

Laser-Mediated Synthesis of a High-Performance Iron Carbide/Nickel Cathode for Efficient Hydrogen Evolution

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ABSTRACT

This study aimed to develop a highly efficient and stable non-noble metal electrocatalyst to overcome the slow kinetics of the hydrogen evolution reaction (HER) during water splitting. To achieve this, a rapid two-step fabrication strategy was employed: solvothermal deposition of an Fe-based material onto a Ni foam, followed by CO₂ laser irradiation. This thermal process drives the *in situ* growth of a uniform iron carbide phase, creating a hierarchically roughened surface with abundant active sites. Material and electrochemical characterizations revealed that the laser-treated electrode retains the original structure of the substrate, while achieving a threefold increase in the electrochemically active surface area compared to that of a pristine Ni foam. Consequently, the laser-treated Fe₃C/Ni electrode demonstrated improved catalytic activity in an alkaline electrolyte, requiring an overpotential of 77 mV to reach a current density of 10 mA/cm⁻², whereas the pristine Ni foam requires 215 mV. The electrode also exhibited a low Tafel slope of 108 mV dec⁻¹ and maintained operational stability over 24 h of continuous use. This laser-mediated manufacturing technology offers a scalable, rapid pathway for designing robust, earth-abundant electrocatalysts for large-scale sustainable hydrogen production.

Keywords: hydrogen evolution reaction, iron-based electrocatalysts, iron carbide, laser-assisted fabrication, nickel foam, alkaline water electrolysis

1. INTRODUCTION

The global transition toward a clean hydrogen economy is currently limited by the efficiency of water electrolysis, as the hydrogen evolution reaction (HER) remains kinetically sluggish in alkaline environments^{1,2}. Although platinum-group metals are highly active, their high cost and scarcity limit industrial scalability, necessitating stable, earth-abundant alternatives³.

Fe-based materials are promising electrocatalyst candidates due to their abundance and tunable electronic structures. Danilovic *et al.*⁴ showed that Fe incorporation into Ni frameworks enhances activity via d-band modulation and optimized adsorption energies. However, their low conductivity and poor stability remain challenges; Lopes *et al.*⁵ reported that metallic Fe passivates to Fe(OH)₂ and dissolves in alkaline electrolytes, causing performance decay.

Transition-metal carbides are promising for HER due to their Pt-like d-band structure, fast charge transport, and robust surfaces⁶. However, synthesizing them on 3D substrates like Ni foam remains challenging, as conventional furnace annealing causes active-site aggregation and support damage⁷. In this regard, laser-based material processing has gained significant interest because it is rapid and scalable and allows for precise surface modification⁸. Tang *et al.* showed that laser-induced processing achieves uniform porous structures with a high density of exposed active sites, while preventing the collapse of 3D Ni foam struts⁹. However, the specific use of CO₂ laser irradiation

for the rapid fabrication of Fe-carbide phases remains largely unexplored.

To address this gap in knowledge, we aimed to develop a highly efficient, stable non-noble metal electrocatalyst for alkaline water electrolysis. We present a rapid two-step strategy: solvothermal precursor deposition followed by an instant CO₂ laser-induced phase transformation. Unlike traditional bulk heating, this laser-assisted approach uses localized high-energy pulses to create a hierarchical Fe₃C/Ni surface¹⁰. The resulting electrode features a high density of active sites and exhibits good stability in an alkaline electrolyte, thereby demonstrating a scalable pathway toward efficient hydrogen production.

2. METHODOLOGY

2.1. Materials. Iron(II) acetate (Fe(CH₃COO)₂), polyvinyl alcohol (PVA, 99–100% hydrolyzed, ACROS Organics), ethanol, ethylene glycol, potassium hydroxide and urea were obtained from Sigma-Aldrich. The Ni foam, obtained from MTI Corp. with 1.6 mm thickness, was cut into 1 cm × 2 cm pieces and ultrasonically cleaned in ethanol prior to use.

2.2. Preparation of Fe₃C/Ni samples. A precursor solution was prepared by combining 0.05 g of PVA, 18 mL of ethanol, 2 mL of ethylene glycol, 0.12 g of urea, and 0.173 g of iron(II) acetate. The mixture was heated to 80 °C and magnetically stirred at 300 rpm until a clear and homogeneous solution was obtained.

