



Ni-Modified Cu–Fe Prussian Blue Analogues as electrochemical catalysts for hydrogen production

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ABSTRACT

The development of novel catalysts for hydrogen evolution reaction (HER) is crucial in clean energy production technology. In this study, $\text{Cu}_2[\text{Fe}(\text{CN})_6]$ (CuFe PB), a Prussian blue analogue (PBA) and Ni-modified CuFe PB (Ni-CuFe PB) were synthesized by co-precipitation. The structural, compositional, and morphological characteristics of the materials were investigated using XRD, FT-IR, SEM, and EDS techniques. The results showed that the Ni-modified materials possess a network without altering the characteristic crystal structure of Prussian blue. The Ni modification also created more active centers, favorable for electrochemical processes. The HER catalytic activity was evaluated in a 0.5 M H_2SO_4 electrolyte. Compared to the CuFe PB sample, the optimized Ni-CuFe PB material exhibited better electrocatalytic activity, with the overpotential at a current density of $10 \text{ mA}\cdot\text{cm}^{-2}$ decreasing by approximately 100 mV. These results demonstrate that transition metal modification is an effective approach to improving the catalytic performance of PBAs materials in electrochemical hydrogen production applications.

Introduction

The escalating demand for clean and sustainable energy sources is driving intensive research into environmentally benign technologies for energy conversion and storage. Hydrogen, in particular, has emerged as a highly attractive energy carrier owing to its high energy density and carbon-neutral nature upon utilization [1]. Water electrolysis coupled with renewable electricity represents one of the most viable pathways for producing green hydrogen; nevertheless, the overall efficiency of this process is governed critically by the catalytic performance of electrode materials toward the

hydrogen evolution reaction (HER) [2]. Noble-metal catalysts, notably Pt-based systems, currently exhibit benchmark HER activity, yet their large-scale deployment is severely hindered by prohibitive cost and limited resource availability [3]. Hence, the design and development of noble-metal-free electrocatalysts that combine high activity, robust durability, and low production cost have attracted to many researchers [3]. Prussian blue analogues (PBAs) have attracted considerable interest in electrochemical applications owing to their three-dimensional open-framework architecture, large accessible surface area, and compositional flexibility afforded by tunable transition-

metal nodes [4,5]. These intrinsic structural advantages provide abundant catalytically active centers and facilitate efficient mass and charge transport, thereby enhancing electrochemical performance across a range of reactions [6,7]. Among the various PBA compositions, $\text{Cu}_2[\text{Fe}(\text{CN})_6]$ is particularly noteworthy due to its excellent chemical stability and facile synthesis [4,8]. However, its intrinsic electrocatalytic activity remains limited by an insufficient density of effective active sites [8]. Transition-metal modification has proven to be an effective strategy for modulating and enhancing the catalytic properties of PBA materials [9]. In particular, Ni is widely recognized as one of the most active non-noble metals for HER, capable of promoting the Volmer step and accelerating overall reaction kinetics [7,10]. The incorporation of Ni into the PBA framework is therefore anticipated to induce synergistic electronic interactions between the metal centers, increase the density of accessible active sites, improve charge-transfer characteristics, and ultimately enhance HER activity. Ni-containing PBAs exhibit markedly superior electrochemical performance in water-splitting and hydrogen-production applications [7,10].

In the present work, Ni-modified $\text{Cu}_2[\text{Fe}(\text{CN})_6]$ was synthesized via a facile aqueous co-precipitation route and used as an electrocatalyst for the HER. The effects of Ni modification on the structural, morphological, and electrochemical properties of the material were examined to assess its potential as a cost-effective, and environmentally friendly HER catalyst.

Experimental

Chemicals

All chemicals were of analytical grade and used as received without further purification. Copper(II) sulfate hexahydrate ($\text{CuSO}_4 \cdot 6\text{H}_2\text{O}$, $\geq 98.0\%$), iron(II) sulfate heptahydrate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, $\geq 98.0\%$), nickel(II) sulfate hexahydrate ($\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$, $\geq 98.0\%$), potassium hexacyanoferrate(II) trihydrate ($\text{K}_4[\text{Fe}(\text{CN})_6] \cdot 3\text{H}_2\text{O}$, $\geq 98.0\%$), sulfuric acid (H_2SO_4 , $\geq 98.0\%$), and ethanol ($\text{C}_2\text{H}_5\text{OH}$, $\geq 99.5\%$) were supplied by Merck (Germany). N-methyl-2-pyrrolidone (NMP, $\text{C}_5\text{H}_9\text{NO}$, $\geq 99.0\%$) and Nafion™ perfluorinated resin solution (5 wt%) were also obtained from Merck.

