Electronic Supplementary Material (ESI) for Sustainable Energy & Fuels.

Supporting Information
For

Fine-tuning of the water oxidation performance of hierarchical Co_3O_4 nanostructures prepared from different cobalt precursors

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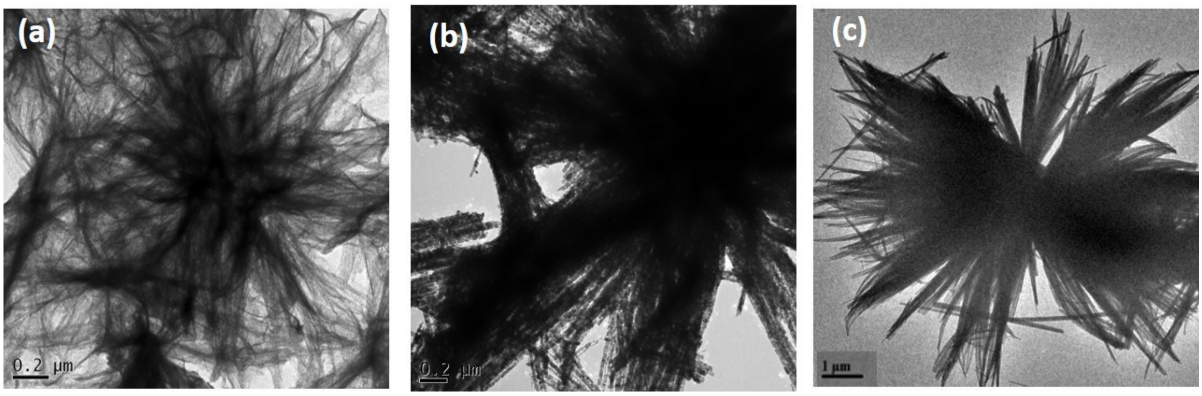

Fig. S1. Low and high magnification SEM and TEM images of Co_3O_4-S (a, b and c); Co_3O_4-Ac (d, e and f); Co_3O_4-N (g, h and i), respectively.

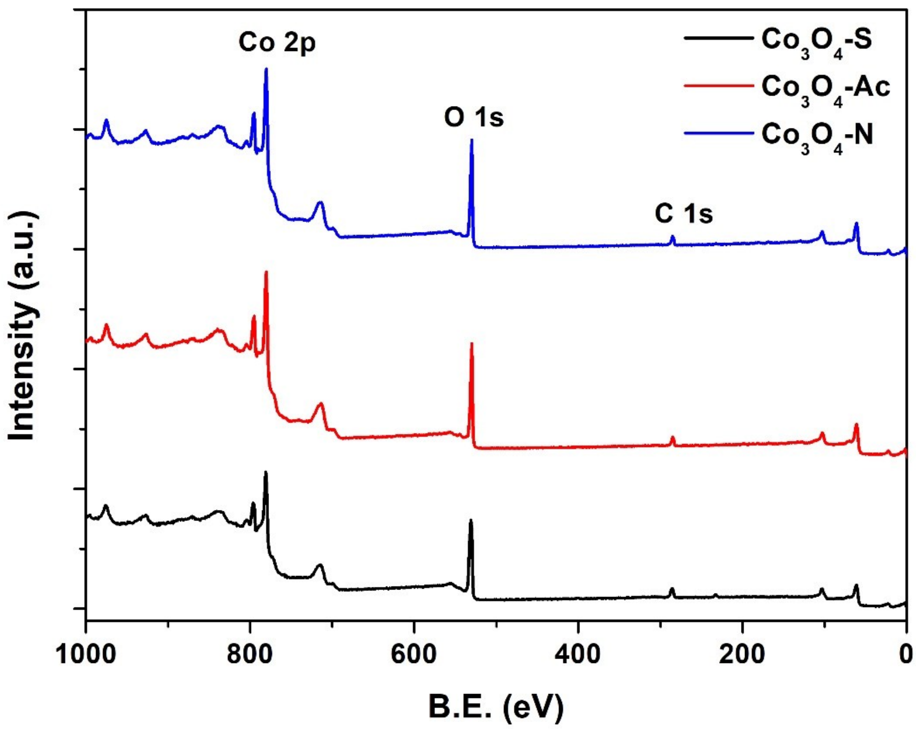

Fig. S2. XPS survey spectra of Co_3O_4-S, Co_3O_4-Ac and Co_3O_4-N nanostructured catalyst.

