

Supporting Information

High-Performance Bifunctional Alkaline Water-Splitting Textile Electrodes Using Monolayer-Enhanced Chemical Reduction of Integrated Electrocatalysts

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S1 Detailed Experimental Section

S1.1 Synthesis of TOA-Cu_xS NPs

TOA-Cu_xS NPs were synthesized using a modified Brust-Schiffrin method. First, a 25 mM TOA solution in toluene (80 mL) and 33 mM CuCl₂ · 2H₂O solution in deionized water (30 mL) were mixed for 15 min at 40 °C. Then, 12 mmol of Na₂S₂O₃ was added to the solution and stirred for 15 min which made the solution to be clear. Subsequently, 0.9 M aqueous solution of NaBH₄ (10 mL) was further added to the mixture for reduction. After 30 min, the aqueous and toluene phases were clearly separated, and the aqueous phase was subsequently removed. The toluene phase with a dark brown color was washed several times with 10 mM HCl, 10 mM NH₄OH, and deionized water.

S1.2 LbL assembly of (TOA-Cu_xS NP/Cys)_n multilayers

Substrates including Si wafers, Au-sputtered Si wafers, quartz glasses, and QCM electrodes were irradiated with a UV ozone cleaner for 30 min. Above mentioned substrates and bare cotton textiles (0.5 x 3 cm²) were first dipped into cysteamine Cys solution (in ethanol, 2 mg mL⁻¹, M_w ~77 g mol⁻¹) for 30 min to form robust underlayer, then washed twice with pure ethanol to remove the weakly adsorbed Cys molecules. The formed Cys-coated substrates were dipped into TOA-Cu_xS NPs solution (in toluene, 30 mg mL⁻¹) for 30 min, then washed with pure toluene to eliminate the weakly adsorbed NPs. In the following process, TOA-Cu_xS NP coated substrates were dipped into Cys solution for 5 min to replace bulky TOA ligands to small Cys ligands. After this ligand exchange reaction-induced adsorption process, weakly adsorbed Cys layer was re-washed out using pure ethanol. These processes were repeated until the desired bilayer number (*n*) of (TOA-Cu_xS NP/Cys)_n multilayers was reached ((TOA-Cu_xS NP/Cys)₄ loading amount : 0.93 mg cm⁻¹).

S1.3 Preparation of the ED Ni

The as-prepared (TOA-Cu_xS NP/Cys)₄ multilayer-coated cotton textile was immersed in a Watt bath (240 g L⁻¹ NiSO₄, 45 g L⁻¹ NiCl₂ and 30 g L⁻¹ H₃BO₃) [S1]. (TOA-Cu_xS NP/Cys)₄ multilayer-coated cotton textile served as the cathode, and a nickel plate was used as the anode. Ni electroplating was performed at a current density of 250 mA cm⁻² for 5 min. Then, the electroplated sample was washed in deionized water and dried in a vacuum oven at room temperature (Ni loading amount: 43.1 mg cm⁻¹).

S1.4 Preparation of the NiP₂ textile

NiP₂ layer was additionally electrodeposited in a traditional 3-electrode electrochemical cell which is composed with ED Ni, graphite rod electrode, and Ag/AgCl (3 M NaCl) as a working, counter, and reference electrode, respectively. Cyclic voltammetry scans were carried out in the range of -1.15 V to 0.247 V vs. Ag/AgCl for 10 cycles under electrodeposition solution (0.5 M NaH₂PO₂, 0.1 M CH₃COONa·H₂O, and 0.05 M NiSO₄ in deionized water). After the process, the electrode was washed with deionized water, and then dried in a vacuum oven at room temperature (NiP₂ loading amount: 6.54 mg cm⁻¹).

S1.5 Preparation of the NiP₂-coated Ti felt

NiP₂ layer was deposited onto the Ti felt in the same manner as the NiP₂ textile described above and then dried in a vacuum oven at room temperature.

S1.6 Preparation of the Ni₂P textile

Ni₂P layer was additionally electrodeposited in a traditional 3-electrode electrochemical cell which is composed with ED Ni, Pt mesh, and Ag/AgCl (3 M NaCl) as a working, counter, and reference electrode, respectively. Electrodeposition was carried out in a growth solution (10 mM NiCl₂, 10 mM NaH₂PO₂, 15 mM NH₄Cl, and 15 mM CO(NH₂)₂ in deionized water) at a constant voltage of -1.0 V for 6 min. After the process, the electrode was washed with deionized water, and then dried in a vacuum oven at room temperature (Ni₂P loading amount: 3.51 mg

cm⁻¹).

S1.7 Preparation of the Ni₂P-coated Ti felt

Ni₂P layer was deposited onto the Ti felt in the same manner as the Ni₂P textile described above and then dried in a vacuum oven at room temperature.

S1.8 Preparation of the TREN-coated textile

The as-prepared NiP₂ textile (for HER) and Ni₂P textile (for OER) were immersed in tris(2-aminoethyl)amine (TREN) solution (in ethanol, 2 mg mL⁻¹, M_w ~ 146 g mol⁻¹) for 10 min. After the process, the electrode was washed with ethanol, and then dried in a vacuum oven at room temperature.

S1.9 Preparation of the PEI-coated textile

The as-prepared NiP₂ textile (for HER) and Ni₂P textile (for OER) were immersed in Poly(ethyleneimine) (PEI) solution (in ethanol, 2 mg mL⁻¹, M_w ~ 800 g mol⁻¹) for 10 min in the same manner as the TREN-coated textile described above. After the process, the electrode was washed with ethanol, and then dried in a vacuum oven at room temperature.

S1.10 Preparation of the Pt/C NF

Pt/C electrodes were prepared by dispersing 1 mg of Pt/C (20 wt.% Pt on Vulcan XC-72) in 300 μL of an EtOH solution containing 10.5 μL of 5 wt.% Nafion [S2]. This resulting catalyst ink solution was deposited onto the commercial Ni foam (0.5 × 0.5 cm²) and then dried at room temperature.

S1.11 Preparation of IrO₂-coated NF

IrO₂ electrodes were prepared by dispersing 1 mg of IrO₂ in 300 μL of an EtOH solution with 10.5 μL of 5 wt.% Nafion [S2]. This IrO₂ catalyst ink solution was loaded onto the commercial Ni foam (0.5 × 0.5 cm²) in the same manner as the Pt/C NF described above and then dried at

room temperature.

S1.12 Characterization

High-resolution transmission electron microscopy (HR-TEM) of synthesized TOA-Cu_xS NPs was conducted using a Tecnai20 microscope (FEI). The UV–vis absorbance spectra of TOA-Cu_xS NP solution were recorded using a Cary 5000 (Agilent Technologies) within a wavelength window ranging from 200 to 1000 nm. Fourier transform infrared (FTIR) spectra of the multilayers were collected using a CARY 600 spectrometer (Agilent Technology) in Advanced Grazing Angle (AGA) mode with a resolution of 4 cm⁻¹, and the obtained data were plotted using spectrum analysis software (OMNIC, Nicolet). The multilayer film growth was quantitatively monitored using a QCM (QCM 200, SRS). In the case of QCM measurement, the mass change (ΔM) per layer was calculated from the QCM frequency change (ΔF) using the Sauerbrey equation [S3],

$$\Delta F(\text{Hz}) = -\frac{2F_0^2}{A\sqrt{\rho_q\mu_q}} \cdot \Delta M \quad (1)$$

where F_0 , A , ρ_q , and μ_q represent the resonant frequency (~5 MHz), the active area (cm²), the density (2.65 g cm⁻³), and the shear modulus (2.95×10¹¹ g cm⁻¹ s⁻²) of the QCM electrode, respectively. This expression can be simplified to $\Delta F(\text{Hz}) = -56.6 \times \Delta M_A$ (M_A indicates mass per unit area).

X-ray diffraction (XRD) patterns of TOA-Cu_xS NPs and all electrodes were obtained using a SmartLab instrument (Rigaku) with Cu K α radiation. X-ray photoelectron spectroscopy (XPS) analysis was performed by X-TOOL (ULVAC-PHI) with monochromatic Al K α radiation as the excitation source. electrodes were obtained using an XPS instrument (X-TOOL, ULVAC-PHI) with an Al K α radiation source. All of the XPS spectra were corrected by calibrating all peaks to the major C-C/C-H binding energy at 284.8 eV. Ultra-violet photoelectron spectroscopy (UPS) measurements were performed using ESCALAB 250Xi

(Thermo Fisher Scientific). Water and bubble contact angles were determined by means of a Phoenix 300 instrument (S.E.O. Co., Ltd.). Scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDX) images were obtained via field-emission SEM (FE-SEM) (Quanta 250 FEG, FEI). The bubbles dynamics on textile and Ni foam-electrodes during water splitting were recorded using a high-speed camera (i-speed 221 iX color 4GB) with video capture of up to 5000 fps. It operated at a frame rate of 2000 fps to visualize the whole gas bubble evolution at the current density of 100 mA cm^{-2} . The measurement was performed in a two-electrode system in 1 M KOH solution. LED lamps were used around the system to illuminate electrodes and bubbles during the experiment.

X-ray absorption spectroscopy (XAS) measurements were conducted at the BL7D beamline of the Pohang Light Source (PLS), operating in top-up mode with a ring current of 300 mA at 3.0 GeV. The incident beam was collimated using a Ru-coated mirror set at 2.8 mrad and monochromatized with a channel-cut Si (111) monochromator. The extended X-ray absorption fine structure (EXAFS) data were processed using standard procedures with the ATHENA module from the IFEFFIT software package. To extract the EXAFS spectra, the post-edge background was subtracted from the total absorption signal, and the data were normalized to the edge-jump step. The resulting $\chi(k)$ data in k-space were then Fourier-transformed into real (R) space using a Hanning window, isolating the EXAFS contributions from distinct coordination shells. Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES, PerkinElmer (Avio500&Avio550)) was performed to detect amount of Cu, Ni, and P ions dissolved in the electrolyte after the full cell stability test. *Operando* surface-enhanced infrared absorption spectroscopy (SEIRAS) spectra were collected using an AIRSight spectroscopic system (Shimadzu Scientific, Japan). The instrument was equipped with a mercury–cadmium–telluride (MCT) detector, and the *in-situ* cell employed a ZnSe crystal as the infrared-transparent window. FT-IR spectra were recorded as a function of potential under continuous

irradiation to probe the dynamic evolution of the electrocatalytic in 1 M KOH.

S1.13 Electrochemical characterization

All electrochemical measurements, including the polarization curves, cyclic voltammetry curves, and electrochemical impedance spectroscopy (EIS) measurements, were conducted with an Ivium-n-Stat electrochemical workstation (Ivium Technologies). For measurements in the three-electrode cell system, a Pt mesh and a reversible hydrogen electrode (RHE) were used as the counter and reference electrodes, respectively, and the electrolyte was 1 M KOH (pH = 14). The electrochemical cell was placed in a thermostatically controlled water bath to maintain the electrolyte temperature at 25 ± 0.5 °C or 60 ± 0.5 °C. A thermocouple was inserted directly into the water bath to ensure accurate monitoring and thermal equilibrium of the system. In addition, the electrolyte was continuously stirred at 300 rpm using a magnetic stirrer to maintain uniform temperature and concentration throughout the electrolyte. Electrochemical measurements were performed using a working electrode with an area of 0.25 and 1 cm². The OER and HER catalytic activities and full-cell electrolyzer were measured by linear sweep voltammetry at scan rates of 2 mV s⁻¹ with 90% *iR* compensation according to the following equation:

$$E_{correction} = E_{measured} - iR_s \quad (2)$$

The EIS measurements were performed with a biased working electrode at frequencies from 100 kHz to 0.01 Hz and potentials of 1.6 V (vs. RHE) for the OER and -0.15 V (vs. RHE) for the HER. In this case, the semicircle diameter indicates the charge transfer resistance (R_{ct}), which can be used to evaluate the charge transfer kinetics on the surface of the electrode. The starting point on the *x*-axis for the semicircle represents the series resistance (R_s), which is the sum of the ionic resistance of the electrolyte, the intrinsic resistance of the active material and the contact resistance at the active material/current collector interface.

Operando Raman spectra were obtained using a Horiba Jobin Yvon LabRam Aramis

with an Ar-ion laser beam at an exciting radiation wavelength of 514.5 nm during LSV experiments. A home-made electrochemical configuration, consisting of a prepared catalyst as a working electrode, Pt mesh as a counter electrode, and RHE as a reference electrode was used. The element components of the electrolyte after water splitting reaction were determined by inductively coupled plasma mass spectrometry (ICP-MS, Elan DRC II)

Faradaic efficiency of water splitting was measured by the eudiometry method in an experimental setup. The working electrode was fixed on the inside of an inverted burette filled with electrolyte. All the metal wires connecting the working electrode were coated with insulating epoxy to prevent charge loss from the side reactions. The evolved gases were directly collected in the headspace of the inverted burette, and the corresponding gas volume was determined by the displacement of the vertical water column. Based on this method, the Faradaic efficiency was calculated by comparing the amount of evolved gas with the theoretical amount of gas, which was calculated by the charge passed through the electrode:

$$\text{Faradaic efficiency } (H_2) = \frac{V_{\text{experiment}}}{V_{\text{theoretical}}} = \frac{V_{\text{experiment}}}{\frac{2}{4} \times \frac{Q}{F} \times V_m} \quad (3)$$

$$\text{Faradaic efficiency } (O_2) = \frac{V_{\text{experiment}}}{V_{\text{theoretical}}} = \frac{V_{\text{experiment}}}{\frac{1}{4} \times \frac{Q}{F} \times V_m} \quad (4)$$

where F is the Faraday constant ($96,485 \text{ C mol}^{-1}$), Q is the summation of the charge passed through the electrodes, the number 4 represents 4 moles of electrons per mole of H_2O , the number 2 represents 2 moles of H_2 per mole of H_2O , the number 1 represents 1 mole of O_2 per mole of H_2O and V_m is the molar volume of gas (24.5 L mol^{-1} , 298 K, 101 kPa) [S4].

S1.14 Fabrication of AEM water electrolyzer

For the AEM water electrolyzer analysis, the membrane electrode assembly (MEA) was fabricated with TREN/NiP₂ textile ($1 \times 1 \text{ cm}^2$) as a cathode electrocatalyst and TREN/Ni₂P ($1 \times 1 \text{ cm}^2$) as anode electrocatalyst, separated by an AEM ($50 \mu\text{m}$, Sustainion® X37-50

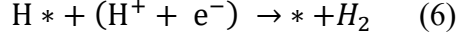
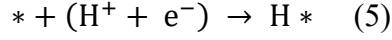
Grade RT; Dioxide Materials). LSV curves were recorded at a scan rate of 10 mV/s with *iR*-correction in 1M KOH electrolyte. Specifically, the anode, cathode, and membrane components were treated with 1 M KOH before forming the MEA. The electrolyzer cell was fed with 1 M KOH electrolyte with a 250 mL/min flow rate.

S1.15 Computational details

Density Functional Theory (DFT) calculations were performed using the Vienna Ab Initio Simulation Package (VASP) version 5.4.4 [S5]. The projected augmented wave (PAW) pseudopotential method and Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional were used [S6-S7]. Grimme's D3 correction method was applied to account for the Van der Waals interactions [S8]. The energy convergence tolerance and kinetic energy cutoff were each set to 10^{-4} eV and 400 eV, respectively. All slab structures consisted of three atomic layers, with the top two layers relaxed and the bottom layer fixed. A 15 Å vacuum layer was added along the z-direction. For Brillouin zone integration, Monkhorst pack k-point grids of $(4 \times 4 \times 1)$ were used for NiP₂, and Ni₂P slabs. Due to the larger unit cells employed in the TREN/NiP₂ for HER and TREN/Ni₂P for OER, a $(2 \times 2 \times 1)$ Monkhorst pack grid was adopted.

The Gibbs free energies were computed by adding free energy correction values to the DFT energies. The corrections were calculated using the ideal gas (harmonic) approximation for gas (adsorbate) molecules as implemented in Atomic Simulation Environment (ASE). i.e., $\Delta G = \Delta E + \Delta ZPE + \int C_p dT - T\Delta S$ ($T = 298$ K), where ΔE , ΔZPE , $\int C_p dT$ and $-T\Delta S$ correspond to changes in DFT energy, zero-point energy, enthalpic and entropic contributions, respectively [S9]. The computational hydrogen electrode (CHE) method was employed, which assumes that the chemical potential of a proton-electron pair is equivalent to that of 0.5H₂(g) i.e., $\mu_{(H^+ + e^-)} = 0.5\mu_{H_2}$. According to the CHE method, the chemical potential $\mu_{(H^+ + e^-)}$ is shifted by $-eU$ when an external potential U is applied.

For the HER, the following two-electron reaction pathway was considered.



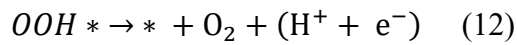
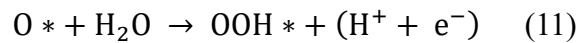
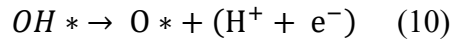
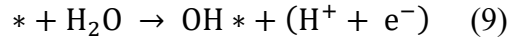
The corresponding Gibbs free energy change is given by

$$\Delta G_{H*} = E(H*) - E(*) - 0.5E(H_2) + G_{corr} \quad (7)$$

where $E(H^*)$, $E(*)$ and $E(H_2)$ are DFT energies of H^* adsorbed surface, bare surface, and H_2 molecule, respectively. The term G_{corr} represents the sum of correction values for the H^* adsorption. The theoretical HER overpotential is defined as

$$\eta_{HER} = |\Delta G_{H*}|/e \quad (8)$$

For the OER, the following four-electron associative pathway was considered to evaluate the reaction energetics.



The binding Gibbs free energies were calculated referenced to H_2O and H_2 molecules as follows.

$$\Delta G_{OH*} = E(OH*) + 0.5E(H_2) - E(*) - E(H_2O) + G_{corr} \quad (13)$$

$$\Delta G_{O*} = E(O*) + E(H_2) - E(*) - E(H_2O) + G_{corr} \quad (14)$$

$$\Delta G_{OOH*} = E(OOH*) + 1.5E(H_2) - E(*) - 2E(H_2O) + G_{corr} \quad (15)$$

where $E(OH*)$, $E(O*)$ and $E(OOH*)$ are DFT energies of OH^* , O^* and OOH^* adsorbed

surfaces, respectively. The theoretical OER overpotential is defined as

$$\eta_{OER} = \max(\Delta G_{OH*}, \Delta G_{O*} - \Delta G_{OH*}, \Delta G_{OOH*} - \Delta G_{O*}, 4.92 - \Delta G_{OOH*})/e - 1.23 \text{ V} \quad (16)$$

where, a lower overpotential corresponds to higher OER catalytic activity.

The Crystal Orbital Hamiltonian Population (COHP) analysis was performed using the Lobster package [S10]. A COHP diagram was constructed to analyze the bonding and antibonding contributions based on density of states calculations. The integrated COHP (ICOHP) represents the COHP summed over a range of energies up to the Fermi level. A stronger bonding interaction between the surface atom and the adsorbate is indicated by a more positive absolute value of ICOHP.

S2 Supplementary Figures and Discussions

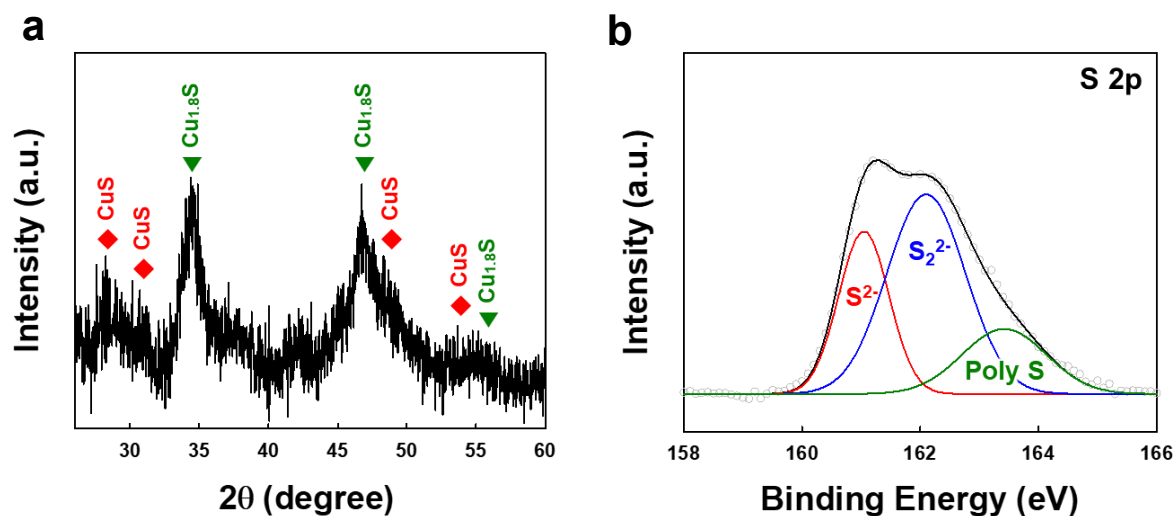


Fig. S1 Chemical structure of TOA-Cu_xS NPs. **a** X-ray diffraction (XRD) patterns of TOA-Cu_xS NPs. **b** X-ray photoelectron spectroscopy (XPS) spectra of TOA-Cu_xS NPs. The S 2p spectrum of TOA-Cu_xS NPs can be deconvoluted into a monosulfide (S²⁻) peak (at a binding energy of 161 eV), a disulfide (S₂²⁻) peak (at a binding energy of 162 eV), and a polysulfide (sulfur in the thiosulfate composition of TOA ligands) peak (at a binding energy of 163 eV), which evidently demonstrated that highly dispersible 8 nm-sized Cu_xS NPs were synthesized using bulky TOA ligands in toluene.

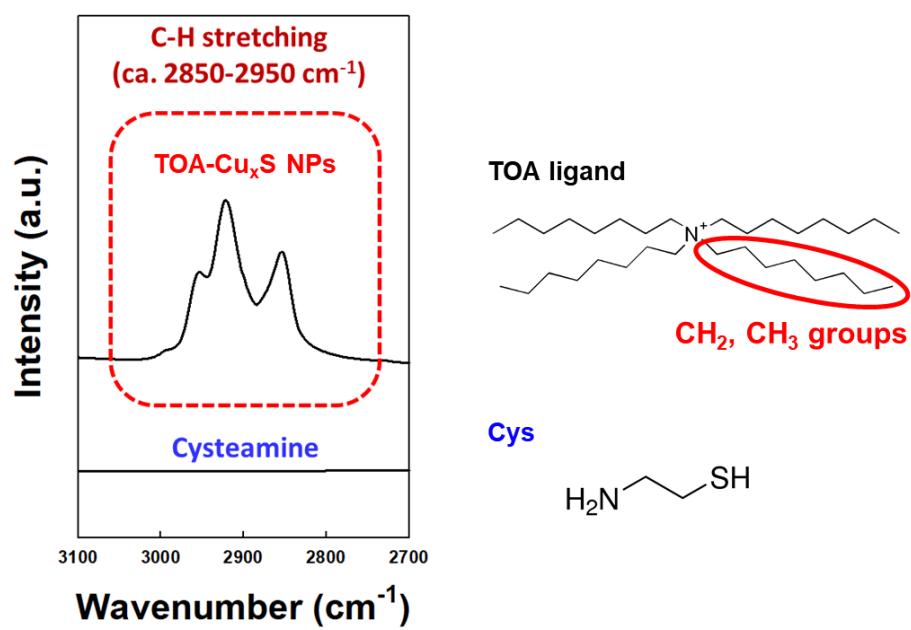


Fig. S2 Characteristic FT-IR spectra of a TOA-Cu_xS NPs and Cys solution. These C-H stretching peaks were monitored to confirm the direct ligand exchange reaction.

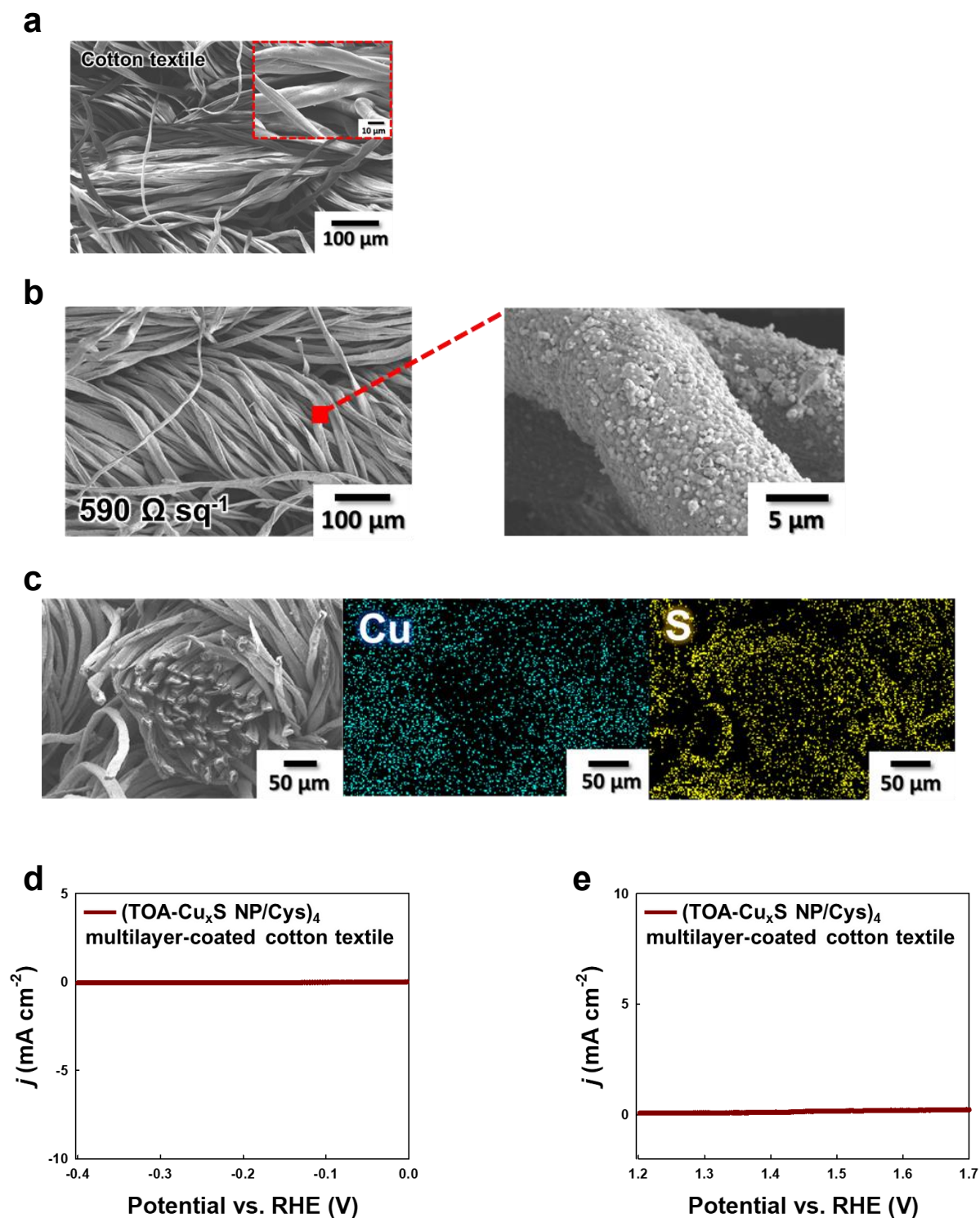


Fig. S3 Morphological characteristics and electrochemical performance. **a** FE-SEM images of bare cotton textile. **b** Planar and **c** cross-sectional FE-SEM images and corresponding EDS mapping images of (TOA-Cu_xS NP/Cys)₄ multilayer-coated cotton textile. **d** HER and **e** OER polarization curve of (TOA-Cu_xS NP/Cys)₄ multilayer-coated cotton textile. The LbL-assembled (TOA-Cu_xS NP/Cys)₄ multilayer showed negligible electrocatalytic activity toward the both HER and OER.

