

Supporting Information

Cobalt Coordination Controlled Carbon Nanospheres Formation and Inclusion of Amorphous Co_3O_4 and AuNPs: Strongly Enhanced Oxygen Evolution Reaction with Excellent Mass Activity

*Pandi Muthukumar,^a Shreya Narasimhan,^a Arunprasanth Panneer Selvam,^b Mariappan Mariappan,^b Mohammed A. Assiri^c and Savarimuthu Philip Anthony^{*a}*

^aDepartment of Chemistry, School of Chemical & Biotechnology, SASTRA Deemed University, Thanjavur-613401, Tamil Nadu, India. Fax: +914362264120;

Tel: +914362264101, E-mail: philip@biotech.sastra.edu.

^bDepartment of Chemistry, SRM IST, Kattankulathur, Chennai-603203, Tamil Nadu, India.

^cDepartment of Chemistry, King Khalid University, Abha 61413, Saudi Arabia.

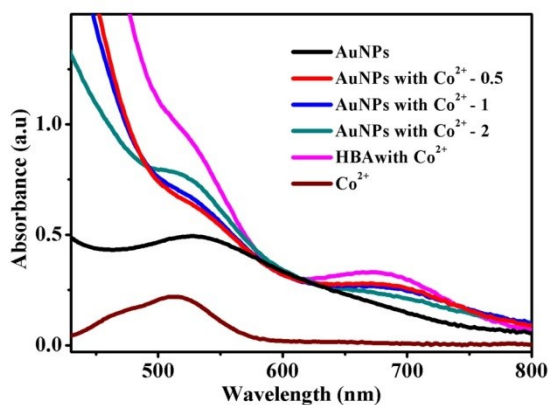


Figure S1. Absorption spectra of HBA, HBA@AuNPs, Co^{2+} ions and coordination with HBA ligand.

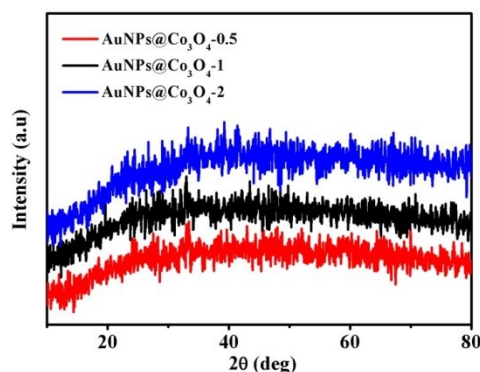


Figure S2. PXRD pattern of 1, 2 and 3.

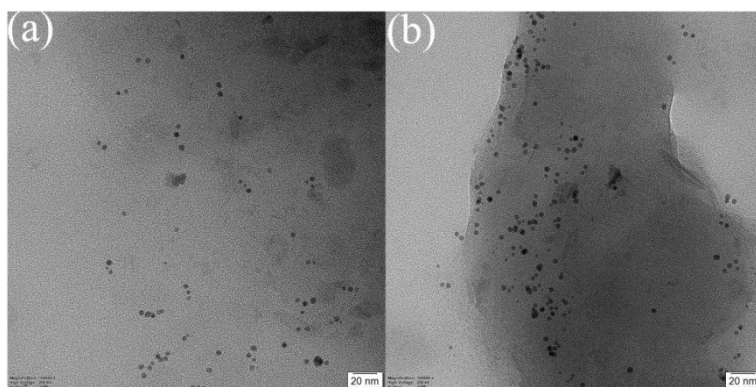


Figure S3. HR-TEM images of AuNPs synthesised using HBA.

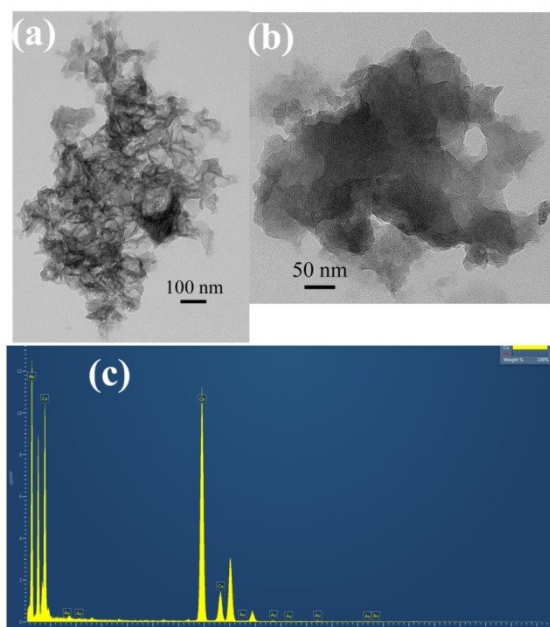


Figure S4. HR-TEM images (a, b) and EDX spectra (c) of **1**.