Table S1. XPS surface atomic % of Co_3O_4-S, Co_3O_4-Ac and Co_3O_4-N hierarchical nanostructured catalysts.

	Surface atomic composition (%) from XPS		
Catalyst	**Co 2p**	**O 1s**	**C 1s**
Co_3O_4-S	23.25	57.91	18.84
Co_3O_4-Ac	27.77	56.46	15.78
Co_3O_4-N	29.01	54.65	16.34

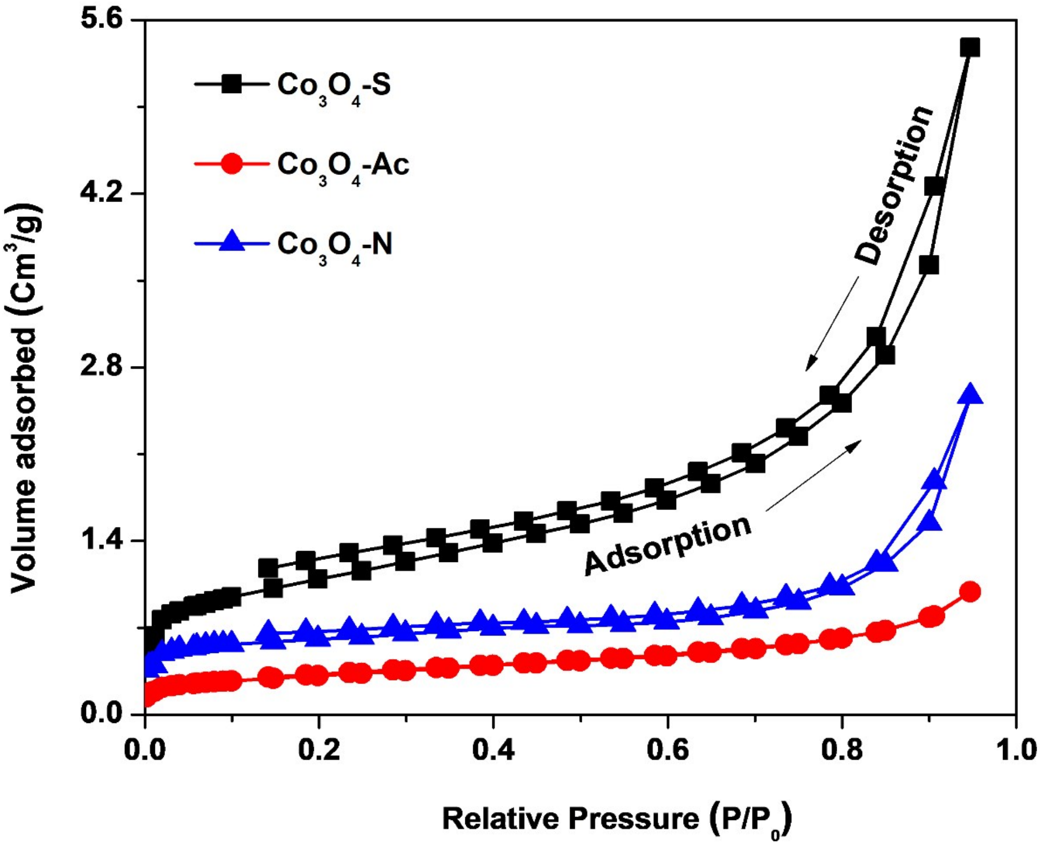

Fig. S3. N_2 Adsorption-desorption isotherm of obtained from BET measurements for Co_3O_4-S, Co_3O_4-Ac and Co_3O_4-N nanostructured catalyst.

