Supporting Information

Enhanced oxygen evolution and urea oxidation reaction using nanosheet-structured NiO@P-doped carbon composite as anode catalyst

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2.4. Materials characterization. While high-resolution transmission electron microscopy (HR-TEM) (JEM-ARM200F, JEOL), energy dispersive X-ray spectroscopy, and atomic force microscopy (AFM) (Innova, Bruker, USA) are at the center of future energy accumulation, all electrocatalysts created were morphologically characterized using these techniques. The generated electrocatalysts X-ray diffraction (XRD) patterns were assessed to use a PANalytical (X'PERT-PRO Powder) (model) and Cu K light (= 0.154 nm). We measured the Raman spectrum of each manufactured electrocatalyst using elevated 3D mapping Scanning Raman spectroscopy with a NANO PHOTON (RAMAN Touch) outfitted with such a 532 nm helium-neon laser at the Jeonbuk National University (JBNU) Center for University-wide Research Facilities (CURF) in South Korea. The chemical state of the materials as-obtained was examined to use an X-ray photoelectron spectroscopy (XPS; Axis-Nova, Kratos Inc.) and a Brunauer-Emmett-Teller (BET) Autosorb-iQ 2ST/MP physisorption analyzer was used to look at the prepared catalysts surface area, at the Korea Basic Science Institute of Jeonju Center (KBSI), South Korea. Using the Ni K-edges, measurements of the extended X-ray absorption fine structure (EXAFS) and the X-ray absorption near edge structure (XANES) based on the R-XAS model (Rigaku, Japan) were carried out using the Sc-detector of Chonnam National University with total electron yield detection.

2.5. Electrochemical analysis. The HER electrochemical performances were investigated using a three-electrode cell with carbon paper-supported electrocatalyst as a working electrode. Graphite rods were employed as the counter electrode while Ag/AgCl was used as the reference electrode. It took about 60 cycles to initially activate the working electrode in a 1.0 M KOH solution until the curve became crisp. The HER polarization curves were measured using linear sweep voltammetry (LSV) in 1.0 M KOH at fixed scanning and sweep rates of 1 mV s^{-1}. The following

equation was used to express all recorded potentials based on the reversible hydrogen electrode (RHE).

$E_{RHE} = E_{AgCl} + (0.197 + 0.059 \times pH)$

Electrochemical impedance spectroscopy (EIS) was carried out within a frequency range of 100 kHz - 0.1 Hz with an amplitude of 5 mV in 1.0 M KOH. The long-term durability test was performed using chronopotentiometry measurements.

Capacitance measurements and comparison of ECSA

Cyclic voltammetry was carried out to probe the electrochemical double layer capacitance (C_{dl}) of various samples at non-Faradaic potentials between 0.05 and 0.25 V (vs. RHE in 0.5 M H_2SO_4) with sweep rates of 10, 20, 30, 40, and 50 mV s^{-1}. The double-layer capacitance (C_{dl}) values of the samples were estimated by plotting $\Delta J = Ja - Jc$ against the CV scan rate, where the slope was twice C_{dl}. The ECSA of each electrocatalyst was then calculated by

$ECSA = C_{dl}/Cs,$

Here, Cs is specific capacitance of the alkaline electrolyte (Cs = 0.04 mF cm^2). The roughness factor (RF) was calculated by

$RF = ECSA/GSA$

where GSA is the geometric surface area of the sample.

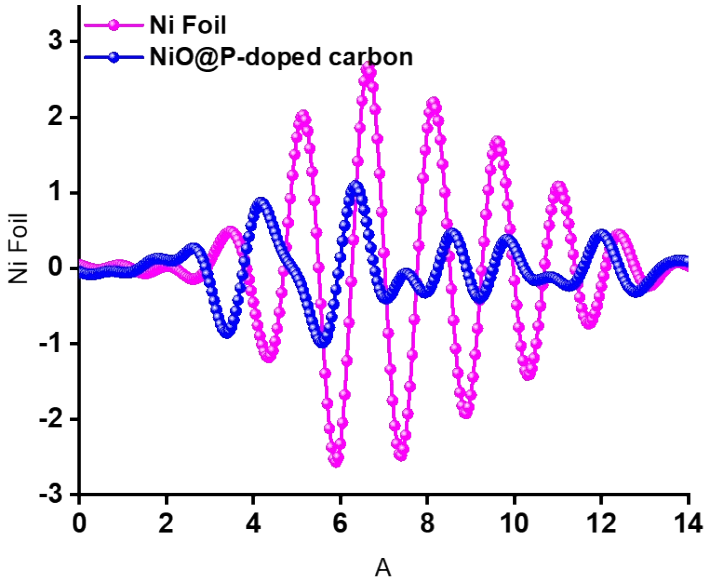

Fig. S1 EXAFS Ni k-edge spectrum of NiO/P-doped carbon composite.

