Electronic Supplementary Information

Iron-nickel oxide: A promising strategy for water oxidation†

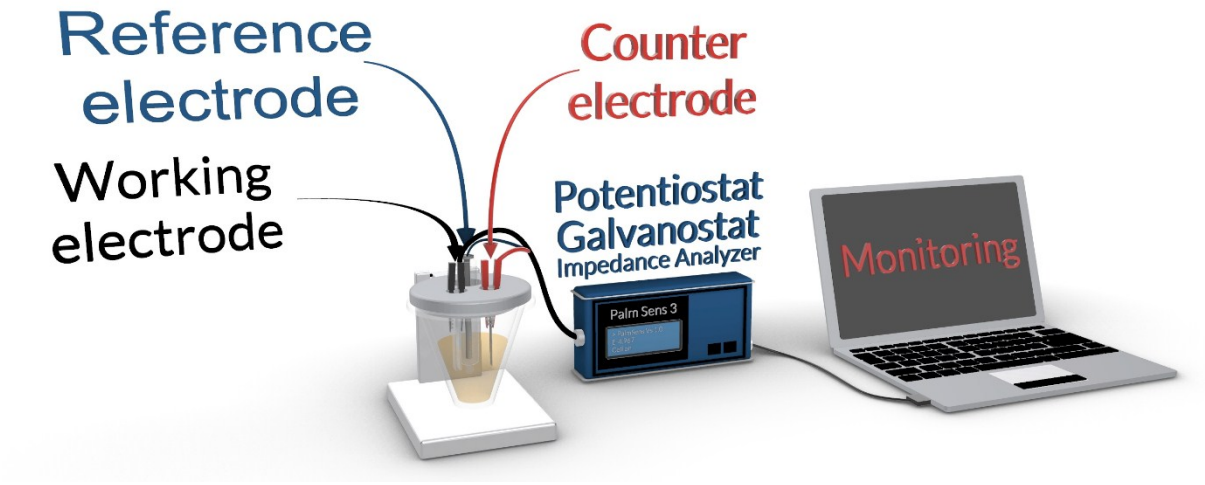
Tohid Safdari [a], Nader Akbari [a¥], Amirreza Valizadeh [a¥], Robabeh Bagheri [b,c], Zhenlun Song [b], Suleyman I. Allakhverdiev [d-h*] and Mohammad Mahdi Najafpour [a,i,j *]

[a]*Department of Chemistry, Institute for Advanced Studies in Basic Sciences (IASBS), Zanjan, 45137-66731, Iran*
[b]*Key Laboratory of Marine Materials and Related Technologies, Zhejiang Key Laboratory of Marine Materials and Protective Technologies, Ningbo Institute of Materials Technology and Engineering, Chinese Academy of Sciences, Ningbo 315201, China*
[c]*School of Physical Science and Technology, College of Energy, Soochow Institute for Energy and Materials Innovations and Key Laboratory of Advanced Carbon Materials and Wearable Energy Technologies of Jiangsu Province, Soochow University, Suzhou 215006, China*
[d]*Controlled Photobiosynthesis Laboratory, K.A. Timiryazev Institute of Plant Physiology, Russian Academy of Sciences, Botanicheskaya Street 35, Moscow 127276, Russia*
[e]*Institute of Basic Biological Problems, Russian Academy of Sciences, Pushchino, Moscow Region 142290, Russia*
[f]*Bionanotechnology Laboratory, Institute of Molecular Biology and Biotechnology, Azerbaijan National Academy of Sciences, Baku, Azerbaijan*
[g]*Department of Plant Physiology, Faculty of Biology, M.V. Lomonosov Moscow State University, Leninskie Gory 1-12, Moscow 119991, Russia*
[h]*Department of Molecular and Cell Biology, Moscow Institute of Physics and Technology, Institutsky lane 9, Dolgoprudny, Moscow region 141700, Russia*
[i]*Center of Climate Change and Global Warming, Institute for Advanced Studies in Basic Sciences (IASBS), Zanjan, 45137-66731, Iran*
[j]*Research Center for Basic Sciences & Modern Technologies (RBST), Institute for Advanced Studies in Basic Sciences (IASBS), Zanjan 45137-66731, Iran*