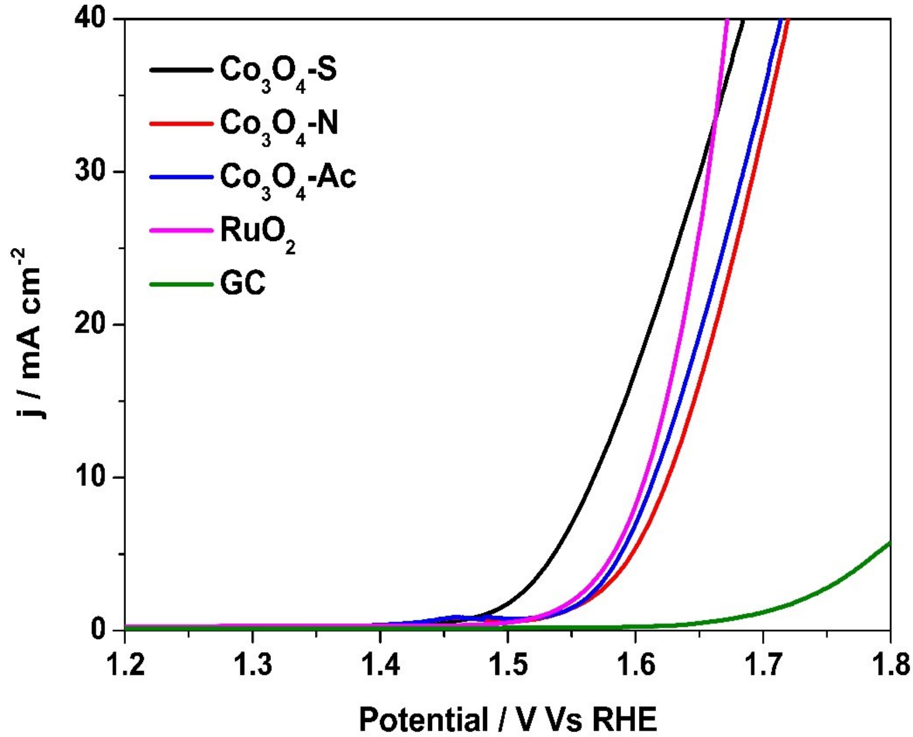

Fig. S4. Linear polarization curves (iR compensated) at a scan rate of 10 mV/s for Co_3O_4-S, Co_3O_4-Ac, Co_3O_4-N, RuO_2, and GC.

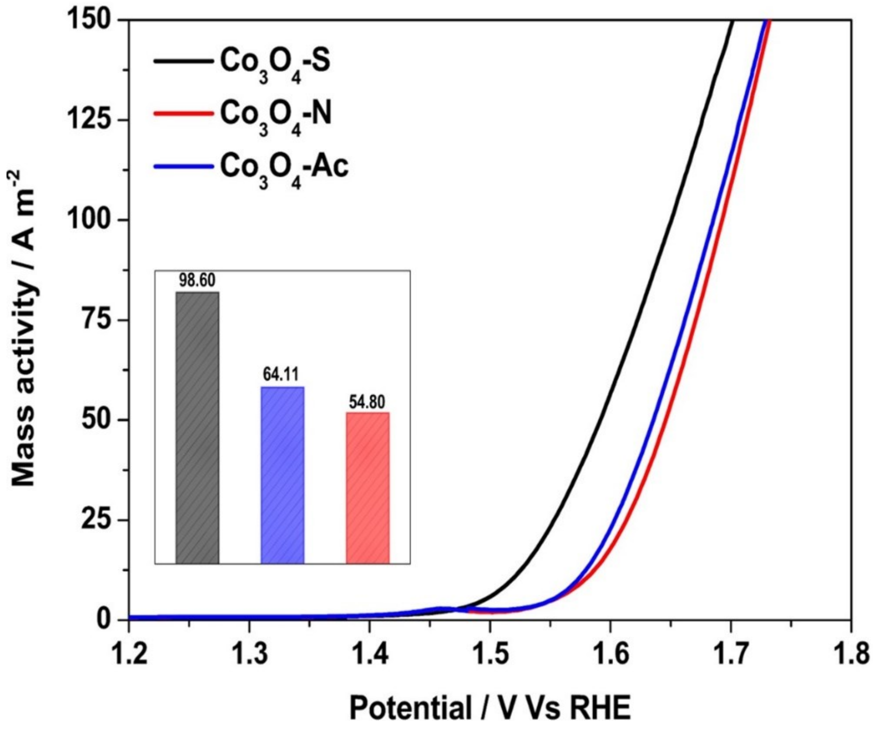

Fig. S5. Potential dependent mass activity curves for Co_3O_4-S, Co_3O_4-Ac, Co_3O_4-N (inset: a bar chart of the mass activity).

