Addressing the OER/HER imbalance by a redox transition-induced two-way electron injection in a bifunctional n-p-n electrode for excellent photoelectrocatalytic water splitting

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Supplementary Information

List of abbreviations and acronyms

DSSC	Dye-sensitized solar cell
EDS	Energy dispersive spectroscopy
FTO	Fluorine-doped tin oxide
HER	Hydrogen evolution reaction
HRTEM	High-resolution transmission electron microscopy
IR	Infrared
LSV	Linear sweep voltammetry
N/N@NF	NiCo ₂ O ₄ /NiFe ₂ O ₄ @Nickel foam
N/W/N@NF	NiCo ₂ O ₄ /WSe ₂ /NiFe ₂ O ₄ @Nickel foam
N/W@NF	NiCo ₂ O ₄ /WSe ₂ @Nickel foam
NF	Nickel foam
OER	Oxygen evolution reaction
QDSC	Quantum dot-sensitized solar cell
SEM	Scanning electron microscopy
SI	Supplementary information
TEM	Transmission electron microscopy
T _F	Fall time
T_R	Rise time
UPS	Ultraviolet photoelectron spectroscopy
UV	Ultraviolet
XPS	X–ray photoelectron spectroscopy
XRD	X–ray diffraction
η	Overpotential

Materials

Nickel nitrate hexahydrate (Ni(NO₃)₂ · 6H₂O, 99%), cobalt nitrate hexahydrate (Co(NO₃)₂ · 6H₂O, 99%), tungsten oxide (WO3, 99%), selenium powder (Se, 99%), ferric nitrate nonahydrate (Fe(NO₃)₃ · 9H₂O, 99%), potassium iodide (KI, 99%), copper sulfate pentahydrate (CuSO₄ · 5H₂O, 99%), trisodium citrate dihydrate (SCD, 99%), fluorine–doped tin oxide glass (FTO, ~7 Ω /sq), and titanium dioxide (TiO₂, 99%) were purchased from Sigma Aldrich (USA). Urea (NH₂CONH₂, 99%), sodium dodecyl benzenesulfonate (SDBS, 99%), bismuth nitrate pentahydrate (Bi (NO₃)₃·5H₂O, 99%), and sodium molybdate dihydrate (Na₂MoO₄ · 2H₂O, 99%) were purchased from Junsei Chemical Co. Ltd. (Japan). Nickel foam (thickness=1.6 mm) was purchased from MTI Corp. (USA).

Characterization

The crystallographic structure of the catalysts was evaluated by X-ray diffraction (XRD, Rigaku D/MAXRINT 000, Japan) using Cu Kα radiation as the X-ray source at 45 kV and 100 mA. Scanning electron microscopy (SEM, Nova NanoSEM 450, FEI-Thermo Fisher Scientific, USA) and transmission electron microscopy (TEM, JEM-2010, Jeol, Japan) were used at an accelerating voltage of 200 kV. Elemental oxidation states were determined by X-ray photoelectron spectroscopy (XPS, K-alpha, Thermo Electron, USA). UV–vis–NIR diffuse reflectance spectroscopy (Lambda 750S, PerkinElmer, USA) was used to determine the light harvesting potential of the catalysts.

Experimental

STEP I: Synthesis of NiCo₂O₄@NF

The organic impurities on the NF surface were removed by heating at 400°C in a tube furnace. The NF was washed with ethanol and deionized (DI) water and dried at 60°C for 10 h. Urea (6 g), Ni(NO₃)₂ · 6H₂O (1.3 g), and Co(NO₃)₂ · 6H₂O (2.61 g) were dissolved in 300 mL of DI water. Trisodium citrate (4 g) was added to the solution under constant stirring. After 3 h, the solution was transferred to a glass dish, and one piece of 10 × 10 cm NF was immersed in it. The glass dish was covered with aluminum foil and placed in an oven at 90°C for 12 h. In the same way, two additional samples were prepared using deposition times of 6 and 18 h. Later, the NF was sonicated, washed with ethanol and DI water, and dried at 60°C for 10 h.

STEP II: Synthesis of NiCo₂O₄/WSe₂@NF

The WSe₂ layer was deposited by thermal evaporation of the precursors in a quartz tube furnace. First, 8 g of WO₃ powder was dissolved in 100 mL of ethanol to form a tungsten–rich suspension. The NiCo₂O₄@NF was soaked in the suspension for 30 min and dried at room temperature for 1 h. Next, 3 g of Se powder was placed near the inlet while the NiCo₂O₄@NF was placed near the outlet of the quartz tube furnace. The quartz tube was closed and flushed with Ar for 10 min before heating. Then, the temperature was increased to 800°C in 50 min and maintained for 4 h in an Ar atmosphere. After heating, the N/W@NF was removed, washed with ethanol and DI water, and dried at 60°C for 10 h.

