
4	NiCo	94	280-350
5	NiCo <sub>2</sub>	85	270-330
6	Ni <sub>2</sub> Co	91	320-420
7	NiMo	144	300-420
8	Ni <sub>2</sub> Mo	144	420-520
9	СоМо	127	130-260
10	Co <sub>2</sub> Mo	128	70-200
11	Ni <sub>2</sub> CoMo	103	250-350
12	NiCo <sub>2</sub> Mo	118	160-230
13	Ni <sub>2</sub> Co <sub>2</sub> Mo	114	200-320
14	NiCoMo	123	290-330
15	NiCo <sub>1.5</sub> Mo	118	270-330

 Table S10: HER Tafel slope values for all materials.

No.	Material	HER overpotential (mV) for 10mA/cm <sup>2</sup> current density	HER overpotential (mV) for 10mA/cm <sup>2</sup> current density	Reference
		(only iR corrected)	(capacitance, redox current and iR corrected)	
1	Cu@CoS <sub>x</sub> /CF	160		Adv. Mater. 2017, 29, 1606200
2	$Co_3O_4$	300		J. Am. Chem. Soc. 2016, 138, 36.
3	CoNi(OH) <sub>x</sub>	280		Adv. Energy Mater. 2016, 6, 1501661
4	CoNi hydroxide UNSs	324		Nano Research. 2016, 9, 1856
5	NiCo <sub>2.7</sub> (OH) <sub>x</sub>	350		Adv. Energy Mater. 2015, 5, 1401880
6	NCO-HNSs	340		Adv. Energy Mater. 2015, 5, 1500091
7	CoMn LDH	280		J. Am. Chem. Soc. 2014, 136, 16481
8	NCNT/CoO-NiO- NiCo	270		Angew. Chem. Int. Ed. 2015, 54, 9654
9	CoNi LDH/CoO nanosheets	300		Nano Research. 2016, 9, 713.
10	$Ni_{0.9}Co_{0.1}O_xH_y$	85		ACS Catal. 2018, 8, 5621
11	NiCo <sub>2</sub> S <sub>4</sub> @NiFe LDH/NF	200		ACS Appl. Mater. Interfaces, 2017, 9, 15364
12	TiN@Ni <sub>3</sub> N nanowire	15		J. Mater. Chem. A, 2016, 4, 5713

**Table S11:** Comparison of NiCo<sub>2</sub>Mo on Cu mesh with reported highly active electrocatalysts towards HER under alkaline conditions.

13	EG/Co <sub>0.85</sub> Se/NiFe- LDH	300		Energy Environ. Sci., 2016, 9, 478
14	Ni <sub>0.82</sub> Co <sub>0.18</sub> O@C/NF	62		Appl. Catal. B, 2019, 252, 214
15	Ni(Cu)@NiFeP/NM	33		J. Catal. 2019, 373, 81
16	NiCo LDH@CoS	100		ACS Sustainable Chem. Eng. 2019, 7, 8255–8264
14	Molybdate incorporated NiCo <sub>2</sub> hydroxide on Cu mesh		125	This Work



**Figure S25:** PXRD pattern (black) of NiCo<sub>2</sub>Mo after HER on Cu mesh substrate. The sharp peaks at 43°, 50° and 74° correspond to metallic Cu (JCPDS: 00-004-0836) and is coming from the substrate. Interestingly, the intensity of the peak at 36° that was earlier arising from Cu<sub>2</sub>O (JCPDS: 00-005-0667) has completely vanished. As the material became very thin during HER, no other significant peak from the material was observed in PXRD.



Figure S26: Post-catalysis microscopic images of  $NiCo_2Mo$ : (a) TEM after 3 hours OER, (b) TEM after 24 hours OER, (c) SEM after 3 hours OER and (d) SEM after 24 hours OER.



**Figure S27:** (A) Survey scan in XPS of NiCo<sub>2</sub>Mo after OER showing the presence of Ni, Co, Mo, O, C and Cu. (B-G) Narrow scan of (B) Co 2p, (C) Ni 2p, (D) Mo 3d, (E) Cu 2p, (F) O 1s, (G) C 1s and (H) K 2p and further deconvolution.

#### **Discussion:**

In XPS, the values for cobalt 2p appear at 783.2 and 798.9 eV with corresponding satellite peaks at 788.1 and 804.1 eV that indicate the presence of only  $Co^{2+}$  species in the material. For nickel, two major peaks appear at 857.9 and 875.5 eV with corresponding satellite peaks at 863.7 and 881.4 eV indicating the presence of both Ni(0) and Ni(II) in the material. In this case, three peaks appear in the molybdenum spectrum at 232.4, 235.4 and 238.5 eV. These indicate the presence

of  $Mo^{6+}$  in the material. For Cu, the XPS spectrum consists of peaks at 932.9 and 952.8 eV that generally arises from Cu(0) and Cu(I) species. However, post-HER PXRD showed that the phase Cu<sub>2</sub>O has completely vanished after electrocatalysis. Thus, we believe that these peaks are arising from metallic Cu. Relatively weaker peaks at 935, 944 and 955.5 eV correspond to Cu(II) and is probably coming from CuO present in the material. The XPS spectrum of O remain almost unchanged w.r.t the initial compound. The C 1s spectrum contains peak at 285.37and 288.48 eV indicating C-O and C=O and at 293.01 and 296.20 eV due to the K<sup>+</sup> ions coming from electrolyte.