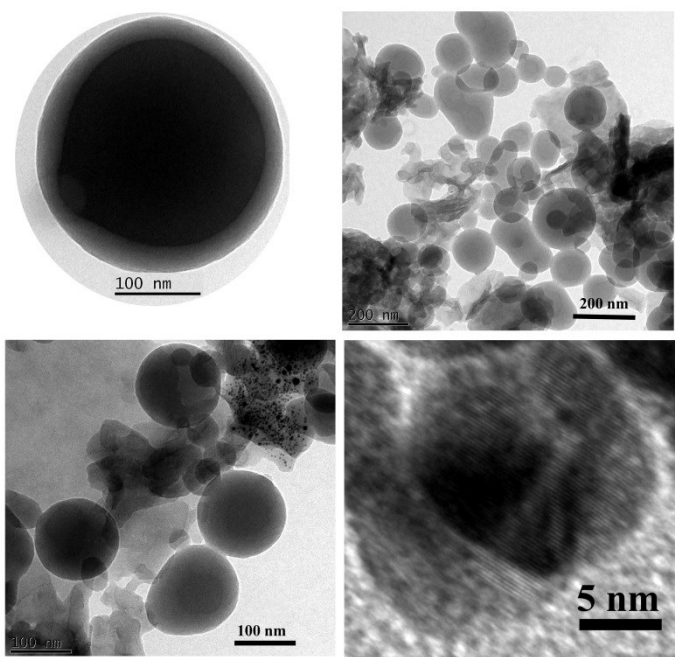


Figure S5. HR-TEM images of **2**.

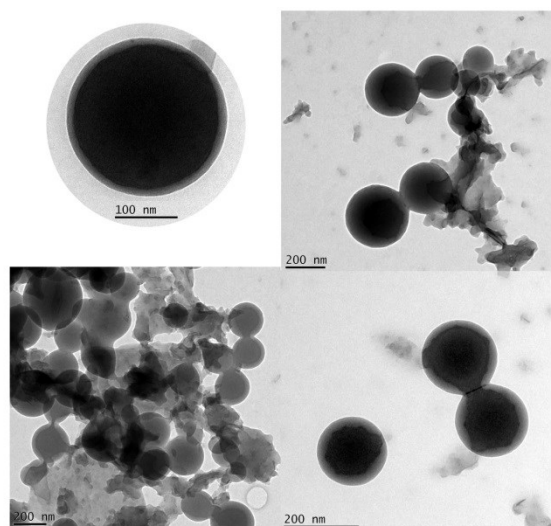


Figure S6. HR-TEM images of **3**.

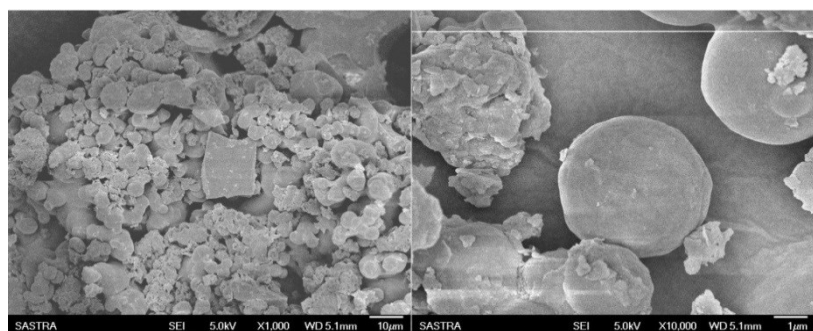


Figure S7. FE-SEM images of **2**.

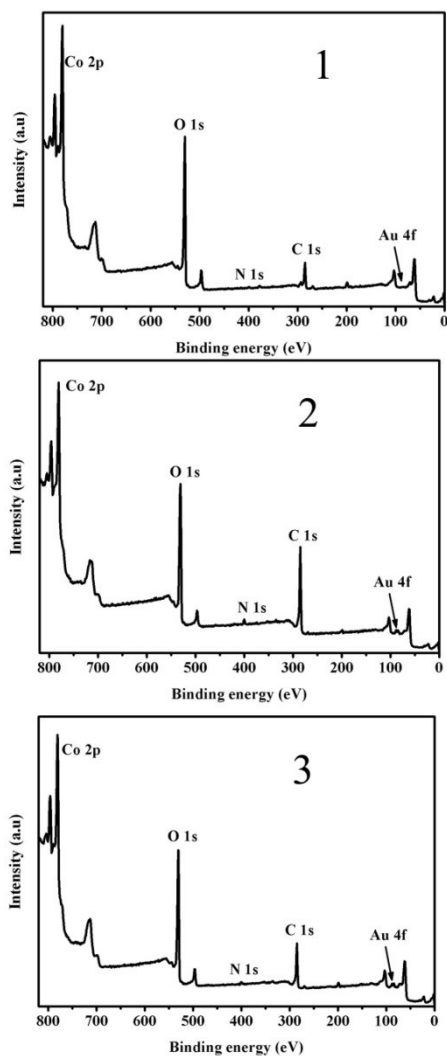


Figure S8. XPS survey spectra of **1-3**.

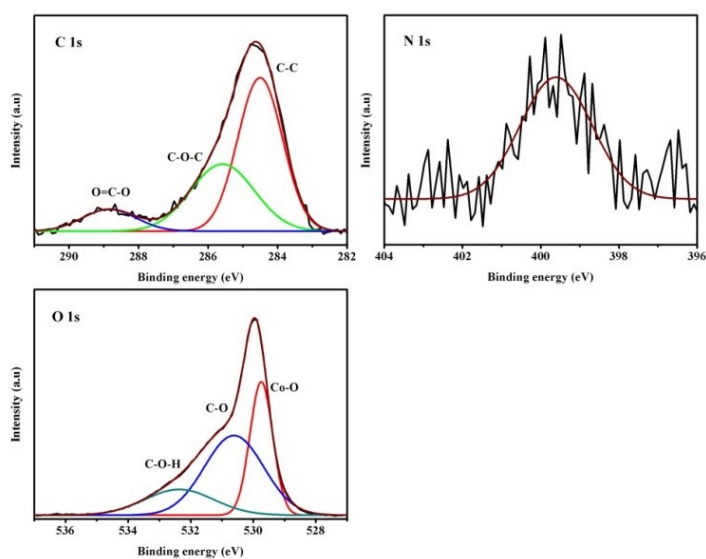


Figure S9. High resolution XPS spectra of C, N and O of **1**.