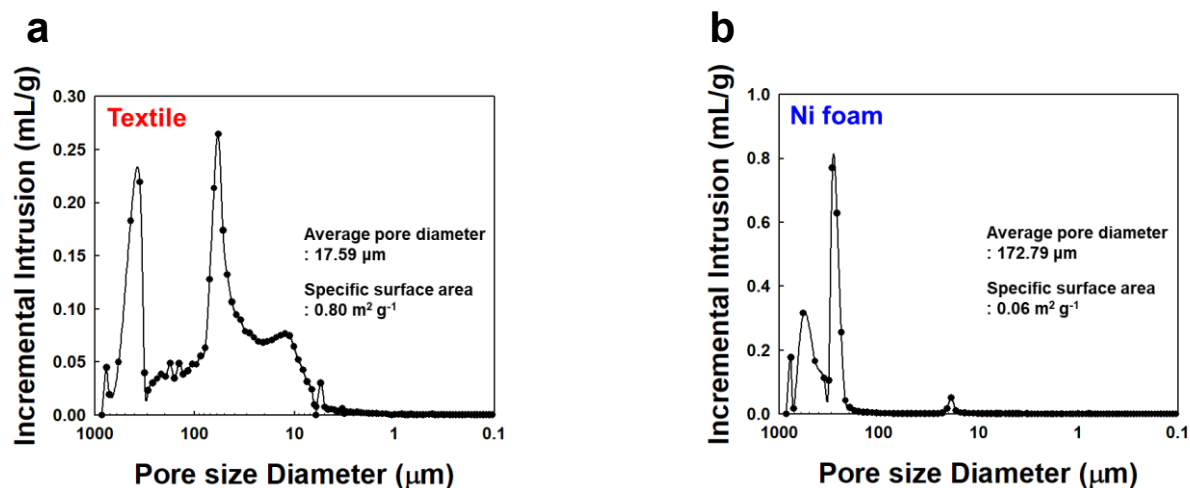


Fig. S4 Pore size distributions. Pore size distribution measured by mercury porosimetry of the **a** textile and **b** commercial Ni foam. In this case, the specific surface area of the textile was measured to be $0.80 \text{ m}^2 \text{g}^{-1}$, which was approximately 13 times higher than that of the commercial Ni foam ($0.036 \text{ m}^2 \text{g}^{-1}$). The density of the cotton textiles used in this study is approximately 0.33 g cm^{-3} , whereas that of Ni foam is about 0.26 g cm^{-3} . Based on these values, the calculated volume-specific surface areas for the cotton textile and Ni foam are approximately $0.26 \text{ m}^2 \text{cm}^{-3}$ and $0.016 \text{ m}^2 \text{cm}^{-3}$, respectively.

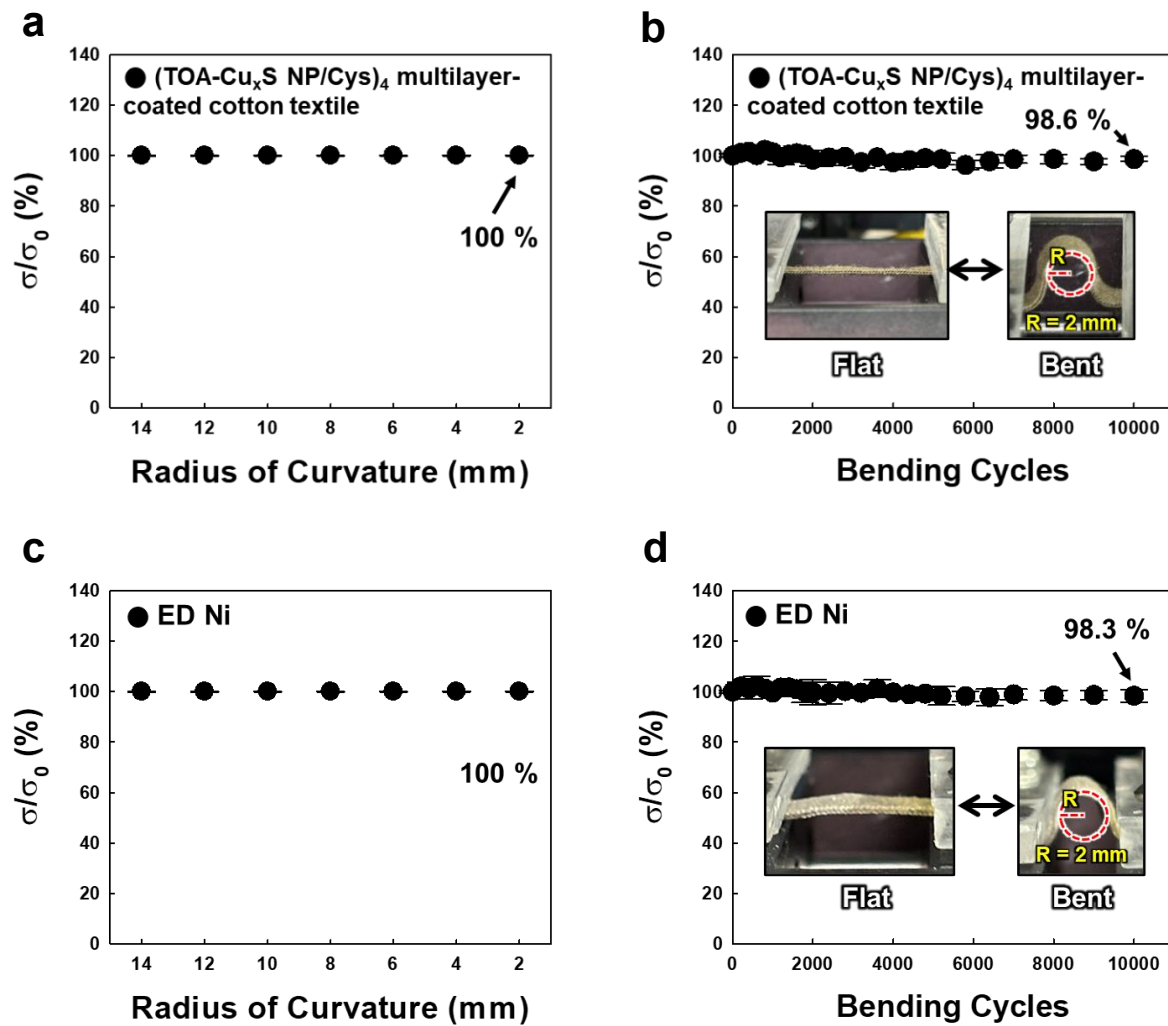


Fig. S5 Mechanical properties of (TOA-Cu_xS NP/Cys)₄ multilayer-coated cotton textile and ED Ni. **a** Relative electrical conductivity (σ/σ_0) of (TOA-Cu_xS NP/Cys)₄ multilayer-coated cotton textile as a function of the radius of curvature and **b** the bending cycle number (bending radius of ~ 2 mm). **c** Relative electrical conductivity (σ/σ_0) of Ni textile as a function of the radius of curvature and **d** the bending cycle number (bending radius of ~ 2 mm).

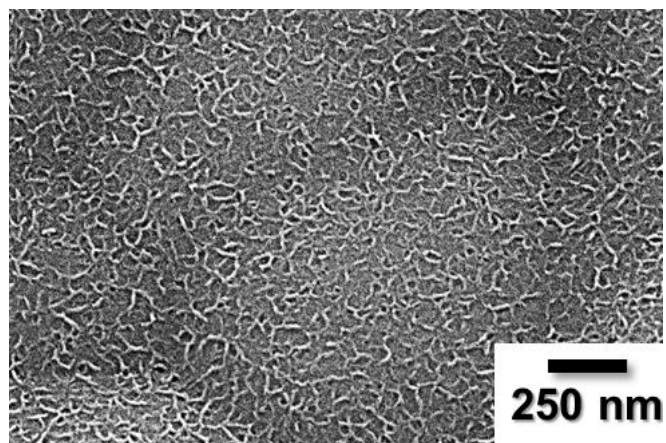


Fig. S6 FE-SEM image. Planar FE-SEM image of NiP_2 textile.

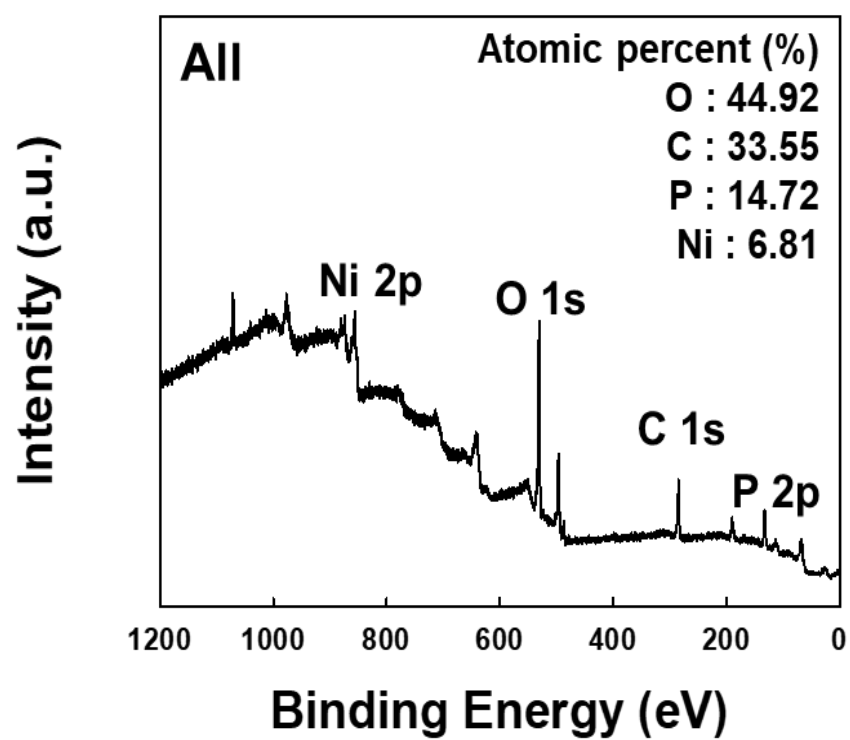


Fig. S7 XPS spectrum. XPS survey spectrum of NiP₂ textile.

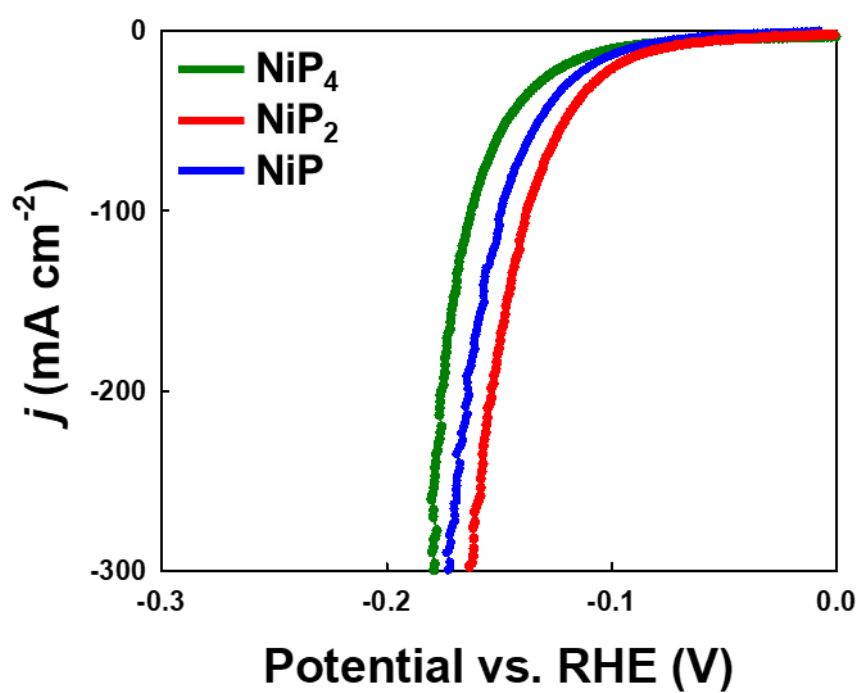


Fig. S8 HER polarization curves. HER performance of the Ni_xP_y-based textile electrodes as a function of the Ni/P chemical composition ratio.

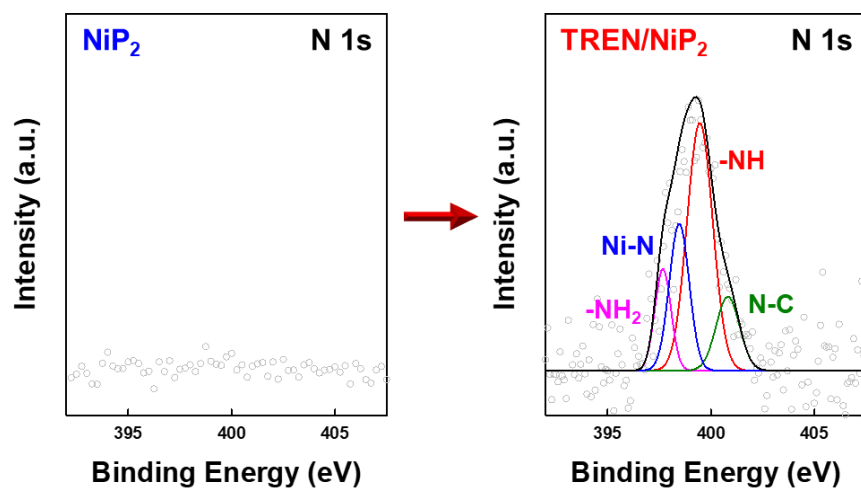
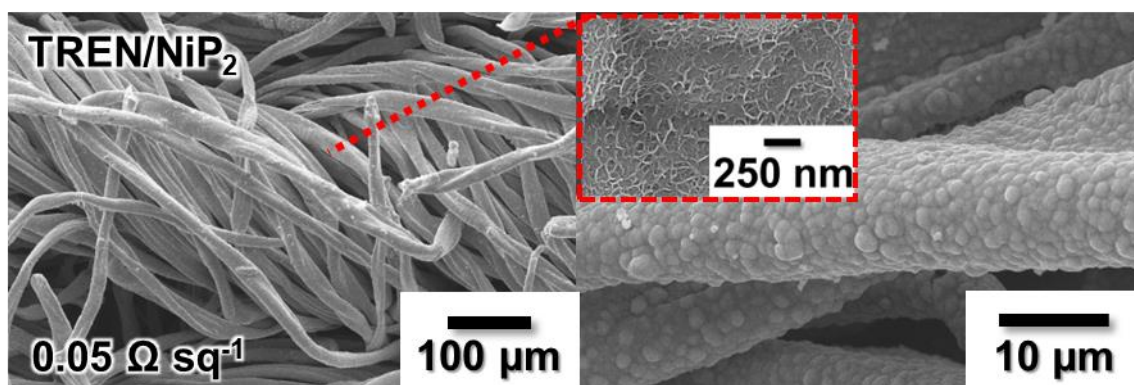


Fig. S9 XPS spectra. XPS spectra of N 1s of NiP₂ and TREN/NiP₂ textile.

a



b

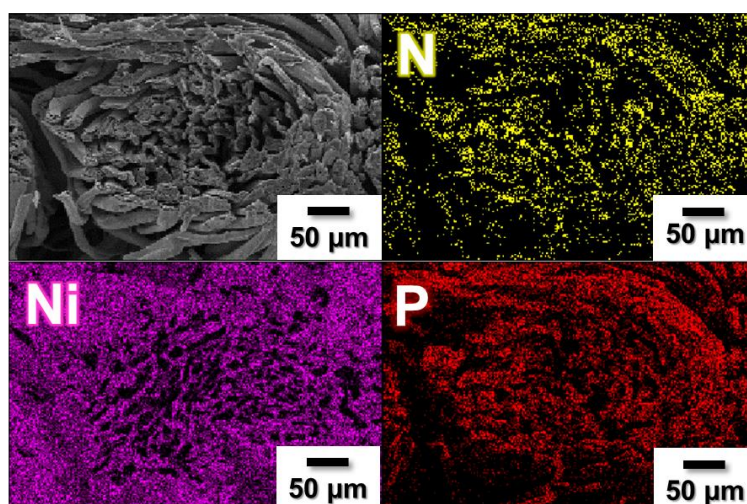


Fig. S10 Morphological characteristics. **a** Planar and **b** cross-sectional FE-SEM images and corresponding EDX mapping images of the TREN/NiP₂ textile (the inset shows the surface morphology).

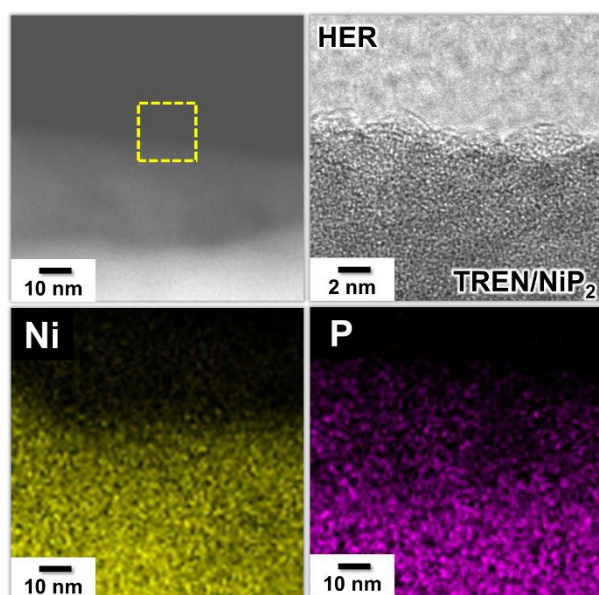


Fig. S11 Crystalline characteristics. HR-TEM image and its corresponding EDS mapping images of TREN/NiP₂ textile.

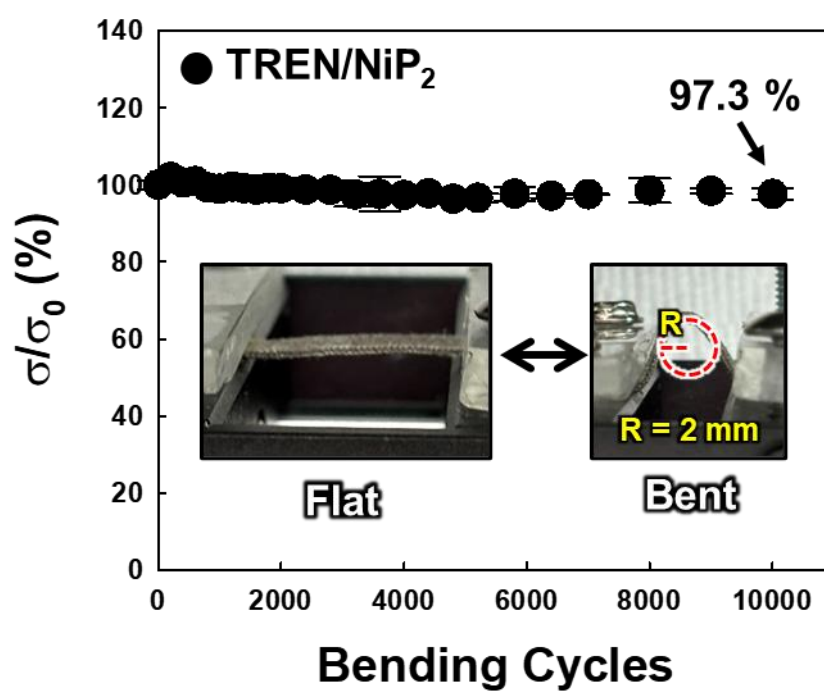


Fig. S12 Mechanical and electrical stability. Relative electrical conductivity (σ/σ_0) of the TREN/NiP₂ textile as a function of as a function of the bending cycle number (bending radius of ~ 2 mm).

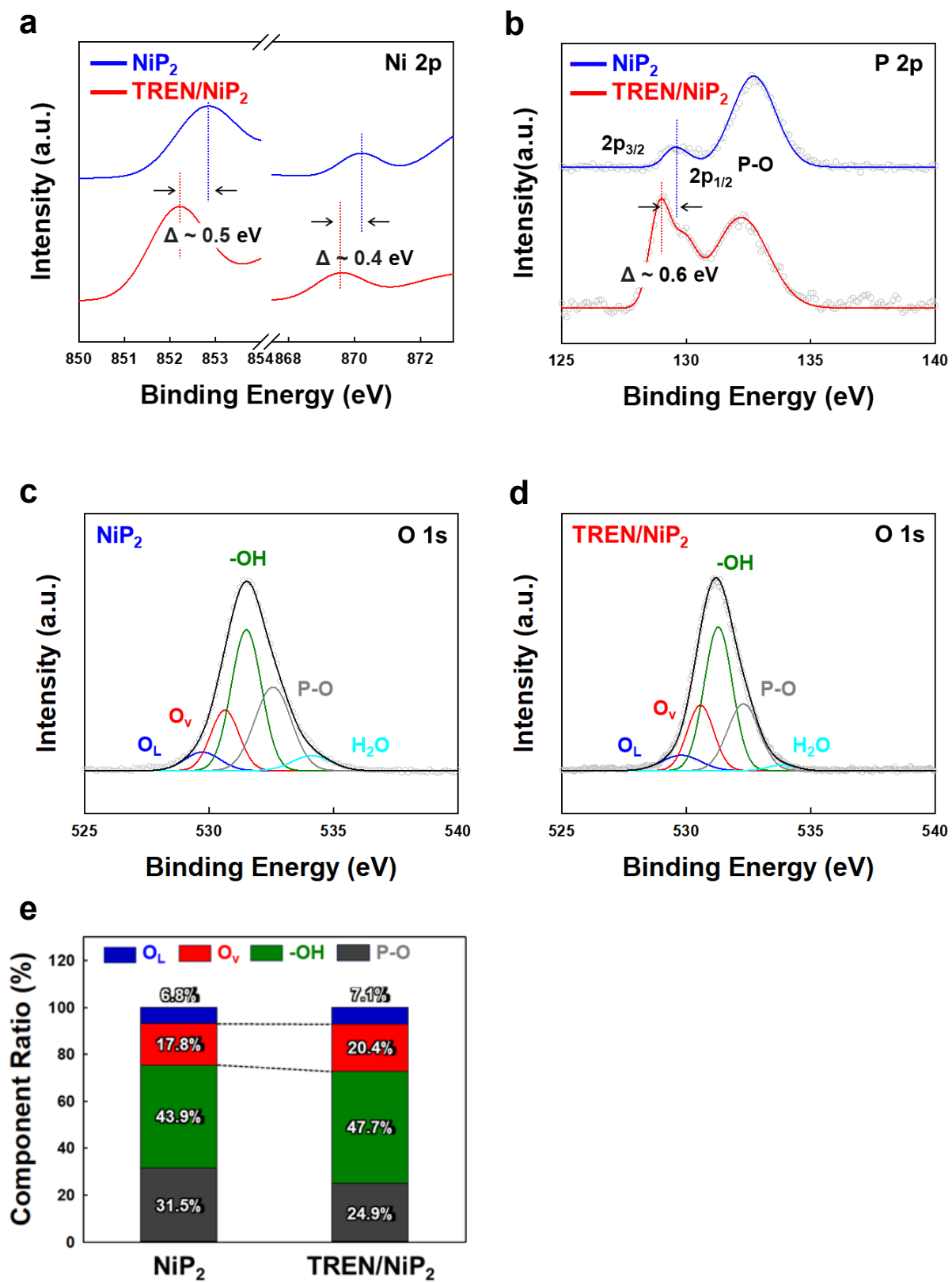


Fig. S13 XPS spectra. **a** XPS spectra of Ni 2p, **b** P 2p, and **c** O 1s for the NiP_2 and **d** TREN/ NiP_2 textile. **e** The comparison of the peak area percentages for each O 1s spectral component.

