



Supporting Information

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Stoichiometric Control of Electrocatalytic Amorphous Nickel Phosphide to Increase Hydrogen Evolution Reaction Activity and Stability in Acidic Medium

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1. Experimental Procedure

Chemicals used

NiCl₂•6H₂O (Fisher chemical, lot #926817); NiSO₄•6H₂O (Fisher chemical, lot #034155); NaH₂PO₂ (Sigma-Aldrich, SKU 243663); NH₄Cl (Sigma-Aldrich); Na₃C₆H₅O₇•2H₂O (Fischer chemical, lot #132789); NH₄OH (Fisher chemical, lot #106935); H₃BO₃ (99.8%, Baker and Adamson); K₂PtCl₆ (Matheson Coleman and Bell, PX1415); HClO₄ (ACS reagent, 70%, Sigma-Aldrich, Batch #08496AP); H₂SO₄ (ACS, 95.0 - 98.0%, Alfa-Aesar, stock #33273); Nafion perfluorinated ion-exchange powder (5 wt% solution in a mixture of lower aliphatic alcohols and water, lot #EN02015PG); Lab distilled water.

Electrodeposition of thin films

All of the electrodepositions were performed in a conventional one-compartment two-electrode system, using a 2 cm width x 5 cm length Cu sheet as the working electrode and a Pt mesh as a counter electrode, with a working distance of 1 cm. Prior to electrodepositions, the Cu substrates were mechanically polished to a mirror finish using P320 sandpapers, followed by sonication in a 1:1 ethanol:water mixture (SHARPERTEK ultrasonic cleaner SH80) for 20 minutes. The Cu substrates were washed again with de-ionized water before use. The area for electrodepositions was 2 cm X 2.5 cm on each side by submersing half the length of the substrate, and a HY1802D DC power supply was used to provide 10 mA cm⁻² cathodic current density for 10 minutes. After the electrodeposition, the films were well washed with de-ionized water. Electrodepositions were performed under ambient conditions (21 ± 1 °C, atmospheric pressure), unless otherwise specified.

Nickel phosphide thin films were electrodeposited using a Brenner type alkaline nickel phosphide electroplating bath (denoted as Ni-P (Brenner)), which is an aqueous solution containing NiCl₂•6H₂O (30 g/L), NaH₂PO₂ (10 g/L), NH₄Cl (50 g/L), Na₃C₆H₅O₇•2H₂O (100 g/L) and NH₄OH (to obtain pH 8-9).^[1] All of the chemicals were used as received without further purification. To investigate the effect of the concentration of NaH₂PO₂ in the electroplating bath, five different modified Brenner solutions were prepared by increasing the amount of NaH₂PO₂ to 20 g/L, 30 g/L, 40 g/L and 50 g/L. The effect of deposition temperature was investigated by electrodepositing Ni-P at varied temperatures of 3 °C, 10 °C, 21 °C (room temperature), 50 °C, and 75 °C. The current density for Ni-P electrodeposition was optimized analyzing the HER catalytic activity of the films made at varied deposition current densities of 2 mA cm⁻², 5 mA cm⁻²

², 10 mA cm⁻², 15 mA cm⁻², and 20 mA cm⁻². Later, optimized Ni-P (Brenner) films (denoted as Ni-P (Brenner: Opt.)) were prepared using the Ni-P (Brenner: NaH₂PO₂: 50 g/L) electroplating bath, with a deposition current density of 10 mA cm⁻² at 3 °C, which were found to be the optimized parameters for Ni-P (Brenner). For comparison, a different type of Ni-P film was prepared using the acidic electroplating bath (denoted as Ni-P (Acidic Bath)), as has been previously used in the literature as a HER catalyst in alkaline medium.^[2] This Ni-P (Acidic Bath) electrolyte consists of NiSO₄•6H₂O (26 g/L), NaH₂PO₂ (26 g/L), H₃BO₃ (9.3 g/L), NH₄Cl (5 g/L) and has a pH of ~ 3-4. Optimized films from the Ni-P (Acidic bath) electrolyte were also prepared (denoted as Ni-P (Acidic Bath: Opt.)) using the same optimized conditions as for Ni-P (Brenner). This optimized bath was prepared by increasing the amount of NaH₂PO₂ in the electroplating bath to 50 g/L and leaving the other constituents unchanged. Electrodeposition was carried out using 10 mA cm⁻² current density at 3 °C.

To compare the catalytic activity of the Ni-P films with Pt and Ni, thin films of these metals were also electrodeposited onto Cu substrates, based on methods reported in the literature. Platinum black films were electrodeposited using an aqueous solution of 2 mM K₂PtCl₆ and 0.1 M HClO₄.^[3] The electroplating bath was deoxygenated by purging the solution with dinitrogen (N₂, industrial grade). Electrodeposition was carried-out under a constant current density of 10 mA cm⁻² for 20 min, under N₂ environment. For electrodeposition of Ni, a Watts type electroplating bath (denoted as Ni(Watts)) consisted of NiSO₄•6H₂O (270 g/L), NiCl₂•6H₂O (90 g/L) and H₃BO₃ (45 g/L) was used.^[4]

The activity of electrodeposited Ni-P films was also compared to Ni₂P, which has been reported as a HER catalyst. For this, Ni₂P powder (100 mesh) was purchased from Sigma-Aldrich, and an ink was prepared by mixing 160 mg of Ni₂P, 5 wt% Nafion (120 μL), ethanol (1.08 mL) and water (800 μL), followed by sonicating for 30 minutes to obtain a homogeneous ink. This ink was painted onto a clean polished Cu foil to yield a ~ 10 mg cm⁻² loading of Ni₂P, and dried under room temperature.

Electrochemical measurements for investigating HER

Electrochemical measurements were performed using a conventional one-compartment three electrode system. A Pt mesh electrode and a Ag/AgCl (3 M NaCl) electrode (BASi, MF-2020) (0.209 V) were used as the auxiliary and reference electrodes, respectively. The reference electrode

was stored in 3 M NaCl, when not in use. The electrolyte for the investigation of the HER was an aqueous solution of 0.5 M H₂SO₄. All of the measurements were performed under normal atmospheric conditions. A Bioanalytical Systems (BAS, West Lafayette, IN) Epsilon-EC electrochemical analyzer was used for all of the electrochemical measurements related to the HER. Linear sweep voltammetry (LSV) and cyclic voltammetry (CV) are two techniques used to investigate the HER activity. Prior to obtaining the polarization plots, the electrocatalysts were activated by cycling through -0.150 to -0.500 V vs Ag/AgCl (3 M NaCl), for 20 cycles with a 100 mV s⁻¹ scan rate, until a stable voltammogram was obtained. The polarization plots were achieved by linearly scanning through -0.2 to -0.7 V vs Ag/AgCl (3 M NaCl), under diffusion controlled conditions with a scan rate of 5 mV s⁻¹. All of the experiments were repeated with a minimum of three samples. The potentials reported in this study are not corrected for *iR* compensation. Distance between the reference electrode and the working electrode was 3 mm.

Maintaining a constant electrochemical surface area is difficult when the working electrode is a flat electrode directly immersed in the electrolyte. One reason is that the edges behave differently than the faces of the electrodes in an electron transfer process, leading to a non-uniform electron transfer. Another reason is the electrolyte solution wicking above the air-electrolyte interface, leading the actual surface area that undergoes electrolysis to become larger. An insulating coating, such as epoxy, could be used to define the surface area, but under the conditions, the epoxy tends to peel off during the electrolysis. A solution to these problems uses a simple O-ring apparatus (Figure S1A and S1B). An O-ring seals the working electrode well enough so there is no leakage of the electrolyte, and the O-ring provides a well-defined and consistent geometric surface area. This also avoids the effect of the edges to the electron transfer, hence a uniform electron transfer process can be achieved. However, one limitation is that the electrolysis experiments cannot be carried out under stirred conditions due to the difficulty in using a magnetic stir bar without affecting the working electrode. Therefore, all of the electrolysis experiments in this study were carried out under non-stirred (diffusion controlled) conditions. In all measurements, the potentials are reported versus Reversible Hydrogen Electrode (RHE), by converting the measured potentials according to the following equation.^[5]

$$E(\text{RHE}) = E_{\text{measured}}(\text{vs Ag/AgCl}(3 \text{ M NaCl})) + 0.059 \text{ pH} + 0.209 \text{ V}$$

The generated gases were collected separately using a custom-built apparatus (Figure S2A and S2B). The apparatus was made as a U-shaped cell collecting dioxygen (O₂) and H₂ gases in situ, without mixing. Gases were collected while passing a current of 85.4 mA through the working electrode for 20 minutes. The theoretical volume of H₂ was calculated based on the cumulative charge assuming 100% Faradaic efficiency for H₂ production.