The solution was then transferred to a polytetrafluoroethylene-lined stainless-steel autoclave (45 mL capacity) and a pre-cleaned Ni foam piece was immersed in the solution. The sealed autoclave was heated at 180 °C for 24 h. After natural cooling to 25 °C, the sample was removed, washed thoroughly with ethanol, and dried in an oven at 60 °C.

The dried, solvothermally treated Ni foam sample was subjected to CO₂ laser irradiation using a Universal Laser Systems CO₂ laser (wavelength of 10.6 μm). The sample supported on nickel foam was irradiated with a 30 W CO₂ laser through an objective lens. Both sides of the Ni foam were irradiated under identical conditions to ensure complete surface modification.

2.3. Material Characterization. Crystalline phases were analyzed through X-ray diffraction (XRD; Rigaku Ultima IV) over a 2θ range of 10°–80° at a scan rate of 2°min⁻¹. Surface morphology and elemental composition were evaluated using a scanning electron microscopy (SEM) device (JEOL 5800LV) equipped with an energy-dispersive X-ray spectroscopy (EDS) system.

2.4. Electrochemical Measurements. The activity of the electrodes were recorded in basic media (1.0 M KOH) at 20–25 °C using a three-electrode setup on a Biologic SP-300 electrochemical workstation. The Fe₃C/Ni foam or Ni foam sample served as the working electrode (cathode), a Pt wire was used as the counter electrode (anode), and a Ag/AgCl electrode was used as the reference. Linear sweep voltammetry (LSV) was performed at a scan rate of 5 mV s⁻¹. Electrochemical impedance (EI) spectroscopy (EIS) was conducted at a frequency ranging of 10⁻⁵–0.01 Hz. To quantitatively analyze the kinetics, the measured EI spectra were fitted using a modified Randles equivalent circuit model. Tafel slopes were subsequently calculated from the EIS data¹¹. The electrochemically active surface area (ECSA) was evaluated by extracting the double-layer capacitance (C_{dl})

from the linear relationship between scan rate and capacitive current density. Cyclic voltammetry (CV) was performed across a non-Faradaic potential window, with scan rates incrementally varied from 10 to 100 mV s⁻¹. The resulting slope of the current density versus scan rate plot was used to quantify (C_{dl}), which serves as a direct indicator of the accessible active sites¹².

2.5. Durability Tests. Long-term durability was evaluated via chronoamperometry at a constant potential for 24 h. Following this continuous operation, electrochemical measurements (LSV and EIS) and microstructural analysis (SEM and EDS) were repeated to assess performance degradation and structural stability¹³.

3. RESULTS AND DISCUSSION

3.1. Crystal Structures of the As-Fabricated Samples.

The crystal structures of bare Ni foam and Fe₃C/Ni foam were characterized by XRD. As shown in Figure 1, the bare Ni foam exhibits three intense diffractions at approximately 44.5°, 51.8°, and 76.3°, which are indexed to the (111), (200), and (220) planes of metallic nickel, respectively. These reflections are in excellent agreement with the standard face-centered cubic (fcc) structure of Ni (JCPDS card No. 04-0850)¹³, confirming that the Ni foam substrate retains its expected crystalline nature.

After Fe-based precursor deposition and subsequent laser treatment, the Fe₃C/Ni foam retains the primary Ni reflections, indicating that the bulk crystalline structure of Ni remains intact during processing. For pure Ni foam, laser processing induces no discernible changes in the XRD pattern, indicating that the crystalline phase remains unchanged. In contrast, the laser-treated FeC/Ni foam exhibits an additional diffraction peak at ~37–38°, which is absent in the pristine Ni foam. This peak is tentatively assigned to Fe₃C (JCPDS No. 35-0772), consistent with reported characteristic reflections of iron carbide in the 37–45°