Synthesis of materials

The pristine $\text{Cu}_2[\text{Fe}(\text{CN})_6]$ was synthesized by a simple aqueous co-precipitation method. In a typical procedure, 1.0720 g of $\text{CuSO}_4 \cdot 6\text{H}_2\text{O}$ was dissolved in 20 mL of deionized water under continuous magnetic stirring to obtain a homogeneous solution (Solution A). In parallel, 1.2672 g of $\text{K}_4[\text{Fe}(\text{CN})_6] \cdot 3\text{H}_2\text{O}$ was dissolved in

20 mL of deionized water (Solution B). Subsequently, Solution B was added dropwise into Solution A under vigorous stirring at room temperature, resulting in the immediate formation of a brownish precipitate. The precipitate was collected by centrifugation, washed repeatedly with deionized water and ethanol, and finally dried at 60 °C for 12 h. The as-obtained product was labeled as CuFe PB.

Ni-modified $\text{Cu}_2[\text{Fe}(\text{CN})_6]$ samples with two different Cu:Ni molar ratios were prepared following an identical co-precipitation protocol, with the exception that Solution A was prepared by dissolving appropriate amounts of $\text{CuSO}_4 \cdot 6\text{H}_2\text{O}$ and $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ simultaneously in 20 mL of deionized water. For the first sample, Solution A₁ contained 0.9000 g of $\text{CuSO}_4 \cdot 6\text{H}_2\text{O}$ and 0.1052 g of $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ (Ni:Cu molar ratio = 1:8.4), yielding the product denoted as Ni-CuFe PB (1:9). For the second sample, Solution A₂ contained 0.5360 g of $\text{CuSO}_4 \cdot 6\text{H}_2\text{O}$ and 0.5260 g of $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ (Cu:Ni molar ratio = 5:5), yielding the product denoted as Ni-CuFe PB (5:5). All other conditions, including the amount of $\text{K}_4[\text{Fe}(\text{CN})_6] \cdot 3\text{H}_2\text{O}$, reaction temperature, and drying procedure, were identical to those employed for the pristine CuFe PB.

Materials characterization

The crystalline structure and phase purity of the as-synthesized samples were examined by powder X-ray diffraction (XRD) using a Bruker D2 Advance diffractometer (Bruker AXS, Germany) equipped with $\text{Cu K}\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$). Measurements were performed at an operating voltage of 40 kV and a tube current of 40 mA, with data collected over a 2θ range of 10° – 80° at a scan rate of $0.02^\circ \cdot \text{s}^{-1}$. The functional groups and chemical bonding characteristics were identified by Fourier-transform infrared spectroscopy (FT-IR) on a Shimadzu IRAffinity-1S spectrophotometer over the wavenumber range of 400 – 4000 cm^{-1} using the KBr pellet technique. The surface morphology and elemental mapping of the samples were investigated by scanning electron microscopy (SEM, JSM-IT800, JEOL Ltd., Japan) at an accelerating voltage of 5–15 kV.

Electrochemical measurements

All electrochemical measurements were carried out at room temperature on a CS350 electrochemical workstation (Corrtest Instruments, China) equipped with a conventional three-electrode configuration. A platinum wire and an Ag/AgCl electrode (saturated KCl) were used as the counter electrode (CE) and reference electrode (RE), respectively. A catalyst-modified glassy carbon electrode (GCE, 3 mm diameter, geometric area

