

Article

Tuning In Situ Growth of CuO-TiO₂/Ti Heterostructure Catalyst for Acceleration of Electrocatalytic Hydrogen Evolution Reaction

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Abstract

Due to the scarcity and high cost of precious metals, development of a noble metal-free, low-cost catalyst for hydrogen generation via water splitting is crucial. To develop an efficient HER catalyst, Ti, the ninth most abundant metal in Earth's crust, was engineered systematically. The pristine transition metal titanium cannot drive an electrocatalytic hydrogen evolution reaction (HER) with an efficient rate in an acidic medium (0.5 M H₂SO₄). However, in situ growth of TiO₂ film on Ti surface achieves HER activity, showing an overpotential for 10 mA cm⁻² at 671.4 mV with a Tafel slope of 163.69 mV dec⁻¹. The electrocatalytic performance was further boosted by immobilizing CuO particles onto the as-developed TiO₂/Ti film, which shows 10 mA cm⁻² overpotential at 543.7 mV with a Tafel slope of 101.09 mV dec⁻¹. The CuO-TiO₂/Ti heterostructured electrode exhibited remarkable long-term stability, with the current density increasing by 36% over 25 h of continuous operation, suggesting gradual electrochemical activation while maintaining robust catalytic performance. In this research, detailed structural, surface, and electrochemical investigations, including SEM-EDX, EIS, OCP, and XPS analyses, verified the optimized formation of the TiO₂ layer and CuO incorporation, underscoring the positive impact of heterointerface engineering on HER enhancement.

Keywords: hydrogen evolution; titanium; electrocatalysis; Tafel slope; turnover frequency

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1. Introduction

Escalating worldwide energy consumption and the depletion of fossil resources have led to a crucial investigation for green, sustainable, and efficient energy preservation alternatives [1]. Since the usage of fossil resources, such as gasoline and coal, increases

ecological pollution and climate change by emitting SO₂, CO₂, and nitrogen oxides, a planned transition to renewable sources is essential in the quest for a sustainable energy solution [2]. The International Energy Agency (IEA) projects that by the year 2040, global energy consumption will increase around 30% and CO₂ emission will reach 35.70 Mt/year [3,4]. Hydrogen is the safest source of energy, as its combustion generates zero carbon emission. The hydrogen evolution reaction (HER), specifically electrocatalytic water dissociation, presents itself as a viable method for transforming renewable energy sources into chemical energy in order to overcome these obstacles [5]. Molecular hydrogen, beyond serving as a power source, plays a key role in oil refinement, ammonia production, and hydrogenation reactions, making it essential to the sustainable “hydrogen economy” [6]. Thus, researchers have looked into electrocatalysts for water electrolysis to produce H₂ in an environmentally acceptable manner in response to the demand for better energy sources.

While electrochemical water splitting can produce pure hydrogen, scalable conversion is limited due to lack of an efficient catalyst to drive the sluggish water-splitting reaction [7]. Platinum (Pt) is recognized as a standard HER electrocatalyst due to its exceptional stability and catalytic activity [8,9]. However, despite its remarkable electrocatalytic capabilities, the expense and constrained supply of Pt severely limit its use and commercialization [10,11]. Therefore, developing alternative catalysts that operate similarly but have higher geological abundance, affordability, and durability is crucial to building a sustainable hydrogen economy [12]. Recent studies have demonstrated that reducing noble metal loading through single-atom engineering is an effective strategy for enhancing catalytic efficiency while minimizing Pt consumption [13]. For example, Lee et al. reported that tailoring the interfacial electronic structure of a single-atom Pt/MoC catalyst through pulsed laser engineering significantly enhanced HER activity and durability, underscoring the importance of catalyst–support interactions in hydrogen evolution electrocatalysis [14].

Note that the ninth most common element in the crust of the planet is titanium. Because of its improved kinetic stability, faster charge carrier separation, and suitable bandgap energy, anatase TiO₂ is said to aid HER [15,16]. Due to their high photosensitivity, non-toxicity, durability across a large pH range, high melting point, low thermal expansion, superior fabrication characteristics, excellent robustness and strength, and corrosion resistance, titanium and its oxides are also favored materials for a variety of potential uses [17,18]. The electrochemical approach produces TiO₂ with less effort and at a lower cost than alternative techniques. The primary disadvantage of employing TiO₂ is that passivation results in a low conductivity of this oxide coating [19]. Therefore, numerous studies have endeavored to boost the conductivity of titanium dioxide (TiO₂) by integrating different heterostructures with TiO₂ to elevate the total catalytic efficiency towards H₂ (hydrogen) evolution [20–26]. Meanwhile, CuO is a suitable p-type semiconductor photocatalyst because of its small bandgap energy, which is between 1.2 and 1.6 eV. CuO is also stable, nontoxic, cheap, and abundant. It also exhibits special chemical and physical characteristics, including field emission, photovoltaic, photoconductivity, and electrochemical and catalytic qualities [24–26]. Consequently, it shows potential for use in energy conversion and environmental remediation applications such as photocatalysis, sensors, nonlinear optical devices, and solar cells [27]. Different forms of CuO have been fabricated including nanorod, nanowire, nanosheet, flower-like, and three-dimensional meso spinels [28–31]. Ashish K. Ranjan et al. synthesized CuO nanoparticles using a hydrothermal technique, and their photoelectrochemical HER properties were studied using cyclic voltammetry [32]. Moreover, the incorporation of heterointerfaces has emerged as an effective strategy for enhancing electrocatalytic activity through accelerated charge transfer and synergistic interactions between distinct phases [33]. In this context, Fatma et al. have

synthesized nonstoichiometric perovskite–swedenborgite nanocomposites, exhibiting enhanced electrocatalytic performance due to strong interfacial coupling and synergistic effects, highlighting the importance of heterostructure engineering [34]. Additionally, Nadeem Asghar Khan et al. developed the CuO/CuS heterostructure catalyst, which boosts the OER that exhibits a current of 10 mA cm^{-2} in an alkaline medium with 270 mV overpotential and a Tafel slope of 67 mV/dec [35]. Thus, considering the efficient catalytic behaviors of TiO_2 and CuO, it is inferred that a heterostructure catalyst comprising these oxide components could drive water reduction reaction with excellent performance.

In this work, we have mounted CuO particles via in situ growth on the surface of a TiO_2/Ti heterostructure surface via electrodeposition to illustrate its implementation towards HER in the acidic medium. This work explores a practical and straightforward approach to developing a Ti-based electrocatalyst that is affordable, durable, and stable for HER. By integrating CuO-modified TiO_2/Ti heterostructures to enhance conductivity under acidic conditions, the catalyst supports efficient electrochemical conversion of energy for fuel cells or hydrogen production via water reduction.