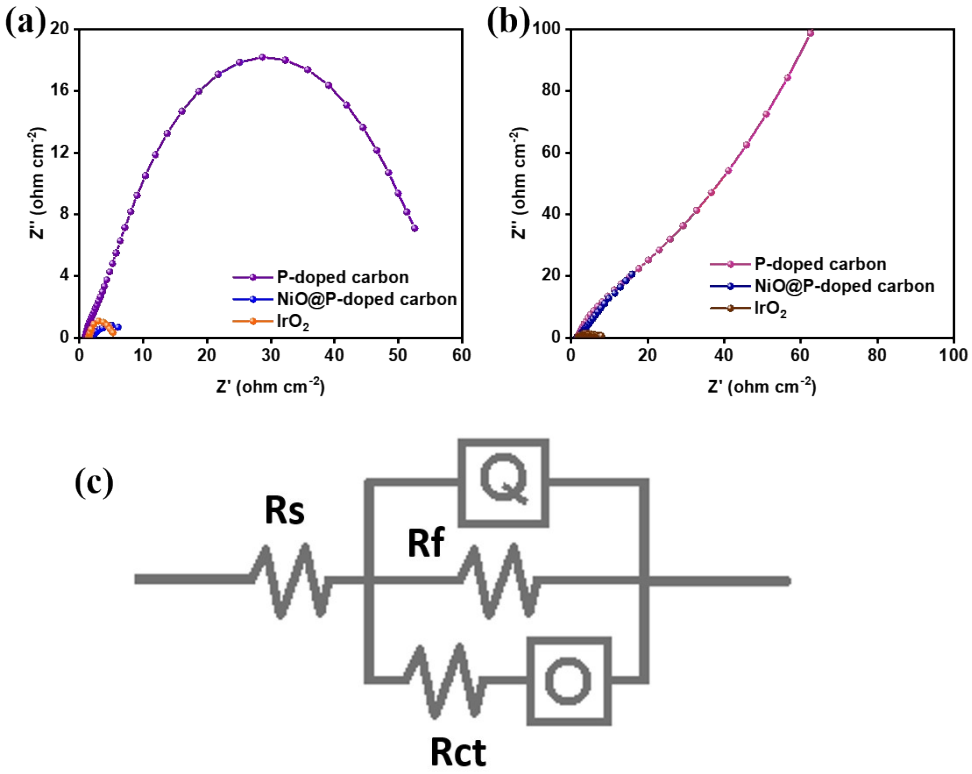

Fig. S2. EIS spectra of NiO@P-doped carbon, P-doped carbon, and IrO_2 electrocatalysts, (a) 1 M KOH solution, (b) 1 M KOH + 0.5 M urea solution, and (c) EIS fitting circuit.