$\approx 0.0707 \text{ cm}^2$) served as the working electrode (WE). The electrolyte was a 0.5 M H_2SO_4 aqueous solution ($\text{pH} \approx 0.3$), which was purged with nitrogen to remove oxygen prior to measurement. To prepare the working electrode, 5.0 mg of the as-synthesized catalyst was dispersed in a mixture containing 950 μL of NMP and 50 μL of NafionTM solution, followed by ultrasonication for 30 min to form a homogeneous ink. Subsequently, 5 μL of the catalyst ink was drop-cast onto the GCE surface polished by 0.05 μm alumina and dried in a vacuum oven at 50 $^\circ\text{C}$ for 24h. Based on the coated volume and electrode area, the catalyst loading was approximately $0.35 \text{ mg}\cdot\text{cm}^{-2}$. Linear sweep voltammetry (LSV) was performed at a scan rate of $5 \text{ mV}\cdot\text{s}^{-1}$ within the cathodic potential window of 0 to -0.8 V (vs. Ag/AgCl). All measured potentials were converted to the reversible hydrogen electrode (RHE) scale according to the Nernst equation: $E(\text{RHE}) = E(\text{Ag}/\text{AgCl}) + 0.059 \times \text{pH} + 0.197 \text{ V}$. The iR compensation was performed using the post-data correction method. Measurements were performed in triplicate, and the mean value was taken. CV measurements were employed to probe the electrochemical double-layer capacitance (Cdl) in the non-Faradaic potential range. In the stability test, the chronopotentiometry curve was measured at a current density of $10 \text{ mA}\cdot\text{cm}^{-2}$.

Results and Discussion

Structural and morphological characterization

The crystalline phases and structural features of CuFe PB, Ni-CuFe PB (1:9), and Ni-CuFe PB (5:5) were examined by powder X-ray diffraction, and the

corresponding patterns are presented in Fig. 1a. All three samples exhibit a series of distinct diffraction peaks located at approximately $2\theta = 18^\circ, 25^\circ, 35^\circ, 39^\circ, 43^\circ, 52^\circ, 57^\circ$, and 59° , which can be readily indexed to the (200), (220), (400), (420), (422), (440), (600), and (620) crystal planes of the face-centered cubic Prussian Blue framework (space group $Fm\bar{3}m$, JCPDS no. 73-0687), respectively [3,8]. The presence of these characteristic reflections in all samples confirms the successful formation of the desired PB phase with high phase purity, as no additional diffraction peaks attributable to secondary phases or impurities were detected within the detection limit of the technique [3,8].

Upon modification of the $\text{Cu}_2[\text{Fe}(\text{CN})_6]$ lattice with Ni, the diffraction peaks of the Ni-modified samples retain essentially the same positions as those of the pristine CuFe PB, indicating that the modification of Ni ions does not disrupt the parent cubic PB framework. Nevertheless, noticeable variations in the relative intensity and sharpness of the diffraction peaks are observed among the three samples. Specifically, the Ni-CuFe PB (1:9) sample exhibits considerably stronger and sharper diffraction peaks than both the pristine CuFe PB and the Ni-CuFe PB (5:5) sample, indicative of a higher degree of crystallinity and enhanced long-range ordering of the crystalline domains. In contrast, Ni-CuFe PB (5:5) displays the broadest and least intense diffraction peaks, suggesting a higher density of structural defects and reduced crystallite size upon increasing Ni content [3,8]. Based on the (200) plane ($2\theta = 18^\circ$) data of the XRD results, the crystallite sizes of CuFe PB, Ni-CuFe PB (1:9), and Ni-CuFe PB (5:5) were determined using the Scherrer equation to be 10.6 ± 1.5 , 15.8 ± 2.5 , and $14.9 \pm 2.0 \text{ nm}$, respectively.