2. Results and Discussion

2.1. Open Circuit Potential (OCP)

Open circuit potential (OCP) reflects an electrode's intrinsic equilibrium potential at the electrode–electrolyte interface in the absence of Faradaic current, where cathodic and anodic reactions proceed at the same rates. It is a crucial parameter for assessing electrode surface properties and evaluating possible changes in electrochemical behavior before and after modification of an electro-active surface. In this study, the polarization plots were investigated for bare Ti, anodized Ti, CuO/Ti, and CuO- TiO_2/Ti electrodes in 0.5 M of H_2SO_4 to assess the distinct electrochemical interfacial characteristics that emerged at the electrode–electrolyte interface prior to and after stepwise modification of the Ti surface, as shown in Figure 1A. The open circuit potential (OCP) of bare Ti was measured at +0.01 V vs. RHE. Upon anodization, i.e., in the case of the TiO_2/Ti surface, the OCP shifted slightly in the negative direction to −0.02 V, whereas modification with CuO/Ti resulted in a positive shift to +0.12 V. Finally, the composite electrode (CuO- TiO_2/Ti) exhibited the most negative OCP value of −0.13 V. The negative shift in OCP in the case of the CuO- TiO_2/Ti electrode suggests increased growth of negative charge on the surface, suggesting that only a small additional negative potential is required to drive a reduction process. This enhanced charge density promotes a more favorable reduction environment, facilitating improved H^+ adsorption and lowering the activation overpotential, thereby enhancing HER activity.

2.2. Impedance Spectroscopy (EIS)

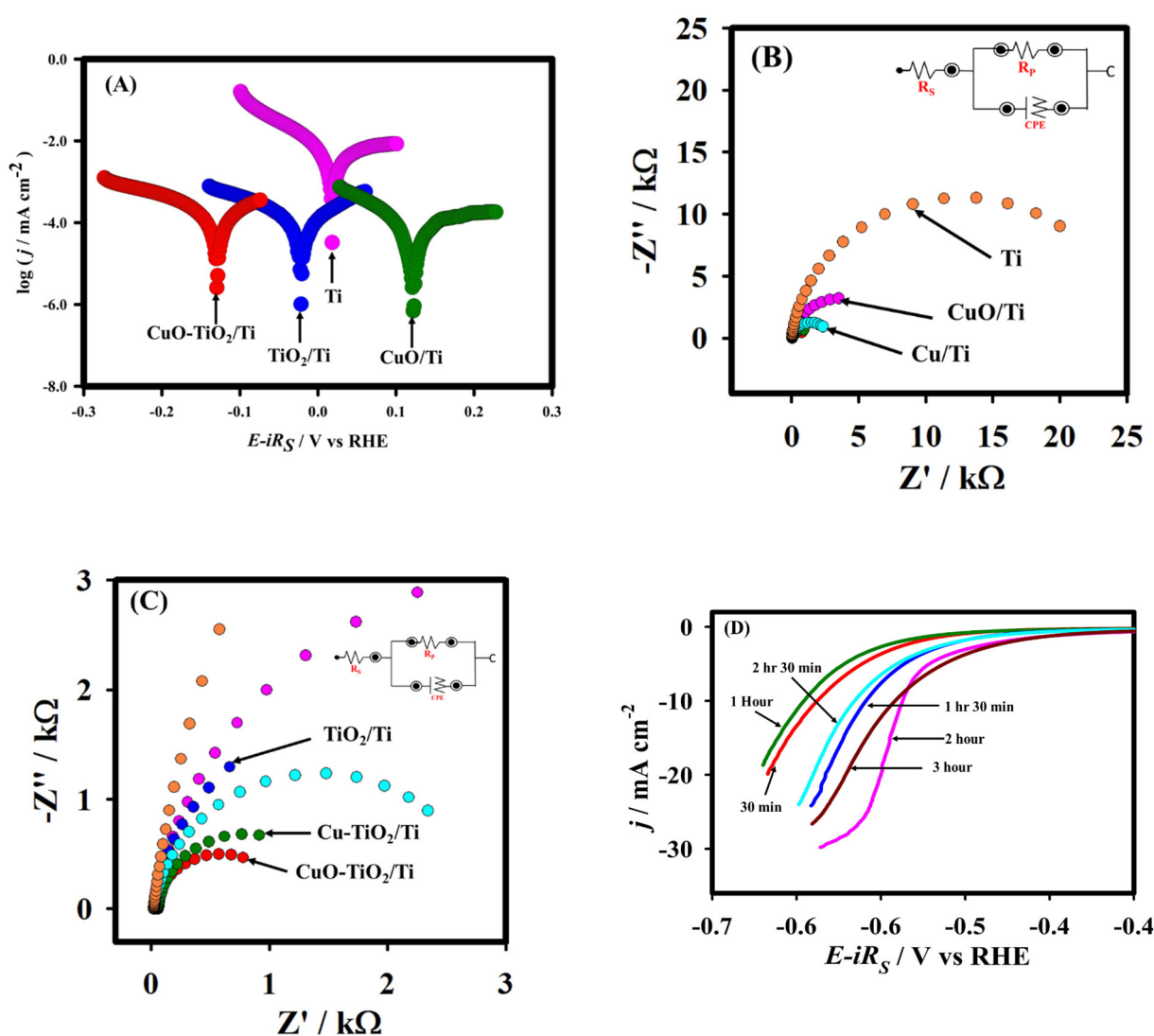
Figure 1B,C illustrates the Nyquist plots for various electrodes recorded in a 0.5 M H_2SO_4 solution. The corresponding EIS parameters are detailed in Table 1. To further validate the EIS analysis, the simulated fitting results for all electrodes, together with the employed equivalent circuit model, have been included in the Supplementary Materials (Figure S1), confirming the reliability of the fitting and the appropriateness of the chosen circuit. The solution resistance (R_s), represented by the semicircle's intersection with the real axis (Z_{re}), reflects the resistance encountered by the electrolyte during ion transport. In contrast, the charge transfer resistance (R_{ct}) is associated with the charge transfer process occurring at the electrode–electrolyte interface, where the semicircle diameter in the Nyquist plot reflects its magnitude. A lower R_{ct} value indicates faster charge transfer kinetics. As per tabulated results (Table 1), the R_{ct} of uncoated Ti markedly declined from 25.9 k Ω to 1.09 k Ω following the development of the CuO- TiO_2/Ti composite. This notable

reduction in R_{ct} implies the improved electron transport kinetics and superior catalytic performance might be offered with the CuO-TiO₂/Ti electrode in hydrogen evolution reactions under the experimental condition. To complement the EIS results, the corresponding Bode plots displaying phase angle and impedance magnitude as a function of frequency are included in the Supplementary Materials (Figure S2). The trends observed in the Bode spectra are in good agreement with the Nyquist plot interpretation and equivalent circuit modeling, further validating the charge-transfer behavior of the studied electrodes.

Table 1. EIS properties recorded with different modified Ti electrodes at -0.60 V potential in in 0.5 M of H₂SO₄.

Catalysts	R_s/Ω	$R_{ct}/k\Omega$
Ti	-26.3 ± 0.05	25.9 ± 0.08
TiO ₂ /Ti	23.8 ± 0.07	4.07 ± 0.10
Cu/Ti	-1.12 ± 0.05	3.21 ± 0.03
CuO/Ti	-17.2 ± 0.05	9.27 ± 0.08
Cu-TiO ₂ /Ti	66.3 ± 0.08	1.47 ± 0.07
CuO-TiO ₂ /Ti	26.8 ± 0.03	1.09 ± 0.04

R_s = Solution resistance; R_{ct} = Charge transfer resistance.