Characterization of the Ni-P films

The morphology and the average composition of electrodeposited Ni-P films were characterized using a JEOL JSM-7500F scanning electron microscope (SEM) with a BRUKER XFlash 5010 series energy dispersive X-ray spectroscopy (EDX) detector, in the Instrumentation Center at the University of Toledo (UT). Powder X-ray diffraction data were collected using a PANalytical X'Pert Pro diffractometer with an X'celerator detector or a Xe Proportional detector, in the Instrumentation Center at UT. X-ray photoelectron spectroscopy (XPS) analysis was performed on both Ni-P (Brenner) and Ni-P (Acidic Bath), using Kratos Axis Ultra X-ray photoelectron spectrometer with a monochromated Al K α as the excitation source, in the EMAL facility at the University of Michigan. X-ray photoelectron spectra of the Ni 2p and P 2p regions were used to examine the chemical states of Ni and P on the surface of as-deposited films and after 5000 cyclic voltammetric sweeps in 0.5 M H₂SO₄. The spectra were calibrated relative to C 1s peak by setting it to be 285.00 eV. All of the 2p peaks were fitted using Shirley background model.

Investigation of the amount of nickel leached into the electrolyte during 5000 CV sweeps of electrolysis

Amount of Ni in the electrolyte was investigated by atomic absorption spectroscopy (AAS), with a Perkin Elmer 5100 PC Atomic Absorption Spectrophotometer. A detailed experimental procedure can be found in the supporting information.

2. Apparatus for electrolysis experiments

Electrolysis experiments on the electrodeposited films were carried-out using an O-ring apparatus, as indicated in Figure S1A and S1B. The O-ring seals a defined surface area on the working electrode and it avoids the effects from the edges to the electron transfer process.

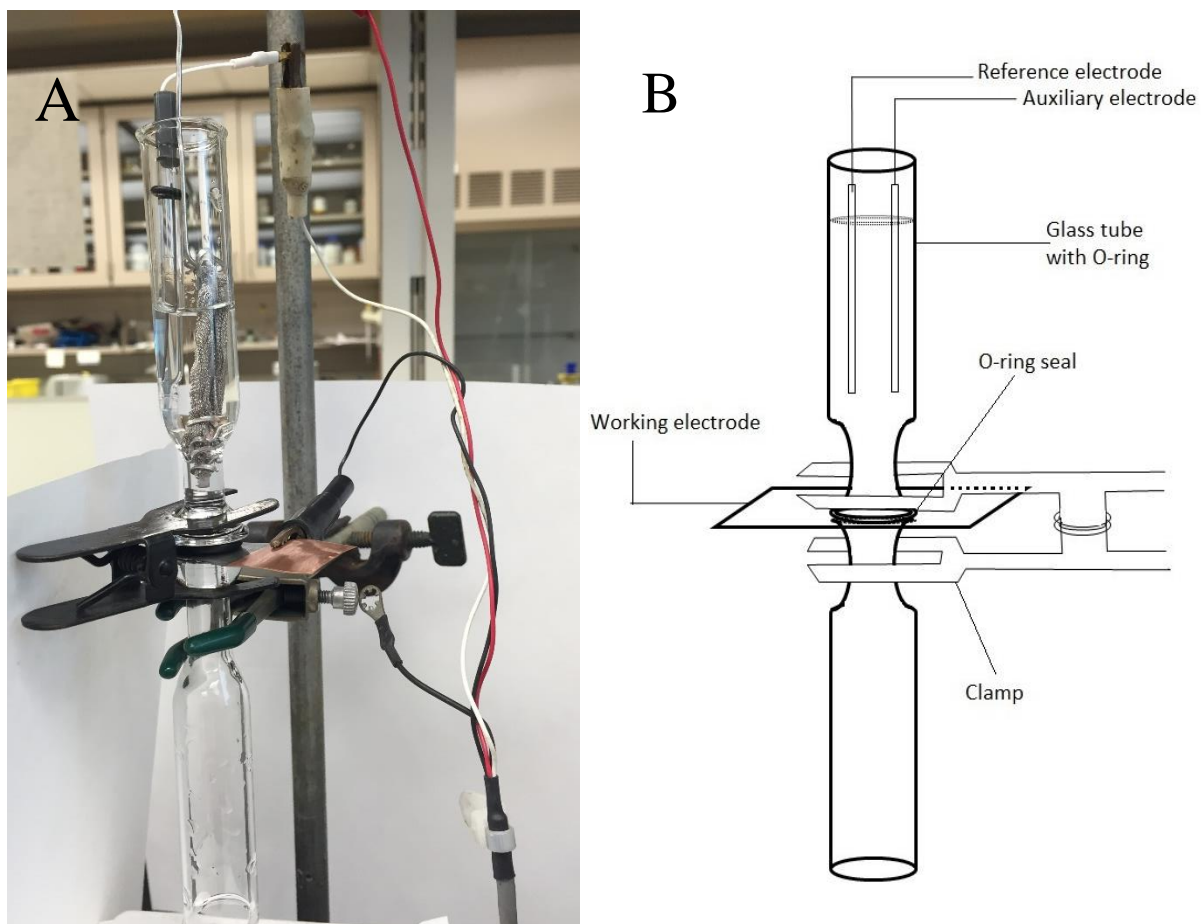


Figure S1. (A) An image and (B) a schematic of the O-ring set-up used for electrolysis experiments.

3. Apparatus for gas collection experiments

A custom-built gas collection apparatus, as illustrated in Figure S2A and S2B was used to evaluate the Faradaic efficiency of the electrodeposited Ni-P (Brenner) films. The generated H_2 at the working electrode is collected in the H_2 collecting graduated cylinder, and to prevent mixing with the O_2 generated at the auxiliary electrode, O_2 is collected in the O_2 collecting graduated cylinder. Since the distance of working electrode to the reference and auxiliary electrodes is larger than that in the electrolysis set-up (Figure S1A), higher voltages are required in the apparatus of Figure S2A, than is required in the apparatus of Figure S1A to achieve the same amount of current density.