**Corresponding authors: E-mails: mmnajafpour@iasbs.ac.ir (MMN); Suleyman.allakhverdiev@gmail.com (SIA);*

[¥] These authors contributed equally to this work

†Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x



Scheme S1 The setup for the electrochemical experiment. A three-electrode setup was used with an Hg/HgO, a Pt sheet, and the operated sheet prepared in this study as the reference, counter and working electrode, respectively. The surface of the working electrode was 4-4.5 mm^2 and the distance between Hg/HgO and the operated sheet was less than 10 mm. The thickness was also 0.75 mm for the operated sheet.

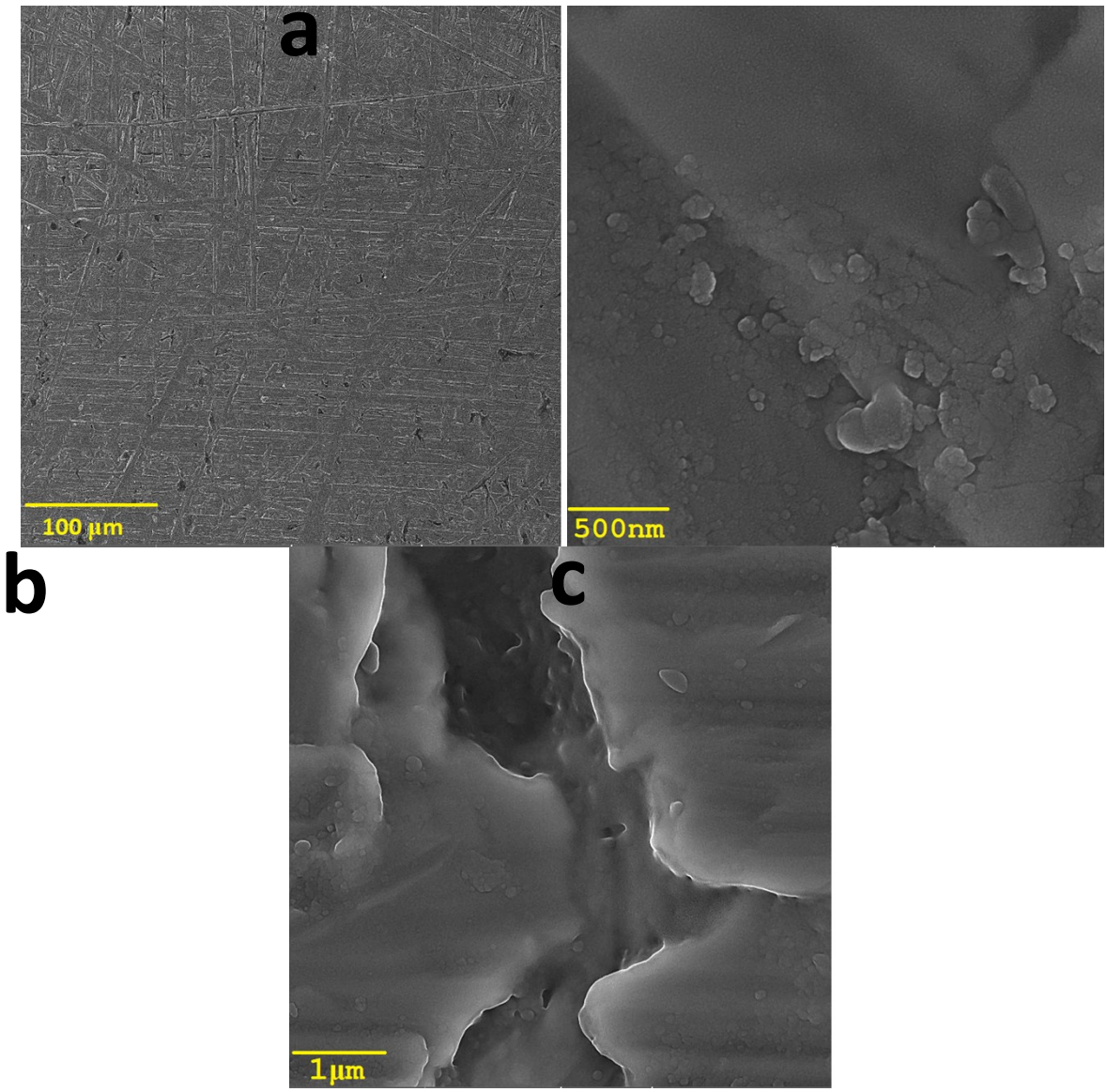


Fig. S1 SEM image of a fresh Fe-Ni alloy with different magnifications (a-c).