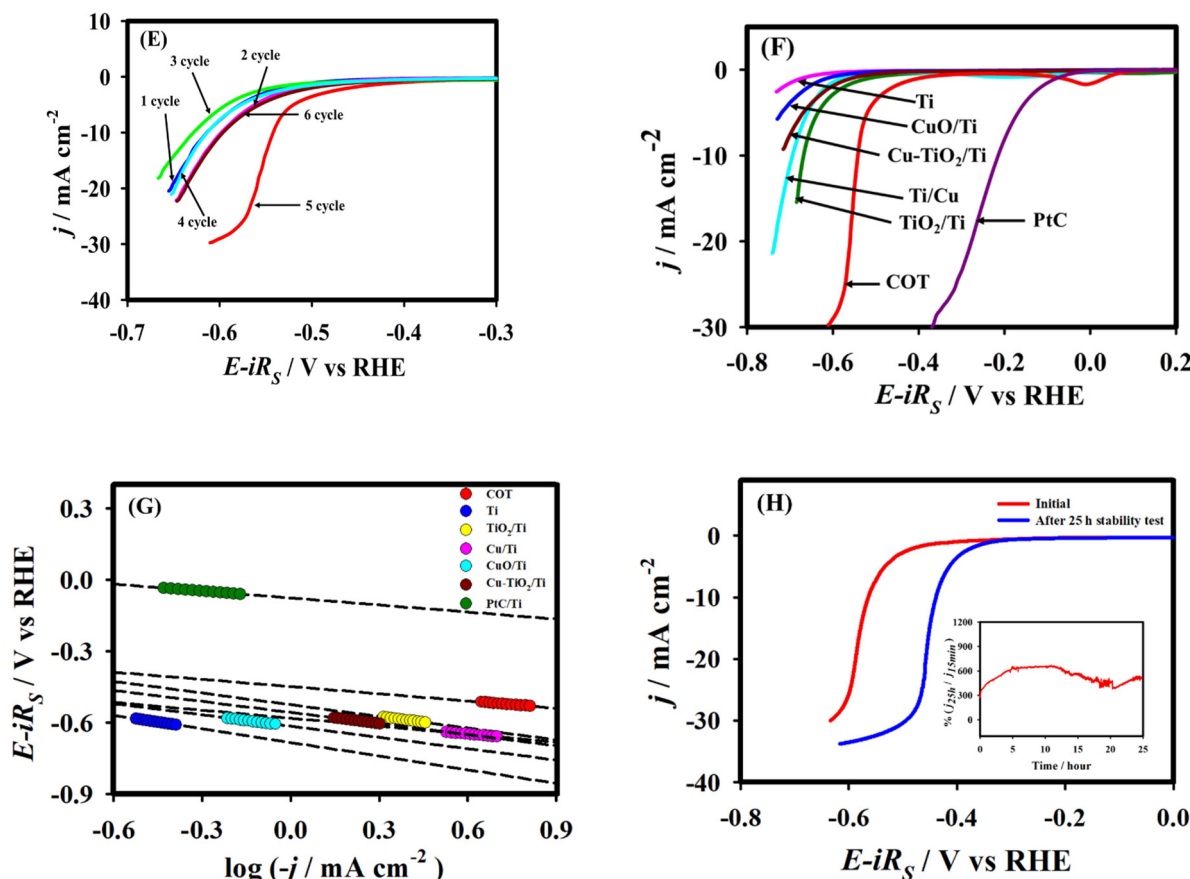


Figure 1. (A) polarization curves for CuO-TiO₂/Ti (COT), TiO₂/Ti, CuO/Ti, and Ti electrodes in a 0.5 M H₂SO₄ electrolyte at a scan rate of 0.1 Vs⁻¹, (B) Nyquist plots for Ti, Cu/Ti, CuO/Ti, (C) Zoomed in Nyquist plots from Figure 1B for TiO₂/Ti, Cu-TiO₂/Ti, CuO-TiO₂/Ti (COT) in 0.5 M of H₂SO₄ electrolyte recorded at −0.60 V excitation potential, (D) Optimization of anodization time on Ti surface, (E) Optimization of cycles of Cu deposited on TiO₂/Ti surface, (F) LSV curves recorded for COT, Cu-TiO₂/Ti, CuO/Ti, Cu/Ti, Ti, TiO₂/Ti, Pt/C electrodes, (G) Tafel plots for modified electrodes in 0.5 M of H₂SO₄ at a scan rate of 0.01 V s⁻¹, (H) LSV of CuO-TiO₂/Ti before and after a 25 h stability test in 0.5 M of H₂SO₄ at a scan rate of 0.01 V s⁻¹; Inset: normalized current density ($j_{25h}/j_{15min} \times 100\%$) as a function of time during the 25 h chronoamperometric test, where j_{15min} represents the stabilized current density measured after 15 min of operation.

2.3. HER Catalysis

Optimization of catalyst composition is a critical aspect for an electrochemical process since an appropriate configuration can enhance yield, reduce energy consumption, and improve economic viability. To determine the optimal composition for HER activity, Ti electrodes anodized for variable durations with a fixed Cu deposition of five cycles were examined. As shown in Figure 1D, the catalyst anodized for 2 h exhibited the lowest onset potential (−0.52 V) in the LSV curve, indicating superior HER performance. Notably, increasing the anodization time up to 2 h improved activity, whereas further anodization led to a shift toward more negative onset potentials, suggesting diminished performance. In addition, TiO₂/Ti catalysts with variable Cu loadings (1–6 deposition cycles) were investigated to identify the optimal Cu content for HER. As presented in Figure 1E, the catalyst with five Cu deposition cycles showed the lowest onset potential (−0.50 V), demonstrating the best HER activity. The performance improved progressively with increasing Cu content up to the fifth cycle; however, further deposition resulted in a negative shift in onset potential, indicating a decline in catalytic efficiency.