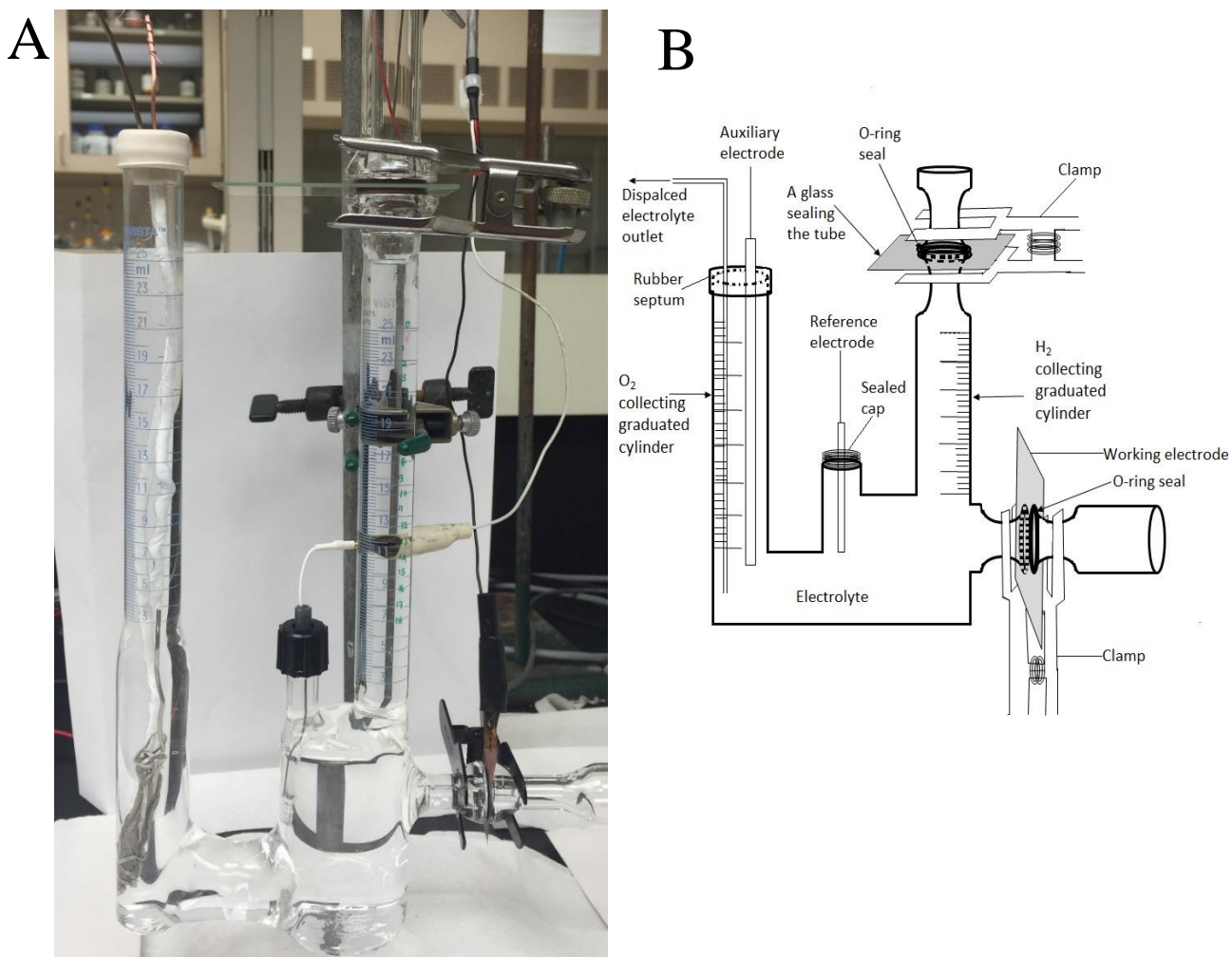


Figure S2. (A) An image and (B) a schematic of the gas collecting apparatus.

4. Energy Dispersive X-ray Spectra (EDX) of the as-deposited Ni-P films and the Ni-P films after 5000 CV sweeps of electrolysis in 0.5 M H₂SO₄

Energy dispersive X-ray spectroscopy of as-deposited Ni-P (Brenner), as-deposited Ni-P (Acidic bath), and the same two films after 5000 CV sweeps of electrolysis are contained in Figure S3, S5, S7 and S9, respectively. All four EDX spectra show the presence of Ni and P. The peak observed for Cu is from the substrate while the peak for O is from the phosphate on the surface as the samples were exposed to air. Other peak observed for C is a contamination from the carbon tape used to mount the samples on sample holder. Peaks for Al and Cl are small contaminations. Energy dispersive X-ray mapping of the four films are shown in Figure S4, S6, S8 and S8, which shows the distribution of both Ni and P is uniform over the film.

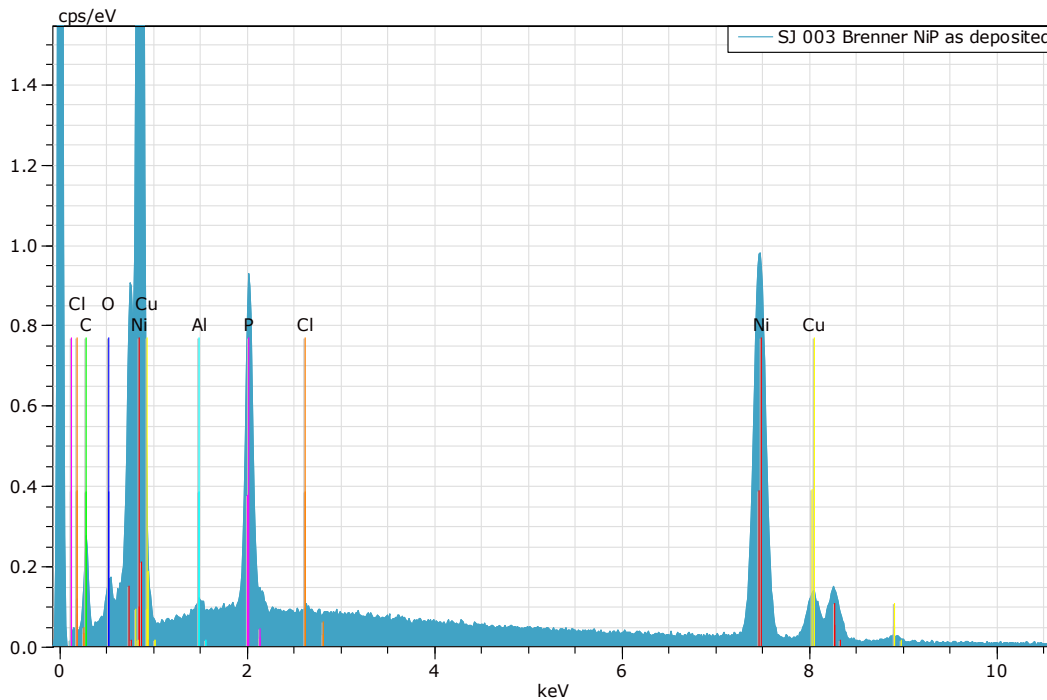


Figure S3. EDX spectra of as-deposited Ni-P (Brenner).

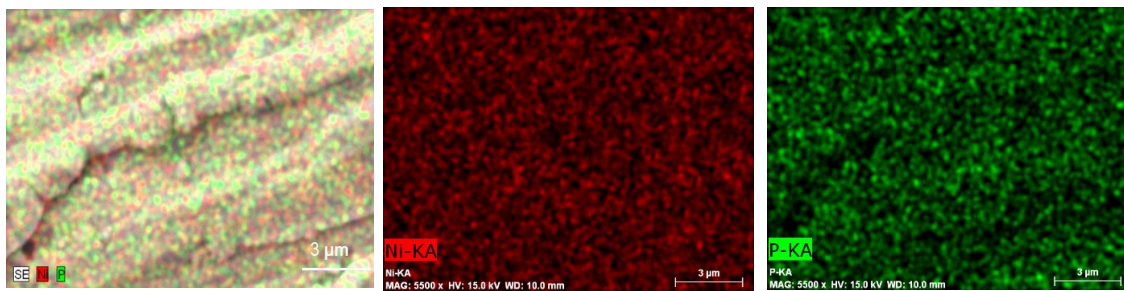


Figure S4. EDX mapping of as-deposited Ni-P (Brenner).