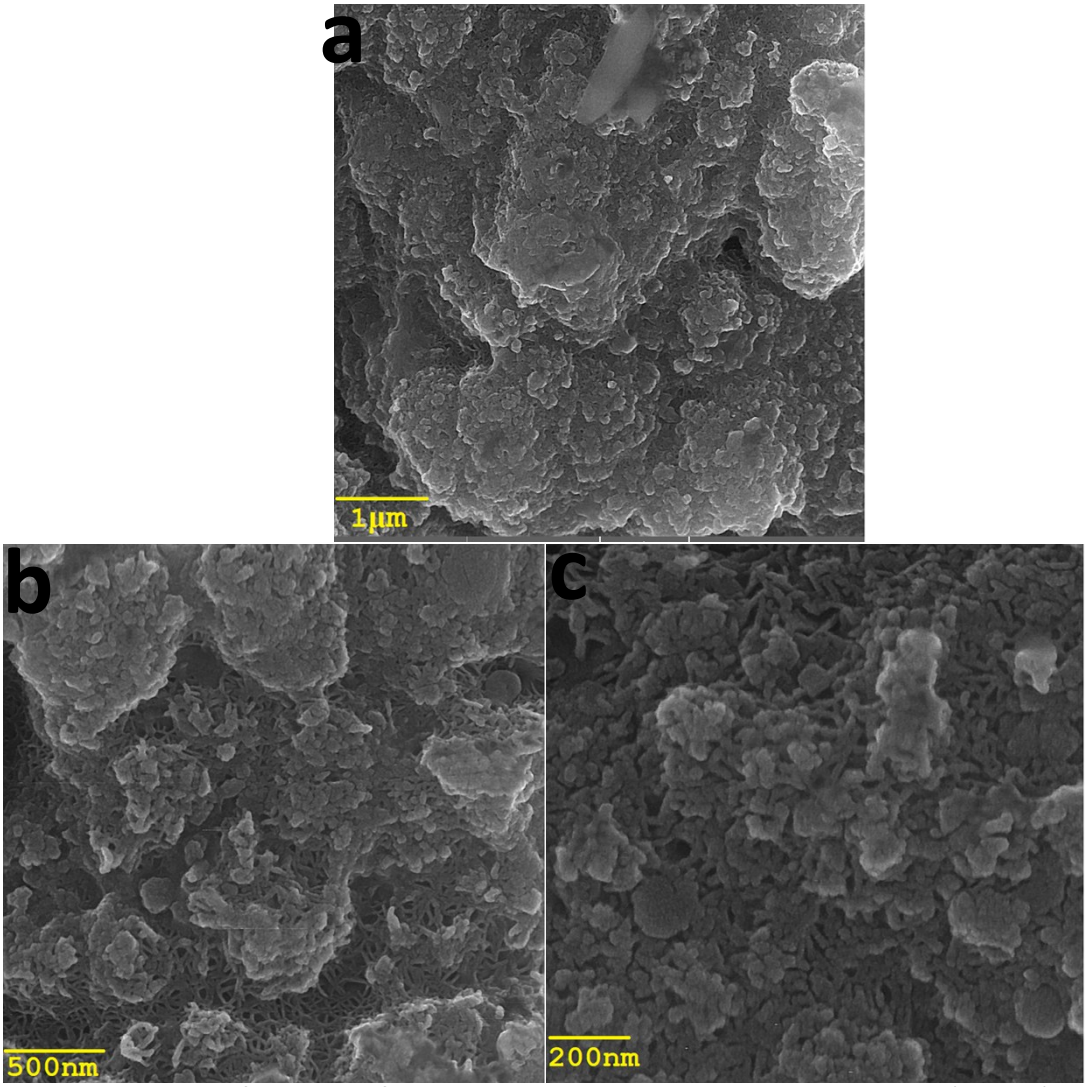


Fig. S2 SEM image of the alloy after the operation at 60.0 V in the KOH solution (0.10 M) with different magnifications (a-c).

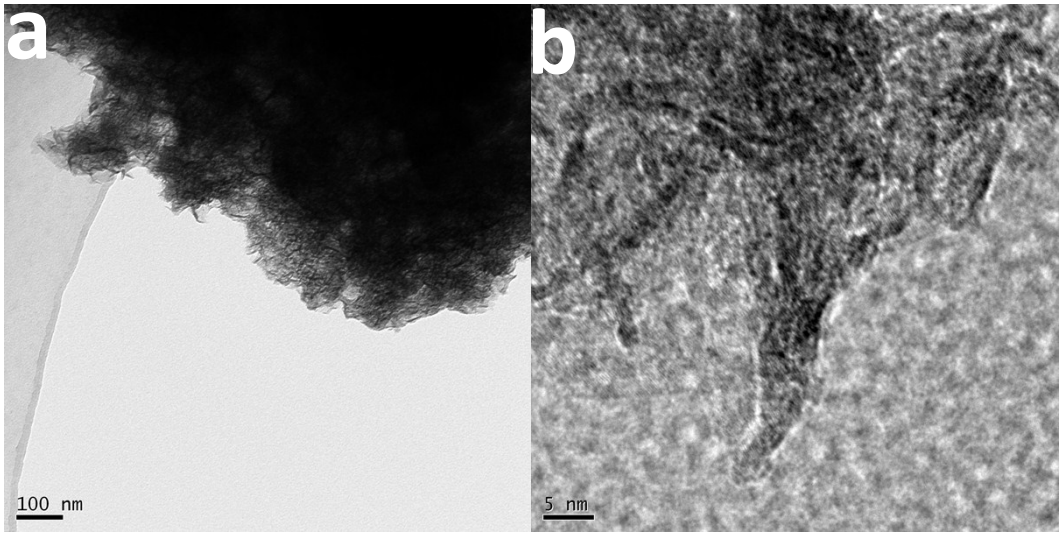


Fig. S3 TEM and HRTEM images of the mechanically separated electrode after the operation at 60.0 V in the KOH solution (0.10 M) with different magnifications (a,b).

Table S1 Comparison of some catalytic parameters for heterogeneous water oxidizing catalysts. Table was modified from ref 1.[1]