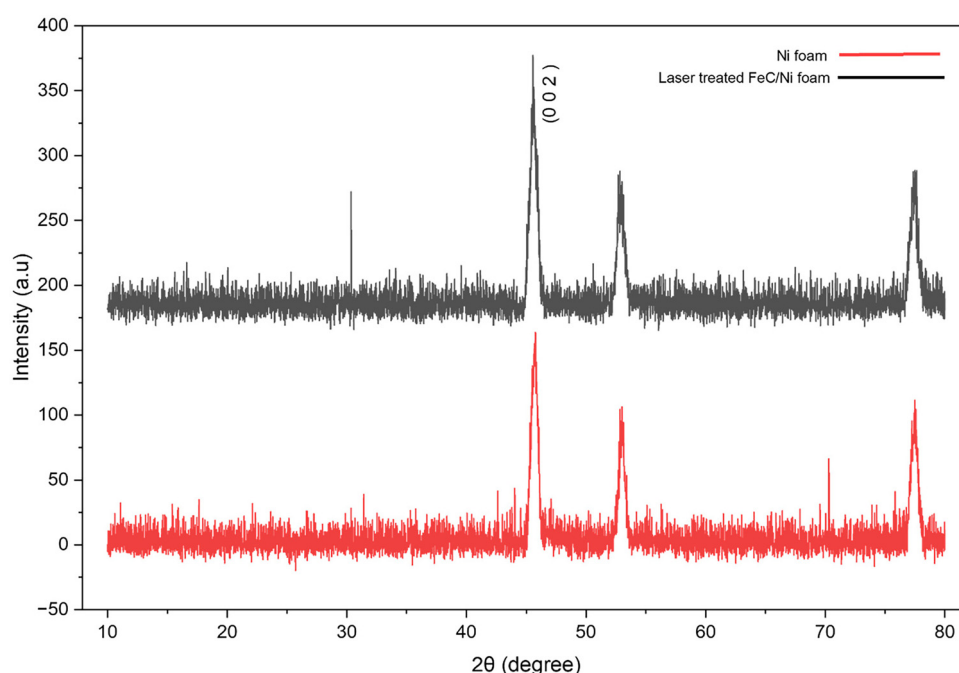


Figure 1. XRD patterns of the pristine Ni foam and laser treated Fe₃C/Ni foam

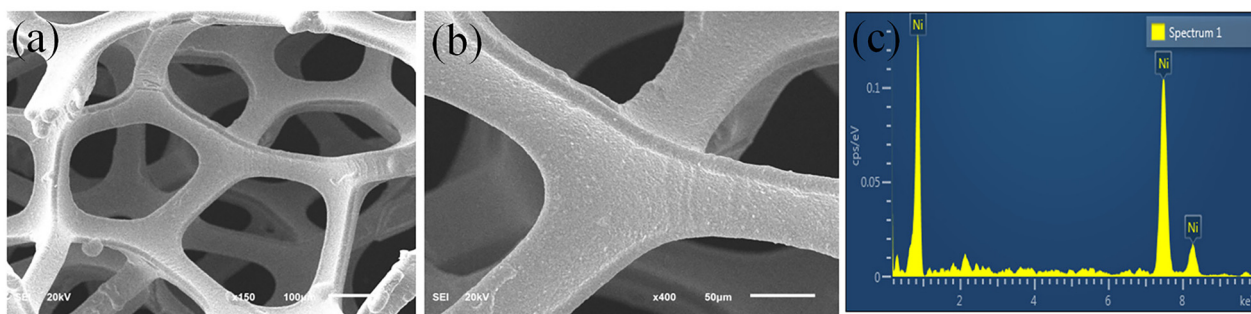


Figure 2. (a) Low- and (b) high-magnification SEM images of the pristine Ni foam at different magnifications. (c) EDS profile confirming that the substrate is pure Ni with no impurities

range¹⁴. The formation of Fe-based carbides is expected because the localized high temperatures produced by CO₂ laser irradiation promote carbon incorporation and the phase conversion of Fe-containing precursors¹⁵.

3.2. Morphology and Elemental Composition. The surface morphology of the pristine Ni foam was examined through SEM to establish a structural baseline prior to solvothermal precursor deposition and laser treatment (Figure 2). At low magnification, the Ni foam exhibits a well-defined 3D porous network characterized by smooth struts and large open macropores ranging from 50 to 500 μm . The higher-magnification SEM image confirms that the Ni walls are smooth, uniform, and free of impurities. Furthermore, its EDS profile displays only intense peaks for Ni, confirming that the substrate is pure and free of impurities. This supports the previous XRD results showing elemental Ni.