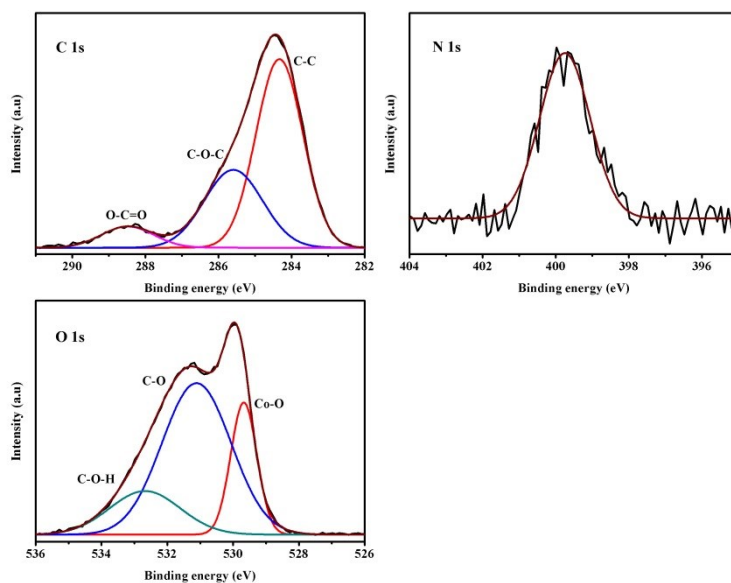


Figure S10. High resolution XPS spectra of C, N and O of **2**.

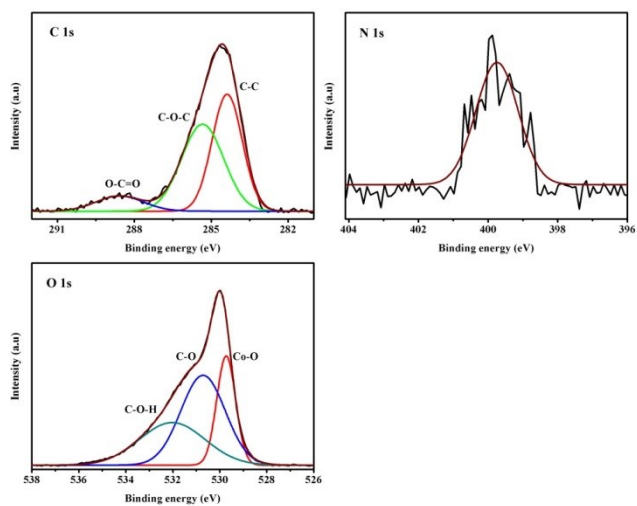


Figure S11. High resolution XPS spectra of C, N and O of **3**.

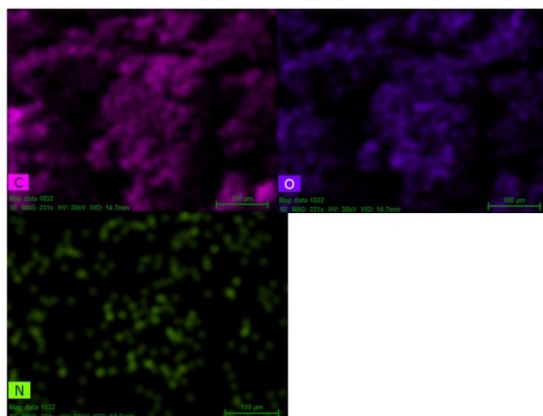


Figure S12. Elemental mapping of **1**.

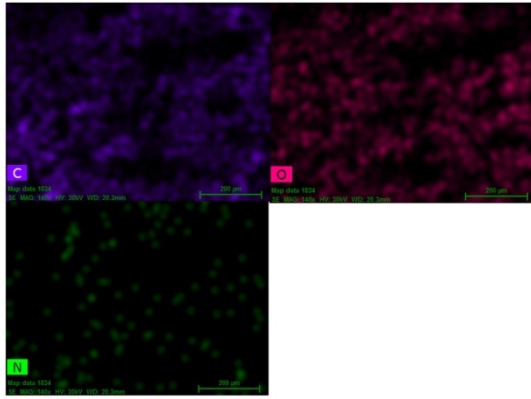


Figure S13. Elemental mapping of **2**.

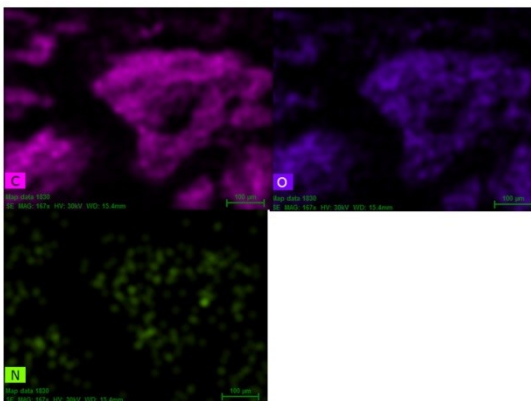


Figure S14. Elemental mapping of **3**.