Comp.	$\eta^{[a]}$ (mV)	$\eta^{[b]}$ (mV)	pH	Ref.
The operated alloy	**195**	**210**	**13**	**This work**
$NiFeO_x$	-	297	14	[2]
NiO_x	> 400	> 1000	14	[3]
NiO_x	-	300	14	[2]
CoO_x	-	381	14	[2]
$NiCoO_x$	-	312	14	[2]
FeO_x	345	445	14	[4]
FeO_x	-	405	14	[2]
Fe_2O_3	< 350	430	14	[5]
MnO_x	320	514	14	[2]
$Fe_3Ni_2O_x$	270	-	13	[6]
$FeNiO_x$	211	-	13	[7]
$Fe_2Ni_3O_x$	190	250	13	[8]
NiO_x	191	280	13	[7]
NiO_x	295	-	13	[9]
$CoFeO_x$[c]	397	-	13	[10]
CoO_x	< 200	< 250	13	[11]
FeO_x	320	410	13	[7]
CoO_x	210	270	13	[7]
CoO_x	295	-	13	[6]
$FeCoO_x$	181	-	13	[7]
$FeCoNiO_x$	191	-	13	[7]
Ni_2FeAlO_x	270	-	13	[6]
$NiFeMo_3O_x$	250	-	13	[6]
$Ni_2FeCr_2O_x$	240	-	13	[6]
$NiFeGa_3O_x$	240	-	13	[6]
$CoSe_2$	373	380	13	[12]
NG-$CoSe_2$	294	320	13	[12]
MnO_x	< 300	> 1000	>11.5	[13]
FeOOH	300	420	11	[14]
NiB_i	300	425	9.2	[15]
MnO_x	< 300	> 1000	8.5-5.5	[13]
CoO_x	< 200	< 300	7	[11]
MnO_x	390	590	7	[16]
MnO_x	441	600	7	[17]
CoFePBA	291	> 600	7	[18]
MnO_x	150	> 1000	7	[19]
CoP_i	281	410	7	[20]
MnO_x	> 700	> 1000	7	[21]
$Li_xMnP_2O_7$	500	-	7	[22]
MnO_x	< 300	> 1000	3.5	[13]
Co^{2+} (1 M)	< 580	600	1	[11]

[a] Onset overpotentiol. [b] @1 $mAcm^{-2}$.