**Figure S28:** Overpotential requirement by different electrocatalysts to reach the mass activity of 2 mA/mg<sub>mass</sub> in HER.



**Figure S29:** OER precondition data of NiCo<sub>2</sub>Mo grown on conductive carbon cloth. Appearance of a capacitive behavior is evident with increase in cycle number.



**Figure S30:** Mass activity of NiCo<sub>2</sub>Mo grown on carbon cloth (red) and Cu mesh (black): (A) OER and (B) HER. All data are from backward LSV scan.



**Figure S31:** Electrochemical impedance spectroscopy (EIS) data of (A) HER used NiCo<sub>2</sub>Mo on Cu mesh, (B) OER used NiCo<sub>2</sub>Mo on Cu mesh, (C) HER used NiCo<sub>2</sub>Mo on C cloth and (D) OER used NiCo<sub>2</sub>Mo on C cloth.

Sample ID	Equivalent Circuit	Fitting Parameters
A	R <sub>1</sub> +Q <sub>2</sub> /R <sub>2</sub>	$R_1 = 2.077 \text{ Ohm}$ $Q_2 = 0.050 \text{ 88 F.s}^{(a - 1)}$ $a_2 = 0.763 \text{ 9}$ $R_2 = 5.921 \text{ Ohm}$
В	R <sub>1</sub> +Q <sub>2</sub> /R <sub>2</sub> +Q <sub>3</sub>	$R_{1} = 4.793 \text{ Ohm}$ $Q_{2} = 1.639 \text{ F.s}^{(a - 1)}$ $a_{2} = 0.903 6$ $R_{2} = 4.75 \text{ Ohm}$ $Q_{3} = 2.405 \text{ F.s}^{(a - 1)}$ $a_{3} = 0.145 8$
С	R <sub>1</sub> +Q <sub>2</sub> /R <sub>2</sub> +Q <sub>3</sub> /R <sub>3</sub>	$R_{1} = 3.154 \text{ Ohm}$ $Q_{2} = 0.024 66 \text{ F.s}^{(a - 1)}$ $a_{2} = 0.48$ $R_{2} = 12.97 \text{ Ohm}$ $Q_{3} = 2.578e-3 \text{ F.s}^{(a - 1)}$ $a_{3} = 0.887 8$ $R_{3} = 105 \text{ Ohm}$
D	R <sub>1</sub> +Q <sub>2</sub> /R <sub>2</sub> +Q <sub>3</sub> /R <sub>3</sub>	$R_{1} = 3.484 \text{ Ohm}$ $Q_{2} = 0.947 \text{ 3 F.s}^{(a - 1)}$ $a_{2} = 1$ $R_{2} = 5.088 \text{ Ohm}$ $Q_{3} = 0.577 \text{ 1 F.s}^{(a - 1)}$ $a_{3} = 0.491 \text{ 8}$ $R_{3} = 2.135 \text{ Ohm}$

**Table S12:** Equivalent circuit and corresponding parameters for EIS data.

Symbol Index:

R= resistance; Q= constant phase element.



Figure S32: Concentration of molybdenum in the electrolyte that was used during chronoamperometry employing  $NiCo_2Mo$  as both cathode and anode in a two-electrode setup.



Figure S33: DLC of different electrocatalysts on Cu mesh.



**Figure S34:** (A) OER and (B) HER of NiCo<sub>2</sub>Mo (black) and stoichiometric mixture (red) comprising (Ni, Co and Mo) on glassy carbon electrode.

Material	Overpotential (mV) for HER $(a)$ 1 mA/cm <sup>2</sup> <sub>geo</sub>	Overpotential (mV) for OER $(a)$ 10 mA/cm <sup>2</sup> <sub>geo</sub>
NiCo <sub>2</sub> Mo on glassy carbon	325	360
Mixture on glassy carbon	353	440

### **Details of electrode fabrication:**

• Preparation of catalyst ink:

OER: 2 mg of NiCo<sub>2</sub>Mo precipitate was mixed in 0.4 ml 1:1 water: ethanol solution by sonication. 20  $\mu$ l PVDF-NMP (8mg/ml) solution was then added and further sonicated to attain homogeneous mixing.

The elemental ratio obtained from elemental analysis was considered to prepare a mixture comprising Ni, Co and Mo. Thereafter, a similar method as stated for NiCo<sub>2</sub>Mo was followed to prepare the catalyst ink.

HER: 4 mg of NiCo<sub>2</sub>Mo precipitate was mixed in 1 ml 1:1 water:ethanol solution by sonication. 50  $\mu$ l 5% Nafion solution (in ethanol) was then added to the mixture, which was then sonicated further for attaining homogeneity. The mixture of Ni, Co and Mo were prepared following the same protocol

 Preparation of electrode: About 4 µl 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.

<sup>[1]</sup> Y. Yoon, B. Yan, Y. Surendranath, J. Am. Chem. Soc. 2018, 140, 2397.

<sup>[2]</sup>Y. Liu, Q. Li, R. Si, G-D. Li, W. Li, D-P. Liu, D. Wang, L. Sun, Y. Zhang, X. Zou, *Adv. Mater.* **2017**, *29*, 1606200.