Supporting Information

Mesoporous K-doped NiCo$_2$O$_4$ derived from Prussian blue analog: High-yielding synthesis and assessment as oxygen evolution reaction catalyst

Nam Woon Kim, a Hyunung Yu b* and Jihun Oh c,d*

a Department of Nature-Inspired Nano Convergence Systems, Korea Institute of Machinery and Materials (KIMM), Daejeon 34103, Republic of Korea

b Surface Analysis Team, Korea Research Institute of Standards and Science (KRISS), Daejeon 34113, Republic of Korea

c Department of Materials Science and Engineering, Korea Advanced Institute of Science and Technology (KAIST), Daejeon 34141, Republic of Korea

d KAIST Institute for NanoCentury, Korea Advanced Institute of Science and Technology (KAIST, Daejeon 34141, Republic of Korea

*Corresponding authors. Emails: peacewithu@kriss.re.kr (H. Y.), jihun.oh@kaist.ac.kr (J. O.)
Figure S1. Fast Fourier transform patterns of (a) NiCo$_2$O$_4$ (white rectangle in Fig. 1b) and (b) KNO$_3$ (red rectangle in Fig. 1b).
Figure S2. Weighing the HK-NCO catalyst powder produced by hydrothermal synthesis.

3.46 g (HK-NCO) / 80 mL (Distilled water)
Figure S3. SEM images of catalysts prepared (a) hydrothermally (KNO$_3$ + high-concentration K-doped NiCo$_2$O$_4$) and (b) non-hydrothermally (KNO$_3$ + low-concentration K-doped NiCo$_2$O$_4$).
Figure S4. XRD pattern of hydrothermally synthesized K-Ni-Co-PBA. Inset shows an expansion of the region of interest, confirming the absence of crystalline KNO₃.
Figure S5. (a) C 1s and (b) N 1s spectra of the synthesized catalysts (calibrated using the C 1s peak of adventitious carbon at 284.4 eV) (c) area calculation of elements derived from KNO$_3$.

\[
\frac{N_{(\text{area})}}{N_{(\text{ASF})}} = \frac{K_{\text{KNO}_3(\text{area})}}{K_{(\text{ASF})}} = \frac{1}{3} \frac{O_{\text{KNO}_3(\text{area})}}{O_{(\text{ASF})}}
\]

Measured in pure KNO$_3$

$N_{(\text{ASF})} = 4.506$, $K_{(\text{ASF})} = 1.466$, $O_{(\text{ASF})} = 3.023$

ASF: Atomic Sensitivity Factor
Figure S6. CV curves of the prepared catalysts recorded at a scan rate of 1 mV s$^{-1}$ to extract overpotentials at 10 mA cm$^{-2}$ and Tafel slopes.
Figure S7. Nyquist plot fitting results for (a) HK-NCO and (b) LK-NCO.
Figure S8. ECSA-normalized LSV polarization curves of the prepared catalysts recorded at a scan rate of 1 mV s$^{-1}$. 
Table S1. Area of peaks corresponding to different chemical states in the X-ray photoelectron spectra of the synthesized catalysts.

| Catalyst | $\text{NH}_3$+ | $\text{NH}_2$+ | $\text{NH}$+ | $\text{NNH}$+ | O1 | O2 | O3 | O2$^+$ | O3$^+$ | N   |
|----------|----------------|----------------|--------------|---------------|----|----|----|--------|--------|-----|
| HK-NCO   | 15003.5        | 14218.2        | 11226.4      | 33370.5       | 23319.6 | 18842.2 | 24618.5 | 2713.2 | 2255.2 | 438.6 | 1348.1 |
| LK-NCO   | 37949.5        | 26733.4        | 30128.4      | 79380.8       | 47448.7 | 24842.6 | 9111.2   | 3976.4 | 1663.3 | 642.8 | 1975.7 |
Table S2. Comparative overpotentials and Tafel slope values of electrocatalysts in this work and other literature.