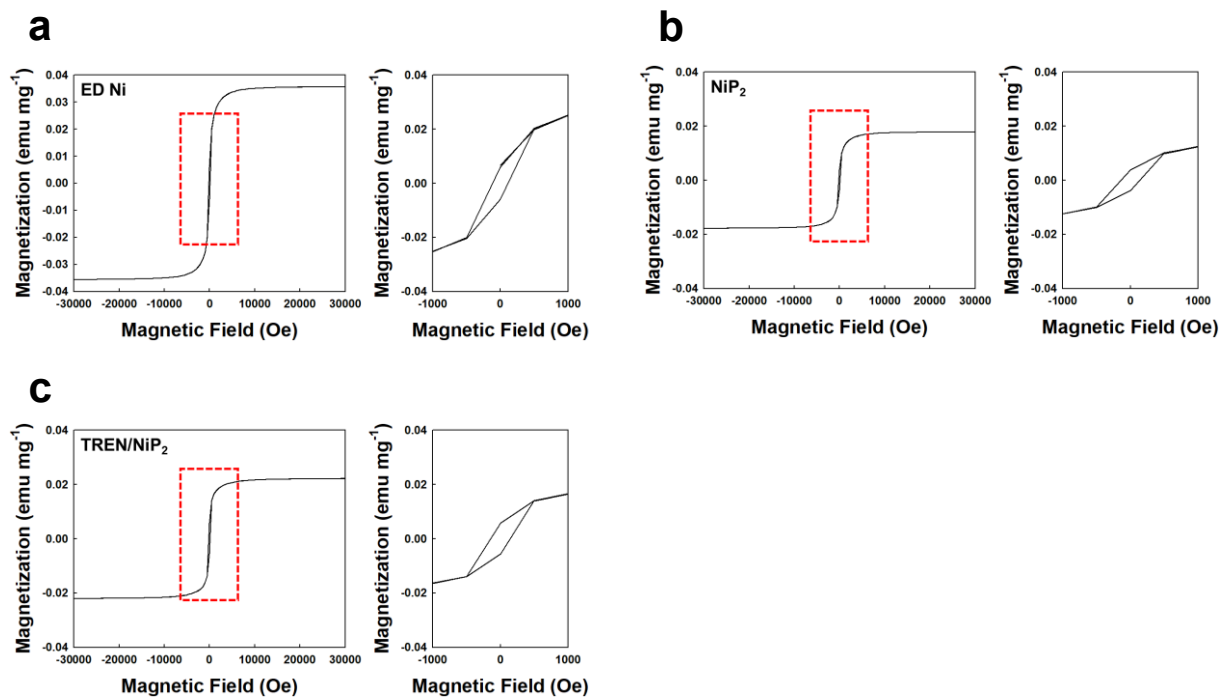


Fig. S14 Magnetization curve. Magnetization curve of **a** ED Ni, **b** NiP₂, and **c** TREN/NiP₂. In this case, all of electrodes exhibit clear ferromagnetic hysteresis loops, which indicates that they are ferromagnetic. Consequently, EPR spectroscopy cannot be used to probe their electronic structures.

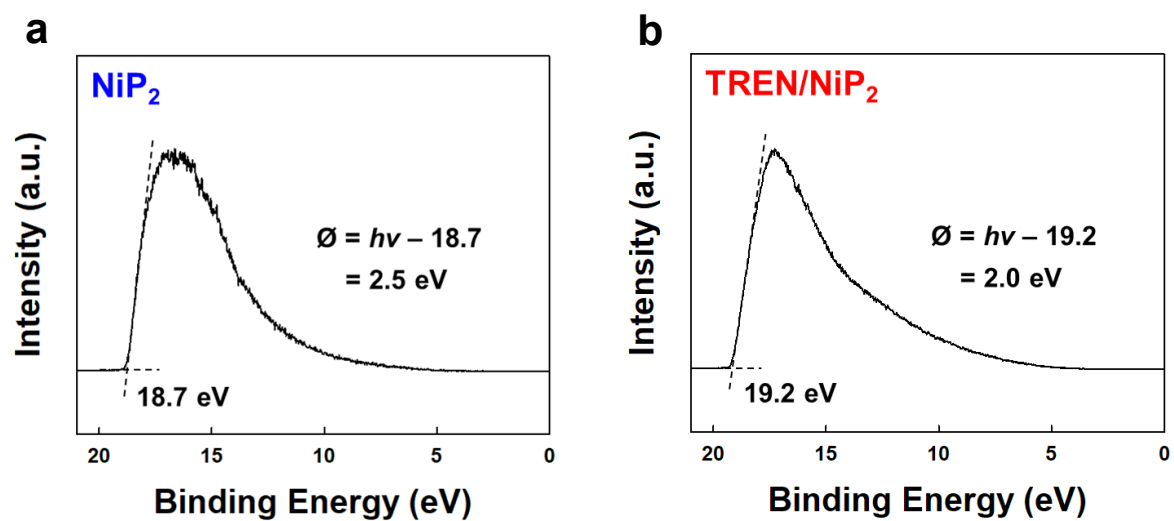


Fig. S15 UPS spectra. **a** Ultraviolet photoemission spectroscopy (UPS) spectra as a function of binding energy for the work function of NiP₂ and **b** TREN/NiP₂.

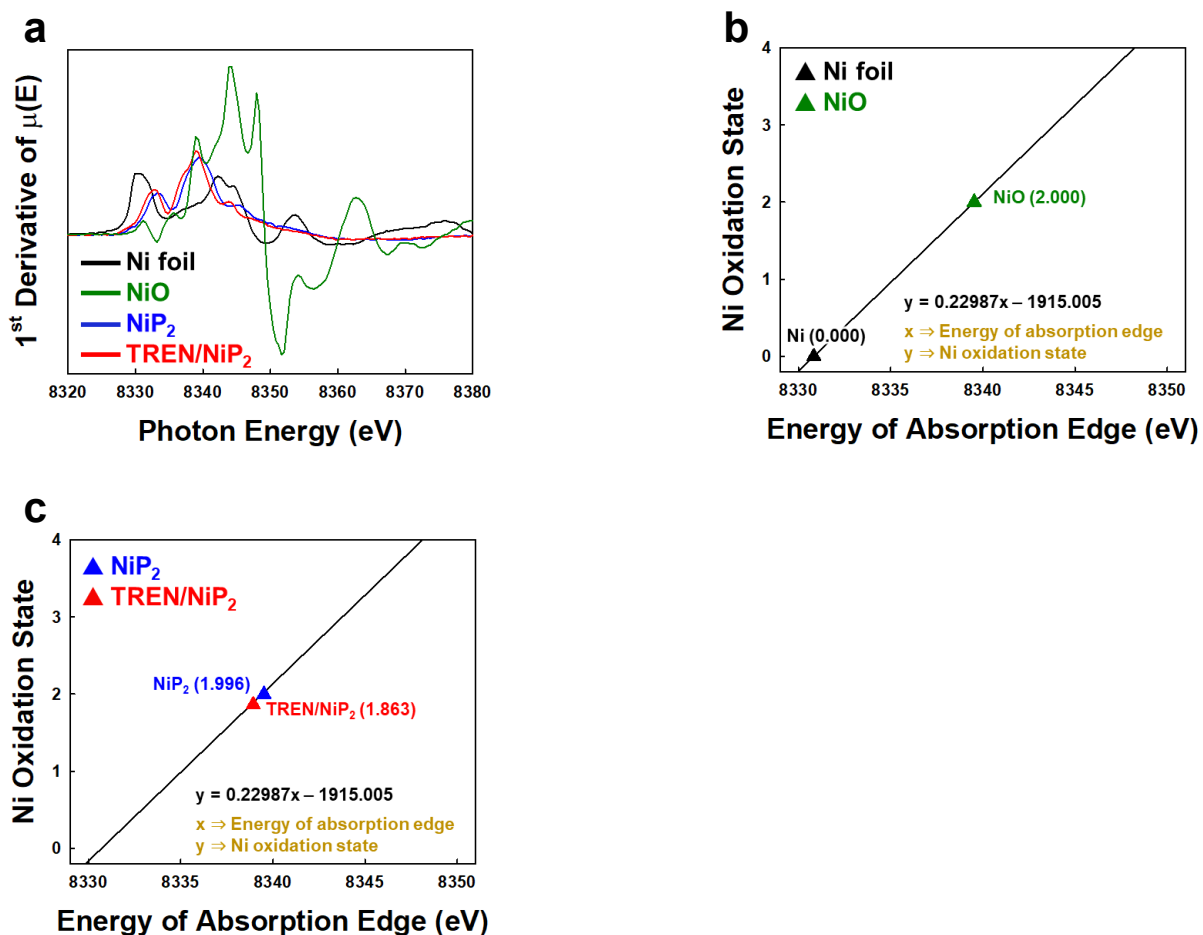


Fig. S16. Ni K-edge XAS characterization of HER electrodes. **a** First derivative of Ni K-edge XANES spectra of Ni foil, NiO, NiP₂ and TREN/NiP₂. **b** Plot of absorption edge position vs Ni valence state for Ni foil and NiO. **c** Plot of absorption edge position vs Ni valence state for NiP₂ and TREN/NiP₂.

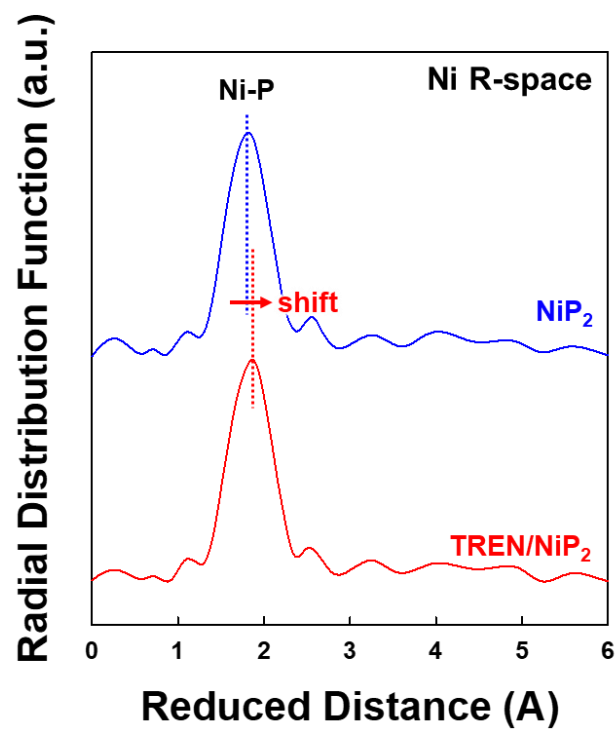


Fig. S17 Ni K-edge XAS characterization of HER electrodes. Extended X-ray absorption fine structure (EXAFS) spectra for the NiP_2 and TREN/NiP_2 textile. The Ni-P coordination shell demonstrates a slight expansion in R-space, reflecting an increased bond distance, after TREN deposition.

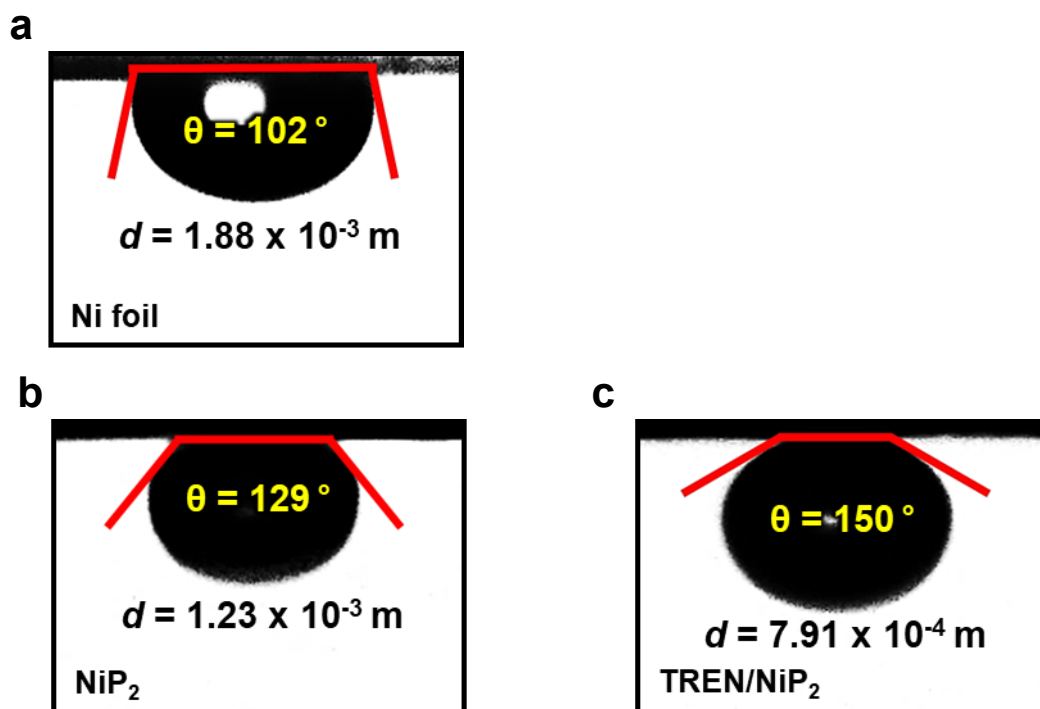


Fig. S18 Air bubble contact angles. **a** The air-bubble contact angles and bubble base diameters of Ni foil, **b** NiP₂, and **c** TREN/NiP₂-deposited Ni foil. Based on these parameters, the bubble adhesion forces (F_s) of NiP₂ and TREN/NiP₂-deposited Ni foil were calculated to be $2.17 \times 10^{-4} \text{ N}$ and $8.95 \times 10^{-5} \text{ N}$, respectively.

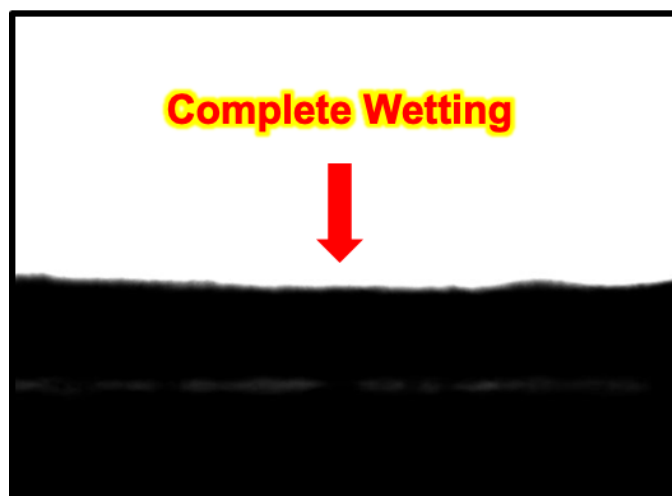


Fig. S19 Hydrophilicity test. Water contact angle of the TREN/NiP₂ textile. The water contact angle was measured using a 1 M KOH droplet.

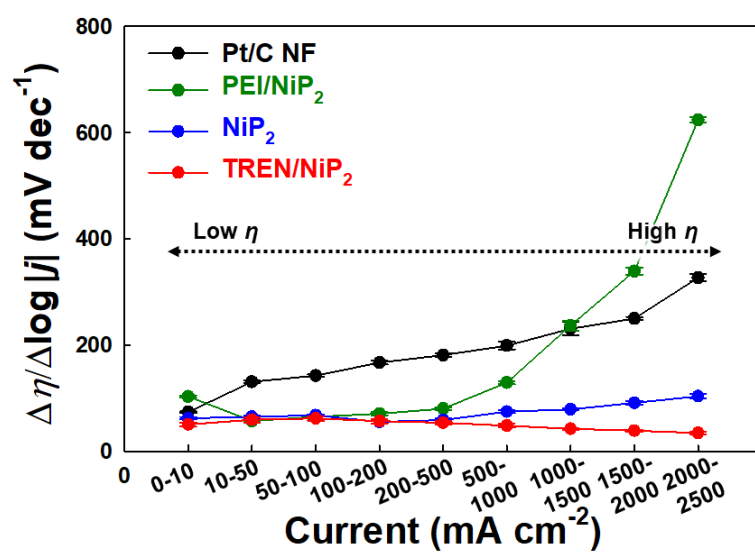


Fig. S20 Ratios of $\Delta\eta/\Delta\log |j|$. Ratios of $\Delta\eta/\Delta\log |j|$ for Pt/C NF, PEI/NiP₂, NiP₂ and TREN/NiP₂ textiles at different current density intervals.

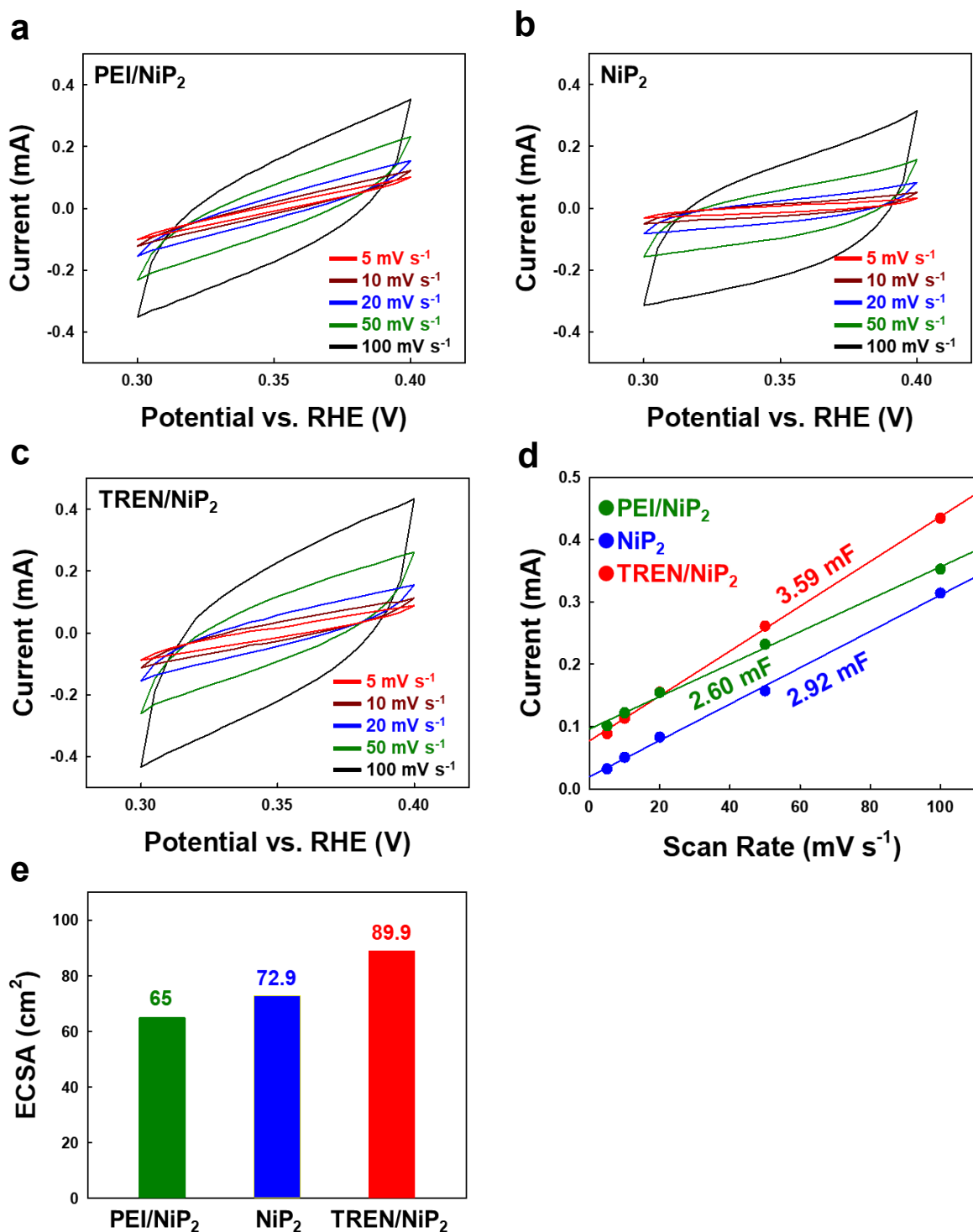


Fig. S21 Comparison of ECSA data of HER electrodes. **a** CV curves recorded in the non-faradaic region (0.3 – 0.4 V) at different scan rates (5, 10, 20, 50 and 100 mV s⁻¹) for the PEI/NiP₂, **b** NiP₂, and **c** TREN/NiP₂ textile. **d** Double-layer capacitance (C_{dl}) for the electrodes measured at different scan rates. **e** Based on the specific capacitance of 0.040 mF cm⁻² of Ni, the ECSA of the PEI/NiP₂, NiP₂, and TREN/NiP₂ textile were calculated to be approximately 65.0, 72.9, and 89.9 cm², respectively.

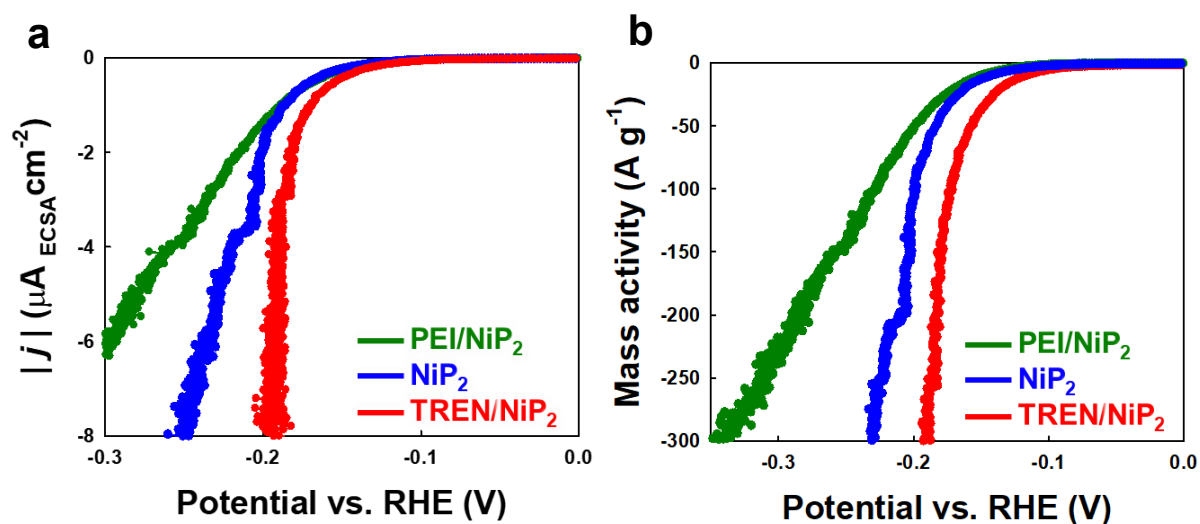


Fig. S22 a Intrinsic electrocatalytic activities of HER electrodes. HER polarization curves normalized with ECSA for the PEI/NiP₂, NiP₂, and TREN/NiP₂ textiles in a 1 M KOH electrolyte. **b** HER polarization curves normalized with mass loading of catalysts for the PEI/NiP₂, NiP₂, and TREN/NiP₂ textile in a 1 M KOH electrolyte. In this case, the catalyst loading amounts for PEI/NiP₂, NiP₂, and TREN/NiP₂ textile each electrode are 6.90, 6.54, and 6.74 mg cm⁻², respectively.

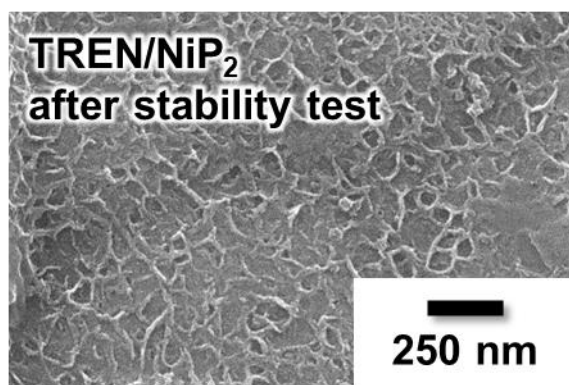


Fig. S23 Morphological characteristics. FE-SEM image of TREN/NiP₂ textile after stability test at current densities ranging from 10 to 4,000 mA cm⁻² over a total duration of 50 h.

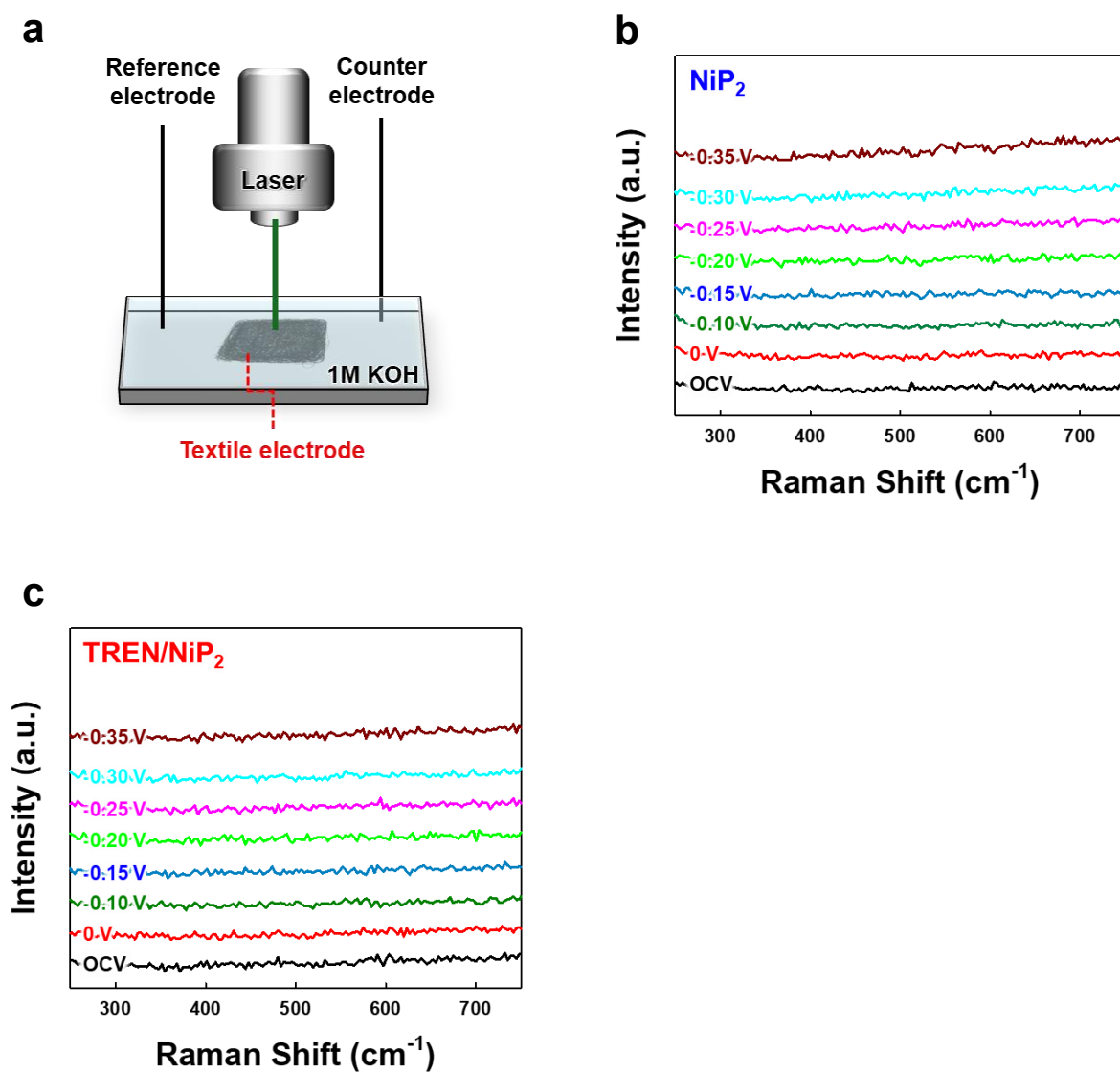


Fig. S24 *Operando* Raman spectra of HER electrodes. **a** Schematic illustration of *Operando* Raman test system. *Operando* Raman spectra of **b** NiP_2 and **c** TREN NiP_2 textile during HER under different potentials.