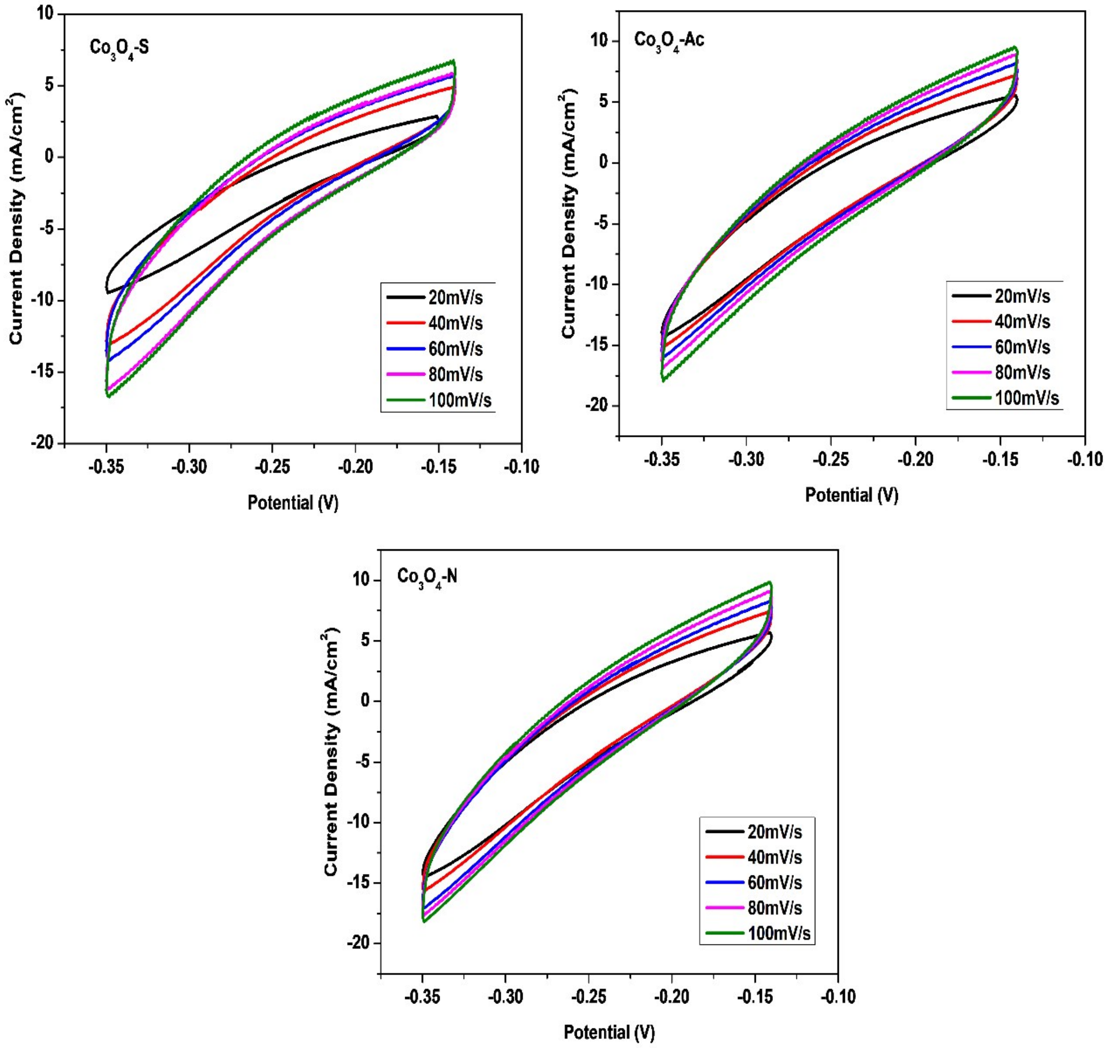

Fig. S6. CV curves at various scan rates to determine the double-layer capacitance (Cdl) of Co_3O_4-S, Co_3O_4-Ac and Co_3O_4-N nanostructured catalysts.