| Catalyst                                      | Substrate                              | η (mV) at 10 mA cm⁻² | Tafel slope (mV dec⁻¹) | Electrolyte | Ref |
|-----------------------------------------------|----------------------------------------|----------------------|------------------------|-------------|-----|
| K-doped NiCo₂O₄ (HK-NCO)                      | Ni foam                                | 292 (reverse current)| 49.9                   | 1 M KOH     | This work |
| Mesoporous NiCo₂O₄                            | KIT-6 (mesoporous silica molecular sieve) | 350                  | 43                     | 1 M KOH     | 1   |
| P-doped NiCo₂O₄ Nanowire                      | Ni foam                                | 300                  | 120                    | 1 M KOH     | 2   |
| Ir-doped (10 at%) NiCo₂O₄ Nanostructure       | Glassy carbon electrode                | 303                  | 78                     | 1 M KOH     | 3   |
| MOF-derived NiCo₂O₄/NiO-rGO                   | Glassy carbon electrode                | 340                  | 66                     | 1 M KOH     | 4   |
| NiMn LDH nanosheets/NiCo₂O₄ nanowires         | Ni foam                                | 310                  | 99                     | 1 M KOH     | 5   |
| NiCo₂O₄ 3-D nanoflowers                       | Graphene nanosheets                    | 383                  | 137                    | 1 M KOH     | 6   |
| 3-D core–shell structured NiCo₂O₄@CoS         | Ni foam                                | 290                  | 92                     | 1 M KOH     | 7   |
| Hierarchical NiCo₂O₄ nanosheet-CNTs           | Ni foam                                | 390                  | 68.1                   | 1 M KOH     | 8   |
| Co₃O₄/NiCo₂O₄                                | Ni foam                                | 320                  | 84                     | 0.1 M KOH   | 9   |
| Hierarchical NiCo₅S₄ nanosheets/rGO           | Glassy carbon electrode                | 366                  | 65                     | 1 M KOH     | 10  |
| Ni₀.₇₅Co₀.₂₅O₂        | Graphite felt                         | 509                  | 119                    | 1 M KOH     | 11  |

MOF (metal organic frameworks), 3-D (Three-dimensional), LDH (layered double hydroxide), CNT (carbon nanotubes), rGO (reduced graphene oxide)
References

1. C. Broicher, F. Zeng, J. Artz, H. Hartmann, A. Besmehn, S. Palkovits and R. Palkovits, *ChemCatChem*, 2019, **11**, 412.
2. W. Chu, Z. Shi, Y. Hou, D. Ma, X. Bai, Y. Gao and N. Yang, *ACS Appl. Mater. Interfaces*, 2020, **12**, 2763.
3. H.-J. Lee, D.-H. Park, W.-J. Lee, S.-B. Han, M.-H. Kim, J.-H. Byeon and K.-W. Park, *Appl. Catal. A Gen.*, 2021, **626**, 118377.
4. Y. Wang, Z. Zhang, X. Liu, F. Ding, P. Zou, X. Wang, Q. Zhao and H. Rao, *ACS Sustain. Chem. Eng.*, 2018, **6**, 12511.
5. L. Yang, L. Chen, D. Yang, X. Yu, H. Xue and L. Feng, *J. Power Sources*, 2018, **392**, 23.
6. Z. Li, B. Li, J. Chen, Q. Pang and P. Shen, *Int. J. Hydrogen Energy*, 2019, **44**, 16120.
7. S. Adhikari, Y. Kwon and D. H. Kim, *Chem. Eng. J.*, 2020, **402**, 126192.
8. H. Cheng, Y. Z. Su, P. Y. Kuang, G. F. Chen and Z. Q. Liu, *J. Mater. Chem. A*, 2015, **3**, 19314.
9. M. Yang, W. Lu, R. Jin, X. C. Liu, S. Song and Y. Xing, *ACS Sustain. Chem. Eng.*, 2019, **7**, 12214.
10. C. Shuai, Z. Mo, X. Niu, X. Yang, G. Liu, J. Wang, N. Liu and R. Guo, *J. Mater. Sci.*, 2020, **55**, 1627.
11. H. Park, B. H. Park, J. Choi, S. Kim, T. Kim, Y. S. Youn, N. Son, J. H. Kim and M. Kang, *Nanomaterials*, 2020, **10**, 1.