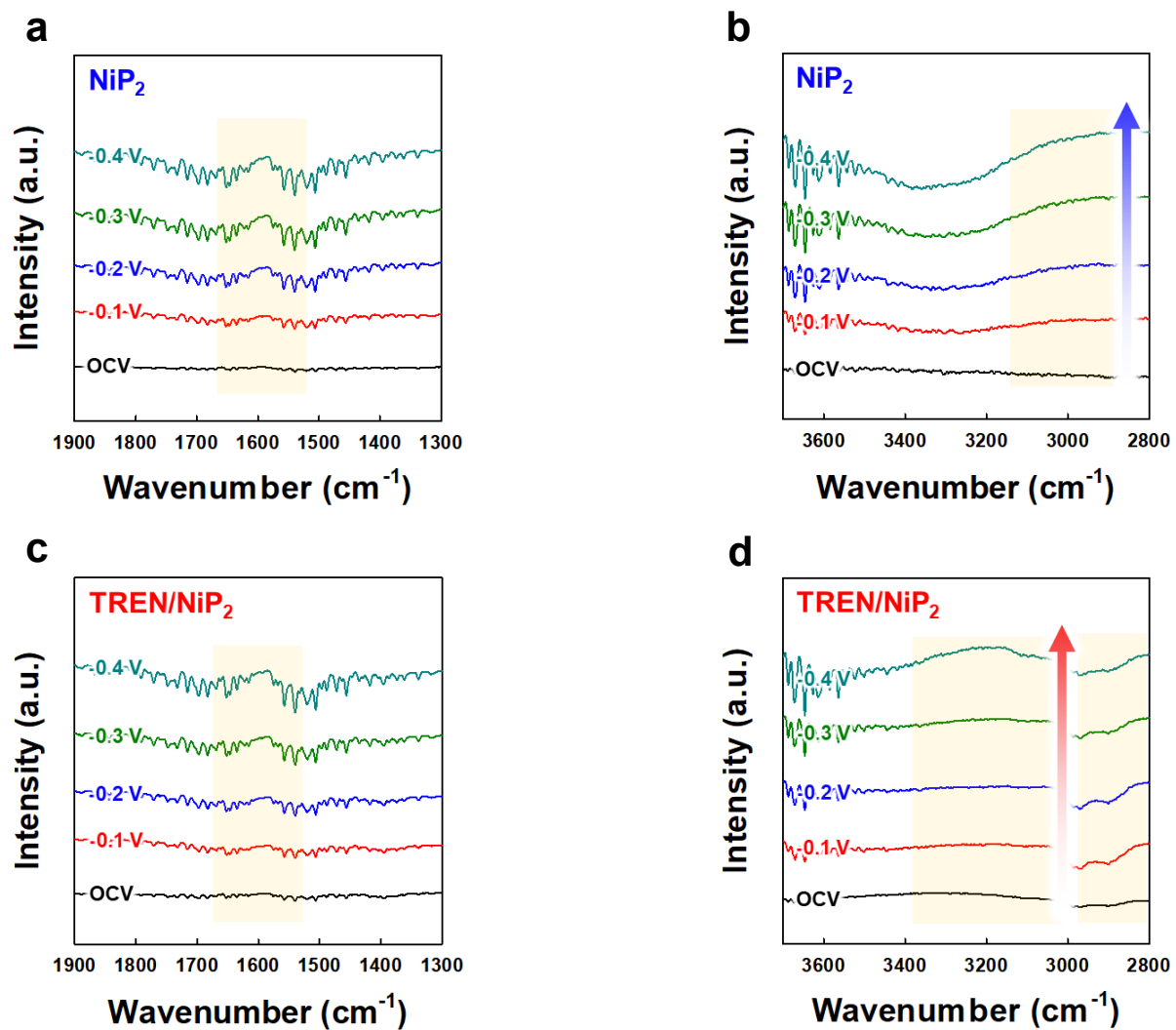


Fig. S25 Operando ATR-SEIRAS spectra. Operando ATR-SEIRAS spectra of **a, b** NiP₂ and **c, d** TREN/NiP₂ under different potential.

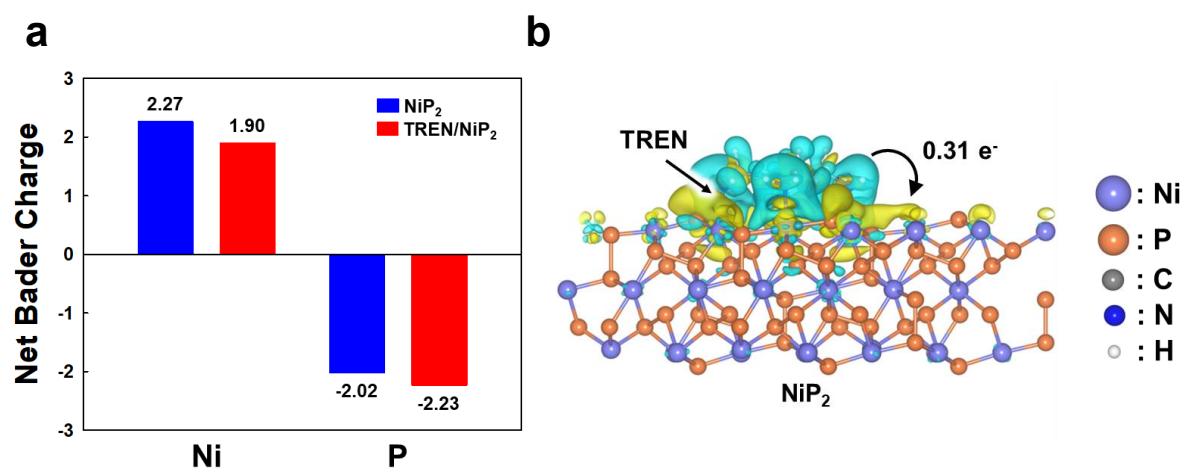


Fig. S26 The calculated net Bader charges. **a** The calculated net Bader charges of surface Ni and P atoms of NiP_2 and TREN/NiP_2 . In this case, the (111) facet was selected as the model surface. For TREN/NiP_2 , a single TREN molecule was deposited on the NiP_2 (111) surface in various configurations. The adsorption configuration in which three NH_2 groups bind to surface Ni atoms was determined to be most stable. **b** The three-dimensional charge density difference (CDD) map of TREN/NiP_2 , where charge accumulation and depletion are shown in yellow and cyan, respectively. Notably, the Bader charge analysis revealed that the Ni and P atoms residing on the NiP_2 surfaces undergo electron accumulation upon TREN adsorption.

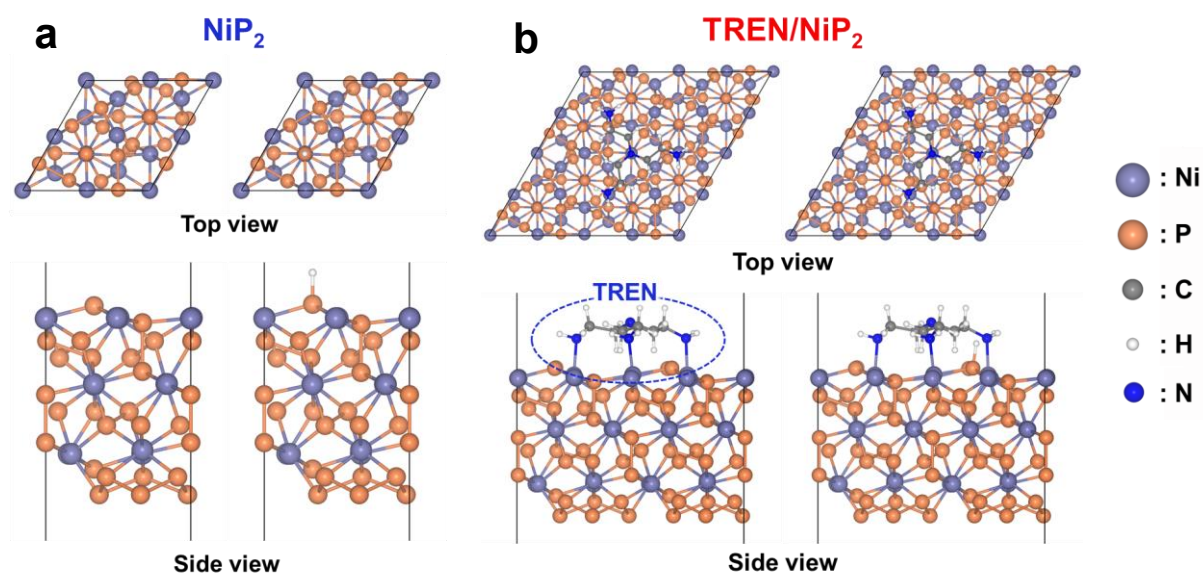


Fig. S27 Structural models for DFT calculation. **a** Atomic models for H adsorption (bare, H^*) on NiP_2 (111) surface. **b** Atomic structures for H adsorption (bare, H^*) on NiP_2 (111) surface after TREN deposition.

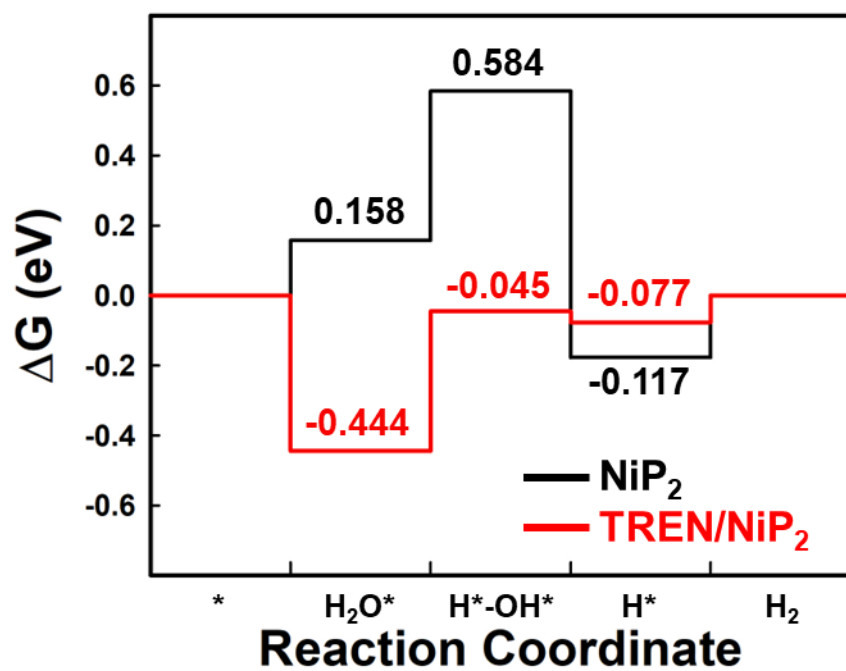


Fig. S28 Gibbs free energy diagram. Gibbs free energy diagram of alkaline HER for NiP_2 (black line) and TREN/NiP_2 (red line).

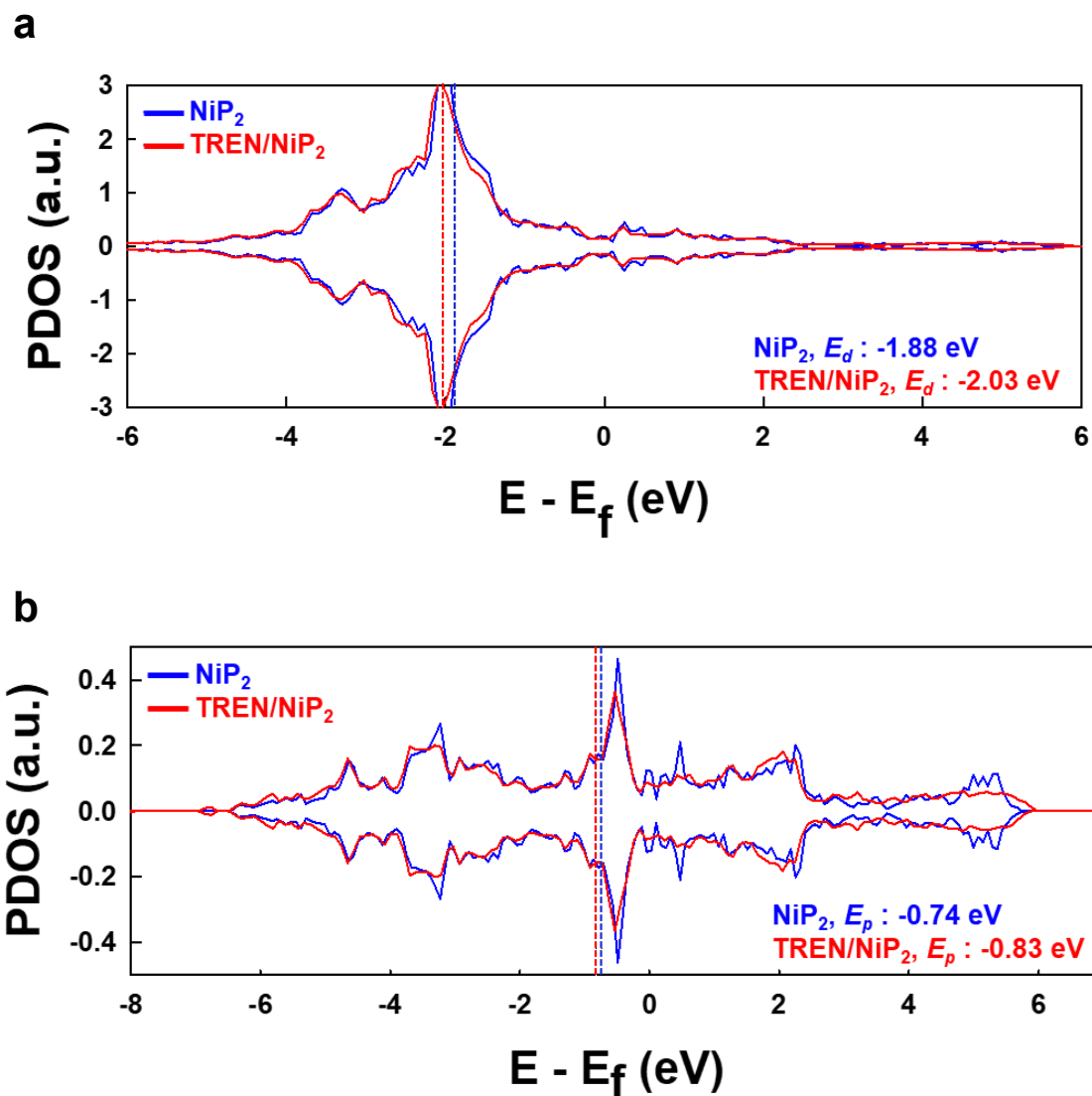


Fig. S29 PDOS analysis of HER electrodes. **a** Projected density of states (PDOS) curves of Ni *d*-orbital for the NiP_2 and TREN/NiP_2 textile. **b** PDOS curves of P *p*-orbital for the NiP_2 and TREN/NiP_2 textile.

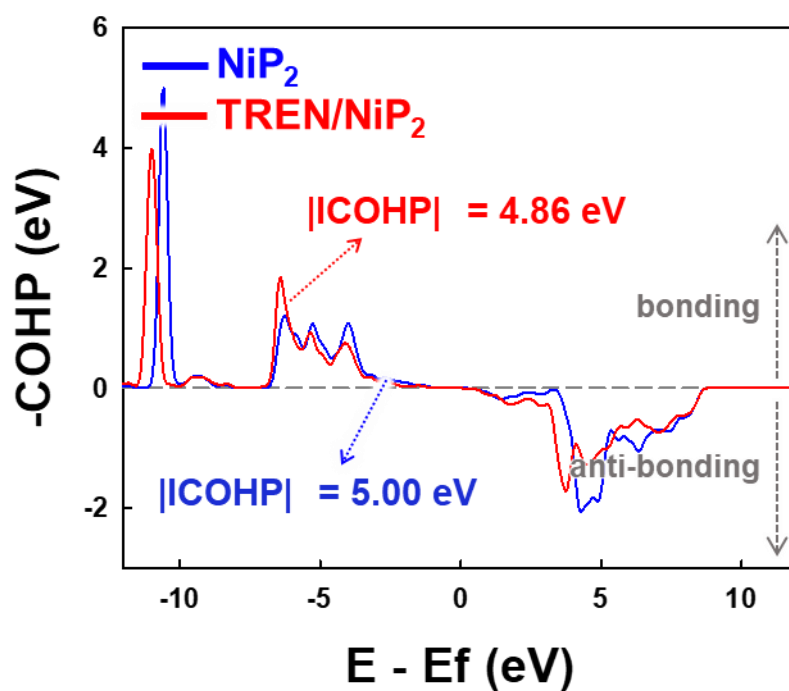


Fig. S30 Integrated Crystal orbital Hamilton populations (ICOHP) of the HER catalysts. In this case, the chemical bond analyzed by ICOHP during the water dissociation on TREN-NiP₂ is the bond between the adsorbed hydrogen intermediate (H*) and the surface phosphorous atom (P). A larger absolute value of the integrated COHP (ICOHP) indicates stronger bonding, as it quantifies the net bonding interactions by integrating the overlap of the orbitals of two atoms over their energy range up to the Fermi level.

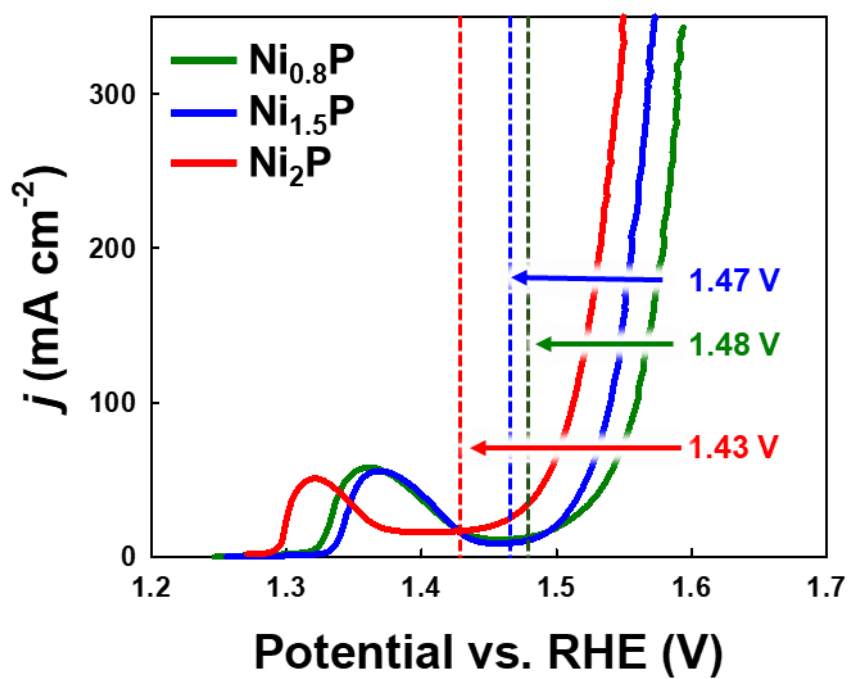


Fig. S31 OER polarization curves. OER performance of the Ni_xP_y -based textile electrodes as a function of Ni/P chemical composition ratio.

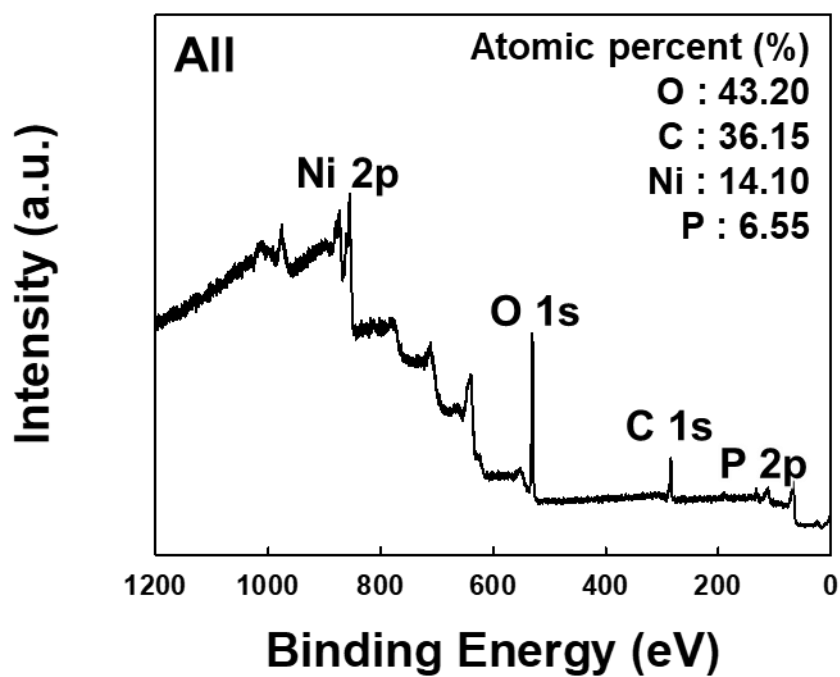


Fig. S32 XPS survey spectra of Ni_2P textile. XPS survey spectra of Ni_xP_y textile for OER electrode. The atomic ratio of $x:y$ was estimated to be approximately 2:1.

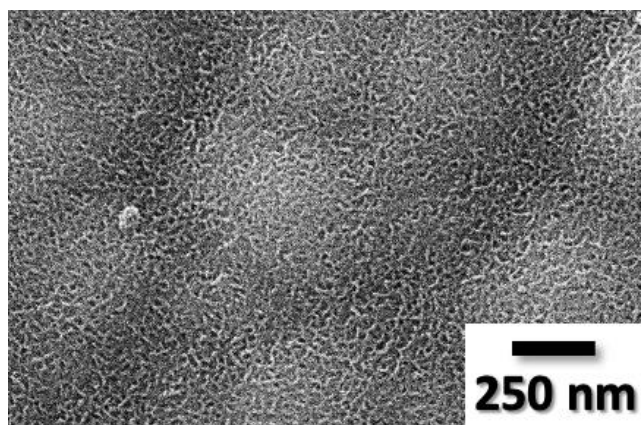


Fig. S33 Planar FE-SEM image. Surface morphology of Ni₂P textile.

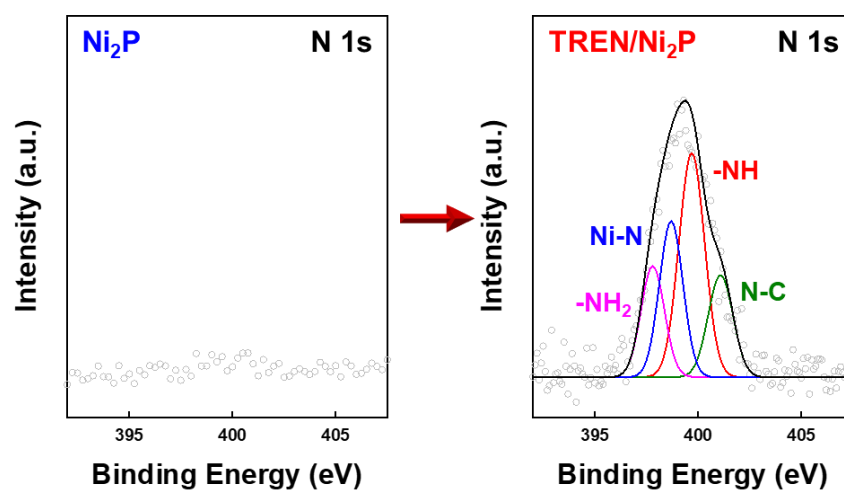
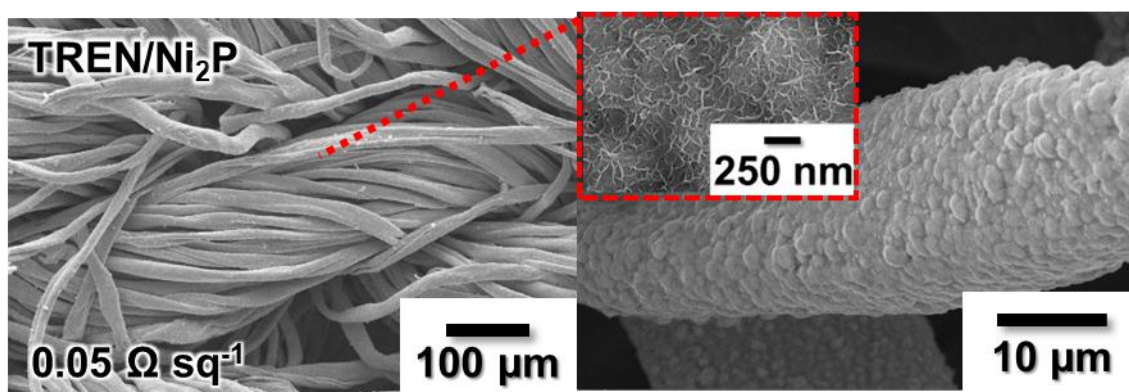


Fig. S34 XPS spectra. This result demonstrates the TREN/ Ni_2P textile is functionalized as hydrophilic amine groups.

a



b

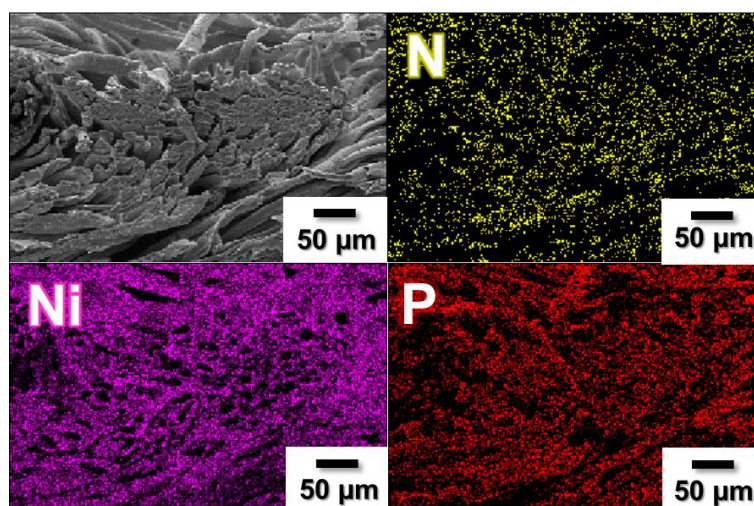


Fig. S35 Morphological characteristics. **a** Planar and **b** cross-sectional FE-SEM images and corresponding EDX mapping images of the TREN/Ni₂P textile (the inset shows the enlarged surface morphology).