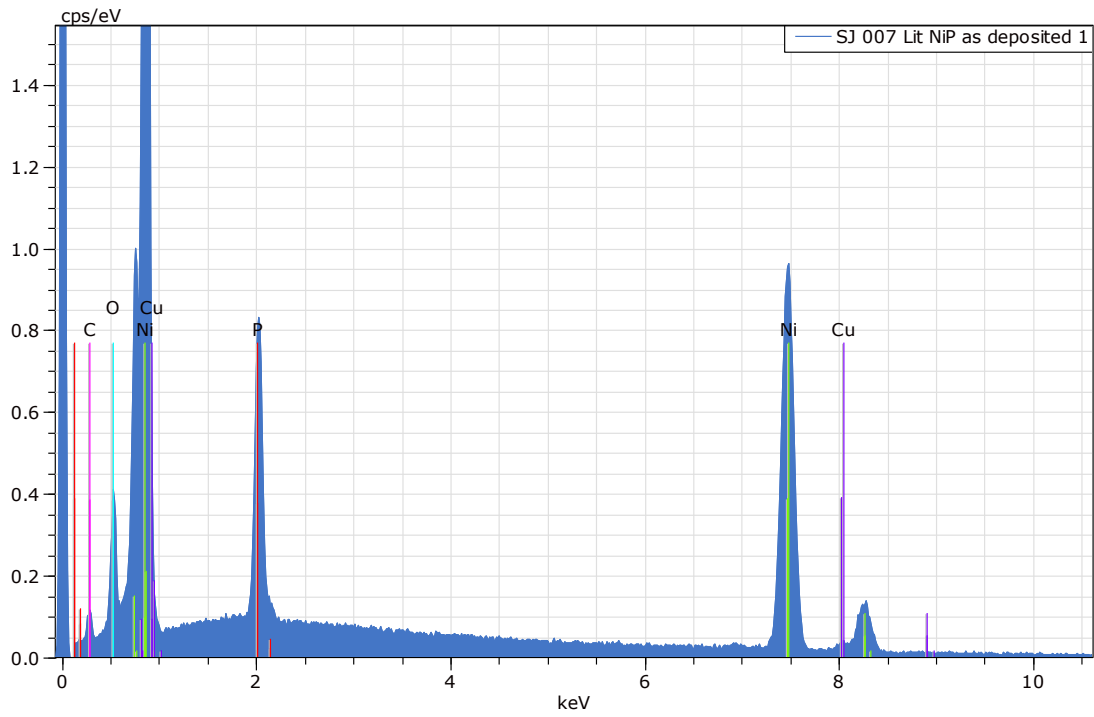


Figure S5. EDX spectra of as-deposited Ni-P (Acidic bath).

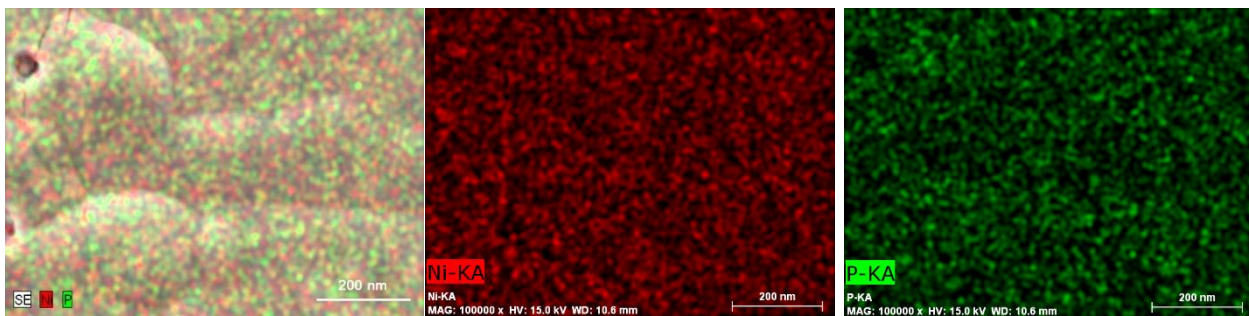


Figure S6. EDX mapping of as-deposited Ni-P (Acidic bath).

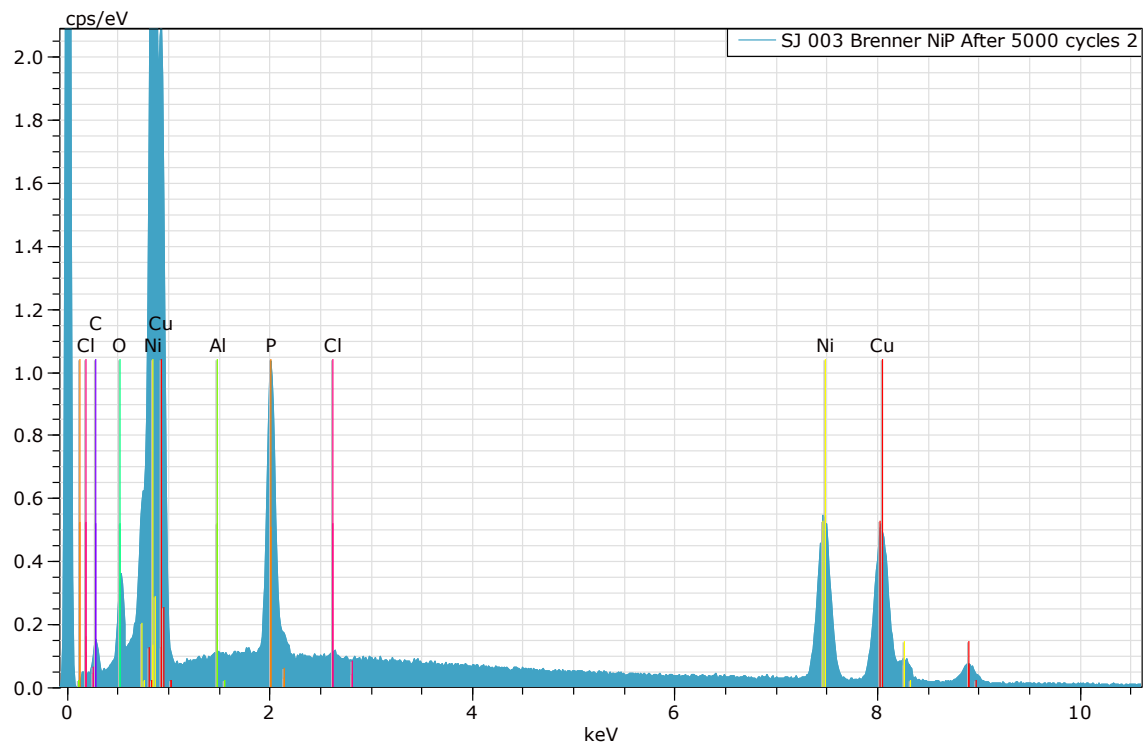


Figure S7. EDX spectra of Ni-P (Brenner) after 5000 CV sweeps of electrolysis.

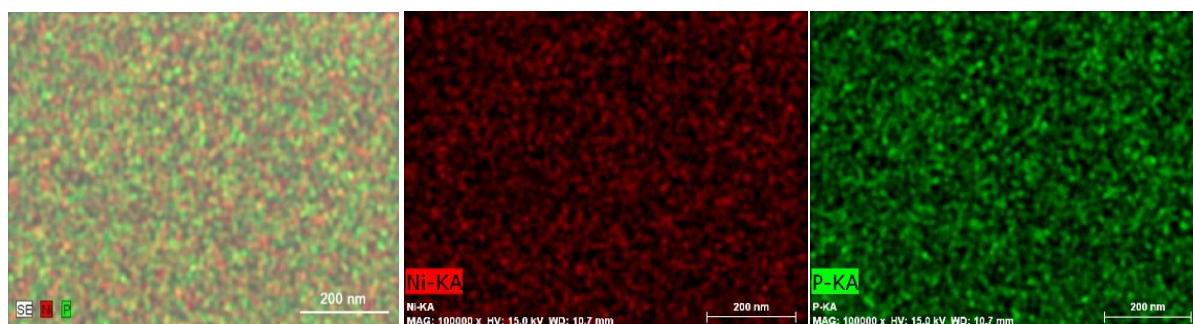


Figure S8. EDX mapping of Ni-P (Brenner) after 5000 CV sweeps of electrolysis.