STEP III: Synthesis of NiCo₂O₄/WSe₂/NiFe₂O₄@NF

To synthesize NiFe₂O₄ nanodots, Ni(NO₃)₂ · $6H_2O$ (1.45 g), Fe(NO₃)₃ · $9H_2O$ (2 g), urea (4 g), and SDBS (1.75 g) were dissolved in 100 mL of DI water. The solution was transferred to a Teflon–lined autoclave along with the N/W@NF template. The autoclave was heated at 140°C for 12 h. After heating, the autoclave was cooled to room temperature, and the N/W/N@NF was removed. Finally, the template was washed with ethanol and DI water and dried at 60°C for 10 h.

Electrochemical measurements

Electrochemical tests were performed using a Bio–Logic electrochemistry workstation. A threeelectrode system was used to record the linear sweep voltammetry curves for the OER and HER. The catalyst synthesized on the NF was used as the working electrode, platinum mesh was the counter electrode, and Hg/HgO was the reference electrode. All measurements were performed in 0.5 M KOH electrolyte. A solar simulator (K201-Lab100, McScience Inc., South Korea) was used as the irradiation source. All the acquired potentials against the Hg/HgO reference electrode were relative to that of the reversible hydrogen electrode (RHE) using the following equation.

 $E_{RHE} = E_{Hg/HgO} + 0.059 pH + E^{0}_{Hg/HgO}$

Here, $E_{Hg/HgO}$ is the potential recorded against the Hg/HgO electrode at pH = 14, and $E^{0}_{Hg/HgO}$ is the standard electrode potential of $E_{Hg/HgO}$ = 0.098 V.

Theoretical computational methods

The geometric modifications and optimizations of the NiFe₂O₄ unit cell were performed using VESTA and Avogadro software. First, the NiFe₂O₄ (110) surface was constructed from its unit cell.

Geometric optimization was performed to obtain a slab with stable energy. The hydrogen intermediates were adsorbed on the exposed 110 surfaces of the NiFe₂O₄ slab. All theoretical calculations were performed using the Quantum Espresso electronic structure code. We used generalized gradient approximations (GGA) with the Perdew–Burke–Ernzerhof (PBE) exchange correlational functional. Brillouin zone integration was approximated using the Monkhorst Pack scheme with a $3\times3\times1$ k–point mesh. The plane–wave energy cutoff was set to 550 eV with a self–consistent field (SCF) tolerance of 5×10^{-7} eV atom⁻¹.

Supplementary Notes

Note 1

Solar cell fabrication

A 5 × 2.5 cm FTO glass was cleaned by sonication. The conductive side of the FTO was identified using a multimeter. The four sides of the FTO glass were covered with adhesive tape. TiO₂ paste was spread on the exposed FTO surface by a doctor blade method. The TiO₂–coated FTO was dried and sintered at 450°C for 1 h.

The NiFe₂O₄ nanodots were grown on TiO₂-coated FTO glass using a hydrothermal method. For this, 1.5 mmol of nickel nitrate (Ni(NO₃)₂·6H₂O) and 2.5 mmol of ferric nitrate (Fe(NO₃)₃·9H₂O) were dissolved in 110 mL of DI water. The solution was stirred for 30 min at room temperature. Next, 10 mmol of sodium dodecyl benzenesulfonate and 5 mmol of urea were added under constant stirring. The mixture was transferred to a Teflon–lined autoclave, and the TiO₂-coated FTO was placed inside the vessel. The autoclave was maintained at 120°C for 12 h in a heating furnace. After 12 h, the FTO was removed and washed with DI water and ethanol to

remove impurities. Finally, the NiFe₂O₄-decorated photoelectrode was dried overnight in an oven at 60° C.

A working solar cell was obtained by combining the photoelectrode in the previous step with a graphite–coated FTO counter–electrode. At this point, potassium iodide electrolyte was added for conductivity. Two clips were used to maintain firm contact between the electrodes.