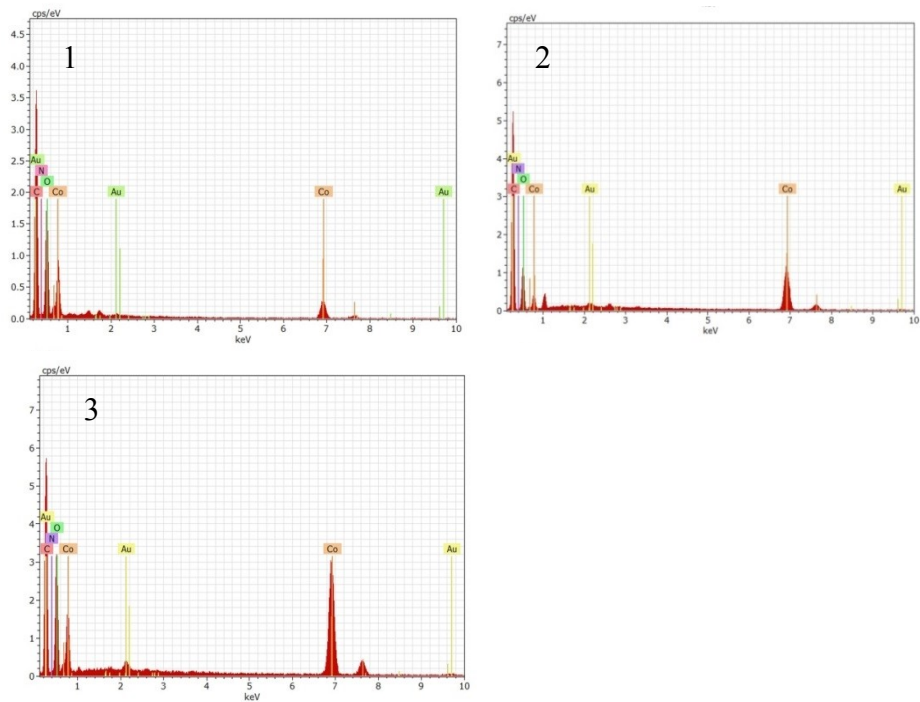


Figure S15. EDX spectra of (a) **1**, (b) **2** and (c) **3**.

Table S1. Au and Co percentage in 1-3.

Catalyst	Element	wt% by EDAX
1	Au	0.01
	Co	0.46
2	Au	0.04
	Co	1.74
3	Au	0.05
	Co	2.86

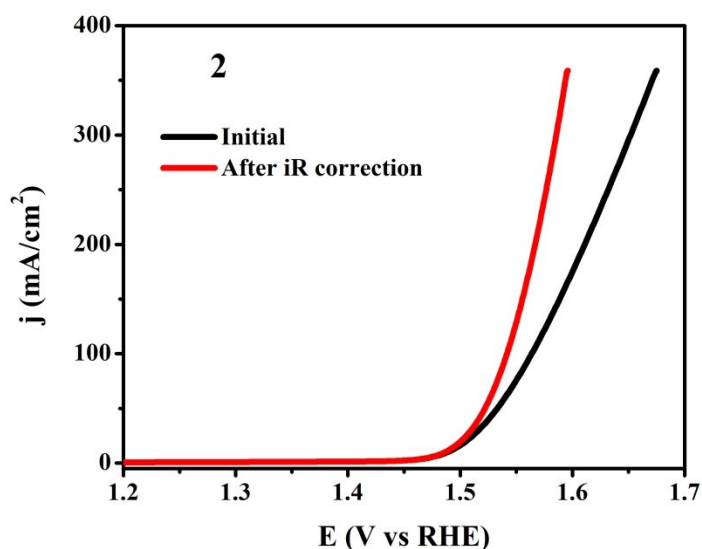


Figure S16. Linear sweep OER polarization curve of 2 before and after iR correction.

Table S2. OER data of different catalysts.

Catalyst	Overpotential (mV)	Tafel slope (mV/dec)	Stability	Reference
2	256	52.4	1000 cycle & 48 h	Present work
Au/NiCo ₂ O ₄	360	63	1000 cycle & 120 min	1
Au/m Co ₃ O ₄	440	46	2000 cycle	2
MnO ₂ /AuNP-4.4	390	~200	NA	3
CNTs-Au@Co ₃ O ₄	350	68	1000 cycle & 25 h	4
AuNCs@Ni(OH) ₂	375	73	600 cycle & 2 h	5
AuNCs@Co(OH) ₂	350	72	600 cycle	6
AuNDs@LDH/GCE	530	53	2000 seconds	7
NiCeOOH/Au	259		NA	8
NiFeOOH/Au	267			8
ZnCo ₂ O ₄ /Au/CNTs	440	46.2	10 h	9
AuCuCo	596	160	4 h	10
Au _{0.89} Fe _{0.11} NPs	800	163	NA	11
Au@NiO _x	394	117	2 h	12