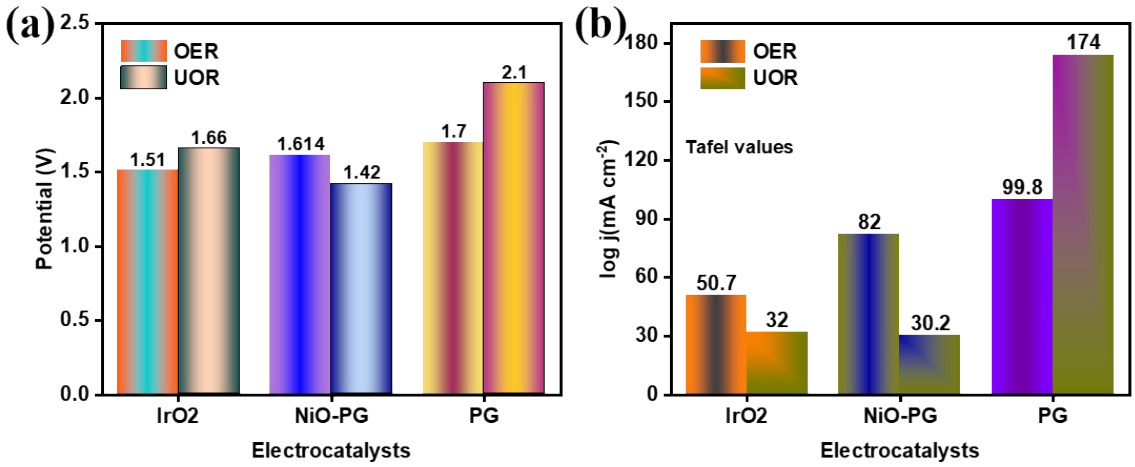

Fig. S3. (a, b) Comparison of overpotential values and Tafel values

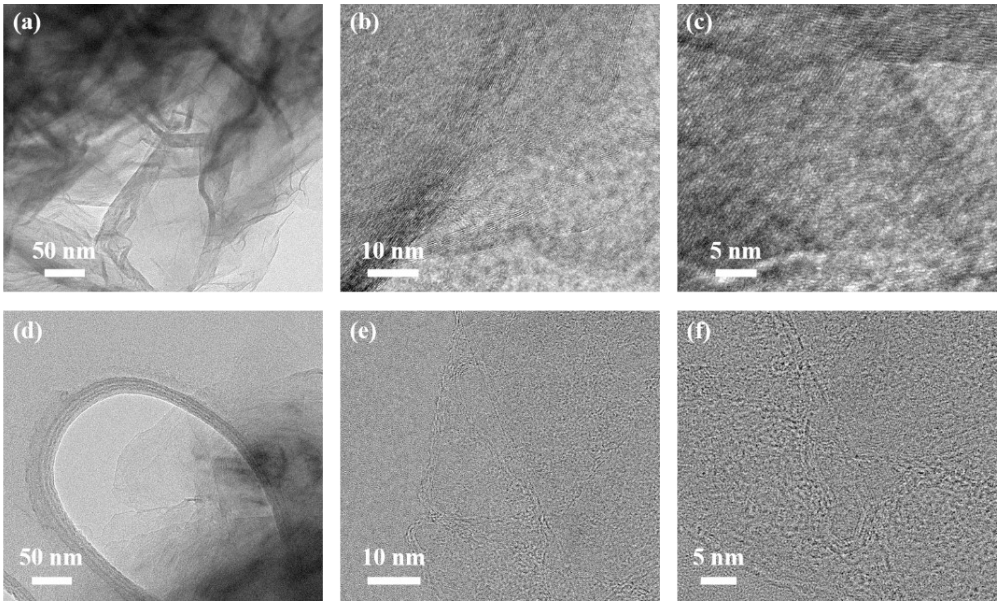

Fig. S4 TEM analysis of (a-c) before stability and (d-f) after HER stability in acid medium of NiO/P-doped carbon electrocatalyst.