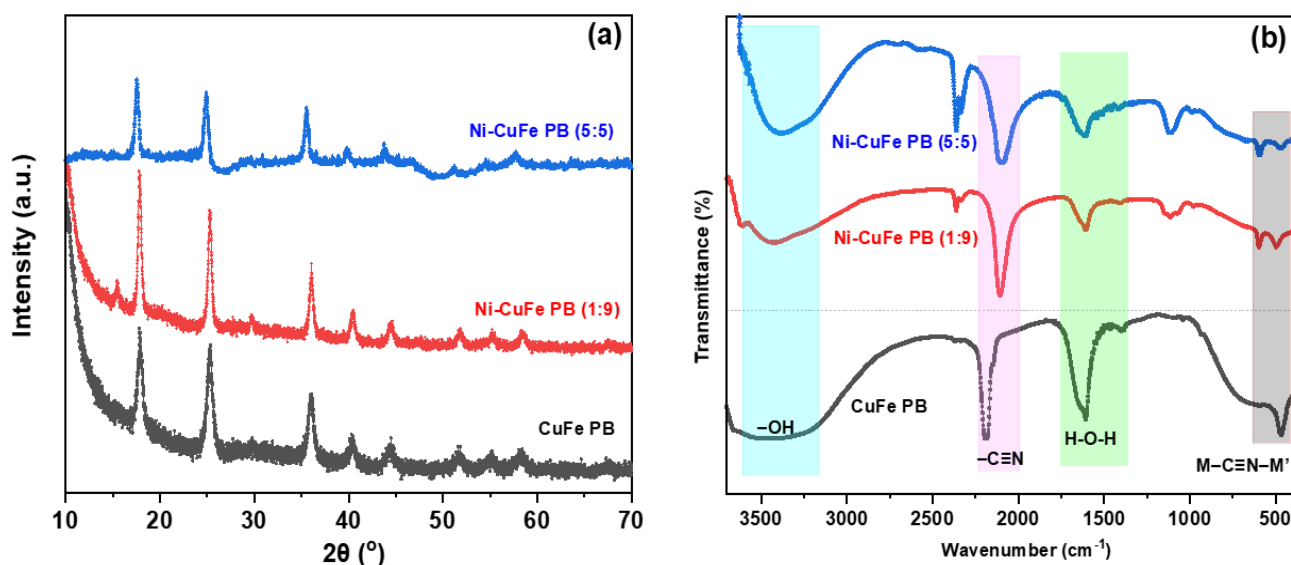


Fig 1: XRD patterns (a) and IR spectra (b) of CuFe PB and Ni-CuFe PB (1:9) and Ni-CuFe PB (5:5).

The chemical bonding characteristics and functional groups of the as-synthesized materials were further investigated by FT-IR spectroscopy, as shown in Fig. 1b. All three samples display a prominent absorption band in the wavenumber region of $2100\text{--}2150\text{ cm}^{-1}$, which is assigned to the stretching vibration mode ($\nu(\text{C}\equiv\text{N})$) of the cyano group ($-\text{C}\equiv\text{N}$) bridging the metal centers in the PBA framework [9]. This observation can confirm that the coordination framework of the PBA lattice remains intact upon Ni modification. More specifically, a subtle yet discernible shift and variation in the relative intensity of the $\nu(\text{C}\equiv\text{N})$ band is observed as a function of Ni content. This can be attributed to the modification of the local electronic environment around the $\text{Fe(II)}-\text{C}\equiv\text{N}-\text{M}$ ($\text{M} = \text{Cu}$ or Ni) linkages. Such electronic perturbations are known to influence the electron density at the metal centers and are expected to play a beneficial role in modulating the adsorption energetics of HER intermediates [3]. In addition, a peak at 2360 cm^{-1} could be due to CO_2 adsorption on the material surface [11]. Furthermore, a broad and intense absorption band centered around $3200\text{--}3600\text{ cm}^{-1}$ is observed in all spectra, which corresponds to the O–H stretching vibration ($\nu(\text{O}-\text{H})$) of water molecules adsorbed within the PBA lattice and on the external surface of the particles. The accompanying band observed in the $1600\text{--}1650\text{ cm}^{-1}$ region is ascribed to the H–O–H