Note 2

OER mechanism and pathways under alkaline conditions

(1) Oxide path

 $D + OH^{-}(aq) \rightarrow D-OH + e^{-}$

 $2D-OH \rightarrow D-O + D + H_2O$

 $2D-O \rightarrow 2D + O_2(g)$

(2) Electrochemical oxide path

 $D + OH^{-}(aq) \rightarrow D-OH + e^{-}$

 $D-OH + OH^{-}(aq) \rightarrow D-O + H_2O + e^{-}$

 $2D-O \rightarrow 2D + O_2(g)$

(3) Krasil Schkov path

 $D + OH^{-}(aq) \rightarrow D-OH + e^{-}$

 $D-OH + OH^{-}(aq) \rightarrow D-O^{-} + H_2O$

 $D-O^- \rightarrow D-O + e^-$

 $2D-O \rightarrow 2D + O_2(g)$

(4) Yeager's path

 $D + OH^{-}(aq) \rightarrow D-OH + e^{-}$

 D^{Z} -OH $\rightarrow D^{Z+1}$ -OH + D + e⁻

 $2D^{Z+1}-OH + 2OH^{-}(aq) \rightarrow 2D + 2H_2O + O_2(g)$

(5) Bockris path

 $D + OH^{-}(aq) \rightarrow D-OH + e^{-}$

 $D-OH + OH^{-}(aq) \rightarrow D-H_2O_2 + e^{-}$

 $D-H_2O_2 + OH^-(aq) \rightarrow D-O_2H^- + H_2O$

 $D-H_2O_2 + D-O_2H^- \rightarrow 2D + OH^-(aq) + O_2(g)$

Note 3

We investigated the effect of p-region thickness on the current density by varying the Se deposition time in the tube furnace. The highest current density of 22 mA cm⁻² was achieved with a deposition time of 6 h, which decreased to 17 mA cm⁻² after 8 h (Table S1). The current density obtained after 4 h was similar to that after 6 h. All samples in this research were fabricated using the optimized 4 h deposition time.

No.	Deposition time	Temperature	Current density
1.	1 h	800ºC	4 mA cm ⁻²
2.	2 h	800ºC	13 mA cm ⁻²
3.	4 h	800ºC	21 mA cm ⁻²
4.	6 h	800ºC	22 mA cm ⁻²
5.	8 h	800ºC	17 mA cm ⁻²

Table S1. Effect of WSe₂ deposition time on current density of the N/W/N@NF electrode.

Table S2. Electronic properties of the catalysts used in this study.

Electronic property	NiCo ₂ O ₄	WSe ₂	NiFe ₂ O ₄
Valence band edge (eV)	2.32	0.23	0.94
Conduction band edge (eV)	-0.37	-1.36	-0.49
Band gap (eV)	2.69	1.59	1.43
Work function (eV)	4.25	4.36	4.14

No.	Catalyst	Support	Voltage @ 10mA cm ⁻²	Referenc
				е
1.	NiCo ₂ S ₄	Nickel foam	1.63 V	1
2.	DRPC	Carbon fiber paper	1.74 V	2
3.	CoMnO	Nickel foam	1.50 V	3
4.	CoMn sulfides	Nickel foam	1.60 V	4
5.	NiCoFe	Nickel foam	1.62 V	5
6.	Co, WO ₃ , Si complex	Copper foam	1.80 V	6
7.	Co(OH) ₂	Cotton fabric	1.64 V	7
8.	CoP complex	Nickel foam	1.65 V	8
9.	Ni-Fe-P-B	Glassy carbon	1.58 V	9
10.	C–CoP	Glassy carbon	1.65 V	10
11.	N/W/N@NF	Nickel foam	1.47 V	This work

Table S3. Comparison of voltage requirement for overall water splitting in a two-electrode system.



Fig. S1. (a) WSe₂ particles grown over NiCo₂O₄ nanowirres by a hydrothermal method. (b) Uniformly grown WSe₂ particles over NiCo₂O₄ nanowires in a tube furnace.



Fig. S2. Response of a conventional binary junction to (a) positive and (b) negative applied potentials.



Fig. S3. (a) Band edge and fermi level positions of the catalysts used to substitute for the p-type WSe₂. (b) Overpotential needed to achieve the benchmark current density.



Fig. S4. The overpotential, Tafel slopes, and time-dependent current density of catalysts fabricated in this study.



Fig. S5. (a) Oxygen evolution at the electron–deficient NiFe $_2O_4$ nanodots. (b) Electron flow toward NiFe $_2O_4$, which provides excellent sites for adsorption/desorption of H–intermediates.



Fig. S6. The five best electrocatalysts for the (a) HER and (b) OER.



Fig. S7. (a, b) Effect of synthesis time on the length of NiCo₂O₄ nanowires. The average lengths of the NiCo₂O₄ nanowires synthesized for 6 and 18 h were 300 and 1,200 nm, respectively. (c) Spherical NiFe₂O₄ nanodots with an average diameter of 10 nm. (d) TEM image of 2–D sheet-like WSe₂.

Fig. S8. (a) Band gaps corresponding to the absorption spectra of catalysts in Fig. 9(a). (b) XPS

survey spectrum of the N/W/N catalyst fabricated in this study.

Fig. S9. (a–d) XRD spectra of pristine catalysts produced in this study.

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