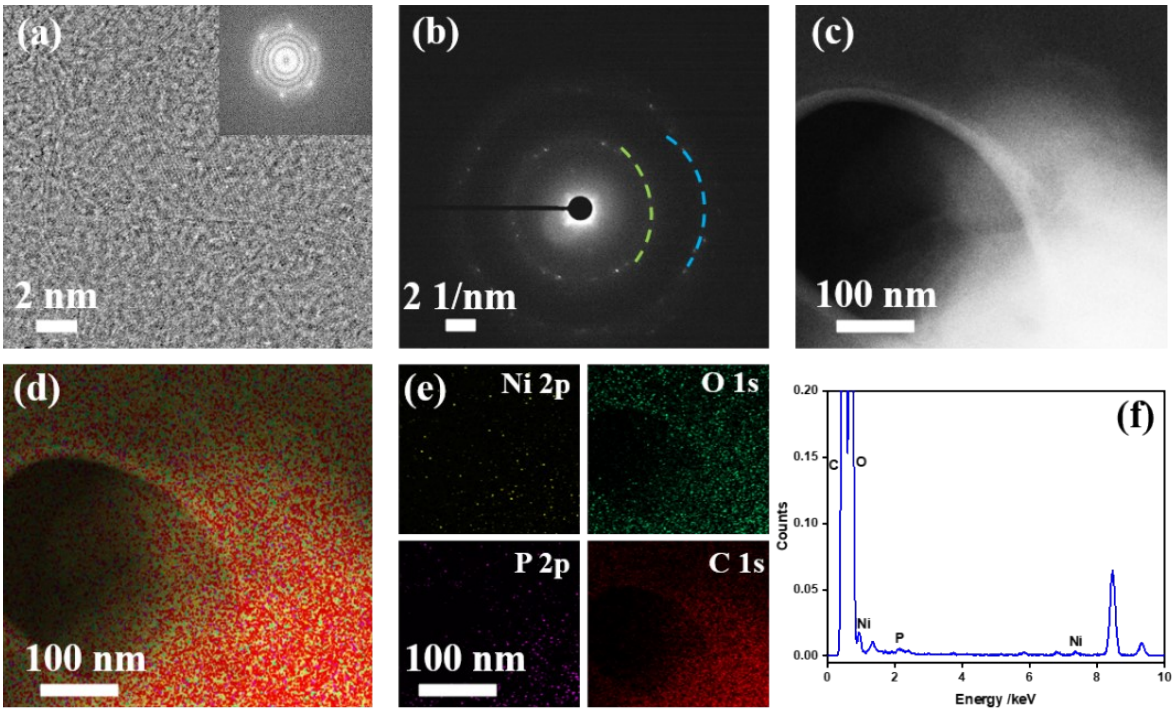

Fig. S5 (a) HR-TEM, (b) SAED pattern, (c) HAADF image, (d) mapping overlap image, (e) color mapping corresponding elemental, and (f) EDS elemental spectrum of NiO/P-doped carbon electrocatalyst evaluating post-HER cyclic stability at 500 mA cm-2 current density corresponding to Ni, O, P, and C.

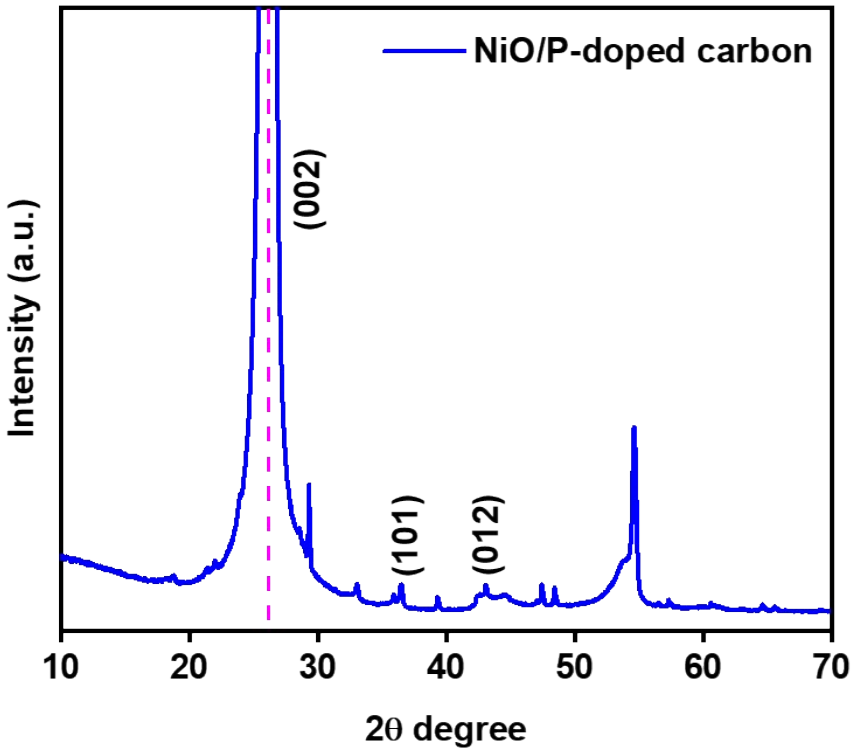

Fig. S6 after long-term stability test XRD analysis of NiO/P-doped carbon

Table S1. Comparison of metal electrocatalysts for OER and UOR performance.

Catalysts	**OER @10mA**	**UOR @10mA**	**Published year**	**Ref**
NiCoP/NF	203	1.13	2023	[1]
2D/2D Ru-Co DAS/NiO	--	1.288	2023	[2]
Ru-Ni_3N@NC	270	1.30	2022	[3]
Co–Ni–S@NF	--	1.31	2022	[4]
NiCo LDH	1.545	1.332	2024	[5]
Ni-MoN NAM	1.52	1.28	2023	[6]
Ce-Ni_3N@CC	279	1.31	2022	[7]
Ni@NiOCN-4	0.33	1.0	2023	[8]
NiO–CrO@N–C	-	1.37	2024	[9]
Ni/NiO-3	1.60	1.42	2022	[10]
Ni-NiO-$Mo_{0.84}Ni_{0.16}$/NF	-	1.33 (50 mA)	2020	[11]
Ni/MNO-10	280	1.37	2023	[12]
NiO@P-doped carbon	**1.62**	**1.42**	**2024**	**Present work**