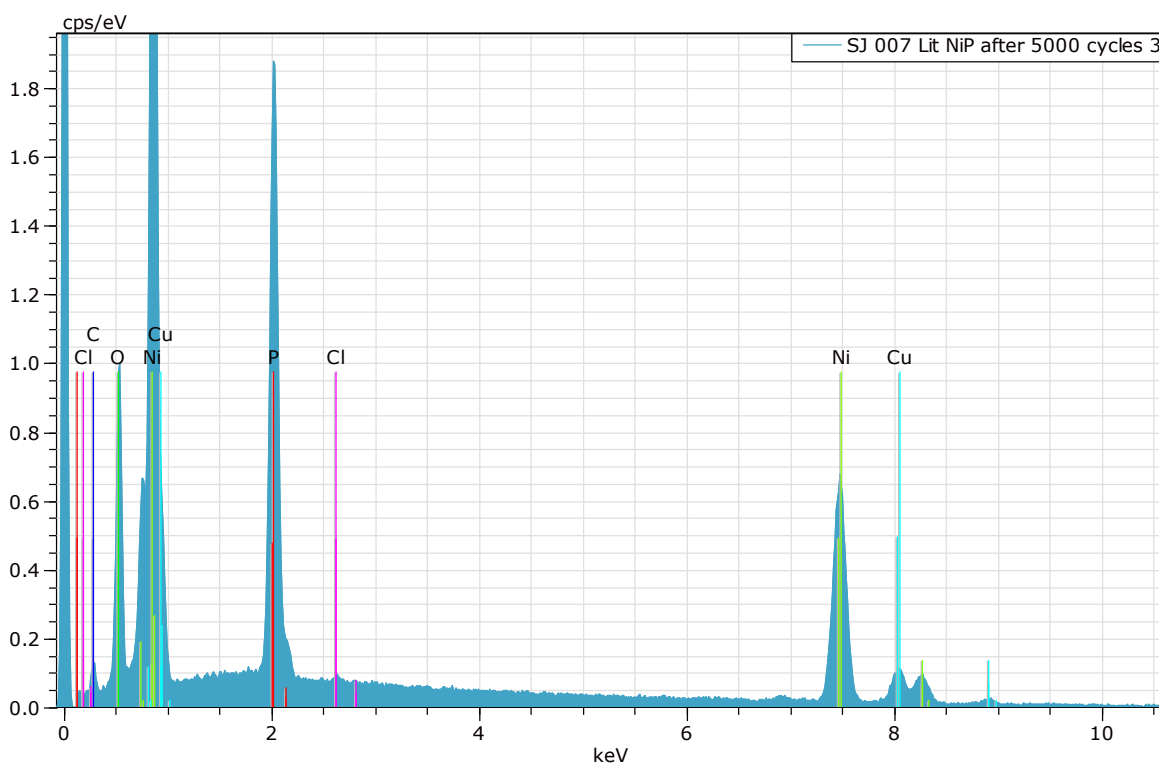


Figure S9. EDX spectra of Ni-P (Acidic bath) after 5000 CV sweeps of electrolysis.

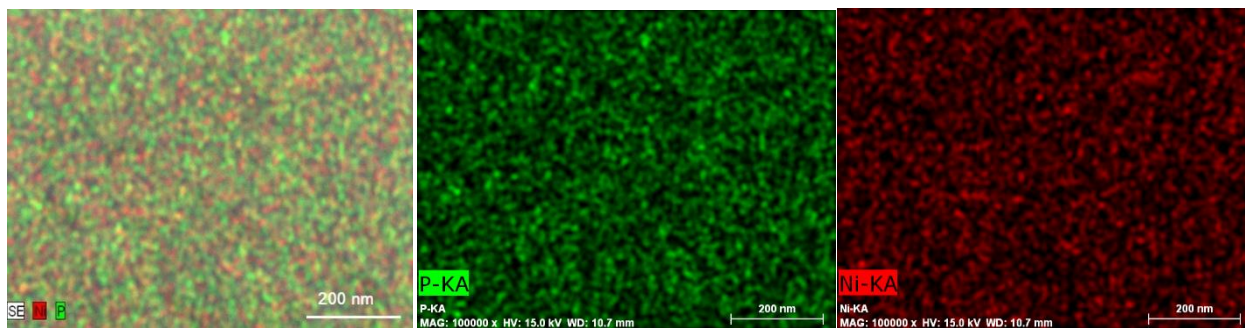


Figure S10. EDX mapping of Ni-P (Acidic bath) after 5000 CV sweeps of electrolysis.

5. Thickness of Ni-P(Brenner) and Ni-P (Acidic Bath) films

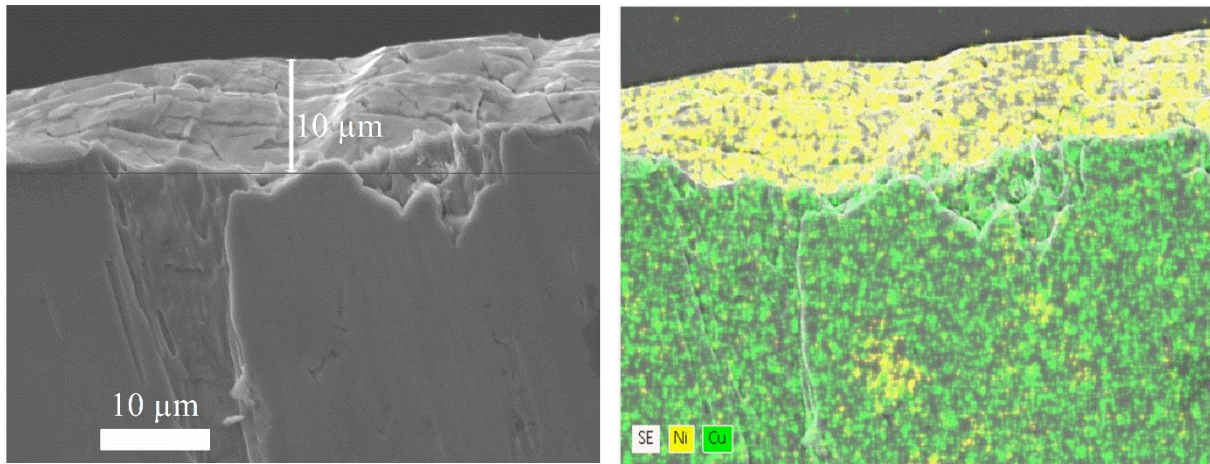


Figure S11. (a) SEM image of a cross section of Ni-P (Brenner), (b) corresponding EDX mapping

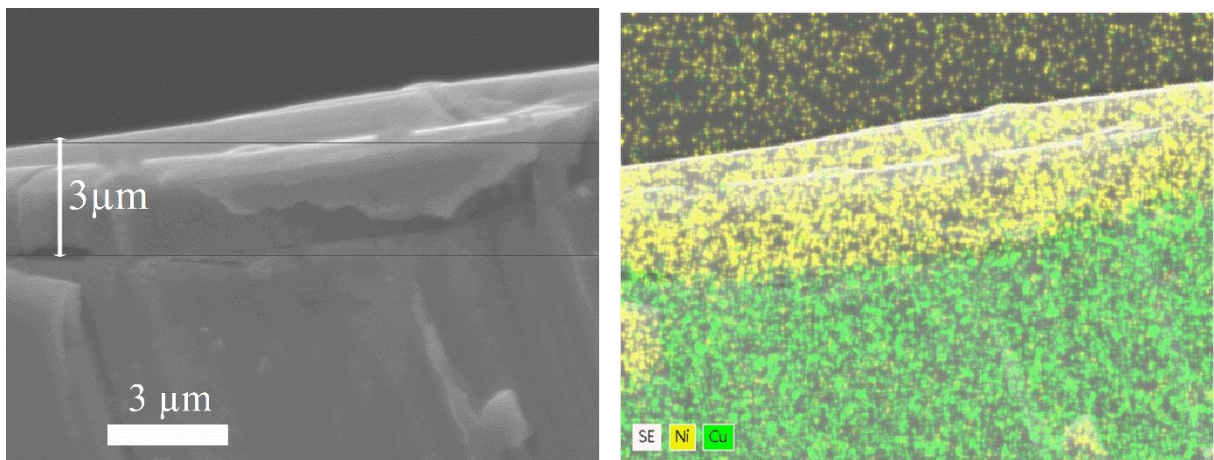


Figure S12. (A) SEM image of a cross section of Ni-P (Acidic Bath), (B) corresponding EDX mapping