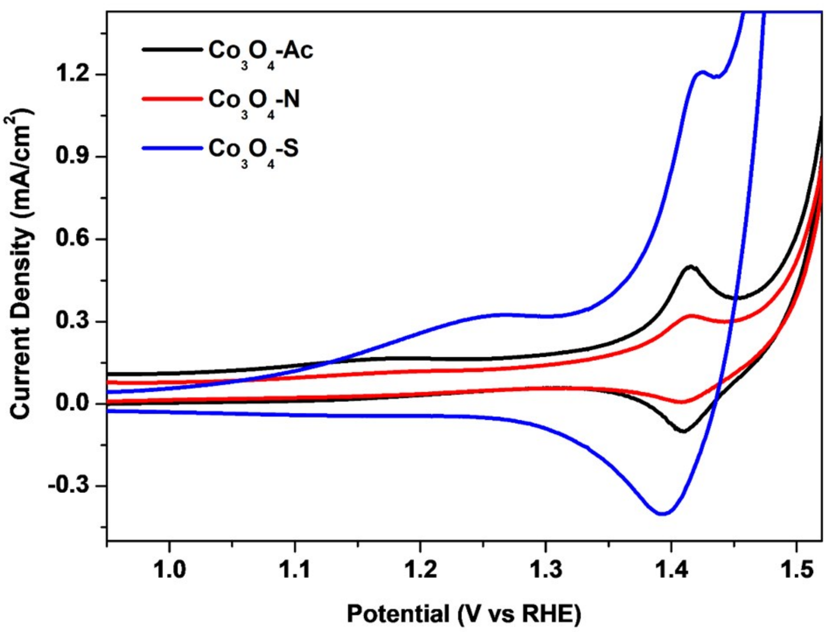

Fig. S7. Cyclic voltammetry scan for Co_3O_4-S, Co_3O_4-Ac and Co_3O_4-N nanostructured catalysts at a scan rate of 2 mV/s in 1M KOH.

Electrochemically active surface area [(ECSA /cm^2)]

ECSA of each catalyst is measured from double layer charging of the catalytic material. Firstly, the non-faradaic region from CV scan is determined. Multiple CV curves at scan rate of 20, 40, 60, 80 and 100 mV/s are recorded. It is assumed that all the current in this region is due to double layer charging capacitance. Following this, a potential value in the middle region is identified and current associated with this potential value is plotted as a function of scan rate. The slope of which gives the value of double layer capacitance according to the equation given below;

$$i_c = \nu \, C_{dl}$$

where i_c is the double layer charging current, ν is scan rate and C_{dl} is double layer charging capacitance. The electrochemically active surface area is calculated from the following relation;

$$ECSA = \frac{C_{dl}}{C_s}$$

Here, C_s is the specific capacitance of the sample or the capacitance of an atomically smooth planer surface of the material per unit area under identical electrolyte conditions. The value of the specific capacitance for various metal electrodes in alkaline electrolyte have been measured and typical reported value lies in the range from 0.022 to 0.130 mF cm^{-2} in KOH solution. We have considered the reported value of 0.027 mF cm^{-2} for Co in alkaline solution and ECSA is calculated accordingly.[1, 2]

Mass activity [MA (A g^{-1})]

MA was calculated using the following equation given below;

$$MA = \frac{J}{Active\ mass\ of\ catalyst}$$

Here, J is the current density in mA cm^{-2} at specific overpotential value of 1.6 V for comparing the electrocatalytic activities of all hierarchical nanostructured electrocatalysts.[3]

Turnover frequency [TOF (S^{-1})]

Following equation is used to calculate the TOF of electrochemical reaction.[4]

$$TOF = \frac{j * N_A}{n * A * F * \Gamma}$$

Where,

j = Current density (A/m^2) at a specified overpotential value.