Au/FeO _x	439	43	2 h	12
Au@CoFeO _x	328	58	2 h	12
Au-Ni ₁₂ P ₅	340	49	2.78 h	13
Au-Co(OH) ₂	320	119	6 h	14
Au ₂₅ /CoSe ₂	430	NA	1000 cycle	15
Au-Ru NPs	220	62	NA	16
AuNPs@LDH	510	61	1.5 h	17
Au/NiFe LDH	237	36	2000 cycle & 20 h	18
AuNi-Cu ₂ O (after 2 nd OER test)	532	NA	10 h	19
AuNi HDs	350	45.9	2 h	20
Au-Fe _x O _y 12	450	132	5 h	21
Au _{0.10} Ir _{0.90} O _y -50	241	55.2	5000 cycle	22
Au/Ir NCs	300	52.94	36 h	23
Au-CoFe ₂ O ₄	312	35	8 h	24
3DG-Au-Ni ₃ S ₂	370 (91.15 j)	106	NA	25
Au-vanadate nanoflute	310	127	NA	26
GMN@Co _x S _y	345	138	6000 seconds	27

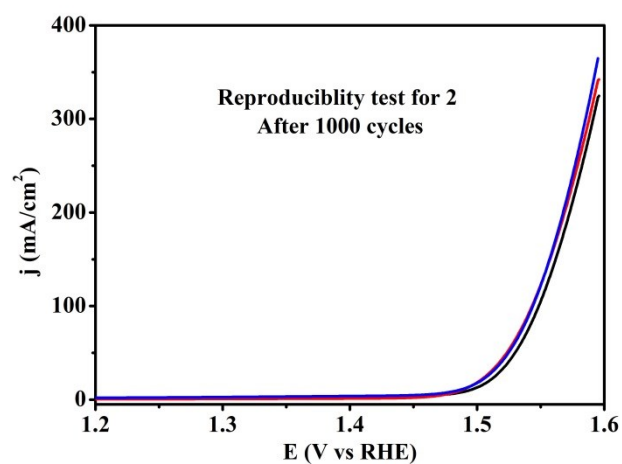


Figure S17. Comparison of linear sweep OER polarization curves of **2** synthesised at three different batches.

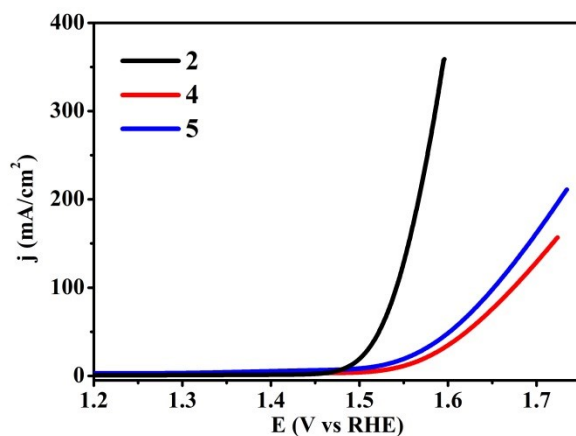


Figure S18. Comparison of linear sweep OER polarization curves of **2,4** and **5**.

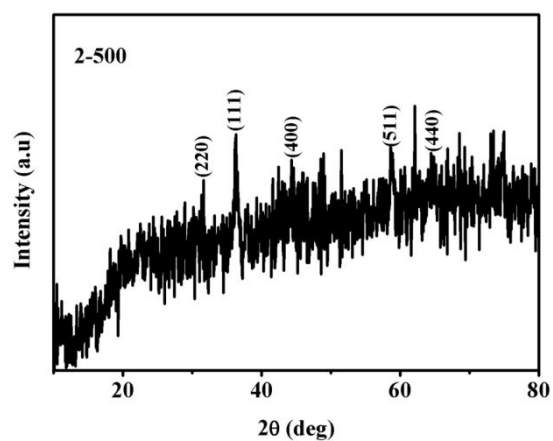


Figure S19. PXRD of **2** after heating at 500 °C.

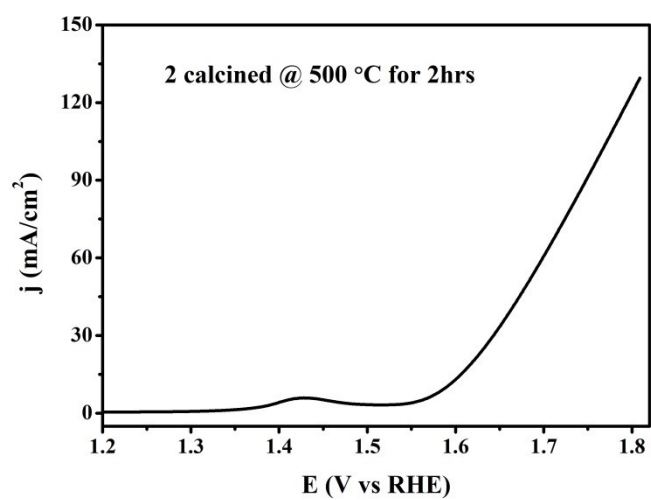


Figure S20. Linear sweep OER polarization curve of **2** after heating at 500 °C.