6. Powder X-ray diffraction (PXRD) data for Ni-P films

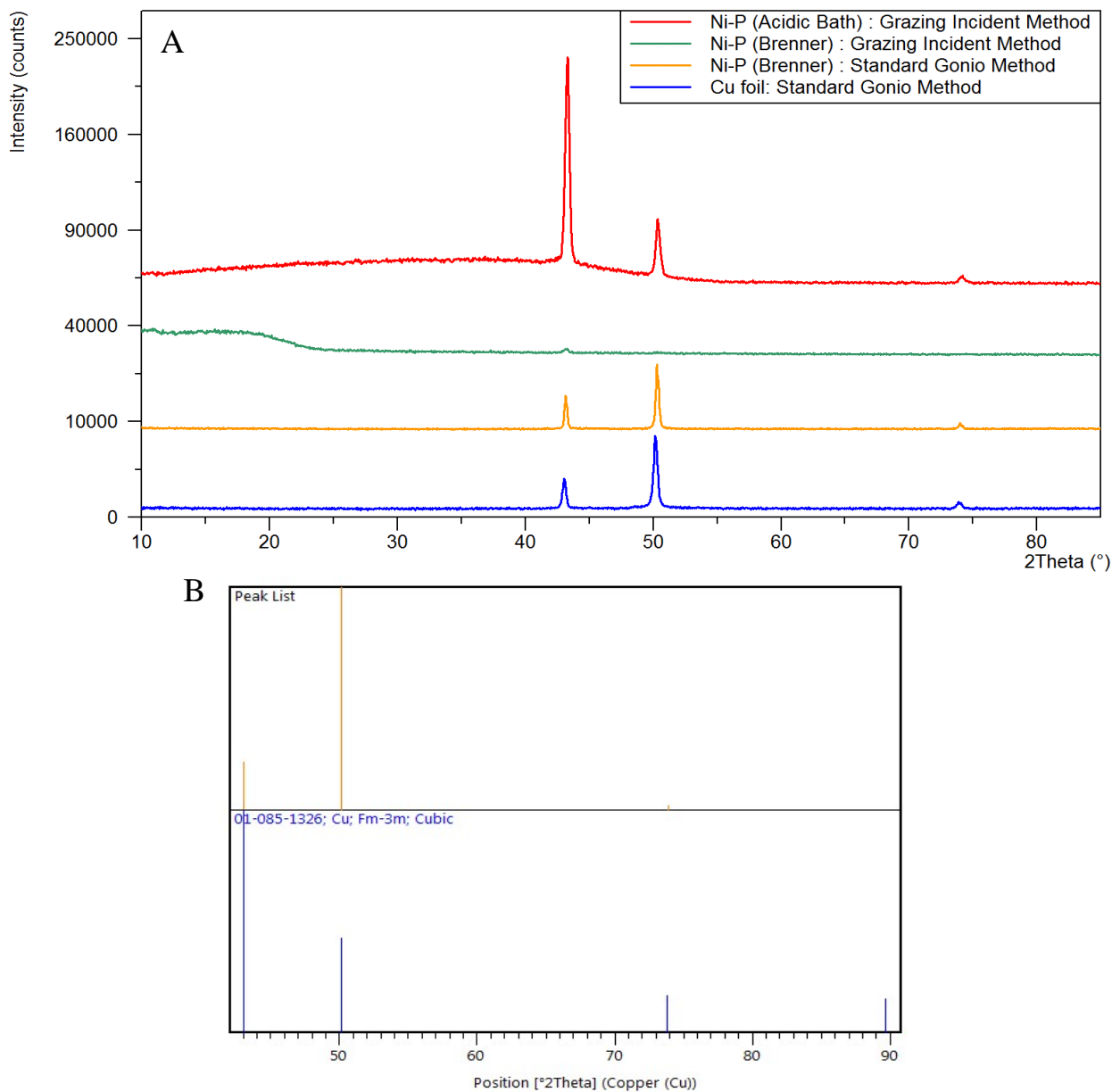


Figure S13. (A) Experimental PXRD pattern for Ni-P (Brenner), Ni-P (Acidic bath) and blank Cu foil. (B) Experimental powder diffraction pattern of Cu foil substrate compared to International Center for Diffraction data (ICDD: 01-085-1326) for pure copper.

Powder X-ray diffraction data were collected for both types of Ni-Ps and for the substrate Cu foil. Grazing incident method (GIXRD) was used for Ni-P films to analyze for any crystalline particles in the thin films of Ni-P. Since, the peaks in the powder pattern of Ni-P (Brenner) on Cu foil had

negligible intensity (which is probably due to higher thickness of the Ni-P film), standard goniometer method was used to enhance the substrate peaks. All of the peaks match with the peaks from the substrate Cu foil, and no peaks characteristic to Ni-P were observed.

7. Cyclic voltammogram of Ni-P (Brenner)

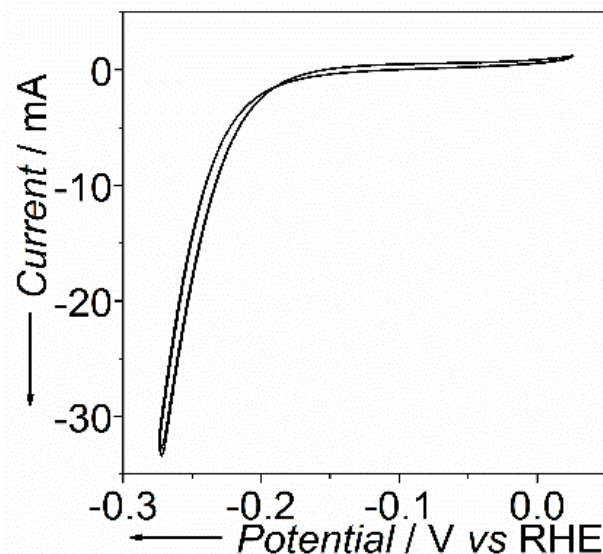


Figure S14. Cyclic voltammogram of Ni-P (Brenner) in 0.5 M H₂SO₄; scan rate is 100 mV s⁻¹.

8. Atomic Absorption Spectroscopic (AAS) determination of the amount of Ni leached during the electrolysis

Procedure: Both Ni-P (Brenner) and Ni-P (Acidic Bath) films were subjected to the electrolysis in 8.0 mL of 0.5 M H₂SO₄, by cycling 5000 CV sweeps from -150 mV to -500 mV vs Ag/AgCl (3 M NaCl). After 5000 CV sweeps, the electrolytes were quantitatively transferred to 25.00 mL volumetric flasks and diluted with DI water upto the mark, which was used as the analyte solution. Method of standard additions was performed in order to analyze the amount of Ni²⁺ in each electrolyte, with a 9.6 μg/mL Ni²⁺ solution as the standard solution. The standard solution was prepared via 2 step dilution procedure. First, 0.02409 g of Ni powder was digested in conc. HNO₃ and diluted upto 250.00 mL with DI water. Then, a 10.00 mL aliquate of the this solution was transferred to another 250.00 mL volumetric flas and diluted with DI water. Table S1 below indicates the amount of each solution added for making the sample solution series.

Table S1: Volume of each solution added for each sampling solution

Sample	Volume of electrolyte (analyte) / mL	Volume of standard Ni ²⁺ solution / mL	Volume of H ₂ O / mL
Unspiked	5.00	0.00	5.00
Spiked 1	5.00	1.00	4.00
Spiked 2	5.00	2.00	3.00
Spiked 3	5.00	3.00	2.00
Spiked 4	5.00	4.00	1.00

Analysis was performed under the conditions of 4 mA lamp current, acetylene fuel, 0.2 nm slit width and 232 nm wavelength (for 0.1 -10 µg/mL working range).