Next, different composite electrodes were developed on Ti and on a 2 h anodized Ti surface to compare overpotential of HER commencement. The HER activities of different electrodes are compiled in Table 2. Among the electrodes, Ti alone exhibited the poorest activity, exhibiting a negligible HER current of only 0.20 mA cm^{-2} at -0.70 V . By contrast, while TiO_2 sites were developed on Ti via 2 h anodization, the resultant TiO_2/Ti surface showed improved HER activity, with an onset potential of -0.60 V with a current density of 0.29 mA cm^{-2} and a 10 mA cm^{-2} overpotential (η_{10}) of 671.4 mV . In comparison, a Cu/Ti electrode exhibited limited catalytic activity with the highest η_{10} value at 699.0 mV , onset potential of -0.61 V , and current density of 0.26 mA cm^{-2} . Meanwhile, CuO/Ti or $\text{Cu}/\text{TiO}_2/\text{Ti}$ electrodes failed to reach a 10 mA cm^{-2} current density, exhibiting only modest current responses with onset potentials of -0.65 V (0.24 mA cm^{-2}) and -0.62 V (0.27 mA cm^{-2}), respectively. Notably, modification of the Ti surface with the CuO/TiO_2 composite significantly improved HER activity, reducing the HER overpotential (543.7 mV) with a lower onset potential of -0.42 V and an increased current density of 0.35 mA cm^{-2} compared to bare Ti and approaching that of the Pt electrode. This marked improvement is attributed to the effective incorporation of CuO nanomaterials onto the TiO_2/Ti surface. Analytically, the overpotential essential to achieve a current density of 10 mA cm^{-2} with the $\text{CuO}-\text{TiO}_2/\text{Ti}$ (COT) electrode was 543.7 mV , which is markedly lower than those of TiO_2/Ti and Cu/Ti electrodes. These results demonstrate that the synergistic integration of the composite components yields a robust electrocatalyst with enhanced HER performance in acidic media, offering a promising alternative to conventional Pt-based catalysts. In contrast, commercially available CuO deposited on TiO_2/Ti exhibited unstable HER performance, as shown in Figure S3 (Supplementary Materials), where the cathodic current density decreased almost completely after the second scan, corresponding to a nearly 100% loss of HER activity. This sharp decline highlights the importance of the synthesized composite structure in achieving enhanced electrocatalytic activity.

To provide deeper understanding of the electrochemical kinetics, Tafel analysis was performed in the kinetically controlled region of the polarization plots. The Tafel slope (b), which is considered a vital intrinsic kinetic parameter of electrocatalysts, is strongly influenced by the so-called rate-determining step (RDS) of the hydrogen evolution reaction (HER). Determining the Tafel slope is essential for understanding the reaction pathways governing HER, as it resembles electron transfer kinetics and catalytic effectiveness. Consequently, Tafel investigation was carried out for all prepared electrodes to investigate the HER kinetics and underlying reaction mechanism. The Tafel slopes were evaluated by adjusting the current density–potential (j – E) data with the Tafel equation Equation (1) [36–38]:

$$\log(j) = \log(j_0) - \frac{1}{b} (E - E^{\circ'}) \quad (1)$$

Here, $E^{\circ'}$ denotes formal potential under room condition, E represents the applied potential with respect to the reversible hydrogen reference electrode (RHE), and $b = 2.303 RT/\alpha F$ corresponds to the Tafel slope. Here, the exchange current density is expressed as $j_0 = nFCK^0$ when $E = E^{\circ'}$. In an acidic electrolyte, HER proceeds through a series of elementary steps, as explained in Equations (2)–(4) [39].

Volmer reaction (Discharge step):



Heyrovsky reaction (Electrochemical desorption step):



Tafel reaction (Recombination step):



It is well established that, in multi-stage reaction systems, the rate-determining step (RDS) has a decisive influence on the charge-transfer coefficient, α . When the reaction proceeds through an RDS, it follows the relationship described in Equation (2), and the value of α is generally considered to be 0.5, yielding a characteristic Tafel slope at 120 mV dec^{−1} in accordance with the conventional HER pathway. Nevertheless, when either Equation (3) or Equation (4) becomes the RDS, the α value deviates from 0.5, resulting in lower Tafel slopes of close to 40 and 30 mV dec^{−1}, respectively. In acidic media, HER may also proceed through coupled pathways involving reactions (2) and (3) or reactions (2) and (4) [40].

Figure 1G presents the Tafel plots obtained for hydrogen evolution reaction on all modified titanium electrodes. The retrieved kinetic parameters, such as charge-transfer coefficient (α), Tafel slope, and exchange current density (j_0), are compiled in Table 2. The altered Ti electrodes demonstrated Tafel slopes varying between 101.09 and 211.59 mV dec^{−1}, accompanied by α values below 0.5. The results suggest that the Volmer step is the governing factor for the HER kinetics on all investigated Ti electrodes. The listed Tafel parameters in Table 2 reveal that CuO-TiO₂/Ti necessitates 101.09 mV to reach a 10-fold increase in HER current. In contrast, the other materials Cu-TiO₂/Ti, CuO/Ti, Cu/Ti, Ti, and TiO₂/Ti, require 155.22 mV, 158.26 mV, 111.11 mV, 191.11 mV, and 163.69 mV, respectively. Thus, among the modified Ti electrodes, CuO-TiO₂/Ti exhibits the fastest charge-transfer rate, as demonstrated by its minimal Tafel slope. Moreover, the exchange current density (j_0) for CuO-TiO₂/Ti is 0.35 mA cm^{−2}, substantially greater compared to that of the other electrodes. Since j_0 correlates directly with catalytic activity and electron-transfer efficiency, this elevated value confirms that the improved charge-transfer characteristics of CuO-TiO₂/Ti boost the hydrogen evolution reaction kinetics. The combination of the highest j_0 and lowest Tafel slope highlights the CuO-TiO₂/Ti electrode's superior efficiency and durability as an electrocatalyst for HER in acidic environments.

Table 2. A comparative evaluation of Tafel slopes, overpotential, exchange current densities, and electro-transfer coefficients for all prepared electrodes.

Catalysts	E _i /V	η_{10} /mV	b/mV dec ^{−1}	α	j_0 /mA cm ^{−2}
Ti	−0.70	−	191.11	0.30	0.20
TiO ₂ /Ti	−0.60	671.4	163.69	0.36	0.29
Cu/Ti	−0.61	699.0	111.11	0.52	0.26
CuO/Ti	−0.65	−	158.26	0.36	0.24
Cu-TiO ₂ /Ti	−0.62	−	155.22	0.38	0.27
CuO-TiO ₂ /Ti(COT)	−0.42	543.7	101.09	0.58	0.35
Pt/C	−0.10	220.8	97.99	0.60	0.83

N.B. E_i: Onset potential, b: Tafel slope, η_{10} : Overpotential at 10 mA cm^{−2}.

At this point, it is worth noting that the electrochemical active surface area (ECSA) offers vital details regarding the catalytic active sites of the electrode. To determine the ECSA, the double-layer capacitance of the C_{dl} value was determined by analyzing the non-Faradaic region of the cyclic voltammetry curves [41]. The ECSA value of the electrocatalyst is significantly impacted by its extremely porous and rough surface. It should be noted that the double-layer capacitance is only controlled by charge accumulation at the electrode–electrolyte interface and does not include any redox activities. The double-layer capacitance is often measured using cyclic voltammetry (CV), which applies within a pre-defined non-Faradaic voltage span at varying scan rates. A linear correlation was

highlighted when the difference between the cathodic and anodic currents was plotted against scan rate [42].