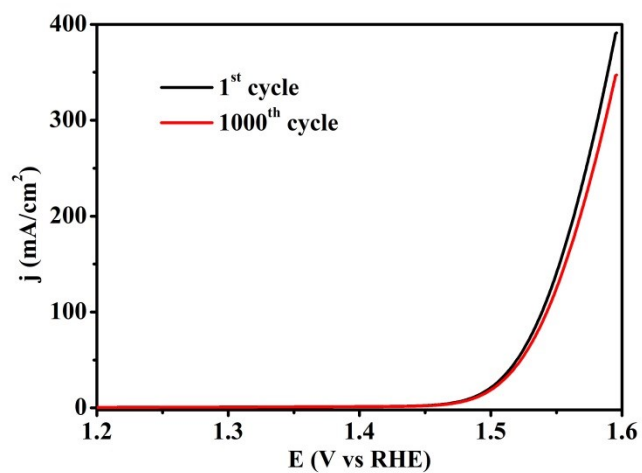


Figure S21. Linear sweep OER polarization curve of **2**.

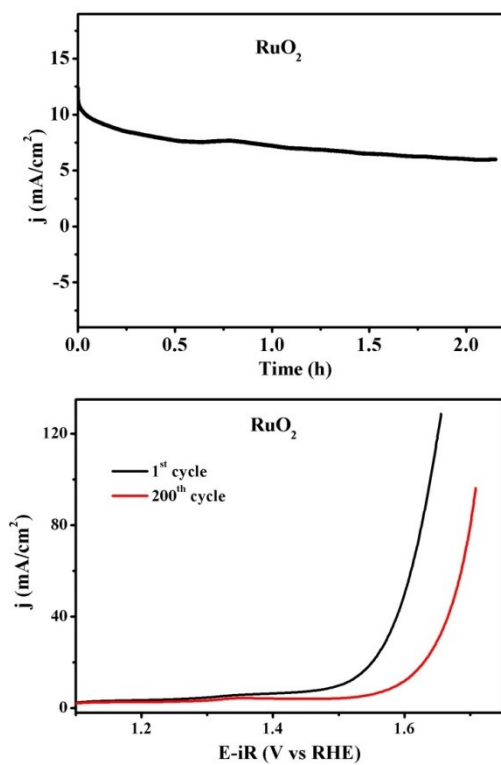


Figure S22. (a) Chronopotentiometric response and (b) OER polarization curve of RuO₂.

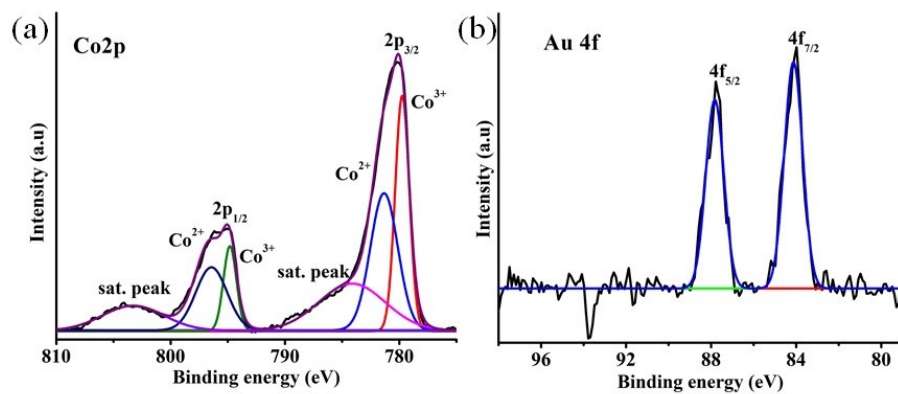


Figure S23. High resolution XPS spectra of (a) Co and (b) Au of **2** after catalytic studies.

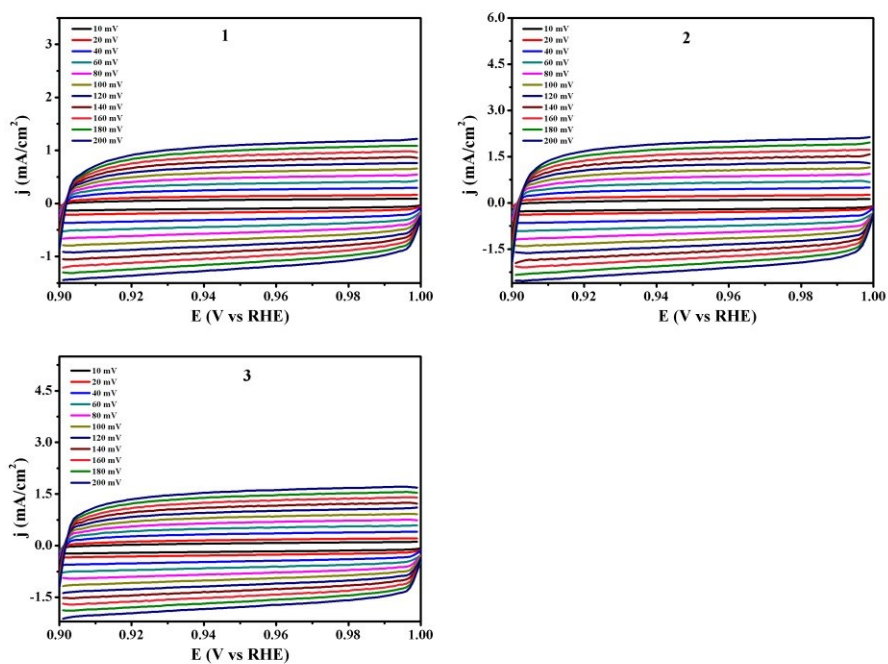


Figure S24. (a) CV of **1**, **2** and **3**.