N_A = Avogadro's constant [$6.022*10^{23}$].

n = Number of electrons.

A= Electroactive surface area.

F = Faraday constant [96485 C].

Γ = Surface concentration of atom on the electrode surface.

Surface concentration of Co_3O_4-S from CV curve

Charge passed calculated by integrating the area under reduction peak from potential vs. current curve.

Calculated area associated with the reduction of Co^{3+} to Co^{2+} = $0.0471*10^{-3}$ VA

Hence, associated charge = $0.0471*10^{-3}$ VA / 0.002 V/s

= 0.02355 As

= 0.02355 C

The number of electrons transferred = 0.02355 C / $1.602*10^{-19}$ C

= $0.0147*10^{19}$

Since, the reduction of Co^{3+} to Co^{2+} is a single electron transfer reaction, the number electrons calculated above is exactly the same as the number of surface active sites.

Hence, the surface concentration of Co^{2+} that participated in OER is = $0.0147*10^{19}$

$$TOF\ at\ 1.53\ V = \frac{6.12 * 10^{-3} * 6.022 * 10^{23}}{4 * 0.089 * 96485 * 0.0147 * 10^{19}} = 0.7\ s^{-1}$$

Table S2. Exchange current density, ECSA, mass activity and TOF values of Co_3O_4-S, Co_3O_4-Ac and Co_3O_4-N hierarchical nanostructured catalysts.

Catalyst	Exchange current density ($A\ cm^{-2}$)	ECSA (cm^2)	Mass activity ($A\ g^{-1}$) at 1.65 V Vs RHE	TOF (s^{-1}) at 1.53 V Vs RHE
Co_3O_4-S	1.723×10^{-3}	892	98.60	0.7
Co_3O_4-Ac	1.682×10^{-3}	666	64.11	0.2
Co_3O_4-N	1.698×10^{-3}	574	54.80	0.1