The ECSA and C_{dl} have a linear relationship; as C_{dl} rises, so does ECSA, adding more active areas for catalytic transformation of H^+ to H_2 . According to Equation (5), the scan rate and the current derived from the CV curve are exactly proportional:

$$i = \nu C_{dl} \quad (5)$$

Figure S4 (Supplementary Materials) shows the voltammograms for Ti, TiO_2/Ti , and $CuO-TiO_2/Ti$ in 0.5M of H_2SO_4 that reveal the double-layer region's capacitive current displayed against scan rate. The C_{dl} values for Ti, TiO_2/Ti , and $CuO-TiO_2/Ti$ were found to be 0.124, 0.147, and 1.93 $\mu F\ cm^{-2}$, respectively, on the basis of the slope of the current density and scan rate plot. Equation (6) was then used to calculate the ECSA of these electrodes:

$$ECSA = \frac{C_{dl(Modified)}}{C_{dl(Ti)}} \times T_i \quad (6)$$

The comparison of ECSA numerals is listed in Table 3. Remarkably, the $CuO-TiO_2/Ti$ catalyst shows the highest ECSA (1.16 cm^2), far exceeding that of bare Ti (0.019 cm^2).

Turnover frequency (TOF) serves as an important metric for assessing the catalytic performance of materials in the hydrogen evolution reaction (HER). It indicates how efficiently each active site participates in hydrogen production over time. A greater TOF means that individual active sites contribute to generating increased hydrogen molecules per unit time. In this work, TOF was determined using Equation (7), where n is the number of electrons involved in the HER process; m ($mol\ cm^{-2}$); j ($A\ cm^{-2}$) represents the current density; F is the Faraday constant and denotes the number of active areas; and ECSA refers to electrochemical active surface area, which was calculated using Equation (8).

$$TOF = \frac{j}{nFm} \quad (7)$$

$$I = \frac{n^2 F^2 ECSA m}{4RT} \nu \quad (8)$$

Among all the catalysts examined, the $CuO-TiO_2/Ti$ electrode demonstrated the highest TOF of 0.150 s^{-1} , markedly surpassing the performance of TiO_2/Ti and Ti, as presented in Table 3. The exceptional TOF of the $CuO-TiO_2/Ti$ catalyst can be linked to its larger ECSA, improved electron-transfer capability, and well-optimized catalytic surface, all of which promote more efficient hydrogen adsorption, evolution, and desorption. Overall, the combined assessments of ECSA, Tafel slope, exchange current density, and TOF confirm that the $CuO-TiO_2/Ti$ electrode acts as a highly effective catalyst for the HER.

Table 3. A comparative assessment of the C_{dl} , ECSA, and TOF characteristics of the modified electrodes.

Parameters	Ti	TiO_2/Ti	$CuO-TiO_2/Ti$
$C_{dl}/\mu F\ cm^{-2}$	1.21	3.50	7.12
ECSA (cm^2)	0.196	0.570	1.161
TOF (s^{-1})	0.007	0.084	0.150

Finally, catalyst stability is a critical parameter for practical electrochemical applications, as it directly governs long-term durability and performance. To assess the electrochemical stability of the as-developed $CuO-TiO_2/Ti$ electrode, chronoamperometric measurements were performed in 0.5 M of H_2SO_4 at a steady potential of $-0.6\ V$ vs. RHE, and the resulting normalized current density–time profile is shown in Figure 1H. During the initial 15 min of electrolysis, a fluctuation in current density was observed, which is

commonly associated with electrode–electrolyte equilibration, surface conditioning, and the establishment of steady-state HER activity [43,44]. Consequently, the stabilized current density recorded after 15 min was selected as the reference point for evaluating the catalyst's long-term performance. Interestingly, the normalized current density increased progressively throughout the electrolysis period, reaching nearly 136% of the reference value after 25 h of continuous operation, equivalent to a 36% improvement in activity. This increase indicates an activation process occurring on the catalyst surface during HER, which may be related to electrochemically driven surface reconstruction and the generation of new active sites. The observed enhancement is in good agreement with the post-HER XPS analysis, which revealed an increased abundance of oxygen-vacancy-related species and modifications in the oxidation states of surface copper species following prolonged electrolysis. To further verify the durability of the catalyst, LSV measurements were performed before and after the 25 h chronoamperometric test (Figure 1H). Only a slight variation in the polarization behavior was observed after extended operation, demonstrating that the catalyst maintained its high HER activity. The combined electrochemical and surface characterization results suggest that the CuO–TiO₂/Ti electrode preserves its structural integrity while experiencing favorable surface modifications during electrolysis. Overall, these findings demonstrate the outstanding durability of the catalyst and emphasize its promise for long-term hydrogen generation in acidic environments.

Table 4 represents a comparative assessment of the HER activity of the synthesized catalyst against several recently published electrocatalysts. The prepared catalyst demonstrates promising electrochemical performance, exhibiting a comparatively low overpotential at 10 mA cm^{−2}, along with favorable HER properties relative to many previously reported Ti-based composite materials. Although its activity is still somewhat lower than that of a few advanced state-of-the-art catalysts, the obtained results establish its potential as an effective electrocatalyst for hydrogen evolution in acidic conditions.

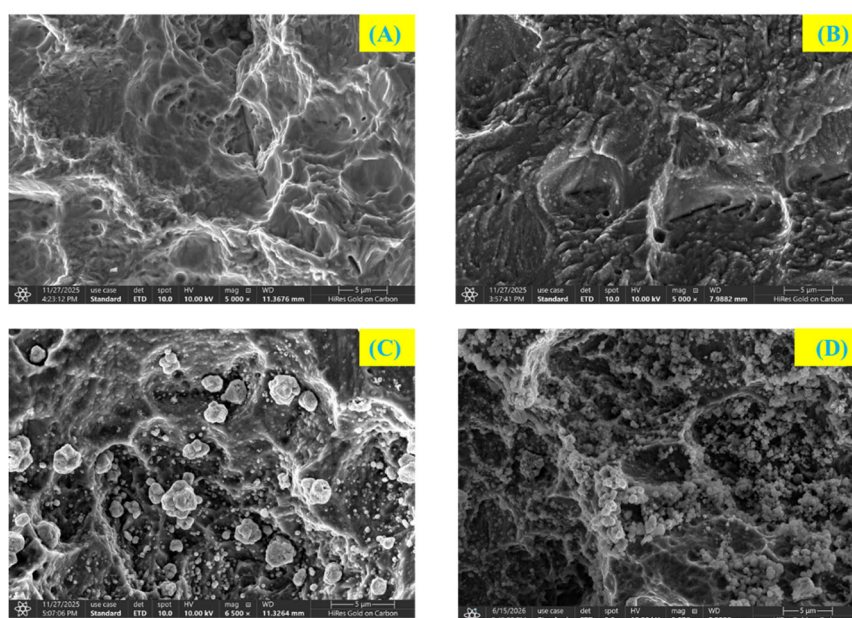
Table 4. Comparison of recently reported composites regarding HER performance.