bending mode ($\delta(\text{H}-\text{O}-\text{H})$) of these adsorbed water molecules, confirming the presence of interstitial and surface-bound H_2O within the open-framework structure [10]. In the lower-wavenumber region ($500\text{--}700\text{ cm}^{-1}$), additional absorption features are detected, which can be attributed to the $\text{M}-\text{C}\equiv\text{N}-\text{M}'$ bending modes and metal–nitrogen ($\text{M}-\text{N}$) stretching vibrations characteristic of the PBA type coordination network [7]. The surface morphology and microstructure of the as-prepared samples were examined by SEM, as illustrated in Fig. 2. The micrographs reveal that all three materials, CuFe PB, Ni-CuFe PB (1:9), and Ni-CuFe PB (5:5), exhibit a hierarchical flower-like architecture composed of interconnected, irregularly shaped nanoparticles that are aggregated into larger porous clusters. Using ImageJ software, the crystallite sizes of CuFe PB, Ni-CuFe PB (1:9), and Ni-CuFe PB (5:5) were manually determined to be 11.9 ± 0.5 , 17.6 ± 2.1 , and $16.5 \pm 1.2\text{ nm}$, respectively. This result is relatively consistent with the XRD results. Notably, no appreciable morphological differences are observed between the pristine and Ni-modified samples, indicating that the modification of Ni^{2+} into the $\text{Cu}_2[\text{Fe}(\text{CN})_6]$ framework does not significantly alter the intrinsic growth habit or the macroscopic morphology of the resulting materials. Additionally, Fig. 2 (d–h) demonstrates the uniform distribution of elements in a representative material, Ni-CuFe PB (1:9).

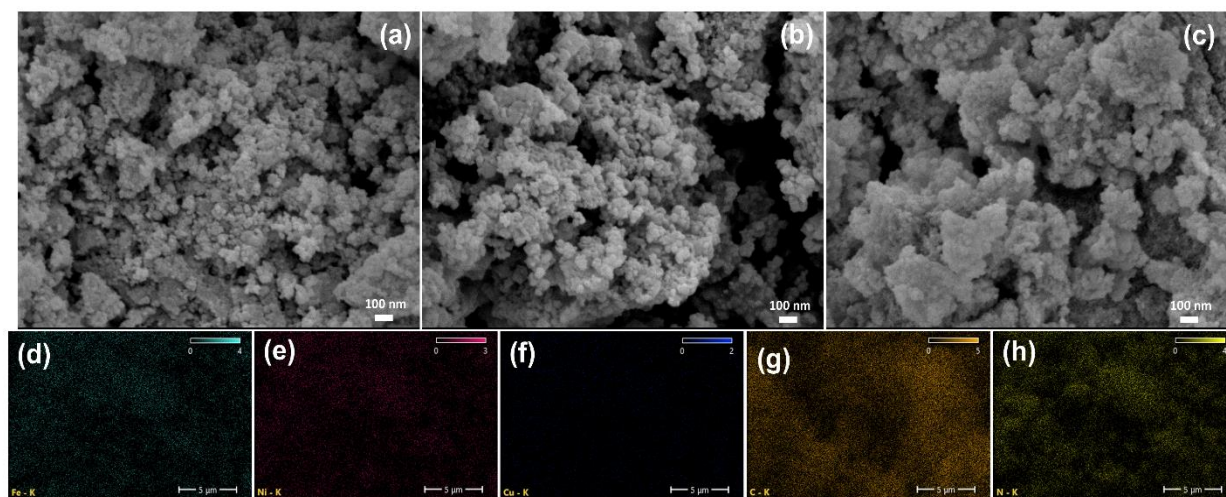


Fig 2: SEM images of CuFe PB (a), Ni-CuFe PB (1:9) (b) and Ni-CuFe PB (5:5) (c). (d–h) EDS elemental mapping of Ni-CuFe PB (1:9).

Electrocatalytic performance

The electrocatalytic HER activity of the as-synthesized materials was evaluated by linear sweep voltammetry (LSV) in $0.5\text{ M H}_2\text{SO}_4$ at a scan rate of $5\text{ mV}\cdot\text{s}^{-1}$. As displayed in Fig. 3a, the LSV polarization curves reveal a clear dependence of HER activity on the Ni modification level. Notably, the Ni-CuFe PB (1:9) electrode exhibits a positive shift in the onset potential compared with the

pristine CuFe PB and the Ni-CuFe PB (5:5) electrodes, indicative of substantially enhanced HER kinetics. The η_{10} values follow the order: Ni-CuFe PB (5:5) (853 mV) > CuFe PB (739 mV) > Ni-CuFe PB (1:9) (639 mV) (Fig. 3b). The optimized Ni-CuFe PB (1:9) sample delivers the lowest overpotential, representing a reduction of approximately 100 mV relative to the unmodified CuFe PB. This significant improvement can be attributed by