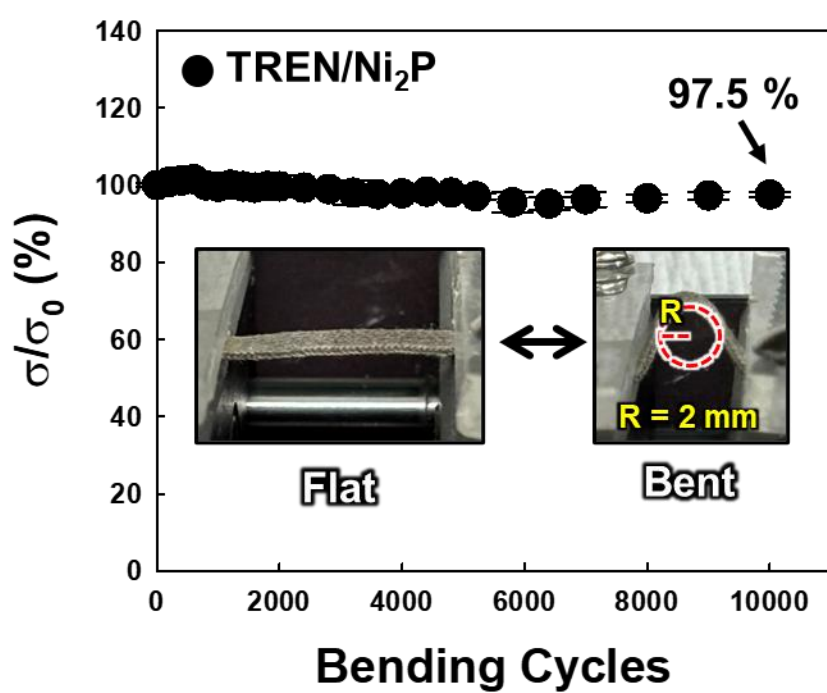


Fig. S36 Mechanical and electrical stability. Relative electrical conductivity (σ/σ_0) of the TREN/ Ni_2P textile as a function of as a function of the bending cycle number (bending radius of ~ 2 mm).

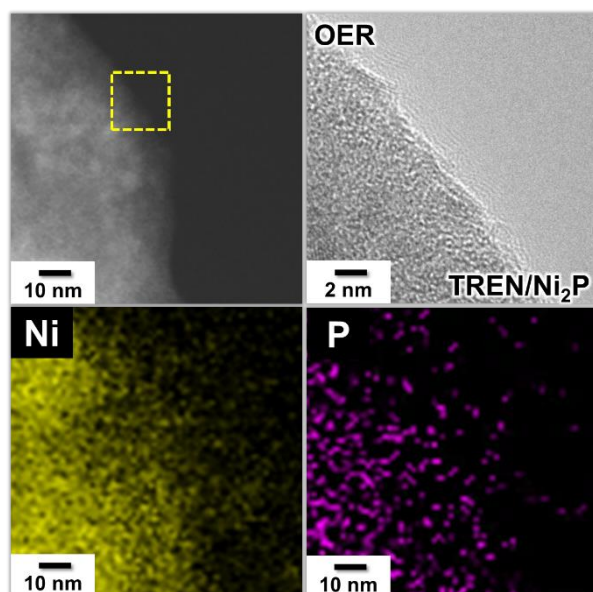


Fig. S37 Crystalline characteristics. HR-TEM image and its corresponding EDS mapping images of TREN/Ni₂P textile.

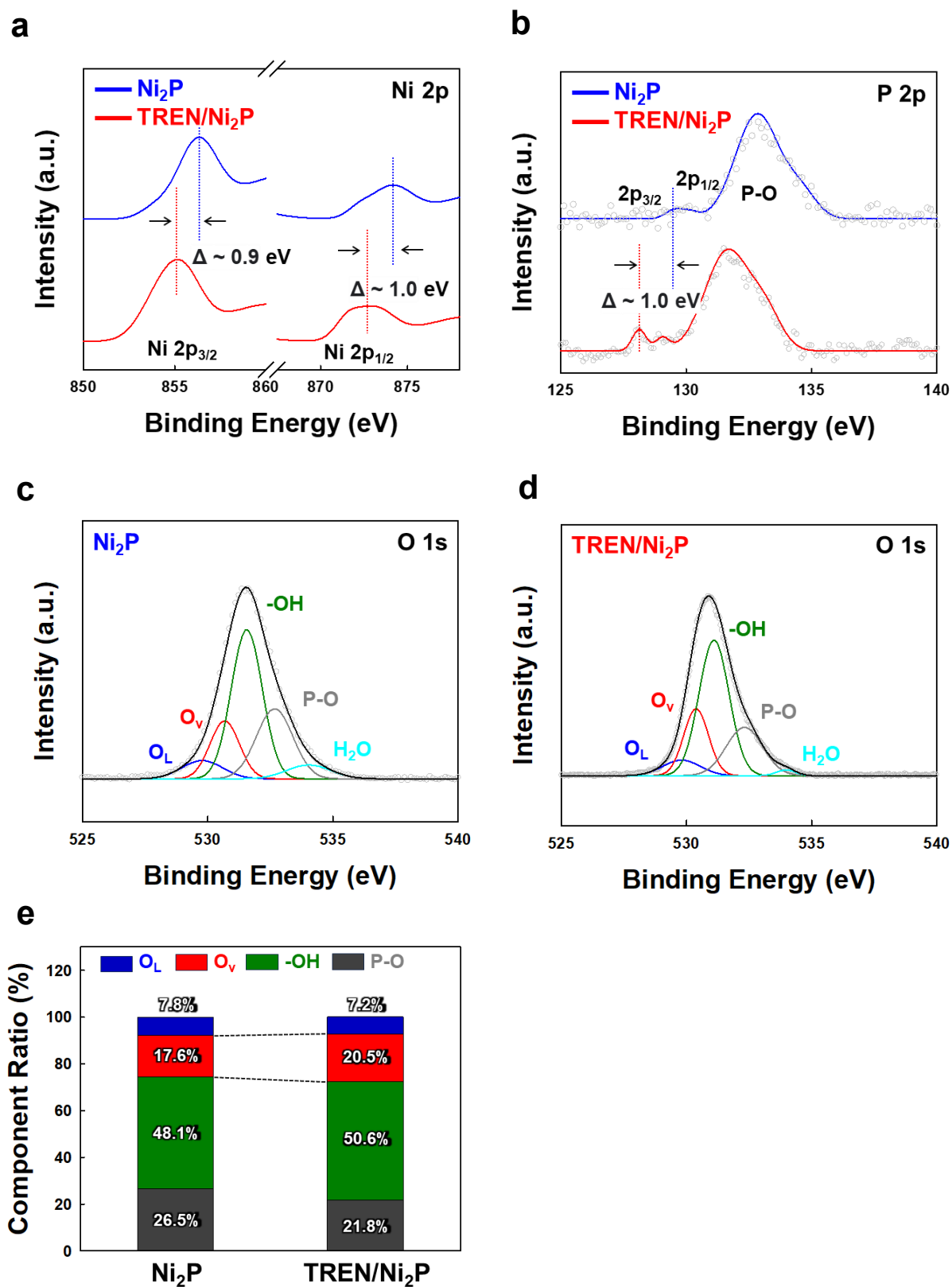


Fig. S38 XPS spectra. **a** XPS spectra of Ni 2p, **b** P 2p, and O 1s for the **c** Ni₂P and **d** TREN/Ni₂P textile. **e** The comparison of the peak area percentages for each O 1s spectral component.

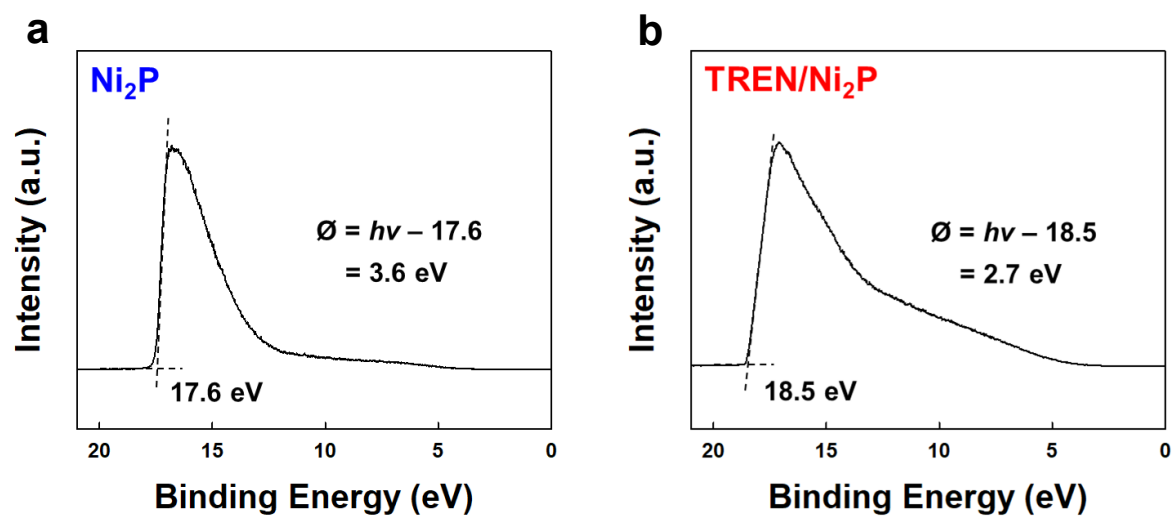


Fig. S39 UPS spectra. **a** UPS spectra as a function of binding energy for the work function of Ni₂P and **b** TREN/Ni₂P.

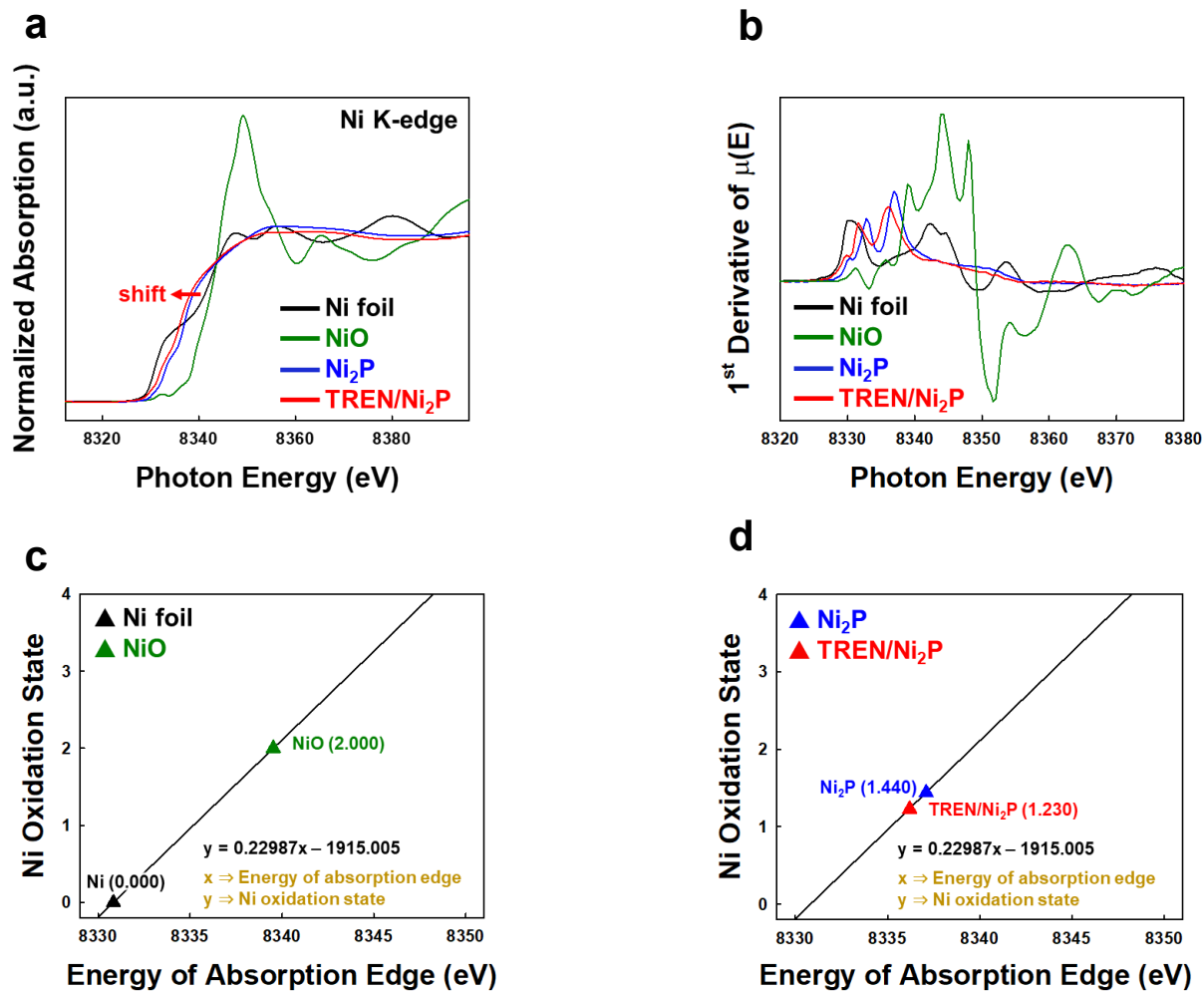


Fig. S40. Ni K-edge XAS characterization of OER electrodes. **a** XANES spectra for the Ni foil, NiO, Ni₂P and TREN/Ni₂P textile. **b** First derivative of Ni K-edge XANES spectra of Ni foil, NiO, Ni₂P and TREN/Ni₂P. **c** Plot of absorption edge position vs Ni valence state for Ni foil and NiO. **d** Plot of absorption edge position vs Ni valence state for Ni₂P and TREN/Ni₂P.

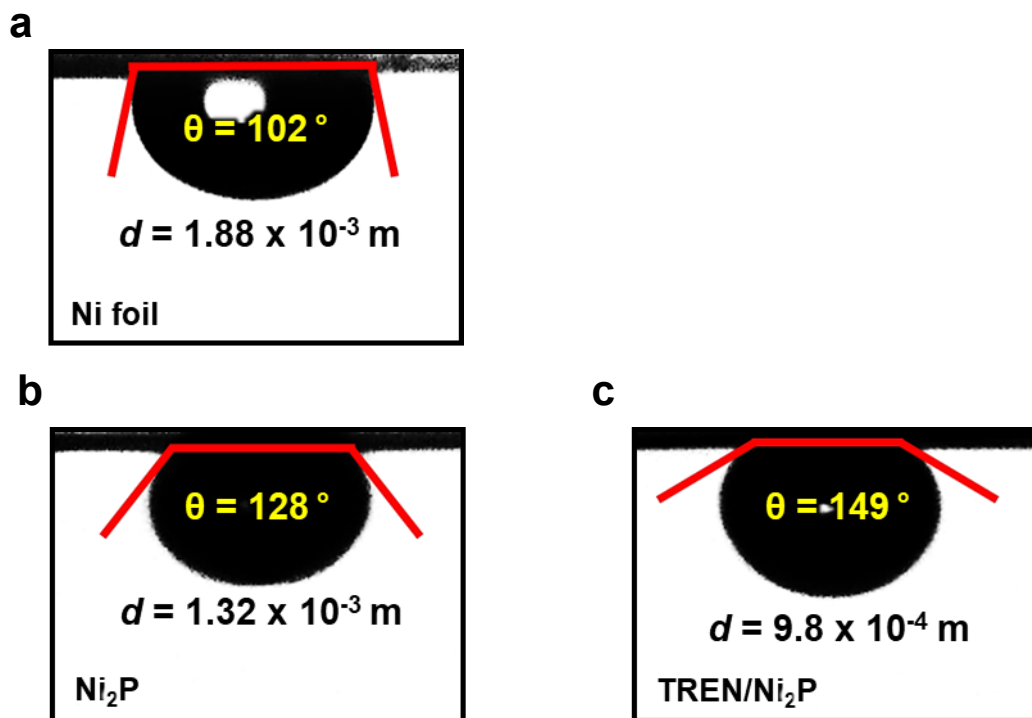


Fig. S41 Air bubble contact angles. **a** The air-bubble contact angles and bubble base diameters of Ni foil, **b** Ni₂P, and **c** TREN/Ni₂P-deposited Ni foil. Based on these parameters, the bubble adhesion forces (F_s) of NiP₂ and TREN/NiP₂-deposited Ni foil were calculated to be $2.35 \times 10^{-4} \text{ N}$ and $1.14 \times 10^{-4} \text{ N}$, respectively.

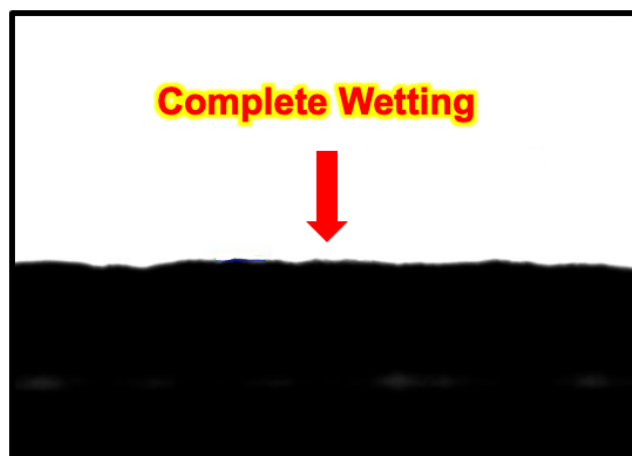


Fig. S42 Hydrophilicity test. Water contact angle of the TREN/Ni₂P textile. The water contact angle was measured using a 1 M KOH droplet.

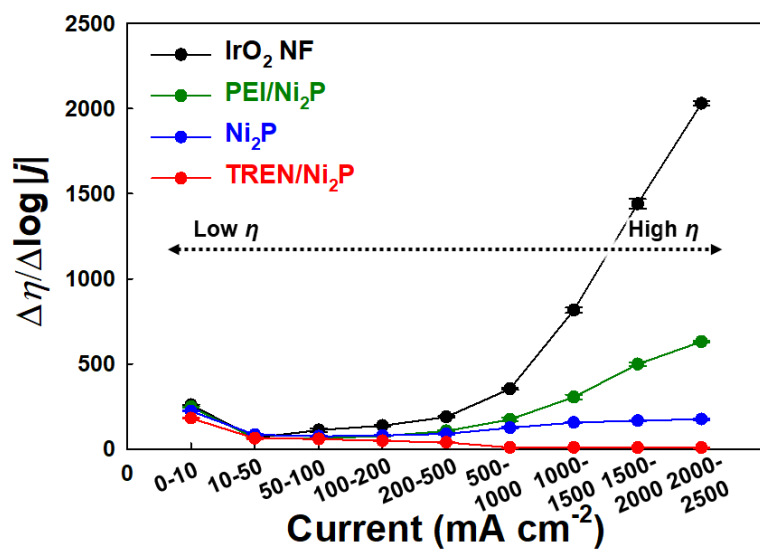


Fig. S43 Ratios of $\Delta\eta/\Delta\log |j|$. Ratios of $\Delta\eta/\Delta\log |j|$ for IrO₂ NF, PEI/Ni₂P, Ni₂P and TREN/Ni₂P textiles at different current density intervals.

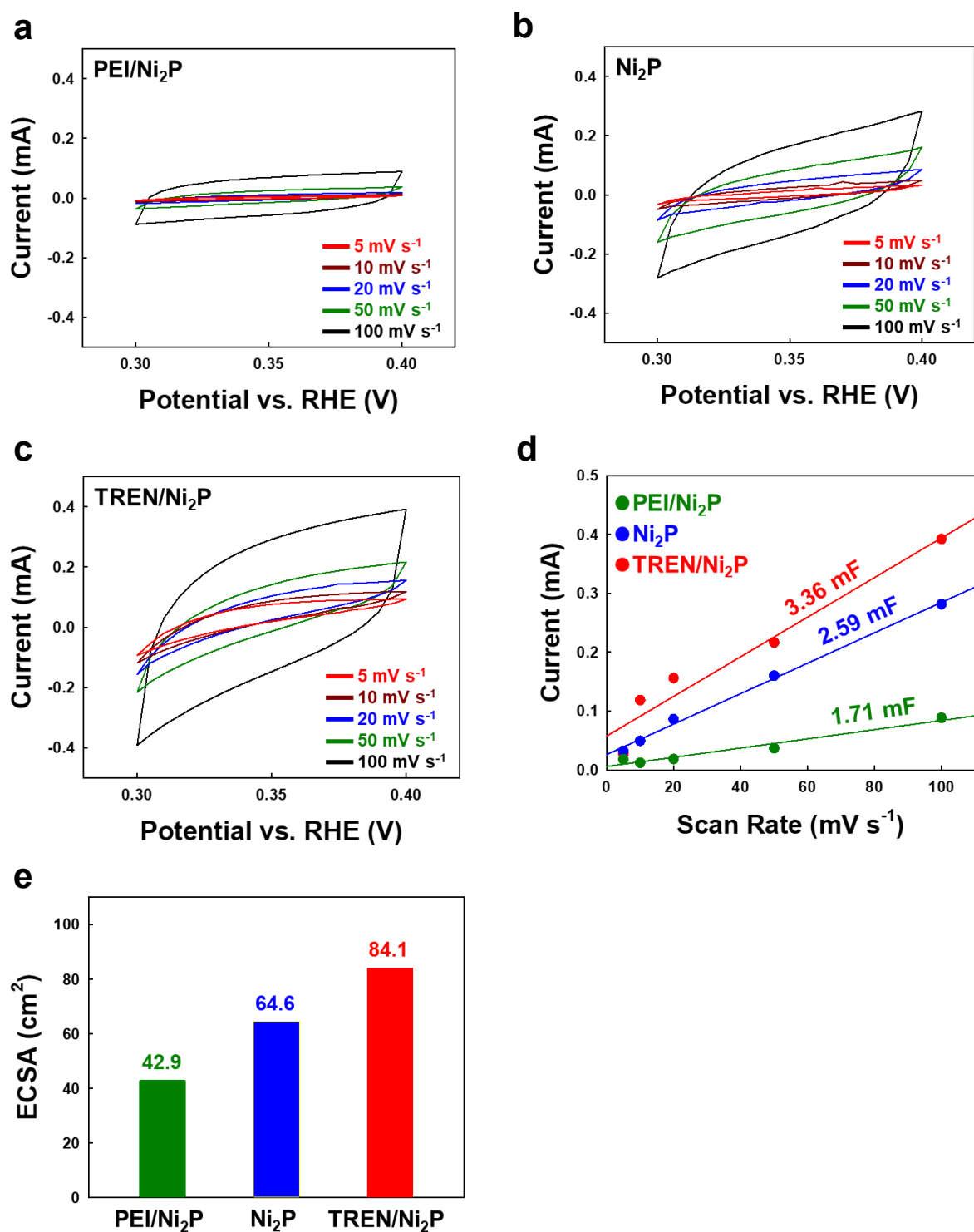


Fig. S44 Comparison of ECSA data of OER electrodes. **a** CV curves recorded in the non-faradaic region (0.3 – 0.4 V) at different scan rates (5, 10, 20, 50 and 100 mV s⁻¹) for the PEI/Ni₂P, **b** Ni₂P, and **c** TREN/Ni₂P textile. **d** Double-layer capacitance (C_{dl}) for the electrodes measured at different scan rates. **e** ECSA of PEI/Ni₂P, Ni₂P, and TREN/Ni₂P textiles. In this

analysis, ECSAs of PEI/Ni₂P, Ni₂P, and TREN/Ni₂P textile electrodes were calculated based on a specific capacitance value of 0.040 mF cm⁻² for Ni. The resulting ECSA values were approximately 42.9, 64.6, and 84.1 cm², respectively.