References

[1] L. Yang, F. Ru, J. Shi, T. Yang, C. Guo, Y. Chen, E. Wang, Z. Du, K.-C. Chou, X. Hou, Trifunctional electrocatalysts based on feather-like NiCoP 3D architecture for hydrogen evolution, oxygen evolution, and urea oxidation reactions, Ceramics International, 49 (2023) 659-668.

[2] X. Zheng, J. Yang, P. Li, Z. Jiang, P. Zhu, Q. Wang, J. Wu, E. Zhang, W. Sun, S. Dou, D. Wang, Y. Li, Dual-Atom Support Boosts Nickel-Catalyzed Urea Electrooxidation, Angewandte Chemie International Edition, 62 (2023) e202217449.

[3] Y. Liu, D. Zheng, Y. Zhao, P. Shen, Y. Du, W. Xiao, Y. Du, Y. Fu, Z. Wu, L. Wang, Ru-doped 3D porous Ni3N sphere as efficient Bi-functional electrocatalysts toward urea assisted water-splitting, International Journal of Hydrogen Energy, 47 (2022) 25081-25089.

[4] Z. Xu, Q. Chen, Q. Chen, P. Wang, J. Wang, C. Guo, X. Qiu, X. Han, J. Hao, Interface enables faster surface reconstruction in a heterostructured Co–Ni–S electrocatalyst towards efficient urea oxidation, Journal of Materials Chemistry A, 10 (2022) 24137-24146.

[5] Z. Zheng, D. Wu, L. Chen, S. Chen, H. Wan, G. Chen, N. Zhang, X. Liu, R. Ma, Collaborative optimization of thermodynamic and kinetic for Ni-based hydroxides in electrocatalytic urea oxidation reaction, Applied Catalysis B: Environmental, 340 (2024) 123214.

[6] H. Shen, T. Wei, Q. Liu, S. Zhang, J. Luo, X. Liu, Heterogeneous Ni-MoN nanosheet-assembled microspheres for urea-assisted hydrogen production, Journal of Colloid and Interface Science, 634 (2023) 730-736.

[7] M. Li, X. Wu, K. Liu, Y. Zhang, X. Jiang, D. Sun, Y. Tang, K. Huang, G. Fu, Nitrogen vacancies enriched Ce-doped Ni3N hierarchical nanosheets triggering highly-efficient urea oxidation reaction in urea-assisted energy-saving electrolysis, Journal of Energy Chemistry, 69 (2022) 506-515.

[8] D.M. Sanke, A.V. Munde, J. Bezboruah, P.T. Bhattad, B.R. Sathe, S.S. Zade, Highly Dispersed Core–Shell Ni@NiO Nanoparticles Embedded on Carbon–Nitrogen Nanotubes as Efficient Electrocatalysts for Enhancing Urea Oxidation Reaction, Energy & Fuels, 37 (2023) 4616-4623.

[9] N. Wu, X. Chi, Y. Zhang, T. Hu, Convenient synthesis and enhanced urea oxidation of NiO–CrO@N–C, New Journal of Chemistry, 48 (2024) 5621-5626.

[10] T.V.M. Sreekanth, G.R. Dillip, X. Wei, K. Yoo, J. Kim, Binder free Ni/NiO electrocatalysts for urea oxidation reaction, Materials Letters, 327 (2022) 133038.

[11] Q. Xu, G. Qian, S. Yin, C. Yu, W. Chen, T. Yu, L. Luo, Y. Xia, P. Tsiakaras, Design and Synthesis of Highly Performing Bifunctional Ni-NiO-MoNi Hybrid Catalysts for Enhanced Urea Oxidation and Hydrogen Evolution Reactions, ACS Sustainable Chemistry & Engineering, 8 (2020) 7174-7181.
[12] V. Maheskumar, A. Min, C.J. Moon, R.A. Senthil, M.Y. Choi, Modulating the Electronic Structure of Ni/NiO Nanocomposite with High-Valence Mo Doping for Energy-Saving Hydrogen Production via Boosting Urea Oxidation Kinetics, Small Structures, 4 (2023) 2300212.