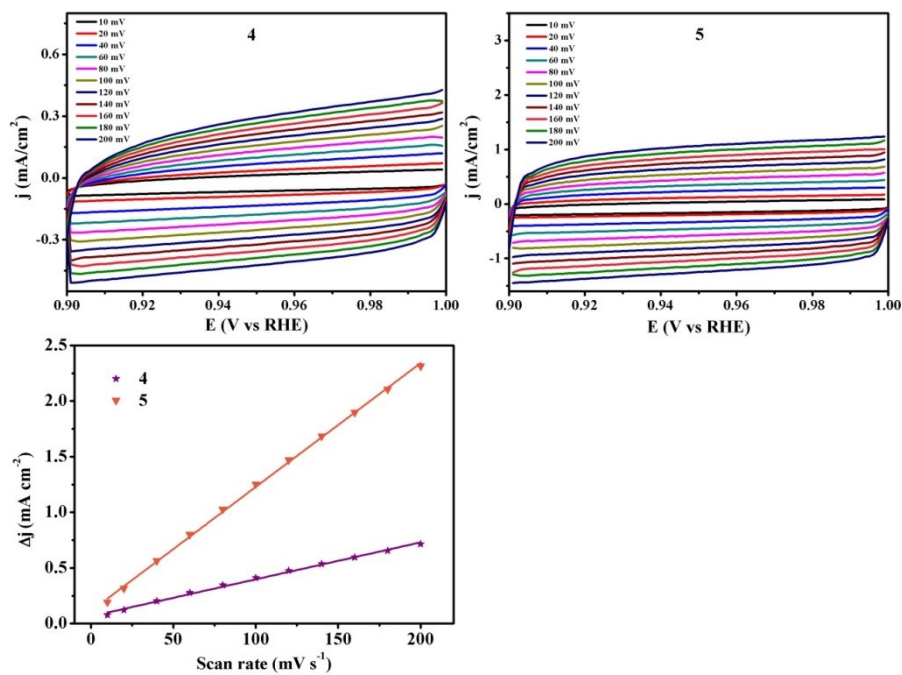


Figure S25. (a) CV of **4** and **5** and capacitive currents as a function of the scan rate for **2** and **4**.

Table S3. Comparison of mass activities of different catalysts.

Catalyst	Loading (mg)	Overpotential (mV)	Current density (mA/cm ²)	Mass activity (mA mg ⁻¹)	Ref
2	0.05	300	67.62	1352.5	This work
α -Ni(OH) ₂	0.2	350	30.02	150.1	28
γ -CoOOH	0.15	300	10	66.6	29
CuCo ₂ S ₄	0.7	310	10	14.29	30
NiFe-LDH/CuO NRs/CF	0.70	300	~105	150	31
Ba ₂ CoMo _{0.5} Nb _{0.5} O _{6-δ}	0.232	440	~10	~43	32
LaCo _{0.8} Fe _{0.2} O _{3-δ} -700	0.245	293	10	40.80	33
Electrochemically activated Co _x Ni _{1-x} S ₂	0.285	340	60	217	34
CeO ₂ /Co ₃ O ₄	0.35	340	~45	128.6	35
Au/NiFe LDH	2	280	129.8	64.9	18
Co-S-130	0.17	350	~13	76	36
CoOOH-NS	2	320	~45	~22.5	37

References:

- 1) X. Liu, J. Liu, Y. Li, Y. Li, X. Sun, *ChemCatChem* **2014**, *6*, 2501 – 2506.
- 2) X. Lu, Y. H. Ng, C. Zhao, *ChemSusChem* **2014**, *7*, 82 – 86.
- 3) C.-H. Kuo, W. Li, L. Pahalagedara, A. M. El-Sawy, D. Kriz, N. Genz, C. Guild, T. Ressler, S. L. Suib, J. He, *Angew. Chem. Inter. Ed.* **2015**, *127*, 2375-2380.
- 4) Y. Fang, X. Li, Y. Hu, F. Li, X. Lin, M. Tian, X. An, Y. Fu, J. Jin, J. Ma, *J. Power Sources* **2015**, **300**, 285-293.
- 5) Y. Zhou, H. C. Zeng, *J. Phys. Chem. C* **2016**, *120*, 29348–29357.
- 6) Y. Zhou, H. C. Zeng, *J. Phys. Chem. C* **2016**, *120*, 29348-29357.
- 7) M. Taci, E. Havakeshian, F. Hasheminasab, *RSC Adv.* **2017**, *7*, 47049–47055.
- 8) P. Chakthranont, J. Kibsgaard, A. Gallo, J. Park, M. Mitani, D. Sokaras, T. Kroll, R. Sinclair, M. B. Mogensen, T. F. Jaramillo, *ACS Catal.* **2017**, *7*, 5399–5409.
- 9) H. Cheng, C.-Y. Su, Z.-Y. Tan, S.-Z. Tai, Z.-Q. Liu, *J. Power Sources* **2017**, *357*, 1-10.
- 10) H. Gong, W. Zhang, F. Li, R. Yang, *Electrochimica Acta* **2017**, *252*, 261–267.
- 11) I. Vassalini, L. Borgese, M. Mariz, S. Polizzi, G. Aquilanti, P. Ghigna, A. Sartorel, V. Amendola, I. Alessandri, *Angew. Chem. Int. Ed.* **2017**, *56*, 6589-6593.
- 12) A. L. Strickler, M. Escudero-Escribano, T. F. Jaramillo, *Nano Lett.* **2017**, *17*, 6040–6046.
- 13) Y. Xu, S. Duan, H. Li, M. Yang, S. Wang, X. Wang, R. Wang, *Nano Res.* **2017**, *10*, 3103-3112.
- 14) M. A. Sayeeda, A. P. O'Mullane, *J. Mater. Chem. A* **2017**, *5*, 23776-23784.
- 15) S. Zhao, R. Jin, H. Abroshan, C. Zeng, H. Zhang, S. D. House, E. Gottlieb, H. J. Kim, J. C. Yang, R. Jin, *J. Am. Chem. Soc.* **2017**, *139*, 1077–1080.