Calculation of the amount of Ni²⁺ in each analyte solution:

A: Absorbance

Munk: Concentration of Ni²⁺ in the electrolyte

Vstd: Volume of 9.6 µg/mL standard Ni²⁺ solution

$$A \propto \frac{(Munk * 5.00 \text{ mL}) + \left(9.6 \frac{\mu\text{g}}{\text{mL}} * Vstd\right)}{10.00 \text{ mL}}$$
$$A = k \frac{(Munk * 5.00 \text{ mL}) + \left(9.6 \frac{\mu\text{g}}{\text{mL}} * Vstd\right)}{10.00 \text{ mL}}$$
$$A = k \frac{\left(9.6 \frac{\mu\text{g}}{\text{mL}}\right)}{10.00 \text{ mL}} * Vstd + k Munk \frac{5.00 \text{ mL}}{10.00 \text{ mL}}$$

Absorbance values were plotted against the volume of standard to give a y = mx + b type plot, and the concentrations of Ni²⁺ in the electrolytes were calculated using the slope and y-intercept. The resulted graphs are contained in Figure S14A and S14B.

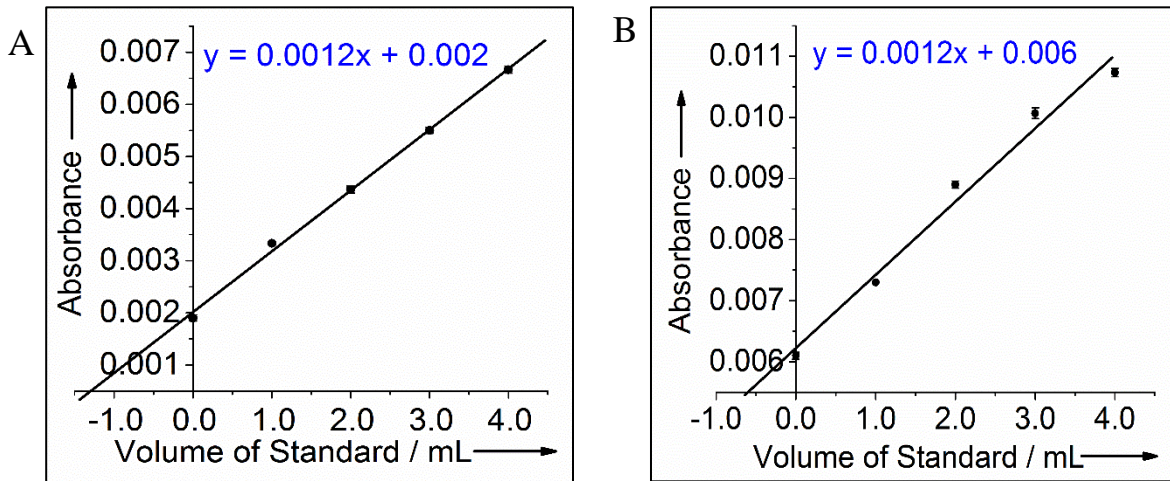


Figure S15. Graphs of absorbance vs volume of standard Ni²⁺ solution obtained for analyzing the dissolved Ni content in (A) Ni-P (Brenner) and (B) Ni-P (Acidic Bath) in 0.5 M H₂SO₄ during 5000 CV sweeps of electrolysis.

For both plots: Slope = 0.0012 mL⁻¹

$$\text{Slope} = 0.0012 \text{ mL}^{-1} = k \frac{\left(9.6 \frac{\mu\text{g}}{\text{mL}}\right)}{10.00 \text{ mL}}$$

$$k = \frac{0.012 \text{ mL}}{9.6 \mu\text{g}}$$

For the plot in Figure S14A (Ni-P (Brenner)):

$$y - \text{intercept} = 0.002 = k * Munk * \frac{5.00 \text{ mL}}{10.00 \text{ mL}}$$

$$Munk = 3.2 \frac{\mu\text{g}}{\text{mL}}$$

Size of the analyte solution = 25.00 mL

$$\text{Amount of Ni leached to the electrolyte} = 3.2 \frac{\mu\text{g}}{\text{mL}} * 25.00 \text{ mL} = 80 \mu\text{g}$$

For the plot in Figure S14B (Ni-P (Acidic Bath)):

$$y - \text{intercept} = 0.006 = k * Munk * \frac{5.00 \text{ mL}}{10.00 \text{ mL}}$$

$$Munk = 9.6 \frac{\mu\text{g}}{\text{mL}}$$

Size of the analyte solution = 25.00 mL

$$\text{Amount of Ni leached to the electrolyte} = 9.6 \frac{\mu\text{g}}{\text{mL}} * 25.00 \text{ mL} = 240 \mu\text{g}$$

9. Ni-P (Brenner) films electrodeposited at varied temperatures

The images of Ni-P (Brenner) films prepared at different deposition temperatures of 3 °C, 10 °C, 21 °, 50 °C and 75 °C are contained in Figure S11A to S11E. The films electrodeposited at higher temperatures appear less lustrous than the films prepared at lower temperatures.

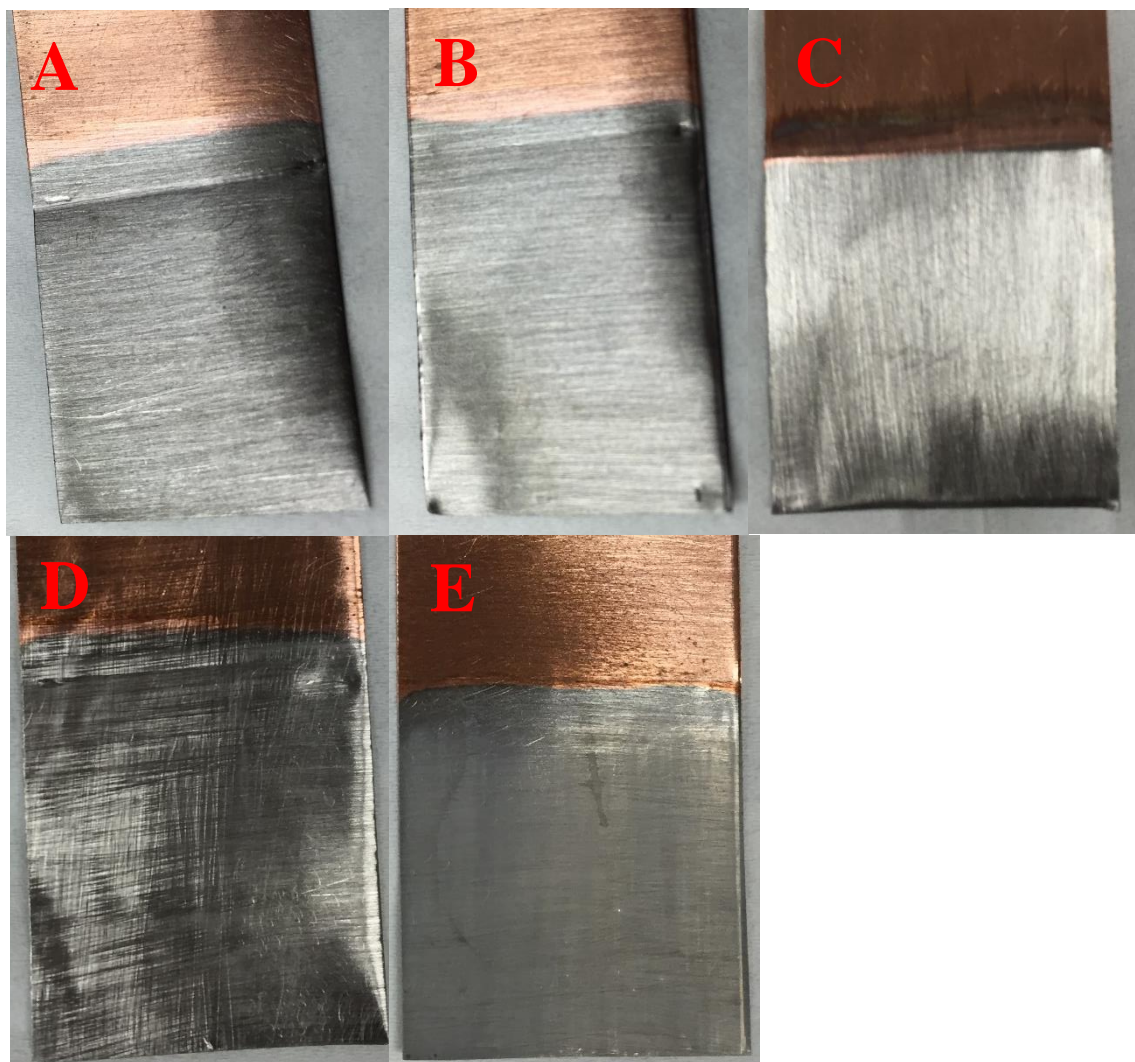


Figure S16. Images of Ni-P (Brenner) films electrodeposited at different temperatures of (A) 3 °C, (B) 10 °C, (C) 21 °C, (D) 50 °C, (E) 75 °C.