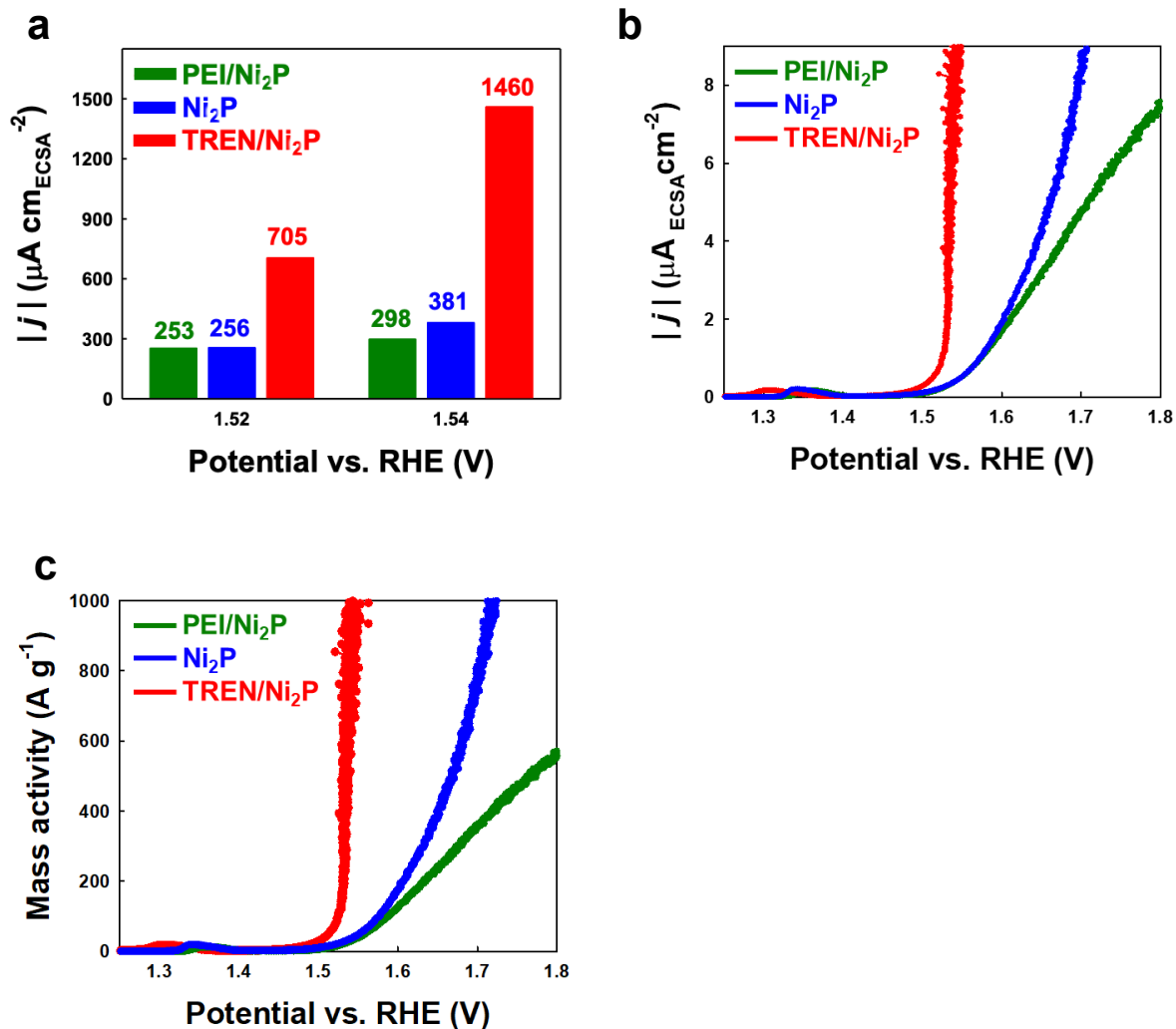


Fig. S45 Intrinsic electrocatalytic activities of OER electrodes. **a** Intrinsic OER activity ($\mu\text{A cm}_{\text{ECSA}}^{-2}$) of the PEI/Ni₂P, Ni₂P, and TREN/Ni₂P textile normalized with respect to the ECSAs of the electrocatalysts at 1.52 and 1.54 V vs. RHE. **b** OER polarization curves normalized with ECSA for the PEI/Ni₂P, Ni₂P, and TREN/Ni₂P textile in a 1 M KOH electrolyte. **c** OER polarization curves normalized with mass loading of catalysts for the PEI/Ni₂P, Ni₂P, and TREN/Ni₂P textile in a 1 M KOH electrolyte. In this case, the catalyst loading amounts for PEI/Ni₂P, Ni₂P, and TREN/Ni₂P textile are 3.99, 3.51, and 3.63 mg cm⁻², respectively.

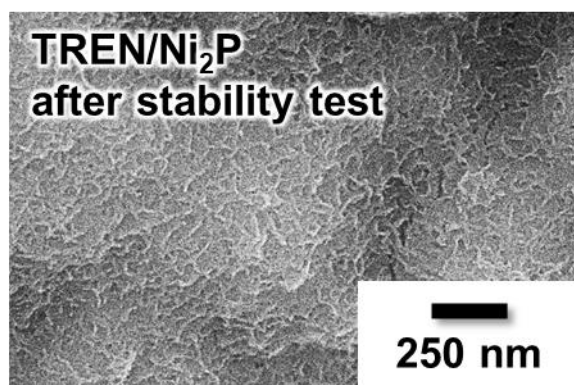


Fig. S46 Morphological characteristics. FE-SEM image of the TREN/Ni₂P textile after OER stability test.

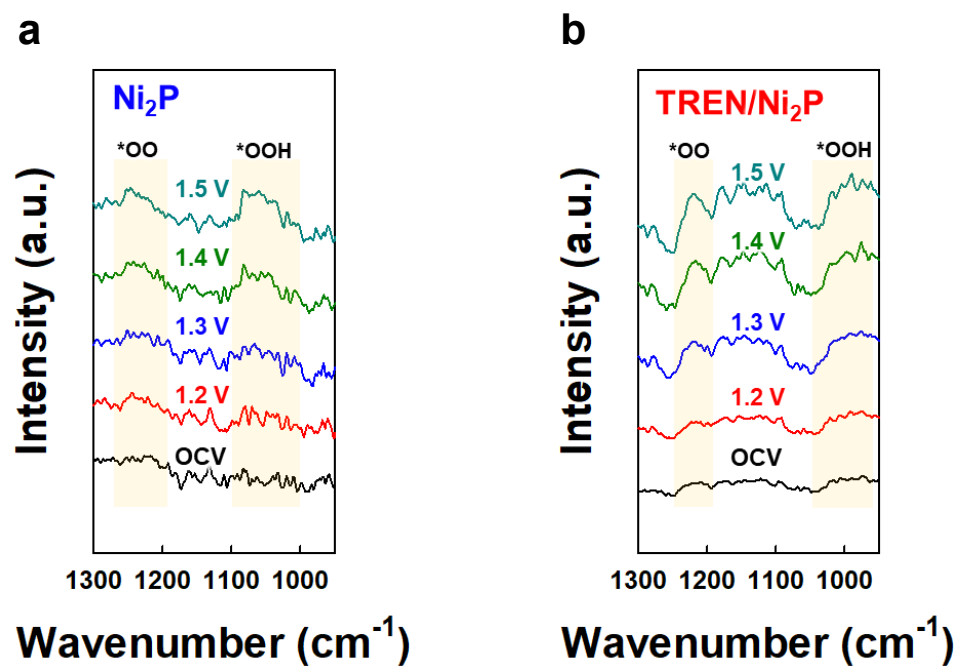


Fig. S47 *Operando* ATR-SEIRAS spectra. *Operando* ATR-SEIRAS spectra of **a** Ni₂P and **b** TREN/Ni₂P under different potential.

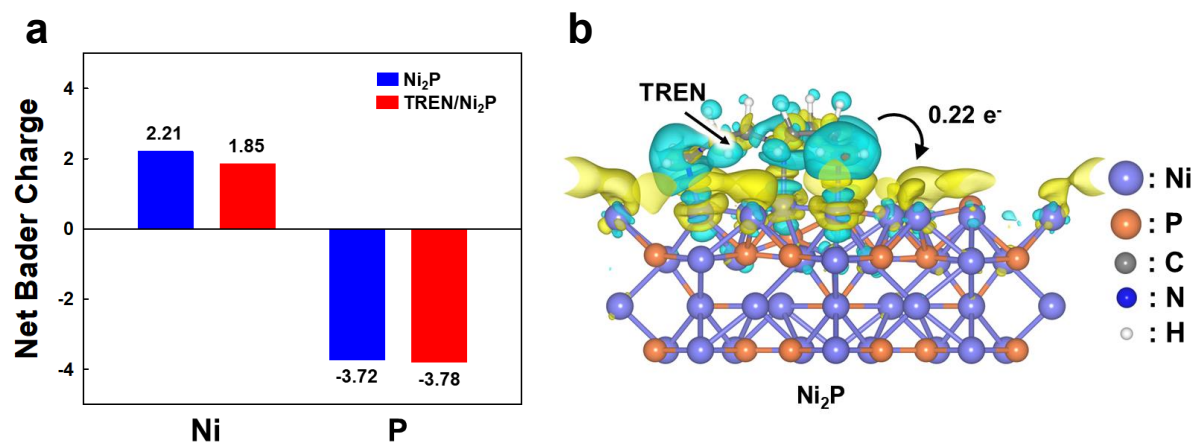


Fig. S48 The calculated net Bader charges. **a** The calculated net Bader charges of surface Ni and P atoms of Ni_2P and TREN/ Ni_2P . For the TREN/ Ni_2P system, a single TREN molecule was positioned with its three amine groups binding to three surface Ni atoms similar to TREN/ NiP_2 system. **b** The three-dimensional CDD map of TREN/ Ni_2P , where charge accumulation and depletion are shown in yellow and cyan, respectively. Notably, the Bader charge analysis revealed that the Ni and P atoms residing on the Ni_2P surfaces undergo electron accumulation upon TREN adsorption.

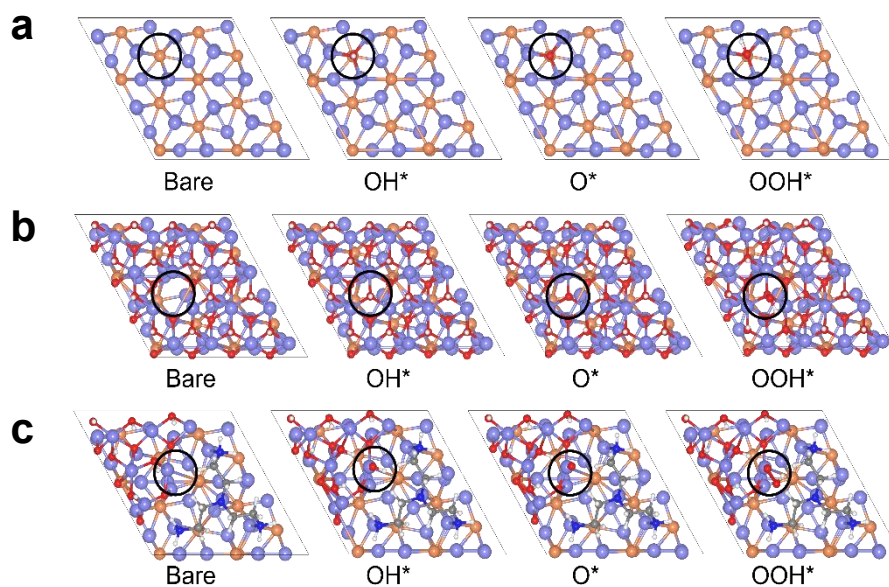


Fig. S49 DFT Calculation. Atomic models of OER with intermediate adsorbates (bare, *OH, *O, and *OOH) adsorbed on **a** Ni₂P, **b** NiOOH/Ni₂P, and **c** TREN-NiOOH/Ni₂P surface.

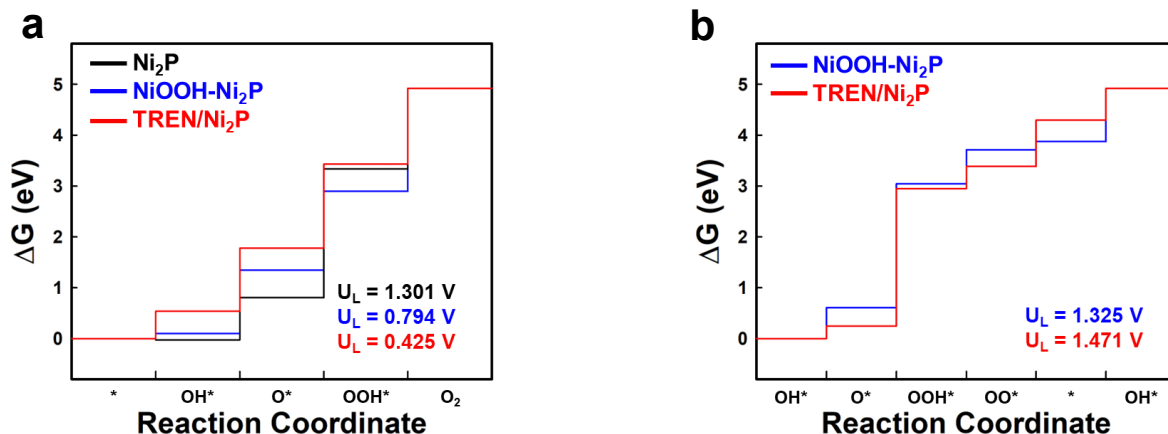


Fig. S50 Gibbs free energy diagram for AEM and LOM pathway. OER mechanism of DFT calculation with the **a** AEM and **b** LOM pathway for Ni_2P (black line), $\text{NiOOH/Ni}_2\text{P}$ (blue line), and $\text{TREN-NiOOH/Ni}_2\text{P}$ (red line). In this case, the LOM pathway exhibited significantly higher limiting potentials ($U_L = 1.325 \text{ V}$ and 1.471 V for $\text{NiOOH-Ni}_2\text{P}$ and $\text{TREN-NiOOH/Ni}_2\text{P}$, respectively) compared to those of the AEM pathway ($U_L = 0.794 \text{ V}$ and 0.425 V for $\text{NiOOH-Ni}_2\text{P}$ and $\text{TREN-NiOOH/Ni}_2\text{P}$, respectively).

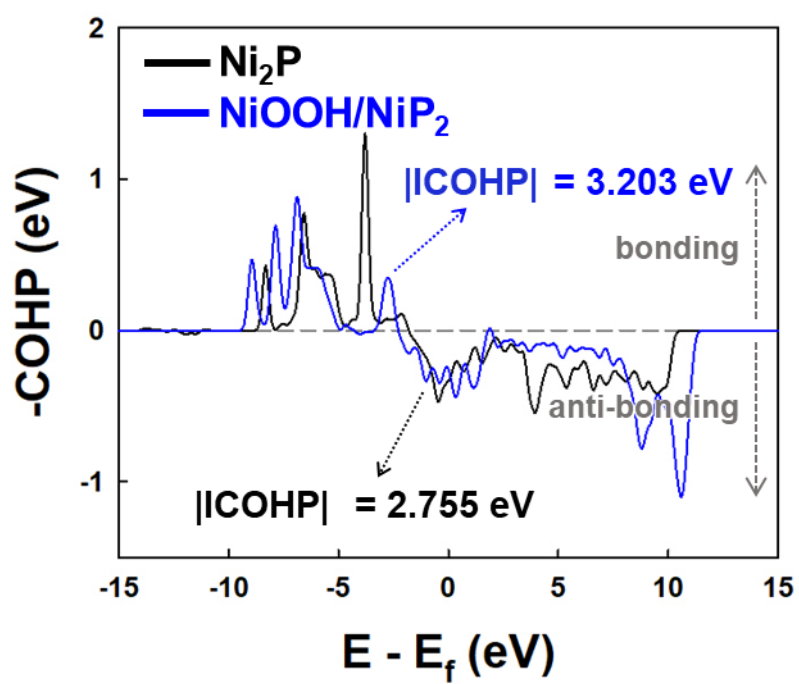


Fig. S51 ICOHP of the OER catalysts. COHP plot of Ni-OOH* bonding of Ni_2P and $NiOOH/Ni_2P$.

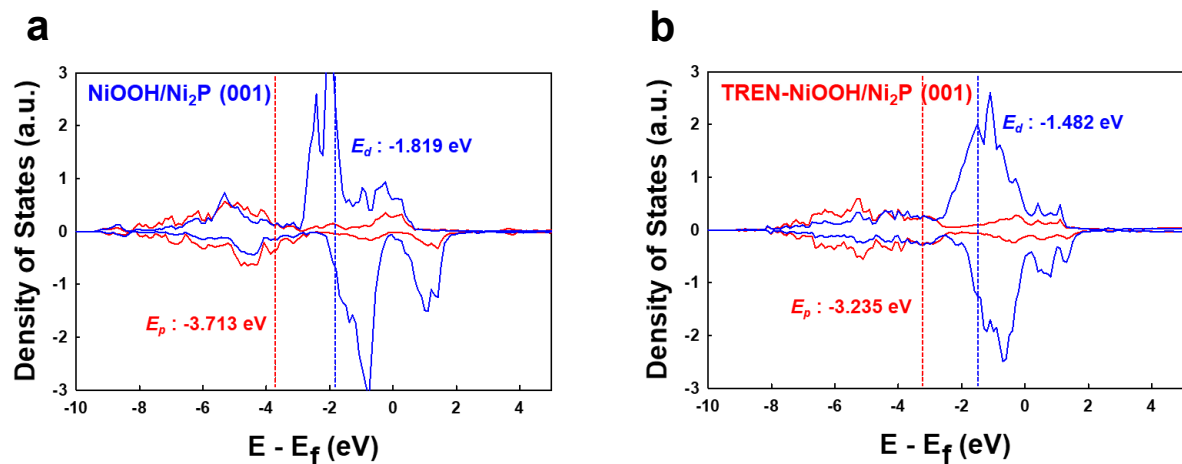


Fig. S52 DOS spectra. **a** DOS plots of NiOOH/Ni₂P and **b** TREN-NiOOH/Ni₂P. It is indicated that the energy gap between *d*-band and *p*-band narrows from 1.894 eV for NiOOH/Ni₂P to 1.753 eV for TREN-NiOOH/Ni₂P. The smaller gap on the TREN-NiOOH/Ni₂P surface indicates a stronger interaction between the Ni sites and their coordinating oxygen atoms. Consequently, the Ni active sites become less favorable for binding with OER intermediates, resulting in the observed weaker adsorption.

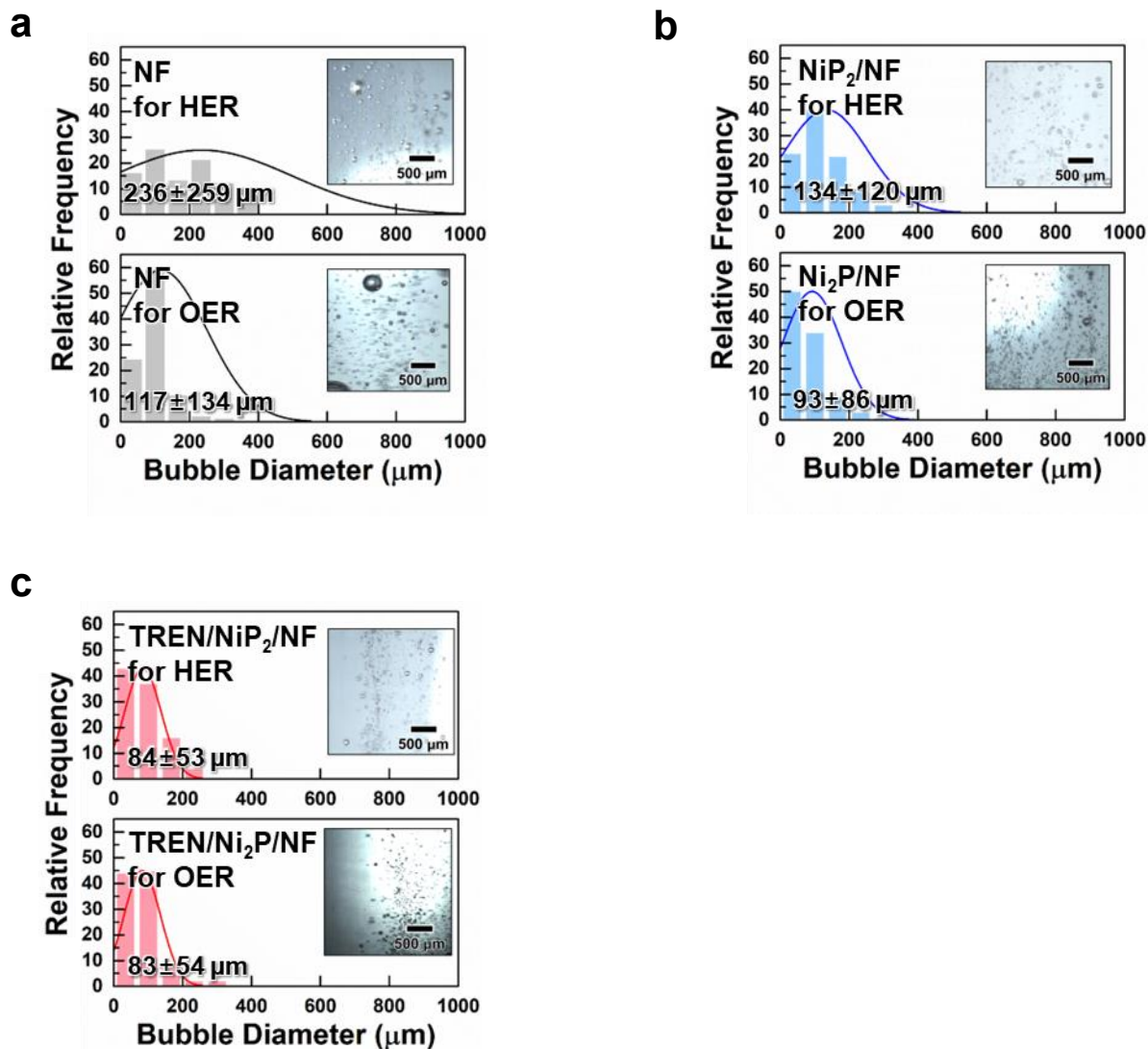


Fig. S53 The bubble size distribution. **a** The bubble diameter distribution of the releasing H₂ and O₂ bubbles from NF || NF, **b** NiP₂-coated NF || Ni₂P-coated NF, and **c** TREN/NiP₂-coated NF || TREN/Ni₂P-coated NF electrodes as a function of a constant current density of 100 mA cm⁻² in a 1 M KOH electrolyte. The insets are the digital images of generated bubbles on various electrode surfaces.

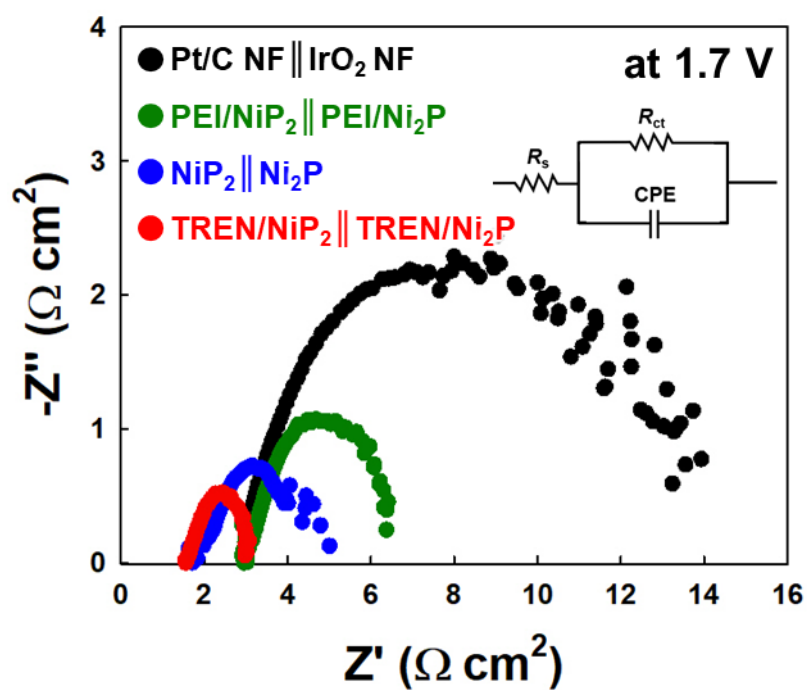


Fig. S54 EIS plots. EIS plots of the TREN/NiP₂ || TREN/Ni₂P-textile, NiP₂ || Ni₂P-textile, the PEI/NiP₂ || PEI/Ni₂P-textile, and the conventional Pt/C-coated NF || IrO₂-coated NF-based devices. In this case, the charge transfer resistance (R_{ct}) values are 1.4, 3.2, 3.4, and 12.3 $\Omega \text{ cm}^2$, respectively.

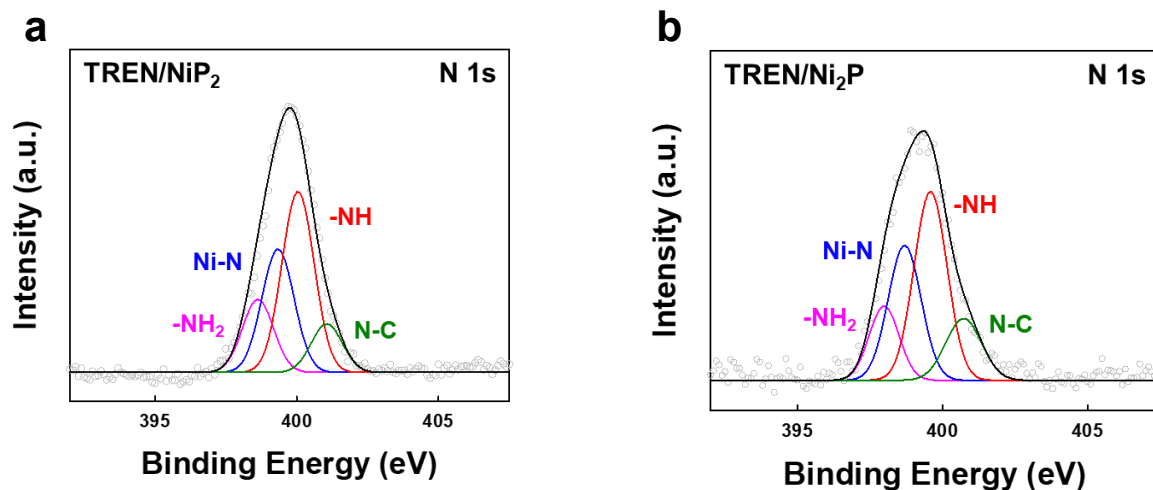


Fig. S55 XPS spectra. **a** N 1s XPS spectra of TREN/NiP₂ and **b** TREN/Ni₂P textile electrodes after overall water-splitting up to 4000 mA cm⁻². These XPS spectra clearly demonstrate that the NH₂ groups of TREN remained preserved on both the NiP₂ and Ni₂P textile electrodes, even under harsh current density conditions.