Following solvothermal deposition and subsequent CO₂ laser treatment, distinct morphological changes are observed in the SEM images of the Fe₃C/Ni foam (Figure 3). The low-magnification SEM image (Figure 3(a)) reveals that although the 3D interconnected porous Ni foam substrate remains intact, its surface is transformed after laser treatment. The initially smooth struts become highly roughened after precursor deposition and laser irradiation, indicating the successful in situ formation and anchoring of the active material layer¹⁶. The higher-magnification SEM image (Figure 3(b)) shows Fe-based nanoparticles deposited on the Ni foam framework, which were not observed for the pristine Ni substrate, confirming the successful deposition of the active phase. The presence of iron carbide,

which is an active site for the HER reaction, enhances the electrocatalytic performance toward the HER¹⁶.

The successful integration of the Fe-based phase is further supported by EDS analysis (Figure 3 (c)). The resulting spectrum reveals an Fe signal along with that of Ni, confirming that the Fe-containing particles are attached to the Ni foam support. No signals corresponding to contaminants or unintended impurities are detected, confirming the chemical purity of the processed electrode surface.

3.3. Electrochemical Performance.

3.3.1. HER activity. LSV was performed to compare the Ni foam and Fe₃C/Ni foam electrodes. As shown in Figure 4(a), the Fe₃C/Ni foam exhibits an enhanced current density and a more positive onset potential than the pristine Ni foam, confirming its improved catalytic activity.

Specifically, the Fe₃C/Ni foam cathode achieves a current density of 10 mA cm⁻² at an overpotential of only 77 mV, substantially lower than the 215 mV required for the bare Ni foam under identical conditions. This marked reduction in overpotential clearly demonstrates the significantly enhanced electrocatalytic activity of the Fe₃C/Ni cathode, which is attributed to its high density of active sites and improved surface reaction kinetics.

3.3.2. ECSA. The CVs for the pristine Ni foam (Figures 4(c)) and Fe₃C/Ni foam (Figure 4(d)) samples reveal distinct capacitive behaviors. The pristine Ni foam exhibits minimal capacitive currents, whereas the Fe₃C/Ni sample demonstrates much larger currents that increase with the scan rate. Derived from the corresponding current density versus scan rate plot

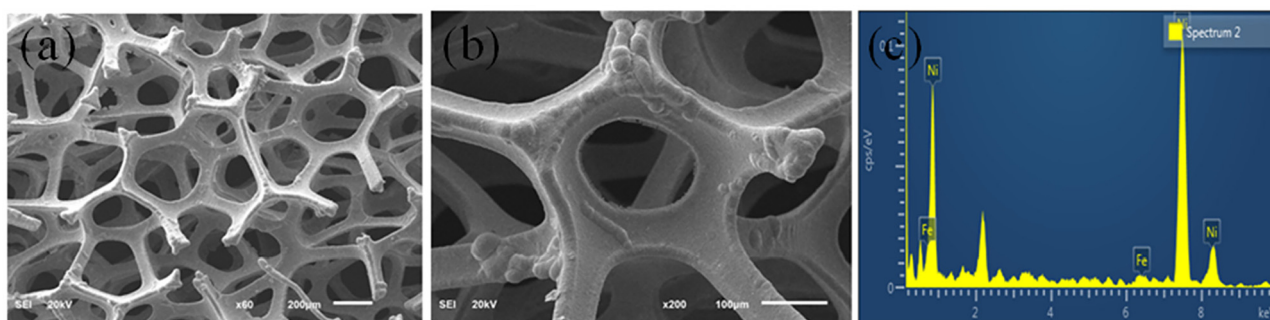


Figure 3. (a) Low- and (b) high-magnification SEM images of laser-treated Fe₃C/Ni showing the rough walls after coating and laser irradiation. (c) EDS profile confirming the presence of Fe with no unwanted elements