References

1. Galan-Mascarós, J. R., Water oxidation at electrodes modified with earth-abundant transition-metal catalysts. *ChemElectroChem* **2015,** *2* (1), 37-50.
2. Trotochaud, L.; Ranney, J. K.; Williams, K. N.; Boettcher, S. W., Solution-cast metal oxide thin film electrocatalysts for oxygen evolution. *J. Am. Chem. Soc.* **2012,** *134* (41), 17253-17261.
3.Trotochaud, L.; Young, S. L.; Ranney, J. K.; Boettcher, S. W., Nickel–iron oxyhydroxide oxygen-evolution electrocatalysts: the role of intentional and incidental iron incorporation. *J. Am. Chem. Soc.* **2014,** *136* (18), 6744-6753.
4. Doyle, R.; Lyons, M., Kinetics and mechanistic aspects of the oxygen evolution reaction at hydrous iron oxide films in base. *J. Electrochem. Soc.* **2013,** *160* (2), H142-H154.
5. Qiu, Y.; Leung, S.-F.; Zhang, Q.; Hua, B.; Lin, Q.; Wei, Z.; Tsui, K.-H.; Zhang, Y.; Yang, S.; Fan, Z., Efficient photoelectrochemical water splitting with ultrathin films of hematite on three-dimensional nanophotonic structures. *Nano lett.* **2014,** *14* (4), 2123-2129.
6. Chen, J. Y.; Miller, J. T.; Gerken, J. B.; Stahl, S. S., Inverse spinel NiFeAlO 4 as a highly active oxygen evolution electrocatalyst: promotion of activity by a redox-inert metal ion. *Energy Environ. Sci.* **2014,** *7* (4), 1382-1386.
7. Smith, R. D.; Prévot, M. S.; Fagan, R. D.; Zhang, Z.; Sedach, P. A.; Siu, M. K. J.; Trudel, S.; Berlinguette, C. P., Photochemical route for accessing amorphous metal oxide materials for water oxidation catalysis. *Science* **2013**, 1233638.
8. Smith, R. D.; Prévot, M. S.; Fagan, R. D.; Trudel, S.; Berlinguette, C. P., Water oxidation catalysis: electrocatalytic response to metal stoichiometry in amorphous metal oxide films containing iron, cobalt, and nickel. *J. Am. Chem. Soc.* **2013,** *135* (31), 11580-11586.
9. Shaidarova, L.; Davletshina, L.; Budnikov, G., Flow-injection determination of water-soluble vitamins B 1, B 2, and B 6 from the electrocatalytic response of a graphite electrode modified with a ruthenium (III) hexacyanoruthenate (II) film. *J. Anal. Chem.* **2006,** *61* (5), 502-509.
10. Abellán, G.; Carrasco, J. A.; Coronado, E.; Romero, J.; Varela, M., Alkoxide-intercalated CoFe-layered double hydroxides as precursors of colloidal nanosheet suspensions: structural, magnetic and electrochemical properties. *J. Mater. Chem. C* **2014,** *2* (19), 3723-3731.
11. Gerken, J. B.; McAlpin, J. G.; Chen, J. Y.; Rigsby, M. L.; Casey, W. H.; Britt, R. D.; Stahl, S. S., Electrochemical water oxidation with cobalt-based electrocatalysts from pH 0–14: the thermodynamic basis for catalyst structure, stability, and activity. *J. Am. Chem. Soc.* **2011,** *133* (36), 14431-14442.