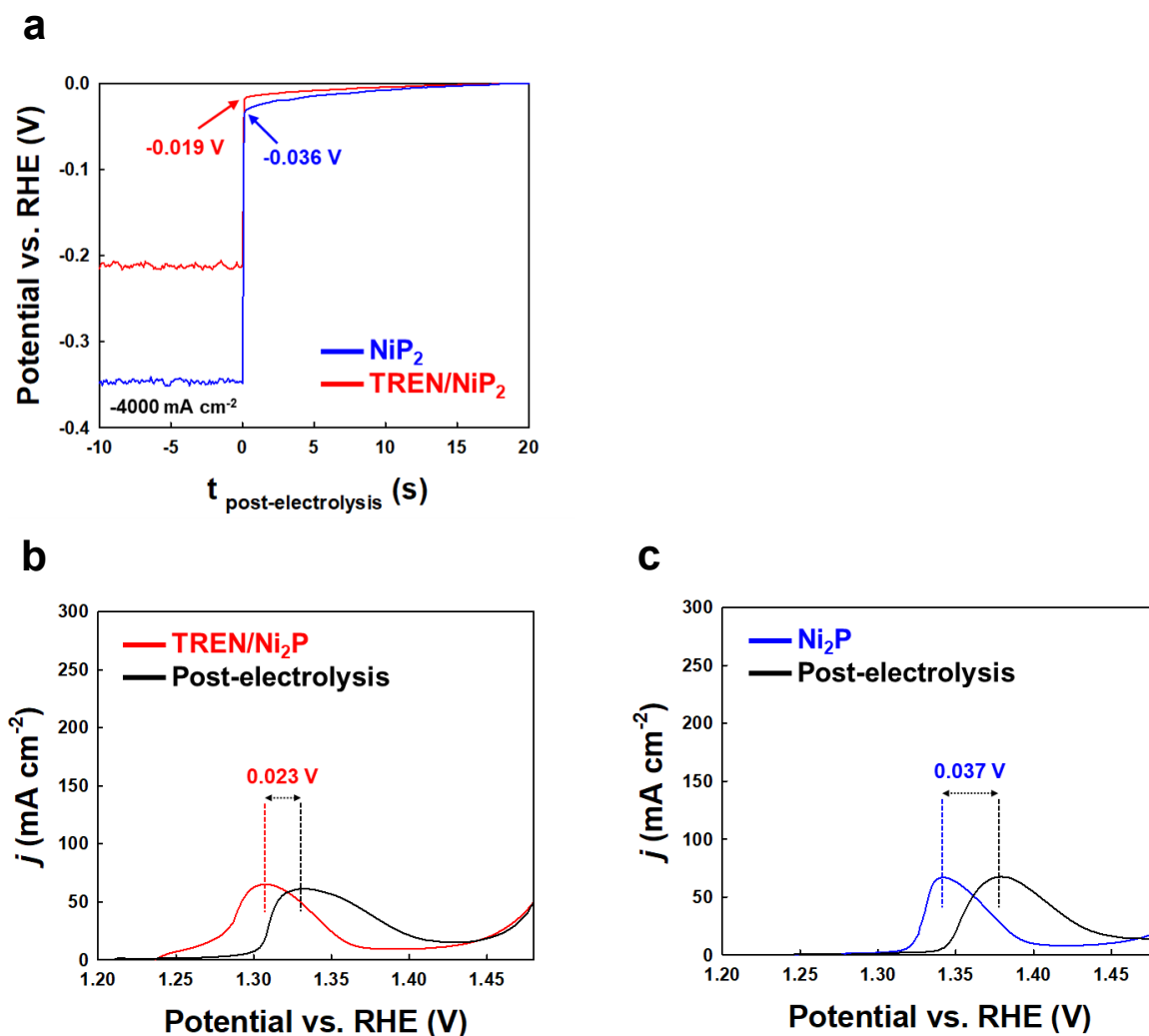
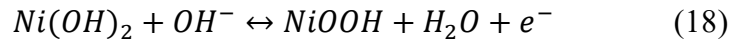


Fig. S56 Determination of interfacial pH swing in 1 M KOH following electrolysis at 4000 mA cm⁻². **a** Open circuit potential decay transients of NiP₂ and TREN/NiP₂ following galvanostatic polarization at -4000 mA cm⁻² in 1 M KOH. **b** LSVs of TREN/Ni₂P and **c** Ni₂P electrodes measured in 1 M KOH before and after electrolysis at 4000 mA cm⁻². For HER, The deviation of the OCP from 0 V vs RHE reflects a transient mismatch between the local interfacial pH and the bulk electrolyte pH, based on the Nernstian dependence of the hydrogen equilibrium potential:

$$\eta_{\Delta pH} = 0.059 \times \Delta pH_{interfacial-bulk} \quad (17)$$

Using this relation, after electrolysis at -4000 mA cm⁻², the bare NiP₂ electrode exhibited an OCP deviation of -36 mV vs RHE, corresponding to a local pH increase of approximately 0.6 units relative to the bulk electrolyte. In contrast, the TREN/NiP₂ electrode showed a smaller OCP deviation of -19 mV, corresponding to a reduced interfacial pH increase of ~0.3 units.

Consistent trends were also observed under OER-relevant conditions by analyzing the anodic $\text{Ni}^{2+}/\text{Ni}^{3+}$ oxidation peak. The $\text{Ni}(\text{OH})_2/\text{NiOOH}$ redox transition in alkaline media can be expressed as:



This redox couple exhibits a Nernstian dependence on hydroxide activity, leading to the following relationship between the oxidation potential and pH:

$$\Delta E_{\text{Ni}^{2+}/\text{Ni}^{3+}} = 0.059 \times \Delta \text{pH}_{\text{interfacial-bulk}} \quad (19)$$

After high-current electrolysis, the oxidation peak of bare Ni_2P shifted by approximately 37 mV toward lower potentials, whereas that of TREN/ Ni_2P shifted by only ~23 mV. By analyzing the shift of the $\text{Ni}^{2+}/\text{Ni}^{3+}$ redox potential according to the Nernst relationship, we quantitatively estimated an interfacial pH increase of ~0.4–0.6 units after OER. Notably, the smaller potential shift observed for TREN/ Ni_2P indicates a mitigated pH swing, suggesting that amine groups in TREN act as an interfacial proton buffer during high-rate OER operation.

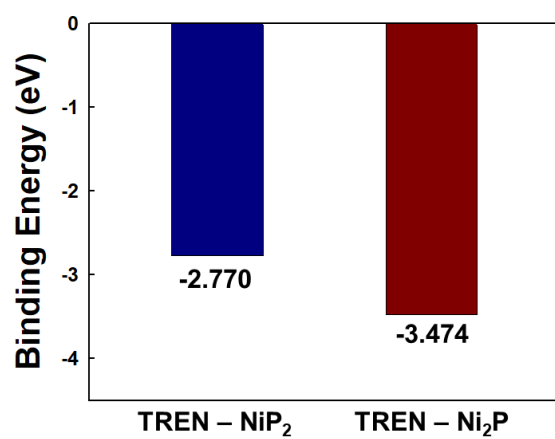


Fig. S57 The calculated binding energy of TREN on the NiP₂ and Ni₂P surface.

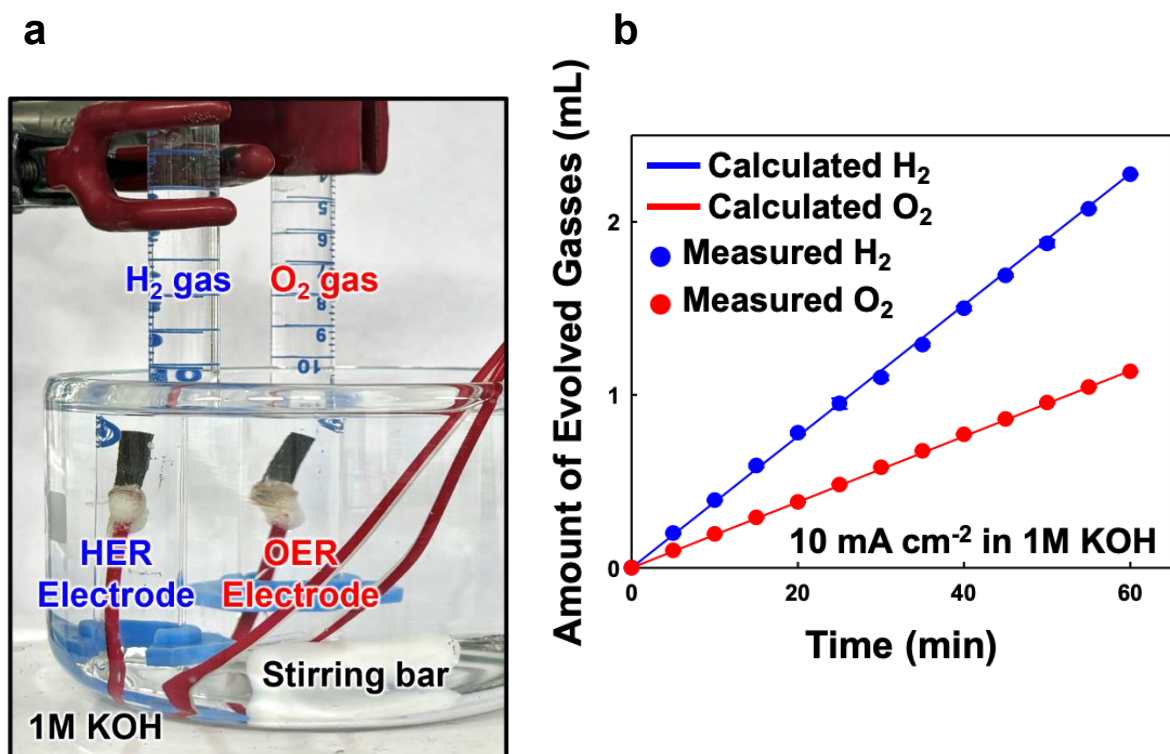


Fig. S58 Faradaic efficiency test of full-cell device. **a** The photographic image of full-cell water splitting device composed of the TREN/NiP₂ || TREN/Ni₂P textile electrodes for collection of the evolved gas. Hydrogen and oxygen gases were generated and collected in the cylinders. **b** Theoretically calculated and experimentally measured amounts of H₂ and O₂ gases from the TREN/NiP₂ || TREN/Ni₂P as a function of the interval time at a constant current density of 10 mA cm⁻².

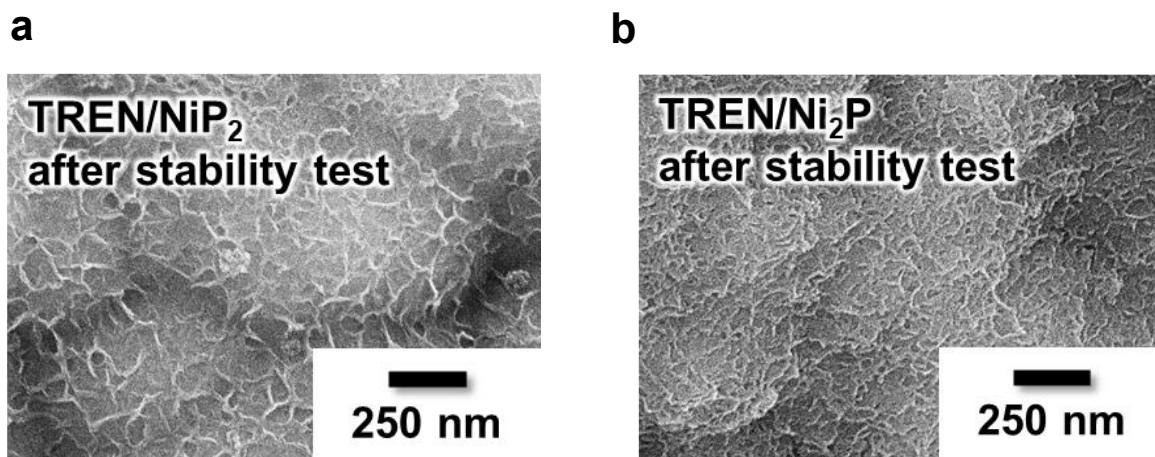


Fig. S59 Morphological characteristics. FE-SEM images of the **a** TREN/NiP₂, and **b** TREN/Ni₂P textile device after full-cell stability test at the current density alternated between 1,000 and 4,000 mA cm⁻² for at least 3,200h.

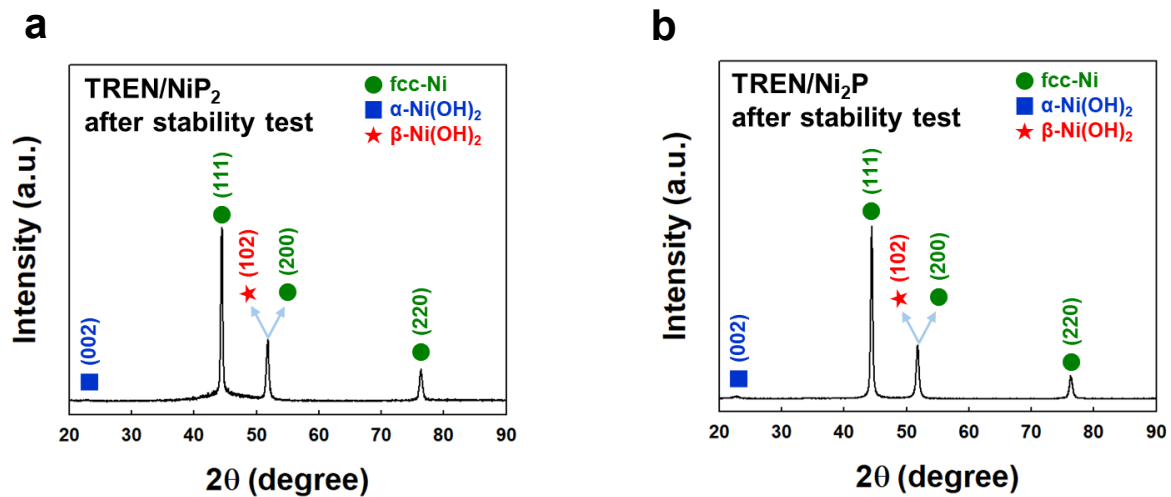


Fig. S60 Structural characteristics. XRD spectra of **a** TREN/NiP₂, and **b** TREN/Ni₂P textile device after full-cell stability test at the current density alternated between 1,000 and 4,000 mA cm⁻² for at least 3,200h.

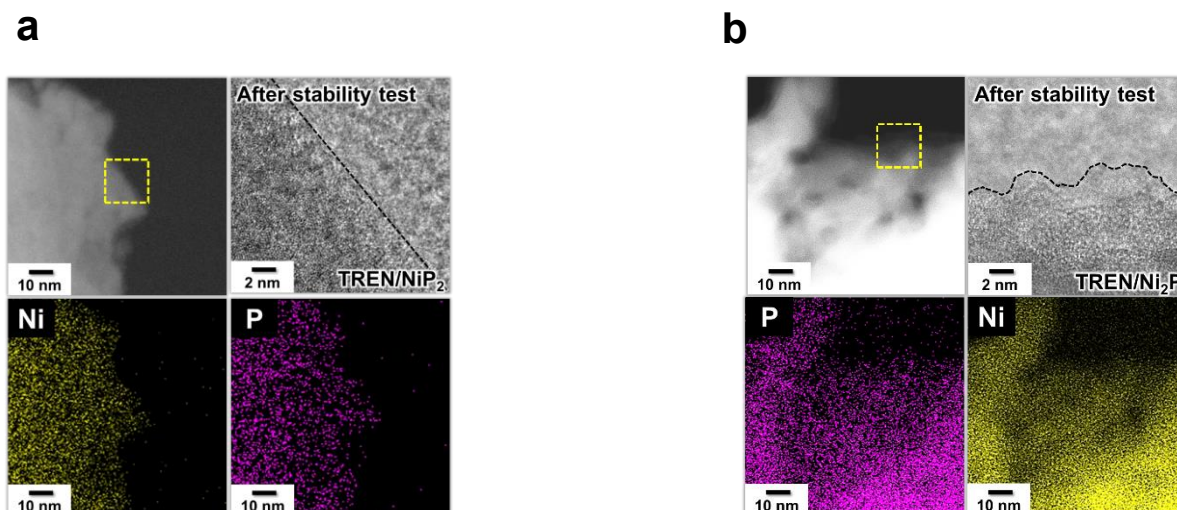


Fig. S61 Crystalline characteristics. **a** HR-TEM image and its corresponding EDS mapping images of TREN/NiP₂ and **b** TREN/Ni₂P textile device after full-cell stability test at the current density alternated between 1,000 and 4,000 mA cm⁻² for at least 3,200h.

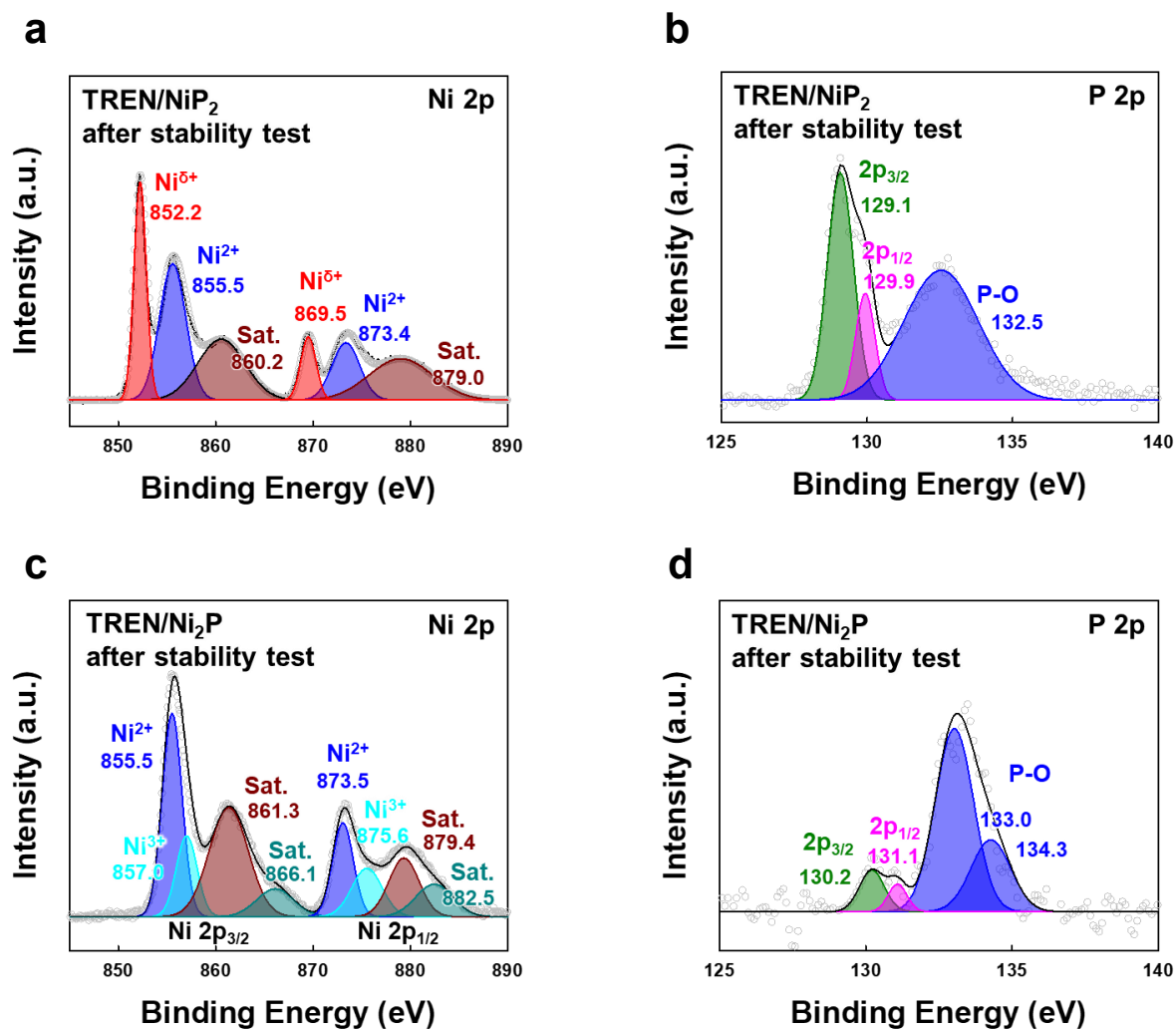


Fig. S62 XPS spectra of TREN/NiP₂ || TREN/Ni₂P textile device. **a** Ni 2p and **b** P 2p XPS spectra of TREN/NiP₂ textile after stability test. **c** Ni 2p and **d** P 2p XPS spectra of TREN/Ni₂P textile after stability test

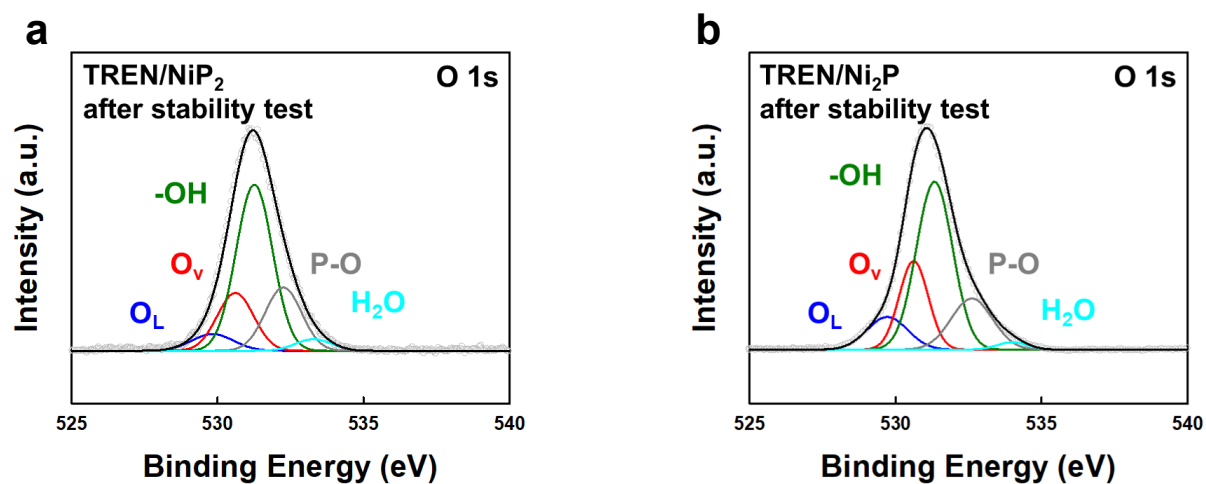


Fig. S63 XPS spectra of TREN/NiP₂ || TREN/Ni₂P textile device. O 1s XPS spectra of **a** TREN/NiP₂ and **b** TREN/Ni₂P textile after stability test.

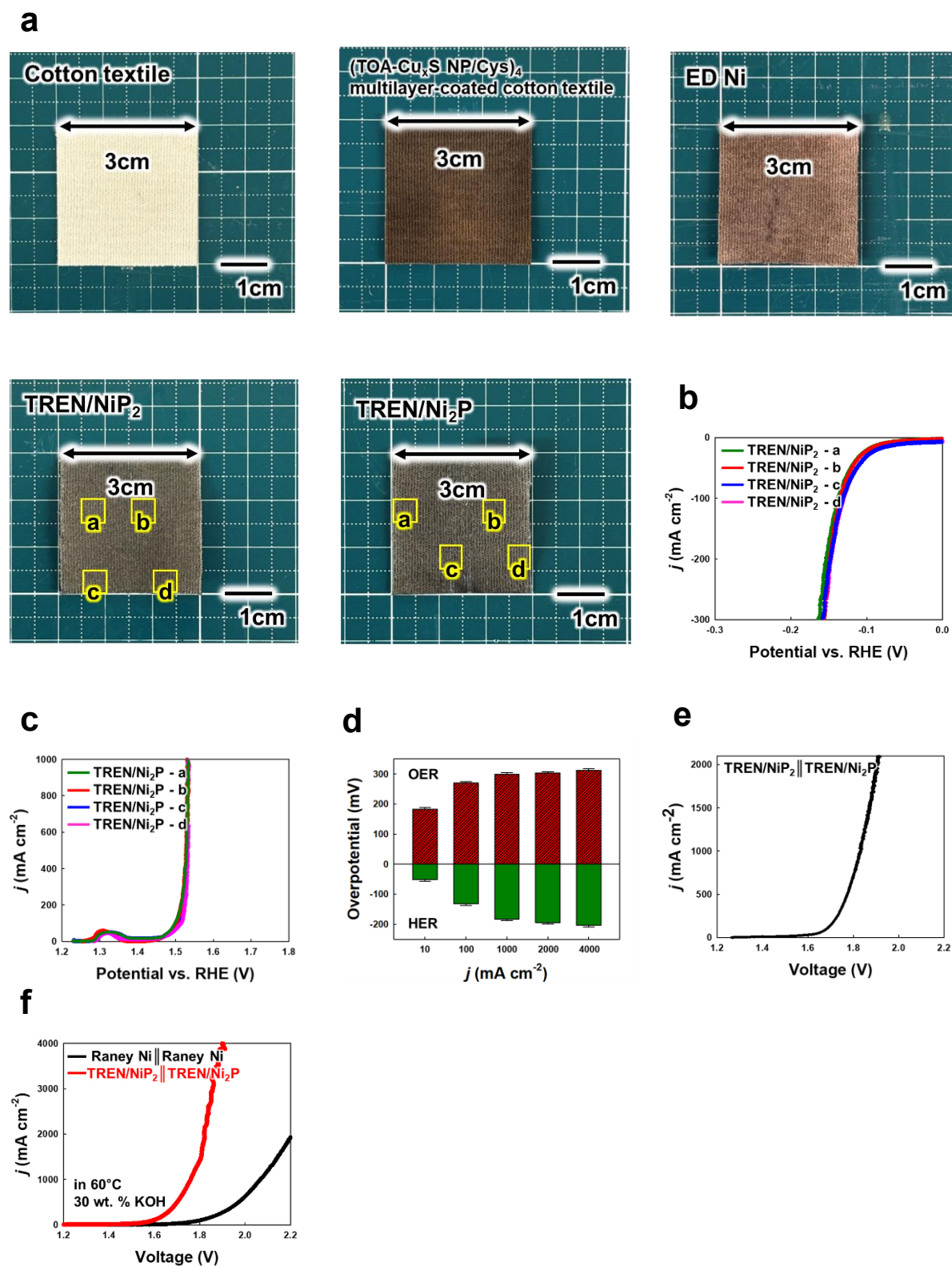


Fig. S64 Verification of applicability in commercially available condition. **a** Photographic image of cotton textile. (TOA-Cu_xS NP/Cys)₄ multilayer-coated cotton textile, ED Ni, TREN/NiP₂, and TREN/Ni₂P textile. Reproducibility and uniformity of the **b** HER (TREN/NiP₂) and **c** OER (TREN/Ni₂P) electrodes. The marked spots in the photographic images were used

for the measurements. **d** Overpotentials obtained from HER and OER polarization curves. **e** The polarization curves of the TREN/NiP₂ || TREN/Ni₂P devices measured with electrode areas of 1 cm². **f** The polarization curves of the TREN/NiP₂ || TREN/Ni₂P, and conventional water splitting electrodes (Raney nickel/Ni foam) measured in a 30 wt.% KOH electrolyte at 60°C.