the synergistic effect arising from the modification of Cu^{2+} by Ni^{2+} within the PBA framework. Specifically, the modification of an appropriate amount of Ni modulates the local electronic structure of the bimetallic Cu/Ni/Fe active centers, and facilitates faster interfacial charge transfer during the HER process. However, a further increase in the Ni content, as exemplified by the Ni-CuFe PB (5:5) sample, leads to a pronounced deterioration of catalytic activity ($\eta_{10} = 853$ mV). This behavior suggests that excessive modified-Ni disrupts the electronic structure of the active centers in a negative manner. These findings establish that a proper Ni doping level (Cu:Ni = 9:1) is critical for achieving enhanced HER activity, whereas over-doping is counterproductive.

To gain insight into the intrinsic reaction kinetics and operative HER mechanism, the Tafel plots were derived from the corresponding LSV polarization curves and are presented in Fig. 3c. The Tafel slopes were calculated by fitting the linear portions of the overpotential (η) versus

log current density ($\log j$) plots to the Tafel equation ($\eta = a + b \cdot \log j$, where b is the Tafel slope). The obtained Tafel slopes are 58, 59, and 84 $\text{mV} \cdot \text{dec}^{-1}$ for CuFe PB, Ni-CuFe PB (1:9), and Ni-CuFe PB (5:5), respectively. Both CuFe PB and Ni-CuFe PB (1:9) display Tafel slopes close to 60 $\text{mV} \cdot \text{dec}^{-1}$, whereas the over-doped Ni-CuFe PB (5:5) sample exhibits a considerably higher value of 84 $\text{mV} \cdot \text{dec}^{-1}$, consistent with its inferior HER activity revealed by the polarization curves. According to the classical Butler-Volmer framework, Tafel slopes of approximately 120, 40, and 30 $\text{mV} \cdot \text{dec}^{-1}$ correspond to rate-determining Volmer, Heyrovsky, and Tafel steps, respectively [12]. The Tafel slopes observed in this work (58–84 $\text{mV} \cdot \text{dec}^{-1}$) fall within the characteristic range of 40–120 $\text{mV} \cdot \text{dec}^{-1}$, indicating that the HER probably proceeds via a Volmer–Heyrovsky mechanism in which the initial electrochemical adsorption of protons onto the active sites (Volmer step, $\text{H}^+ + \text{e}^- \rightarrow \text{H}^*$) is coupled with the subsequent electrochemical desorption step (Heyrovsky step, $\text{H}^* + \text{H}^+ + \text{e}^- \rightarrow \text{H}_2$).

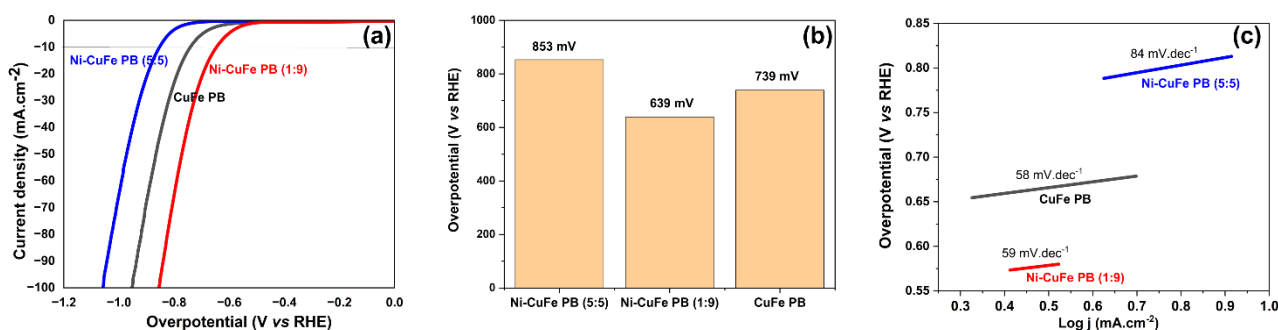


Fig 3: LSV curves (a), overpotential at $10 \text{ mA} \cdot \text{cm}^{-2}$ (b) and Tafel plots (c) of CuFe PB, Ni-CuFe PB (1:9) and Ni-CuFe PB (5:5).