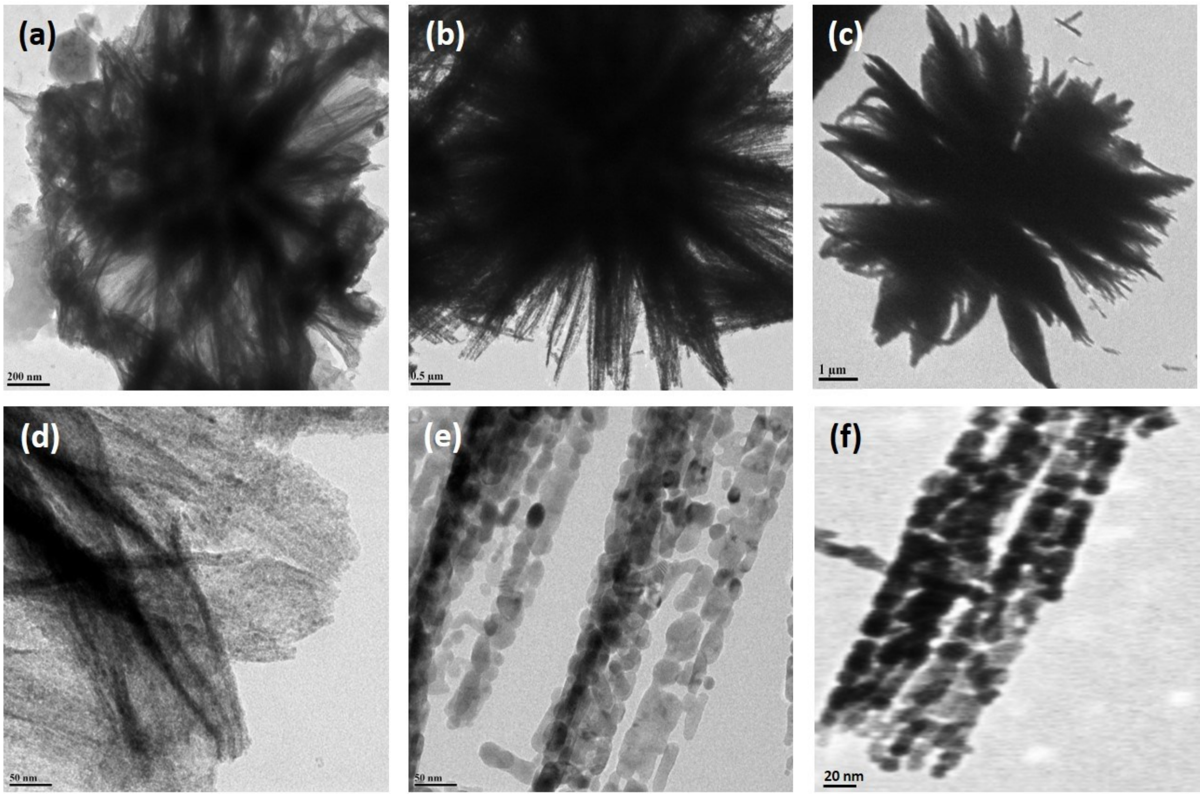

Fig. S8. Post-OER low and high magnification TEM image of Co_3O_4-S (a & d), Co_3O_4-Ac (b & e) and Co_3O_4-N (c & f) respectively.

Table S3: Comparison of recent Co based electrocatalysts for OER active in alkaline media.

Catalyst	Morphology	Electrolyte	Onset potential	Over-potential	Tafel slope	Ref.

			(V)	(mV) at 10 mA cm^{-2}		
AuCoCu alloy	Branched nanostructure	0.1M KOH	1.57	596	60	[5]
$Ni_{0.7}Co_{0.3}O_x$	Hexagon nanoplate	0.1M KOH	1.62	394	-	[6]
Ce-$MnCo_2O_4$	Microrod	1M KOH	-	390	125	[7]
$CuCoO_2$	Nanoplate	1M KOH	1.55	390	70	[8]
Co-Nitrogen co-doped Graphene	Nanosheet	0.1M KOH	-	426	69	[9]
$Co_{1-x}S$/N-S-G	Crumpled, silk-like	0.1M KOH	-	371	63	[10]
Co_3O_4@BP	Lamellar	1M KOH	-	400	128	[11]
CeO_2/Co_3O_4	Spherical	0.3M KOH	-	386	165.7	[12]
$Co_3V_2O_8$	Nanoparticles	1M KOH	1.58	359	65	[13]
Co_3O_4	Semi spherical	1M KOH	1.52	425	44	[14]
Co_3O_4	flower-shaped	1M NaOH	1.51	356	68	[15]
Co_3O_4	Thin film	1M NaOH	-	377	58.1	[16]
Co_3O_4-F127	Sheetlike	1 M NaOH	-	350	90	[17]
Co_3O_4	Nanosheets	1M KOH	1.52	374	60	[18]
Porous Co_3O_4	Wrinkled shee-tlike	1M KOH	1.48	368	59	[19]
Co_3O_4	Nanoflakes	1M KOH	1.60	380	46	[20]
Co@NS/CN Ts-MCFs	Hybrid fibers	0.1M KOH	1.53	362	54	[21]
Co_3O_4@GF_	Flat sheets	1M KOH	0.82 V	440	60.3	[22]

$KMnO_4$						
Co-N/Co-O@N-C nanohybrid	Hierarchical porous nanoarchitecture	0.1M KOH	-	370	81.12	[23]
$LiCoO_2$	-	0.1M KOH	1.55	350	52	[24]
Co_3O_4-S	**Marigold flower-like**	**1M KOH**	**1.45**	**330**	**78**	**This work**
Co_3O_4-Ac	**Self-assembled flower**	**1M KOH**	**1.54**	**380**	**86**	**This work**
Co_3O_4-N	**Urchin-like**	**1M KOH**	**1.55**	**390**	**90**	**This work**