Catalysts	Medium	η (mV)	b (mV dec ^{−1})	Ref.
Fe-doped TiO ₂ /MWNCT	0.5M H ₂ SO ₄	221	152	[45]
MXene-TiO ₂ nanotube composite	0.5M H ₂ SO ₄	681	112	[46]
TiO ₂ /SrMoO ₄	0.5M H ₂ SO ₄	313	152	[47]
CuWO ₄ @rGO	0.5M H ₂ SO ₄	565	192	[48]
Cu ₂ S micro-hexagons	1.0M KOH	330	107	[49]
M-NC-CoCu (CoCu/N-doped C)	1.0M KOH	240	164	[50]
CuO/TiO ₂ /Ti	0.5M H ₂ SO ₄	543.7	101.09	This work

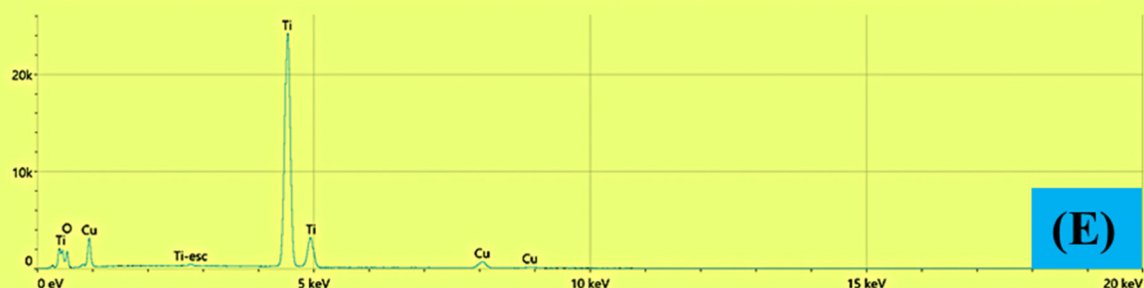
2.4. Morphological Analysis Using SEM-EDX

Scanning electron microscopy (SEM) was performed at a magnification of 10 μ m to investigate the surface morphology of the as-prepared samples, as illustrated in Figure 2A–D. The micrographs reveal a highly porous, sponge-like architecture accompanied by pronounced surface roughness, suggesting an enlarged effective surface area, which is advantageous for electrochemical hydrogen evolution reaction (HER) activity. The SEM image of the bare substrate (Figure 2A) exhibits an inherent porous framework. Upon anodization (Figure 2B), the surface becomes markedly more porous, indicating the successful formation of a TiO₂ layer and a significant increase in the density of exposed active

sites. Subsequent modification with CuO leads to the formation of uniformly distributed particles on the TiO₂/Ti surface (Figure 2C), reflecting successful and homogeneous incorporation of CuO within the composite matrix. Following 25 h of continuous HER operation (Figure 2D), the CuO/TiO₂/Ti electrode undergoes a distinct morphological transformation, evidenced by the emergence of porous and hollow-like surface architectures. This evolution is attributed to dynamic surface reconstruction driven by prolonged electrolysis, continuous hydrogen bubble generation, and electrode–electrolyte interactions under cathodic conditions. Notably, despite these structural modifications, the catalyst coating remains firmly adhered to the substrate without signs of severe degradation or delamination. Furthermore, post-electrocatalysis EDS and XPS analyses confirm the sustained presence of Cu- and O-containing species, indicating that the active CuO/TiO₂ phase is preserved throughout the HER process. These findings suggest that the observed morphological changes arise from beneficial surface reorganization and activation rather than catalyst loss, contributing to the excellent durability and sustained electrocatalytic performance of the electrode.



Element	Atomic %	Atomic % Error	Weight %	Weight % Error	Net Counts
O	20.6	0.9	7.8	0.3	3 290
Ti	73.5	0.3	83.4	0.3	317 436
Cu	5.8	0.2	8.8	0.2	11 175



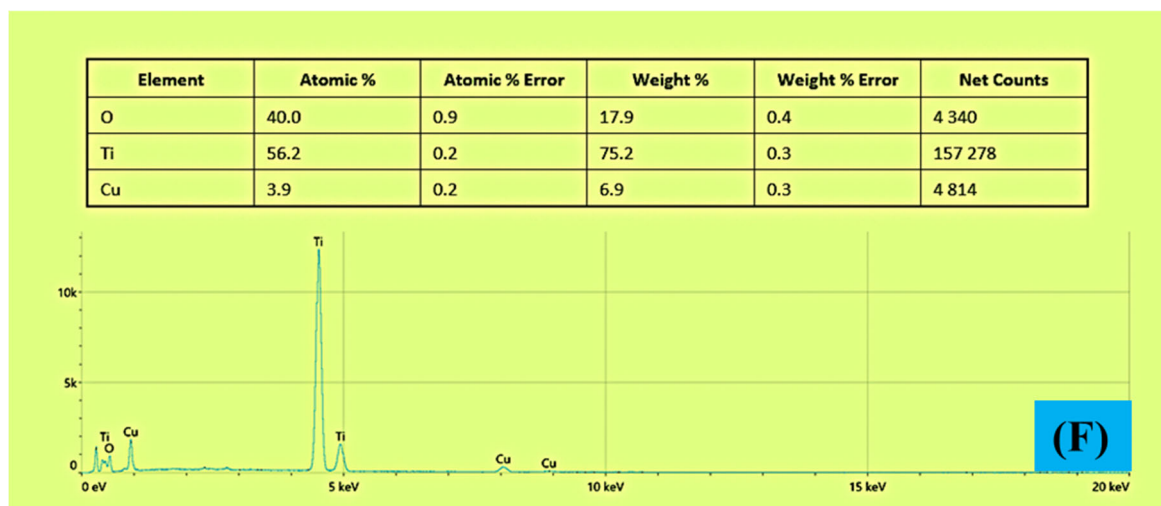


Figure 2. SEM images of (A) bare Ti, (B) TiO₂/Ti, (C) CuO/TiO₂/Ti before electrocatalysis, and (D) CuO-TiO₂/Ti after 25 h chronoamperometric electrocatalysis at 5 μ m magnification; (E) presents the corresponding EDX spectrum of CuO/TiO₂/Ti before analysis, (F) CuO/TiO₂/Ti after 25 h analysis.

Energy-dispersive X-ray spectroscopy (EDX) results (Figure 2E,F) demonstrated evident modifications in the surface elemental composition of the electrode after 25 h of HER testing. Prior to electrochemical operation, the surface consisted of 73.5 at.% Ti, 20.6 at.% O, and 5.8 at.% Cu. After the long-term HER experiment, the oxygen concentration increased significantly to 40.0 at.%, while the relative amounts of Ti and Cu decreased to 56.2 and 3.9 at.%, respectively. The enrichment of oxygen on the catalyst surface can be associated with the formation of hydroxylated species as well as the adsorption of water-derived oxygen-containing intermediates during prolonged electrolysis. The presence of these surface species may enhance proton accessibility and accelerate interfacial electron-transfer processes, thereby contributing positively to hydrogen evolution activity. The reduced relative abundance of Ti and Cu is likely a consequence of surface restructuring and the development of an oxygen-rich overlayer that partially masks the underlying metallic components. Despite these compositional variations, the clear detection of Ti and Cu after extended operation indicates that the catalyst retains its structural integrity, highlighting its excellent durability and resistance to degradation under HER conditions.