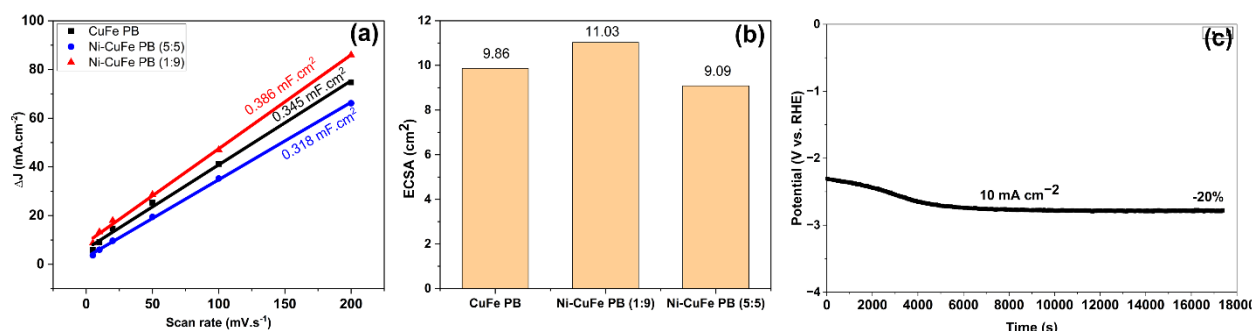


Fig 4: C_{dl} of different electrodes in $0.5 \text{ M H}_2\text{SO}_4$ (a), ECSA of different electrodes (b) and stability test of Ni-CuFe PB (1:9) for HER (c).

Table 1: Comparison of the HER performances of Ni-CuFe PB (1:9) electrodes with different PBA-derived catalysts

Material	Substrate	Electrolyte	Overpotentials (mV) at $10 \text{ mA} \cdot \text{cm}^{-2}$	Ref.
CNBO-NSs	GCE	1.0 M KOH	300	[13]
NG-NiFe@MoC ₂	NF	1.0 M KOH	320	[14]
(Ni,Co)Se ₂ -GA	NF	1.0 M KOH	320	[15]
Fe ₈ Cu ₂ CN	NF	1.0 M KOH	150	[16]
Ni ₂ Fe ₈ CN	NF	1.0 M KOH	142	[7]
Ni-CuFe PB (1:9)	GCE	0.5 M H ₂ SO ₄	639	Present work

C_{dl} and ECSA were calculated from the cyclic voltammetry (CV) curve and shown in Figure 4a,b. The C_{dl} of Ni-CuFe PB (1:9) is 0.386 mF.cm^{-2} , which is higher than those of CuFe PB and Ni-CuFe PB (5:5). This result partially supports the superior catalytic activity of Ni-CuFe PB (1:9). Chronopotentiometry measurement was used to study the stability of Ni-CuFe PB (1:9) at an applied current of 10 mA.cm^{-2} versus RHE in acid solution (Fig. 4c). Stability decreased by 20% after 5 hours. This indicates that the catalyst is not stable under the measurement conditions. Table 1 shows that our results remain modest compared to published studies. Therefore, these materials are needed to further improve.

Conclusions

In summary, pristine $\text{Cu}_2[\text{Fe}(\text{CN})_6]$ (CuFe PB) and two Ni-modified analogues with Ni:Cu molar ratios of 1:8.4 and 5:5 (denoted Ni-CuFe PB (1:9) and Ni-CuFe PB (5:5), respectively) were successfully synthesized via a facile aqueous co-precipitation route. The characterization confirmed that all three samples crystallize in the characteristic face-centered cubic Prussian Blue framework (space group $Fm-3m$) with high phase purity. The electrocatalytic HER performance demonstrated a dependence on the Ni modification extent with the optimally modified Ni-CuFe PB (1:9) sample delivered the lowest overpotential of 639 mV at a geometric current density of 10 mA.cm^{-2} . This work demonstrates a trend in PBA electrocatalyst modification for the hydrogen evolution reaction. However, improvements in activity and durability for these materials are needed to further investigate.

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