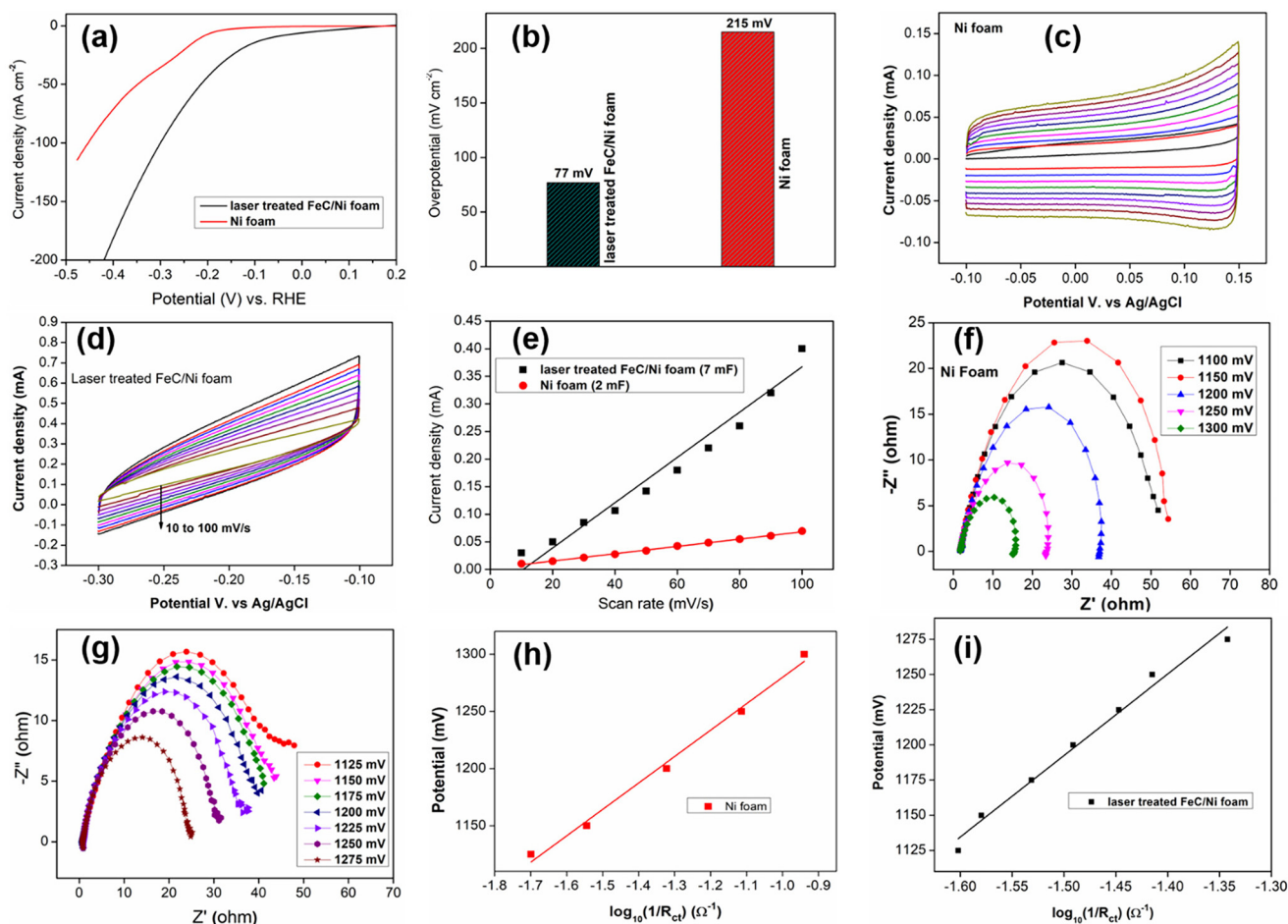


Figure 4. Electrochemical performance of the pristine Ni foam and $\text{Fe}_3\text{C}/\text{Ni}$ foam. (a) LSV curves showing HER activity and (b) overpotential at 10 mA cm^{-2} for both electrodes; CVs in the non-Faradaic region for the (c) Ni foam and (d) $\text{Fe}_3\text{C}/\text{Ni}$ foam; (e) C_{dl} comparison showing a larger ECSA for the $\text{Fe}_3\text{C}/\text{Ni}$ foam; Nyquist plots obtained with various applied potentials used to obtain the R_{ct} for the (f) pristine Ni foam and (g) $\text{Fe}_3\text{C}/\text{Ni}$ foam; Tafel plots for (h) pristine Ni foam and (i) $\text{Fe}_3\text{C}/\text{Ni}$ foam

(Figure 4(e)), the C_{dl} of the pristine Ni foam is 2 mF, whereas the $\text{Fe}_3\text{C}/\text{Ni}$ foam achieves a threefold higher C_{dl} of 7 mF. This improved HER activity is attributed to the laser-assisted deposition of Fe_3C creating a rougher, Fe-rich surface with more active sites.