2.5. X-Ray Photoelectron Spectroscopy (XPS) Analysis

To ascertain the chemical states of the elements, X-ray photoelectron spectroscopy (XPS) is a great instrument. As a result, XPS was employed to determine the electrical state and chemical makeup of the developed materials. The oxidation state and chemical bonding environment of each element have a significant impact on the XPS signals. The survey XPS spectra shown in Figure 3A confirm the presence of Cu, Ti, and O species on the electrode surface. Following electrolysis, only minor variations in the intensity of several weak spectral features were observed, whereas the characteristic Cu 2p, Ti 2p, and O 1s peaks remained clearly discernible without noticeable binding-energy shifts. These findings indicate that the catalyst largely retains its chemical identity and structural integrity throughout the HER process, with only limited surface reconstruction occurring under operating conditions. Further insight into the electronic states of the constituent elements was obtained through high-resolution analysis of the Ti 2p, Cu 2p, and O 1s regions. Figure 3B displays high-resolution Ti 3p core-level spectra along with their fits. Two peaks are seen to appear at 458.8 eV for Ti 2p_{3/2} and at 464.5 eV for Ti 2p_{1/2} [51]. The peaks emerge from spin-orbit coupling, which divides the Ti 2p core level into two separate components. The energy difference between these peaks, known as spin-orbit splitting, generally falls

between 5.7 eV and 6.0 eV for Ti^{4+} , which corresponds well with the observed separation of 5.7 eV in the present analysis. The area ratio of the $2p_{1/2}$ to $2p_{3/2}$ peaks is anticipated to be 1:2, indicating the relative statistical likelihood of these spin-orbit transitions [51]. The existence of these particular binding energies is a conclusive sign of fully oxidized titanium, differentiating it from lesser oxidation states like Ti^{3+} or metallic Ti^0 , which have peaks at reduced binding energies [52]. It is worth noting that TiO_2 particles demonstrate stability and serve as an efficient support material by enhancing charge separation between Cu and Ti, thereby improving electronic conductivity and generating active sites for hydrogen evolution reactions. This might facilitate effective electron transfer between Cu and Ti and enhance catalyst efficiency [53]. While titanium in titanium dioxide is not active enough for hydrogen evolution reactions, it serves as a conductive platform that facilitates effective charge extraction from the catalyst to the external pathway [54].

Figure 3C presents high-resolution Cu 2p spectra accompanied by their corresponding fits. Two primary peaks for Cu(I) are observed at 932.5 eV for Cu^+ $2p_{3/2}$ and 952.6 eV for Cu^+ $2p_{1/2}$, with no satellite features present in the 940–945 eV range [55]. The peaks at 932.5 and 952.6 eV can be assigned to Cu^+ species, although a contribution from Cu^0 cannot be completely excluded because of the close proximity of their binding energies [56]. The simultaneous presence of Cu^{2+} satellite peaks confirms that mixed-valence copper species coexist on the catalyst surface [57]. Figure 3C displays additional features at 934.7 eV for Cu^{2+} $2p_{3/2}$, 955.1 eV for Cu^{2+} $2p_{1/2}$, as well as notable satellite peaks at 943.9 eV for Cu^{2+} $2p_{3/2}$ and 962.6 eV for Cu^{2+} $2p_{1/2}$ [58,59]. These satellite structures are well known signatures of divalent copper (Cu^{2+}), signifying the existence of CuO-type species [60]. The ability of Cu to exist in both Cu^+ and Cu^{2+} oxidation states is essential for augmenting catalytic activity. This redox pair can promote electron transport during the hydrogen evolution reaction, hence reducing the activation energy necessary for the process [61]. The coexistence of Cu^+ and Cu^{2+} species may facilitate charge transfer and provide favorable electronic environments for HER [62]. Cu^+ and Cu^{2+} have greater activity in hydrogen adsorption and activation compared to Ti^{4+} , which demonstrates reduced reactivity in the hydrogen evolution reaction (HER) [63]. The Cu species may interact with protons more efficiently, facilitating the adsorption and reduction of H^+ to produce H_2 , thus facilitating HER [64]. The prominent Cu^{2+} features observed in the pristine catalyst become considerably diminished after HER operation, as evidenced by the weakening of the shake-up satellite peaks. This behavior suggests a cathodically driven surface reconstruction involving the reduction of Cu^{2+} species to Cu^+ and/or Cu^0 during the electrocatalytic process. Figure 3D displays high-resolution O 1s core-level spectra along with their fits. Prior to electrochemical operation, the O 1s profile can be resolved into two distinct contributions located at approximately 529.9 and 531.7 eV. The peak at approximately 529.9 eV is generally attributed to lattice oxygen (O^{2-}) in a fully coordinated metal oxide lattice structure [65]. The peak at approximately 531.7 eV often corresponds to oxygen vacancies or structural defects within the lattice [65]. The presence of these defect sites is expected to influence the electronic structure of the catalyst and provide favorable pathways for charge transport.