12. Gao, M.-R.; Cao, X.; Gao, Q.; Xu, Y.-F.; Zheng, Y.-R.; Jiang, J.; Yu, S.-H., Nitrogen-doped graphene supported CoSe2 nanobelt composite catalyst for efficient water oxidation. *ACS Nano* **2014,** *8* (4), 3970-3978.
13. Huynh, M.; Bediako, D. K.; Nocera, D. G., A functionally stable manganese oxide oxygen evolution catalyst in acid. *J. Am. Chem. Soc.* **2014,** *136* (16), 6002-6010.
14. Chemelewski, W. D.; Lee, H.-C.; Lin, J.-F.; Bard, A. J.; Mullins, C. B., Amorphous FeOOH oxygen evolution reaction catalyst for photoelectrochemical water splitting. *J. Am. Chem. Soc.* **2014,** *136* (7), 2843-2850.
15. Dincă, M.; Surendranath, Y.; Nocera, D. G., Nickel-borate oxygen-evolving catalyst that functions under benign conditions. *Proc. Natl. Acad. Sci.* **2010,** *107* (23), 10337-10341.
16. Zaharieva, I.; Chernev, P.; Risch, M.; Klingan, K.; Kohlhoff, M.; Fischer, A.; Dau, H., Electrosynthesis, functional, and structural characterization of a water-oxidizing manganese oxide. *Energy Environ. Sci.* **2012,** *5* (5), 7081-7089.
17. Indra, A.; Menezes, P. W.; Zaharieva, I.; Baktash, E.; Pfrommer, J.; Schwarze, M.; Dau, H.; Driess, M., Active Mixed-Valent MnOx Water Oxidation Catalysts through Partial Oxidation (Corrosion) of Nanostructured MnO Particles. *Angew. Chem. Int. Ed.* **2013,** *52* (50), 13206-13210.
18. Pintado, S.; Goberna-Ferrón, S.; Escudero-Adán, E. C.; Galán-Mascarós, J. R. n., Fast and persistent electrocatalytic water oxidation by Co–Fe Prussian blue coordination polymers. *J. Am. Chem. Soc.* **2013,** *135* (36), 13270-13273.
19. Singh, A.; Hocking, R. K.; Chang, S. L.-Y.; George, B. M.; Fehr, M.; Lips, K.; Schnegg, A.; Spiccia, L., Water oxidation catalysis by nanoparticulate manganese oxide thin films: probing the effect of the manganese precursors. *Chem. Mater.* **2013,** *25* (7), 1098-1108.
20. Kanan, M. W.; Nocera, D. G., In situ formation of an oxygen-evolving catalyst in neutral water containing phosphate and Co^{2+}. *Science* **2008,** *321* (5892), 1072-1075.
21. Bergmann, A.; Zaharieva, I.; Dau, H.; Strasser, P., Electrochemical water splitting by layered and 3D cross-linked manganese oxides: correlating structural motifs and catalytic activity. *Energy Environ. Sci.* **2013,** *6* (9), 2745-2755.
22. Park, J.; Kim, H.; Jin, K.; Lee, B. J.; Park, Y.-S.; Kim, H.; Park, I.; Yang, K. D.; Jeong, H.-Y.; Kim, J., A new water oxidation catalyst: lithium manganese pyrophosphate with tunable Mn valency. *J. Am. Chem. Soc.* **2014,** *136* (11), 4201-4211.