3.3.3. Electrochemical performance and kinetics. EIS was conducted to evaluate the charge-transfer dynamics at the electrode–electrolyte interface. Nyquist plots pristine reveal that the $\text{Fe}_3\text{C}/\text{Ni}$ electrode (Figure 4(g)) displays a much smaller semicircle radius across the investigated potential range than the

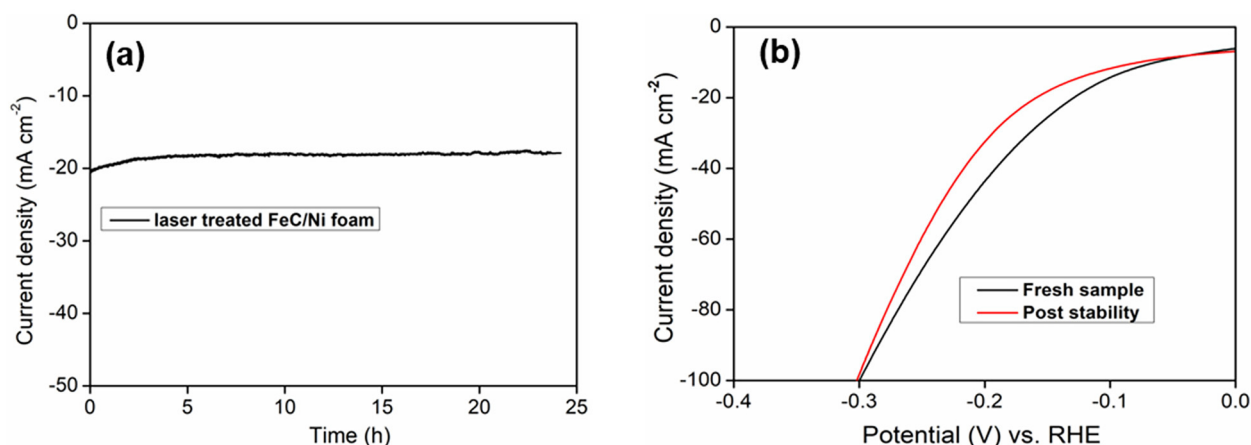


Figure 5. Stability of $\text{Fe}_3\text{C}/\text{Ni}$ electrode performance: (a) chronoamperometry profile and (b) LSV curves before and after the stability test

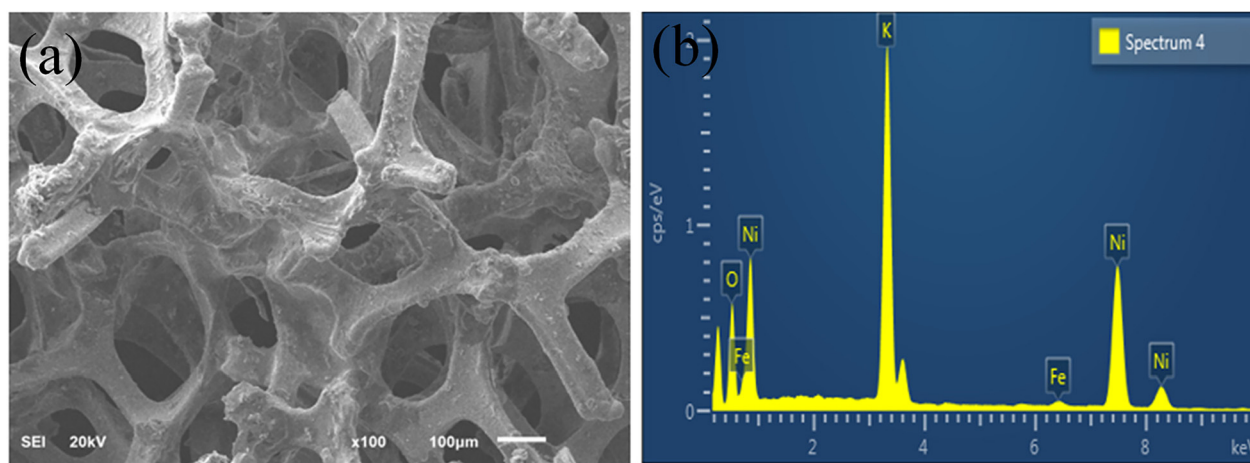


Figure 6. (a) SEM image and (b) EDS profile of the $\text{Fe}_3\text{C}/\text{Ni}$ foam after 24 h electrochemical testing