- 16) L. Gloag, T. M. Benedetti, S. Cheong, Y. Li, X.-H. Chan, L.-M. Lacroix, S. L. Y. Chang, R. Arenal, I. Florea, H. Barron, A. S. Barnard, A. M. Henning, C. Zhao, W. Schuhmann, J. J. Gooding, R. D. Tilley, *Angew. Chem. Int. Ed.* **2018**, *54*, 10241-10245.
- 17) M. Tabei, E. Havakeshian, F. Hasheminasab, *J. Electroanal. Chem.* **2018**, *808*, 75–81.
- 18) J. Zhang, J. Liu, L. Xi, Y. Yu, N. Chen, S. Sun, W. Wang, K. M. Lange, B. Zhang, *J. Am. Chem. Soc.* **2018**, *140*, 3876–3879.
- 19) H. Gong, S. Lu, P. Strasser, R. Yang, *Electrochimica Acta* **2018**, *283*, 1411-1417.
- 20) B. Ni, P. He, W. Liao, S. Chen, L. Gu, Y. Gong, K. Wang, J. Zhuang, Li Song, G. Zhou, X. Wang, *Small* **2018**, *14*, 1703749.
- 21) S. A. Lone, S. Ghosh, K. K. Sadhu, *ACS Omega* **2019**, *4*, 3385–3391.
- 22) S. Moon, Y.-B. Cho, A. Yu, M. H. Kim, C. Lee, Y. Lee, *ACS Appl. Mater. Inter.* **2019**, *11*, 1979–1987.
- 23) Z. Ke, L. Li, Q. Jia, Y. Yang, H. Cui, *App. Surf. Sci.* **2019**, *463*, 58-65.
- 24) G. Zhu, X. Li, Y. Liu, W. Zhu, X. Shen, *App. Surf. Sci.* **2019**, *478*, 206-212.
- 25) H. Glatz, E. Lizundia, F. Pacifico D. Kundu, *ACS Appl. Ener. Mater.* **2019**, *22*, 1288-1294.
- 26) B. Das, M. Sharma, A. Hazarika, K. K. Bania, *ChemistrySelect* **2019**, *4*, 7042-7050.
- 27) H. D. Mai, V. C. T. Le, H. Yoo, *ACS Appl. Nano Mater.* **2019**, *2*, 678–688.
- 28) Minrui Gao, W. Sheng, Z. Zhuang, Q. Fang, S. Gu, J. Jiang, Y. Yan, *J. Am. Chem. Soc.* **2014**, *136*, 7077–7084.
- 29) J. Huang, J. Chen, T. Yao, J. He, S. Jiang, Z. Sun, Q. Liu, W. Cheng, F. Hu, Y. Jiang, Z. Pan, S. Wei, *Angew. Chem. Int. Ed.* **2015**, *54*, 8722–8727.
- 30) M. Chauhan, K. P. Reddy, C. S. Gopinath, S. Deka, *ACS Catal.* **2017**, *7*, 5871–5879.
- 31) Q. Zhou, T.-T. Li, J. Qian, W. Xu, Y. Hu, Y.-Q. Zheng, *ACS Appl. Ener. Mater.* **2018**, *1*, 1364–1373.
- 32) H. Sun, G. Chen, J. Sunarso, J. Dai, W. Zhou, Z. Shao, *ACS Appl. Mater. Inter.* **2018**, *10*, 16939–16942.
- 33) S. Song, J. Zhou, X. Su, Y. Wang, J. Li, L. Zhang, G. Xiao, C. Guan, R. Liu, S. Chen, H.-J. Lin, S. Zhang J.-Q. Wang, *Ener. Environ. Sci.* **2018**, *11*, 2945-2953.
- 34) Y.-R. Hong, S. Mhin, K.-M. Kim, W.-S. Han, H. Choi, G. Ali, K. Y. Chung, H. J. Lee, S.-I. Moon, S. Dutta, S. Sun, Y.-G. Jung, T. Song, H. Han, *J. Mater. Chem. A* **2019**, *7*, 3592-3602.
- 35) B. Qui, C. Wang, N. Zhang, L. Cai, Y. Xiong, Y. Chai, *ACS Catal.* **2019**, *97*, 6484-6490.
- 36) S. Ju, Y. Liu, H. Chen, F. Tan, A. Yuan, X. Li, G. Zhu, *ACS Appl. Ener. Mater.* **2019**, *2*, 4439-4449.
- 37) J. Zhou, Y. Wang, X. Su, S. Gu, R. Liu, Y. Huang, S. Yan, J. Li, S. Zhang, *Ener. Environ. Sci.* **2019**, *12*, 739-746.