References

1. G. Wu, N. Li, D.-R. Zhou, K. Mitsuo and B.-Q. Xu, *Journal of Solid State Chemistry*, 2004, **177**, 3682-3692.
2. C. C. McCrory, S. Jung, J. C. Peters and T. F. Jaramillo, *Journal of the American Chemical Society*, 2013, **135**, 16977-16987.
3. N.-U.-A. Babar and K. S. Joya, *ACS Omega*, 2020.
4. S. Anantharaj, S. Ede, K. Karthick, S. S. Sankar, K. Sangeetha, P. Karthik and S. Kundu, *Energy & Environmental Science*, 2018, **11**, 744-771.
5. H. Gong, W. Zhang, F. Li and R. Yang, *Electrochimica Acta*, 2017, **252**, 261-267.
6. J. Chi, H. Yu, G. Li, L. Fu, J. Jia, X. Gao, B. Yi and Z. Shao, *RSC advances*, 2016, **6**, 90397-90400.
7. X. Huang, H. Zheng, G. Lu, P. Wang, L. Xing, J. Wang and G. Wang, *ACS Sustainable Chemistry & Engineering*, 2018, **7**, 1169-1177.
8. D. Xiong, Z. Du, H. Li, J. Xu, J. Li, X. Zhao and L. Liu, *ACS Sustainable Chemistry & Engineering*, 2018, **7**, 1493-1501.
9. X. Qiao, S. Liao, R. Zheng, Y. Deng, H. Song and L. Du, *ACS Sustainable Chemistry & Engineering*, 2016, **4**, 4131-4136.
10. X. Qiao, J. Jin, H. Fan, Y. Li and S. Liao, *Journal of Materials Chemistry A*, 2017, **5**, 12354-12360.
11. F. Shi, K. Huang, Y. Wang, W. Zhang, L. Li, X. Wang and S. Feng, *ACS applied materials & interfaces*, 2019, **11**, 17459-17466.
12. S. A. Khan, S. B. Khan and A. M. Asiri, *Journal of Materials Science: Materials in Electronics*, 2016, **27**, 5294-5302.
13. M. Xing, L.-B. Kong, M.-C. Liu, L.-Y. Liu, L. Kang and Y.-C. Luo, *Journal of Materials Chemistry A*, 2014, **2**, 18435-18443.
14. S. Asadizadeh, M. Amirnasr, S. Meghdadi, F. F. Tirani and K. Schenk, *International Journal of Hydrogen Energy*, 2018, **43**, 4922-4931.

15. C. Ranaweera, C. Zhang, S. Bhoyate, P. Kahol, M. Ghimire, S. Mishra, F. Perez, B. K. Gupta and R. K. Gupta, *Materials Chemistry Frontiers*, 2017, **1**, 1580-1584.
16. H. S. Jeon, M. S. Jee, H. Kim, S. J. Ahn, Y. J. Hwang and B. K. Min, *ACS applied materials & interfaces*, 2015, **7**, 24550-24555.
17. P. Jash, V. Aravind and A. Paul, *New Journal of Chemistry*, 2019, **43**, 6540-6548.
18. B. Sidhureddy, J. S. Dondapati and A. Chen, *Chemical communications*, 2019, **55**, 3626-3629.
19. Z. Li, X.-Y. Yu and U. Paik, *Journal of Power Sources*, 2016, **310**, 41-46.
20. S. Chen, Y. Zhao, B. Sun, Z. Ao, X. Xie, Y. Wei and G. Wang, *ACS applied materials & interfaces*, 2015, **7**, 3306-3313.
21. Z. Wang, S. Peng, Y. Hu, L. Li, T. Yan, G. Yang, D. Ji, M. Srinivasan, Z. Pan and S. Ramakrishna, *Journal of Materials Chemistry A*, 2017, **5**, 4949-4961.
22. M. P. Araújo, M. Nunes, I. M. Rocha, M. Pereira and C. Freire, *ChemistrySelect*, 2018, **3**, 10064-10076.
23. K. J. Lee, D. Y. Shin, A. Byeon, A. Lim, Y. S. Jo, A. Begley, D.-H. Lim, Y.-E. Sung, H. S. Park and K. H. Chae, *Nanoscale*, 2017, **9**, 15846-15855.
24. T. Maiyalagan, K. A. Jarvis, S. Therese, P. J. Ferreira and A. Manthiram, *Nature communications*, 2014, **5**, 1-8.