pristine Ni electrode (Figure 4(f)). To quantitatively analyze the interface kinetics, the impedance plots were fitted using a modified Randles equivalent circuit. This fitting reveals that at a potential of 1200 mV, the R_{ct} of the $\text{Fe}_3\text{C}/\text{Ni}$ foam is markedly lower than that of the pristine Ni foam. The potential versus $1/R_{ct}$ plot (Figure 4(h)) further illustrates that the pristine Ni foam suffers from high resistance, whereas the $\text{Fe}_3\text{C}/\text{Ni}$ foam supports efficient electron transfer during the HER¹⁷.

To accurately assess the reaction kinetics while controlling for solution resistance, Tafel slopes were estimated via EIS by plotting the applied potential against $\log_{10}(1/R_{ct})$ (Figures 4(h) and (i)). This method yields a lower Tafel slope of 108 mV dec^{-1} for the $\text{Fe}_3\text{C}/\text{Ni}$ foam compared to 190 mV dec^{-1} for the pristine Ni foam. This confirms that the synergistic effect between the Fe_3C phase and the Ni foam substrate lowers kinetic barriers to the Volmer and Heyrovsky steps of the HER¹⁸.

3.3.4. Electrode stability. The electrochemical durability of the $\text{Fe}_3\text{C}/\text{Ni}$ foam electrode was evaluated using chronoamperometry test (Figure 5(a)). The current remained stable throughout continuous HER operation. This sustained performance demonstrates that the in situ formed Fe_3C particles are strongly anchored to the Ni foam substrate, effectively resisting any mechanical removal and electrochemical dissolution in the alkaline electrolyte. To further confirm this catalytic stability, an LSV curve was recorded after the stability test (Figure 5b). The curves obtained for the electrodes before and after stability testing are similar, confirming that the electrode maintains its catalytic activity over 24 h.

3.3.5. Post-stability morphology and composition. To assess the structural integrity of the laser-treated electrode after the HER test, the morphology and elemental composition of the $\text{Fe}_3\text{C}/\text{Ni}$ foam electrode were re-examined using SEM and EDS. As a baseline, the SEM image of the freshly prepared $\text{Fe}_3\text{C}/\text{Ni}$ foam (Figure 3) exhibits a rough surface with uniformly distributed nanoscale clusters across the Ni framework, confirming the successful laser-induced formation of high-density catalytic sites. After the 24-h stability test, the main 3D structure of the foam remained intact; however, surface differences are observed: the surface becomes notably rougher, exhibiting flake-like characteristics and minor fragmentation. Such structural evolution

is frequently observed in transition-metal-based HER catalysts owing to the continuous production of hydrogen bubbles in the presence of electrolytes¹⁹. Critically, no large-scale peeling or structural collapse of the Fe-based coating is evident, demonstrating the mechanical and chemical stability of the laser-engineered coating.

This structural robustness is supported by post-test EDS analysis. The Fe and Ni peaks in the EDS spectrum of the freshly prepared electrode (Figure 3(c)) are maintained in the spectrum for the post-test sample (Figure 6), confirming that the active elements are still present. However, signals for oxygen (O) and potassium (K) are also present. The O signal is likely associated with partial surface oxidation during long-term operation in an alkaline electrolyte, while the K signal likely originates from residual KOH adsorbed onto the electrode surface¹⁴.

4. CONCLUSIONS

In summary, we developed a facile strategy for fabricating $\text{Fe}_3\text{C}/\text{Ni}$ foam HER electrodes by combining solvothermal deposition with CO_2 laser processing. The laser treatment produced a rough, Fe_3C -rich surface strongly adhered to the Ni foam while preserving the crystalline structure of the substrate, as confirmed by XRD. The resulting $\text{Fe}_3\text{C}/\text{Ni}$ electrode exhibited significantly enhanced HER performance compared with pristine Ni foam, owing to a threefold increase in electrochemically active surface area and reduced charge-transfer resistance, while maintaining stable operation over 24 h. This laser-mediated fabrication approach offers a simple and scalable route for producing robust, non-noble-metal HER electrodes for sustainable hydrogen production.

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