10. Ni-P films electrodeposited onto stainless steel substrates

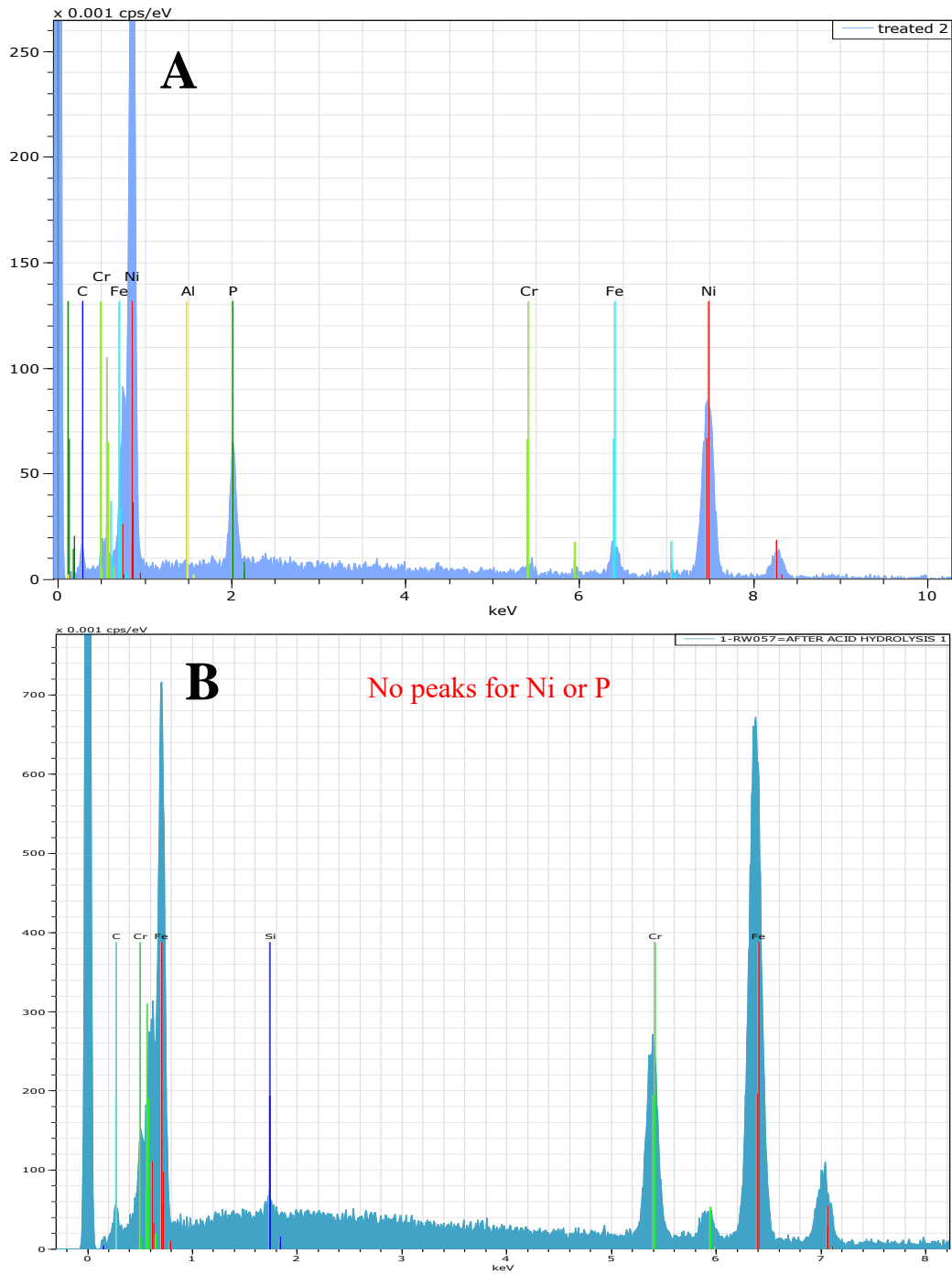


Figure S17. EDX spectra of electrodeposited Ni-P on stainless steel substrate (A) before and (B) after electrolysis in 0.5 M H₂SO₄.

Energy dispersive X-ray spectra of as-deposited Ni-P (Brenner) on stainless steel substrate and the same film after electrolysis in 0.5 M H₂SO₄ are contained in Figure S12. Before electrolysis, EDX shows the presence of Ni and P on the film, however there are no Ni and P peaks in the EDX spectrum of the film after electrolysis. This indicated that the Ni and P are being removed from the substrate during the electrolysis in acidic medium. However, as explained in the main article, with further experiment we could determine that the galvanic dissolution of stainless steel substrate causes the delamination of Ni-P film.

11. X-ray photoelectron spectra of the as-deposited Ni-P films and the Ni-P films after 5000 CV sweeps of electrolysis in 0.5 M H₂SO₄

Table S2 summarizes the binding energy assignment for all the peaks observed for as-deposited Ni-P films and those after 5000 CV sweeps of electrolysis in 0.5 M H₂SO₄.

Table S2. Peak assignment for XPS data in electrodeposited Ni-P films

Sample	Peak Positions (eV) & Assigned binding energies											
	Ni 2p region								P 2p region			
	Nickel phosphide/ Ni ^{δ+}		Nickel phosphate		Satellite peaks		Shake-up peaks		Nickel phosphide/ P ^{δ-}		Nickel phosphate/ oxidized P	
Ni-P (Brenner) As- deposited	852.8 Ni 2p _{3/2}	870.1 Ni 2p _{1/2}	856.4 Ni 2p _{3/2}	874.6 Ni 2p _{1/2}	853.2 Ni 2p _{3/2}	873.1 Ni 2p _{1/2}	860.0 Ni 2p _{3/2}	879.8 Ni 2p _{1/2}	129.4 P 2p _{3/2}	130.2 P 2p _{1/2}	131.2 P 2p _{3/2}	133.2 P 2p _{1/2}
Ni-P (Brenner) After 5000 CV sweeps	853.2 Ni 2p _{3/2}	870.4 Ni 2p _{1/2}	856.3 Ni 2p _{3/2}	874.4 Ni 2p _{1/2}	853.4 Ni 2p _{3/2}	873.9 Ni 2p _{1/2}	860.7 Ni 2p _{3/2}	879.4 Ni 2p _{1/2}	129.3 P 2p _{3/2}	130.1 P 2p _{1/2}	131.0 P 2p _{3/2}	133.0 P 2p _{1/2}
Ni-P (Acidic bath) As- deposited	852.9 Ni 2p _{3/2}	870.2 Ni 2p _{1/2}	856.5 Ni 2p _{3/2}	874.8 Ni 2p _{1/2}	854.7 Ni 2p _{3/2}	873.6 Ni 2p _{1/2}	860.3 Ni 2p _{3/2}	879.9 Ni 2p _{1/2}	129.4 P 2p _{3/2}	130.2 P 2p _{1/2}	131.6 P 2p _{3/2}	133.1 P 2p _{1/2}
Ni-P (Acidic bath) After 5000 CV sweeps	853.4 Ni 2p _{3/2}	870.7 Ni 2p _{1/2}	856.3 Ni 2p _{3/2}	875.6 Ni 2p _{1/2}	855.2 Ni 2p _{3/2}	873.6 Ni 2p _{1/2}	861.3 Ni 2p _{3/2}	879.9 Ni 2p _{1/2}	129.3 P 2p _{3/2}	130.1 P 2p _{1/2}	132.4 P 2p _{3/2}	132.9 P 2p _{1/2}

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