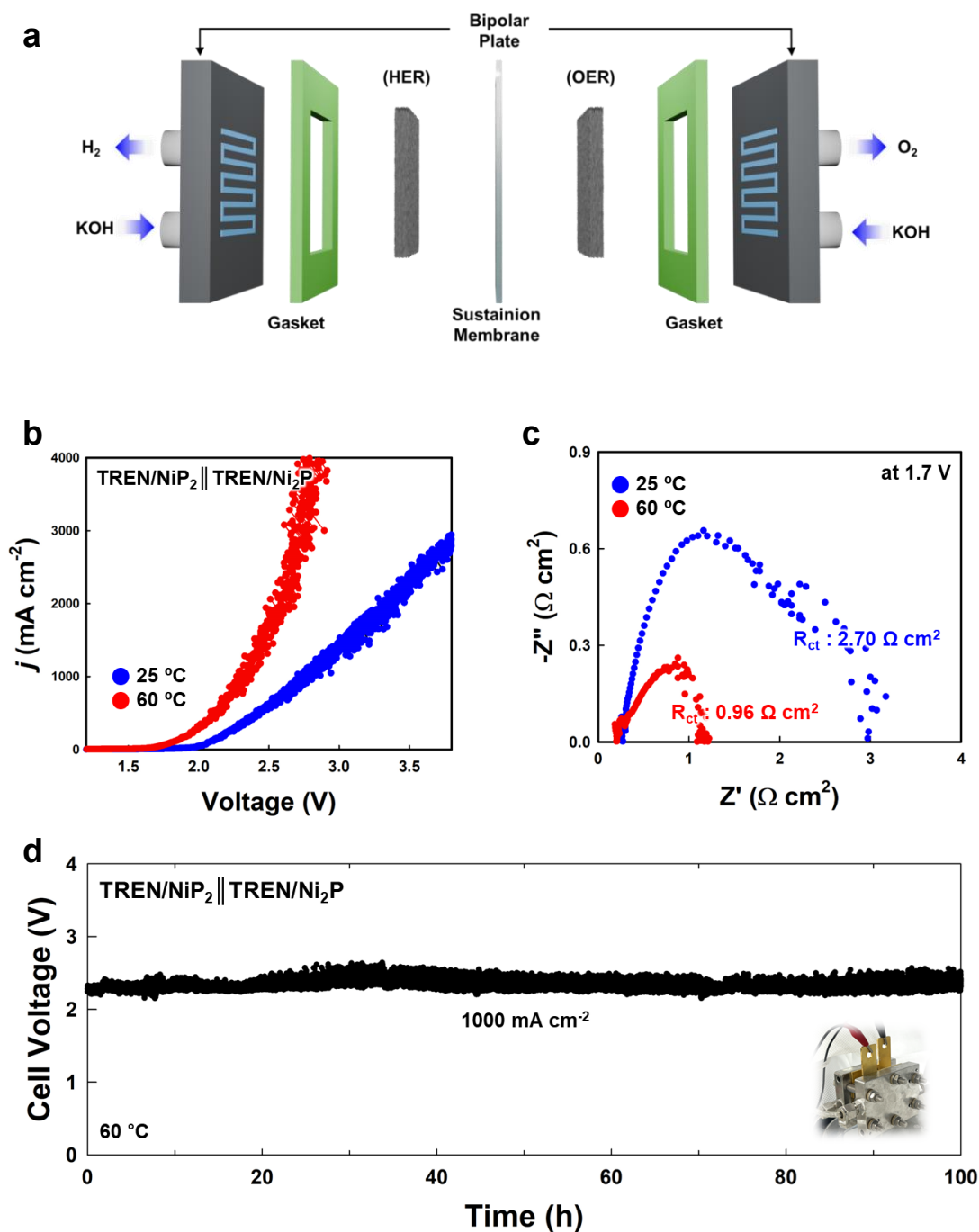


Fig. S65 AEM electrolyzer. **a** Schematic illustration of the AEM water electrolyzer. **b** LSV polarization curves of TREN/ NiP_2 || TREN/ Ni_2P MEA in 1 M KOH, at 25 °C and 60 °C. **c** area-specific resistance spectra of TREN/ NiP_2 || TREN/ Ni_2P MEA in 1 M KOH at 25 °C and 60 °C. **d** Chronopotentiometry stability measurements at a current density of 1,000 mA cm^{-2} for 100 h in 1 M KOH at 60 °C.

Table S1. ICP-OES data of NiP₂-electrodeposited Ti felt electrodes.

	NiP₂
Ni mass (mg L⁻¹)	38826
P mass (mg L⁻¹)	38767.5
Ni: P atomic ratio	1 : 1.9

The NiP₂ textile electrode structure involves electroplating a Ni layer onto textiles embedded with Cu_xS nanoparticles, followed by the electrodeposition of a NiP₂ layer on the Ni-coated surface. As a result, the total Ni content includes contributions from both the underlying metallic Ni layer and the overlying NiP₂ layer. To eliminate the influence of this Ni background, NiP₂ was directly electrodeposited onto Ti felt, which contains no metallic Ni layer.

Table S2. EXAFS fitting parameters at the Ni K-edge for NiP₂ and TREN/NiP₂.

Sample	Atomic scatter	Coordination Number (CN)	Interatomic distance (Å)	Debye-Waller factor (Å²)
NiP₂	NI-P	5.5 ± 0.2	2.282 ± 0.026	0.007 ± 0.003
TREN/NiP₂	NI-P	5.4 ± 0.2	2.297 ± 0.028	0.009 ± 0.003

Table S3. HER Performance comparison of HER overpotential (η) for the TREN/NiP₂-textile, pristine NiP₂-textile, PEI/NiP₂-textile, and conventional Pt/C-coated NF at diverse current densities.

Electrode	η_{10} (mV)	η_{100} (mV)	$\eta_{1,000}$ (mV)	$\eta_{2,000}$ (mV)	$\eta_{3,000}$ (mV)	$\eta_{4,000}$ (mV)
TREN/NiP₂	50	131	181	193	195	204
NiP ₂	72	155	203	231	-	-
PEI/NiP ₂	102	161	250	333	-	-
Pt/C NF	76	224	367	-	-	-

- : not recorded

Table S4. Performance comparison of non-noble metal phosphide-based HER electrodes.

HER catalyst	Method	Overpotential (mV)	Reference
TREN/NiP₂	LbL assembly, Electrodeposition	50 @10 mA cm⁻²	Our work
(Mn-(Co,Ni) ₂ P/CoP/(N,S)-C)	Hydrothermal, Chemical vapor deposition	61 @10 mA cm ⁻²	[S11]
Co@CoFe-P NB ^{a)}	Chemical vapor deposition	104 @10 mA cm ⁻²	[S12]
MoS ₂ /NiPS ₃	Hydrothermal	112 @10 mA cm ⁻²	[S13]
CoP/Co ₂ P-H	Hydrothermal, Phosphorization	97 @10 mA cm ⁻²	[S14]
MoCoP-NPC	Electroless deposition	91 @10 mA cm ⁻²	[S15]
Cu ₃ P/Ni ₂ P	In situ oxidation, Hydrothermal, Phosphidation	88.1 @10 mA cm ⁻²	[S16]
CoP/N,P-CNT	Acid treatment, Carbonization,Phosphidation	101.9 @10 mA cm ⁻²	[S17]
a)	NB : nanoboxes		

Table S5. The comparison of HER catalysts mass loading.

Catalyst	NiP₂	TREN/NiP₂	PEI/NiP₂
Mass loading (mg cm⁻²)	6.54	6.74	6.90

Table S6. ICP-OES data of Ni₂P-electrodeposited Ti felt electrodes.

	Ni₂P
Ni mass (mg L⁻¹)	95074
P mass (mg L⁻¹)	20752
Ni: P atomic ratio	2.4 : 1

The Ni₂P textile electrode structure involves electroplating a Ni layer onto textiles embedded with Cu_xS nanoparticles, followed by the electrodeposition of a Ni₂P layer on the Ni-coated surface. As a result, the total Ni content includes contributions from both the underlying metallic Ni layer and the overlying NiP₂ layer. To eliminate the influence of this Ni background, Ni₂P was directly electrodeposited onto Ti felt, which contains no metallic Ni layer.

Table S7. EXAFS fitting parameters at the Ni K-edge for Ni₂P and TREN/Ni₂P.

Sample	Atomic scatter	Coordination Number (CN)	Interatomic distance (Å)	Debye-Waller factor (Å²)
Ni₂P	Ni-P	1.7 ± 0.2	2.262 ± 0.033	0.004 ± 0.002
	Ni-Ni	3.7 ± 0.2	2.603 ± 0.031	0.011 ± 0.003
TREN/Ni₂P	Ni-P	1.6 ± 0.2	2.281 ± 0.032	0.005 ± 0.004
	Ni-Ni	3.8 ± 0.2	2.605 ± 0.029	0.016 ± 0.006

Table S8. Performance comparison of non-noble metal phosphide-based OER electrodes.

OER catalyst	Method	Overpotential (mV)	Reference
TREN/Ni₂P	LbL assembly, Electrodeposition	180 @10 mA cm⁻²	Our work
(Mn-(Co,Ni) ₂ P/CoP/(N,S)-C)	Hydrothermal, Chemical vapor deposition	213 @10 mA cm ⁻²	[S11]
MoCoP-NPC	Electroless deposition	316 @10 mA cm ⁻²	[S15]
Zn-Ni ₂ P/FeOOH	Phosphorization	207 @10 mA cm ⁻²	[S18]
Ni ₂ P/FeP	Phosphorization	217 @10 mA cm ⁻²	[S19]
Ni ₂ P/WS ₂ /Co ₉ S ₈ @C	Pyrolysis, Phosphorization	204 @10 mA cm ⁻²	[S20]
Fe-Co ₂ P@NPDC ^{a)}	Etching, Calcination	320 @10 mA cm ⁻²	[S21]
Cr-Co-P	Etching, Phosphorization	203@10 mA cm ⁻²	[S22]
a)	NPDC : N/P co-doped carbon		

Table S9. OER Performance comparison of OER overpotential (η) for the TREN/Ni₂P-textile, pristine Ni₂P-textile, PEI/Ni₂P-textile, and conventional IrO₂-coated NF at diverse current densities.

Electrode	η_{10}	η_{100}	$\eta_{1,000}$	$\eta_{2,000}$	$\eta_{3,000}$	$\eta_{4,000}$
	(mV)	(mV)	(mV)	(mV)	(mV)	(mV)
TREN/Ni₂P	180	268	300	302	310	313
Ni ₂ P	220	302	397	448	-	-
PEI/Ni ₂ P	244	310	420	540	-	-
IrO ₂ NF	258	335	546	-	-	-

Table S10. The comparison of OER catalysts mass loading.

Catalyst	Ni ₂ P	TREN/Ni ₂ P	PEI/Ni ₂ P
Mass loading (mg cm ⁻²)	3.51	3.63	3.99

Table S11. The overall water splitting performance comparison of TREN/NiP₂ || TREN/Ni₂P, NiP₂ || Ni₂P, the PEI/NiP₂ || PEI/Ni₂P, and the conventional Pt/C-coated NF || IrO₂-coated NF-based devices at diverse current densities.

Electrode	Cell voltage (V)					
	10 mA cm ⁻²	100 mA cm ⁻²	1000 mA cm ⁻²	2000 mA cm ⁻²	3000 mA cm ⁻²	4000 mA cm ⁻²
TREN/NiP₂ TREN/Ni₂P	1.48	1.65	1.81	1.88	1.93	1.98
NiP ₂ Ni ₂ P	1.56	1.71	1.94	2.12	-	-
PEI/NiP ₂ PEI/Ni ₂ P	1.59	1.73	2.11	2.35	-	-
Pt/C NF IrO ₂ NF	1.60	1.81	2.64	-	-	-

Table S12. Performance comparison of metal phosphide-based bifunctional water splitting electrodes.

Bifunctional electrodes	Voltage (V) at 10 mA cm ⁻²	Reference
TREN/NiP ₂ TREN Ni ₂ P	1.48	Our work
MoS ₂ /NiPS ₃ /Glassy Carbon MoS ₂ /NiPS ₃ /Glassy Carbon	1.64	[S13]
Cu ₃ P/Ni ₂ P/Cu foam Cu ₃ P/Ni ₂ P/Cu foam	1.56	[S16]
NiP ₂ /NiSe/Carbon fiber NiP ₂ /NiSe/Carbon fiber	1.56	[S23]
Fe-CoP NF Fe-CoP NF	1.65	[S24]
Mn-Ni ₂ P/Fe ₂ P NF Mn-Ni ₂ P/Fe ₂ P NF	1.55	[S25]
CoP _x Carbon Paper CoP _x Carbon Paper	1.60	[S26]

Table S13. ICP-OES data of electrolyte (1 M KOH) after stability test.

TREN/NiP₂ TREN/Ni₂P	
Cu	Not detected
Ni	Not detected
P	Not detected

Table S14. Stability comparison of metal phosphide-based bifunctional water splitting electrodes.

Bifunctional electrodes	Stability (h)	Reference
TREN/NiP₂ TREN Ni₂P	>3200 h @ 1000,4000 mA cm⁻²	Our work
(Mn-(Co,Ni) ₂ P/CoP/(N,S)-C)/NF (Mn-(Co,Ni) ₂ P/CoP/(N,S)-C)/NF	50 h @ 100 mA cm ⁻²	[S11]
Co@CoFe-P NB ^{a)} /Glassy Carbon Co@CoFe-P NB/Glassy Carbon	220 h @ 100 mA cm ⁻²	[S12]
MoS ₂ /NiPS ₃ /Glassy Carbon MoS ₂ /NiPS ₃ /Glassy Carbon	100 h @ 10 mA cm ⁻²	[S13]
Cu ₃ P/Ni ₂ P/Cu foam Cu ₃ P/Ni ₂ P/Cu foam	85 h @ 500 mA cm ⁻²	[S16]
CoP/N, P-CNT/Carbon textile CoP/N, P-CNT/Carbon textile	72 h @ 20 mA cm ⁻²	[S17]
Zn-Ni ₂ P/FeOOH/NF Zn-Ni ₂ P/FeOOH/NF	50 h @ 15 mA cm ⁻²	[S18]
NiP ₂ /NiSe/Carbon fiber NiP ₂ /NiSe/Carbon fiber	30 h @ 10 mA cm ⁻²	[S23]
NiCoP/NF NiCoP/NF	600 h @ 1000 mA cm ⁻²	[S27]
Fe-NiCoP/NF Fe-NiCoP/NF	200 h @ 1000 mA cm ⁻²	[S28]
Ni _{0.96} Co _{0.04} P/NF Ni _{0.96} Co _{0.04} P/NF	500 h @ 500 mA cm ⁻²	[S29]
Fe-Ni ₅ P ₄ /NF Fe-Ni ₅ P ₄ /NF	2700 h @ 500 mA cm ⁻²	[S30]

a) NB : nanoboxes

References

- [S1] O. P. Watts, Rapid Nickel Plating, *Trans. Am. Electrochem. Soc.* 29 (1916) 395-403.
- [S2] J. Yin, Y. Li, F. Lv, Q. Fan, Y.-Q. Zhao, Q. Zhang, W. Wang, F. Cheng, P. Xi, S. Guo, NiO/CoN Porous Nanowires as Efficient Bifunctional Catalysts for Zn–Air Batteries, *ACS Nano* 11 (2017) 2275-2283. <https://doi.org/10.1021/acsnano.7b00417>.
- [S3] K. K. Kanazawa, J. G. Gordon, II. Frequency of a Quartz Microbalance in Contact with Liquid. *Anal. Chem.* (Wash. DC) 57 (1985) 1770-1771.
- [S4] S. Zhao, J. Huang, Y. Liu, J. Shen, H. Wang, X. Yang, Y. Zhu, C. Li, Multimetallic Ni–Mo/Cu nanowires as nonprecious and efficient full water splitting catalyst, *J. Mater. Chem. A* 5 (2017) 4207-4214. <https://doi.org/10.1039/C6TA10749D>.
- [S5] G. Kresse, J. Furthmüller, Efficiency of ab-initio total energy calculations for metals and semiconductors using a plane-wave basis set, *Comput. Mater. Sci.* 6 (1996) 15-50. [https://doi.org/10.1016/0927-0256\(96\)00008-0](https://doi.org/10.1016/0927-0256(96)00008-0).
- [S6] P. E. Blöchl, Projector augmented-wave method, *Phys. Rev. B.* 50 (1994) 17953-17979. <https://doi.org/10.1103/PhysRevB.50.17953>.
- [S7] J. P. Perdew, K. Burke, M. Ernzerhof, Generalized Gradient Approximation Made Simple, *Phys. Rev. Lett.* 77 (1996) 3865-3868. <https://doi.org/10.1103/PhysRevLett.77.3865>.
- [S8] S. Grimme, Semiempirical GGA-type density functional constructed with a long-range dispersion correction, *J. Comput. Chem.* 27 (2006) 1787-1799. <https://doi.org/10.1002/jcc.20495>.
- [S9] A. Hjorth Larsen, J. Jørgen Mortensen, J. Blomqvist, I. E Castelli, R. Christensen, M. Dułak, J. Friis, M. N Groves, B. Hammer, C. Hargus et al., The atomic simulation environment—a Python library for working with atoms, *J. Phys: Condes. Matter.* 29 (2017) 273002. <https://doi.org/10.1088/1361-648X/aa680e>.

- [S10] V. L. Deringer, A. L. Tchougréeff, R. Dronskowski, Crystal Orbital Hamilton Population (COHP) Analysis As Projected from Plane-Wave Basis Sets, *J. Phys. Chem. A* 115 (2011) 5461-5466. <https://doi.org/10.1021/jp202489s>.
- [S11] M. R. Kandel, U. N. Pan, P. P. Dhakal, R. B. Ghising, S. Sidra, D. H. Kim, N. H. Kim, J. H. Lee, Manganese-Doped Bimetallic (Co,Ni)₂P Integrated CoP in N,S Co-Doped Carbon: Unveiling a Compatible Hybrid Electrocatalyst for Overall Water Splitting, *Small* 20 (2024) 230724. <https://doi.org/10.1002/sml.202307241>.
- [S12] Y. Zhao, N. Dongfang, C. A. Triana, C. Huang, R. Erni, W. Wan, J. Li, D. Stoian, L. Pan P. Zhang et al., Dynamics and control of active sites in hierarchically nanostructured cobalt phosphide/chalcogenide-based electrocatalysts for water splitting, *Energy Environ. Sci.* 15 (2022) 727-739. <https://doi.org/10.1039/D1EE02249K>.
- [S13] Y. Liu, Y. Chen, Y. Tian, T. Sakthivel, H. Liu, S. Guo, H. Zeng, Z. Dai, Synergizing Hydrogen Spillover and Deprotonation by the Internal Polarization Field in a MoS₂/NiPS₃ Vertical Heterostructure for Boosted Water Electrolysis, *Adv. Mater.* 34 (2022) 2203615. <https://doi.org/10.1002/adma.202203615>.
- [S14] X. Cao, J. Tian, Y. Tan, Y. Zhu, J. Hu Y. Wang, E. Liu, Z. Chen, Interfacial Electron Potential Well Facilitates the Design of Cobalt Phosphide Heterojunctions for Hydrogen Evolution. *Small* 20 (2024) 2306113. <https://doi.org/10.1002/sml.202306113>.
- [S15] S. Zhao, S. Ran, N. Shi, M. Liu, W. Sun, Y. Yu, Z. Zhu, Structural Design Induced Electronic Optimization in Single-Phase MoCoP Nanocrystal for Boosting Oxygen Reduction, Oxygen Evolution, and Hydrogen Evolution. *Small* 19 (2023) 2302414. <https://doi.org/10.1002/sml.202302414>.
- [S16] H. Liu, J. Gao, X. Xu, Q. Jia, L. Yang, S. Wang, D. Cao, Oriented construction Cu₃P and Ni₂P heterojunction to boost overall water splitting. *Chem. Eng. J.* 448 (2022) 137706. <https://doi.org/10.1016/j.cej.2022.137706>.

- [S17] D. Kong, Q. Xu, N. Chu, H. Wang, Y. V. Lim, J. Cheng, S. Huang, T. Xu, X. Li, Y. Wang et al., Rational Construction of 3D Self-Supported MOF-Derived Cobalt Phosphide-Based Hollow Nanowall Arrays for Efficient Overall Water Splitting At large Current Density, Small 20 (2024) 2310012. <https://doi.org/10.1002/sml.202310012>.
- [S18] J. Nie, J. Shi, T. Huang, M.-Y. Xie, Z.-Y. Ouyang, M.-H. Xian, G.-F. Huang, H. Wan, W. Hu, W.-Q. Huang et al., Cation-Induced Deep Reconstruction and Self-Optimization of NiFe Phosphide Precatalysts for Hydrogen Evolution and Overall Water Splitting. Adv. Funct. Mater. 34 (2024) 2314172. <https://doi.org/10.1002/adfm.202314172>.
- [S19] M. Jiang, H. Zhai, L. Chen, L. Mei, P. Tan, K. Yang, J. Pan, Unraveling the Synergistic Mechanism of Bi-Functional Nickel–Iron Phosphides Catalysts for Overall Water Splitting, Adv. Funct. Mater. 33 (2023) 2302621. <https://doi.org/10.1002/adfm.202302621>
- [S20] F.-C. Pan, H. He, Z.-X. Yang, Q. Zheng, D. Lin, Y. Huo, Rationally designed Ni₂P/WS₂/Co₉S₈@C multi-interfacial electrocatalyst for efficient overall water splitting. Chem. Eng. J. 446 (2022) 136961. <https://doi.org/10.1016/j.cej.2022.136961>.
- [S21] L. Li, L. Zhang, Z. Nie, W. Ma, N. Li, T. Wågberg, G. Hu, Tailoring charge reconfiguration in dodecahedral Co₂P@carbon nanohybrids by triple-doping engineering for promoted reversible oxygen catalysis. J. Mater. Chem. A 10 (2022) 21659-21671. <https://doi.org/10.1039/D2TA04482J>.
- [S22] Z. Lv, H. Zhang, C. Liu, S. Li, J. Song, J. He, Oxygen-Bridged Cobalt–Chromium Atomic Pair in MOF-Derived Cobalt Phosphide Networks as Efficient Active Sites Enabling Synergistic Electrocatalytic Water Splitting in Alkaline Media, Adv. Sci. 11 (2024) 2306678. <https://doi.org/10.1002/advs.202306678>.

- [S23] L. Yang, L. Huang, Y. Yao, L. Jiao, In-situ construction of lattice-matching NiP₂/NiSe₂ heterointerfaces with electron redistribution for boosting overall water splitting, Appl. Catal. B: Environ. 282 (2021) 119584. <https://doi.org/10.1016/j.apcatb.2020.119584>.
- [S24] Y. Yuan, K. Wang, B. Zhong, D. Yu, F. Ye, J. Liu, J. Dutta, P. Zhang, MOF-Derived Iron-Cobalt Phosphide Nanoframe as Bifunctional Electrocatalysts for Overall Water Splitting, Energy Environ. Mater. 7, (2024) e12747. <https://doi.org/10.1002/eam2.12747>.
- [S25] Y. Luo, P. Wang, G. Zhang, S. Wu, Z. Chen, H. Ranganathan, S. Sun, Z. Shi, Mn-doped nickel-iron phosphide heterointerface nanoflowers for efficient alkaline freshwater/seawater splitting at high current densities. Chem. Eng. J. 454 (2023) 140061. <https://doi.org/10.1016/j.cej.2022.140061>.
- [S26] W. Zhang, N. Han, J. Luo, X. Han, S. Feng, W. Guo, S. Xie, Z. Zhou, P. Subramanian, K. Wan et al., Critical Role of Phosphorus in Hollow Structures Cobalt-Based Phosphides as Bifunctional Catalysts for Water Splitting, Small 18 (2022) 2103561. <https://doi.org/10.1002/sml.202103561>.
- [S27] D. Chen, H. Bai, J. Zhu, C. Wu, H. Zhao, D. Wu, J. jiao, P. ji, S. Mu, Multiscale Hierarchical Structured NiCoP Enabling Ampere-Level Water Splitting for Multi-Scenarios Green Energy-to-Hydrogen Systems, Adv. Energy Mater. 13 (2023) 2300499. <https://doi.org/10.1002/aenm.202300499>.
- [S28] X. Wang, Z. Wang, B. Jia, C. Li, S. Sun, S. Hu, Concerted proton-coupled electron transfer promotes NiCoP nanowire arrays for efficient overall water splitting at industrial-level current density. Chem. Eng. J. 479 (2024) 147450. <https://doi.org/10.1016/j.cej.2023.147450>.
- [S29] X. Lv, S. Wan, T. Mou, X. Han, Y. Zhang, Z. Wang, X. Tao, Atomic-Level Surface Engineering of Nickel Phosphide Nanoarrays for Efficient Electrocatalytic Water

Splitting at Large Current Density, *Adv. Funct. Mater.* 33 (2023) 2205161.
<https://doi.org/10.1002/adfm.202205161>.

- [S30] Y. Long, P. Jiang, P. Liao, C. Yang, S. Li, J. Xian, Y. Sun, Q. Liu, G. Li, Electronic Structure Regulation by Fe Doped Ni-Phosphides for Long-term Overall Water Splitting at Large Current Density, *Small* 20 (2024) 2403991.
<https://doi.org/10.1002/sml.202403991>.