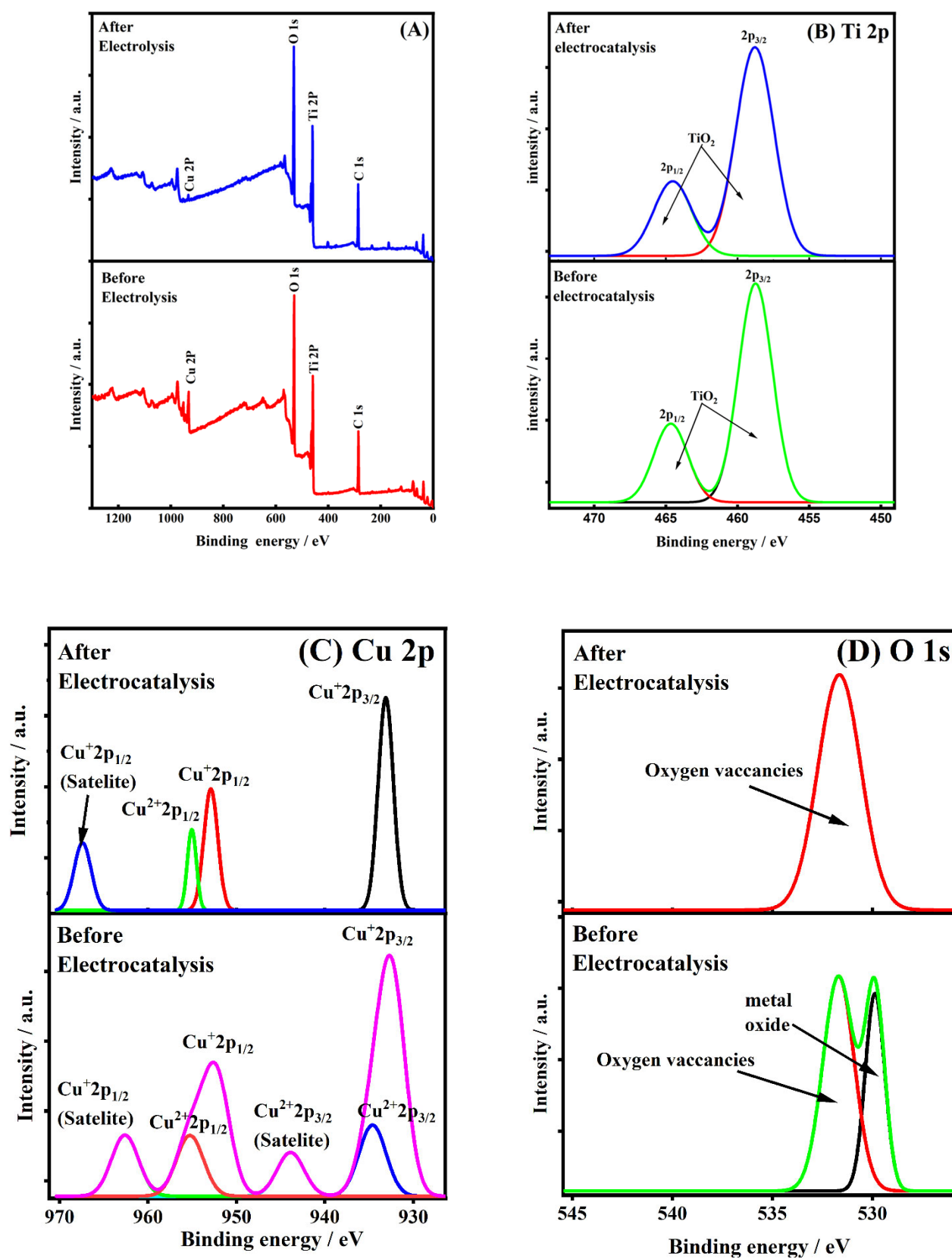


Figure 3. XPS spectrum for CuO-TiO₂/Ti (A) survey scan, (B) Ti 2p, (C) Cu 2p, (D) O 1s before and after 25 h chronoamperometric electrocatalysis.

After prolonged HER operation, a significant change in the O 1s spectral profile is observed, with the higher-binding-energy component becoming predominant and the lattice oxygen signal showing a marked decrease in intensity. This evolution suggests that the catalyst surface undergoes electrochemically induced restructuring during HER, leading to an increased concentration of oxygen-deficient sites together with the adsorption of hydroxyl species and water-derived intermediates [66]. The enrichment of oxygen-containing surface species agrees well with the EDS analysis, which showed a notable increase in oxygen content after extended electrolysis. Such defect-rich and hydroxylated surface environments are known to improve proton accessibility and facilitate interfacial electron-transfer processes, thereby supporting enhanced HER performance and catalyst durability [67].

Hence, the superior HER activity of the CuO-TiO₂/Ti catalyst arises from the synergistic effects between the mixed-valence copper species and the TiO₂/Ti substrate. The simultaneous presence of Cu⁺ and Cu²⁺ creates active centers for proton adsorption and subsequent hydrogen generation, while the Cu⁺/Cu²⁺ redox couple promotes efficient electron transport throughout the reaction. Although TiO₂ exhibits limited intrinsic HER activity, it serves as a robust support that enhances charge separation and facilitates electron conduction. Furthermore, oxygen-vacancy-related defects contribute to improved electronic properties and charge-transfer processes. Following HER operation, the partial reduction of Cu²⁺ species, together with the increased formation of oxygen-deficient sites, suggests electrochemically induced surface restructuring. This defect-enriched, hydroxylated surface environment can enhance proton accessibility and accelerate interfacial electron-transfer kinetics, thereby contributing to sustained HER performance and catalyst durability. Prior to HER testing, the O 1s XPS spectrum could be resolved into contributions associated with lattice oxygen and defect-related oxygen species. Following 25 h of continuous electrolysis, the O 1s signal exhibited significant broadening, reflecting a wider range of oxygen chemical states on the catalyst surface. The increase in full width at half maximum (FWHM) is indicative of the formation of additional defect sites, particularly oxygen-vacancy-associated species, during prolonged HER operation. Moreover, EDS measurements showed a slight increase in the oxygen content after electrolysis. This increase is likely related to the adsorption of oxygen-containing surface species, including hydroxyl groups and water molecules, at vacancy-rich regions. Taken together, the XPS and EDS findings suggest that the catalyst experiences mild surface restructuring under HER conditions while preserving its overall structural framework. Such surface evolution may be beneficial for maintaining the long-term electrocatalytic activity and stability of the catalyst.

3. Experimental

3.1. Instrumentation and Chemicals

In this work, the reagents used were of analytical grade and sourced in their maximum available purity. Sulphuric acid (H₂SO₄), hydrochloric acid (HCl), sodium hydroxide (NaOH), copper(II) sulfate (CuSO₄·H₂O), and acetone were purchased from Sigma Aldrich (St. Louis, MO, USA). Ultrapure Milli-Q Millipore water was used to prepare the required solutions in order to ensure the accuracy of the results. The Ti sheet (2 mm thick) was collected from Shanghai Chemical Co. (Shanghai, China).

CHI 660 potentiostats and an Autolab 128 N potentiostat were employed to carry out electrochemical research. Because all potentials were recorded relative to the Ag/AgCl (sat. KCl) reference electrode, they were transformed to reversible hydrogen electrode (RHE) values using the formula as presented by Equation (9) [68]:

$$E_{\text{RHE}} = [E_{\text{Ag/AgCl}} + 0.059 \times \text{pH} + 0.197]/V \quad (9)$$

3.2. Fabrication of Electrode

3.2.1. Development of TiO₂/Ti Surface

Titanium (Ti) sheets with a 0.196 cm² geometric surface area were first cleaned by ultrasonication in acetone and deionized water for about 10 min each. The cleaned Ti sheets were then immersed in 6.0 M of HCl and then heated at 85.0 °C for 10 min in a hot plate. After treatment in acid, the electrodes were again ultrasonically washed in deionized water for another 10 min. Subsequently, the pretreated Ti sheets were placed in a Pyrex electrochemical cell filled with 1.0 M of H₂SO₄ and treated anodically at an applied voltage of 12.0 V using a DC adapter for 2 h. During this electrochemical oxidation process, the outer surface of the Ti sheets was converted into anatase TiO₂, which was visually evidenced by a color transition from grey to brown [69]. In this article, we refer to it as the TiO₂/Ti assembly.

3.2.2. Fabrication of CuO-TiO₂/Ti Heterostructures

Exactly 0.01 M of CuSO₄·5H₂O solution was made by dissolving the requisite amount of CuSO₄·5H₂O in 10 mL of deionized water. The TiO₂/Ti assembly was placed in a CuSO₄·5H₂O solution containing a three-electrode setup. Copper deposition was carried out by sweeping the electrode from 0 to −1.0 V at a scan rate of 0.1 V s^{−1} for 10 consecutive scans (5 cycles). During this step, Cu was electrodeposited onto the pre-formed TiO₂/Ti assembly by applying a potential sweep from 0 to −1.0 V at a scan rate of 0.1 V s^{−1} for 10 consecutive scans (5 cycles). The deposited Cu was then oxidized by scanning the potential from 0 to 1.0 V at the same scan rate for 20 scans (10 cycles). The resultant surface in this article is referred to as the CuO-TiO₂/Ti electrode (COT), as shown in Figure S5 (Supplementary Materials).

3.2.3. Surface Characterization

Using a Kratos Axis-Ultra apparatus (Kratos Analytical Ltd.) and an Al Kα radiation source (1486.68 eV), X-ray photoelectron spectroscopy (XPS) was used to assess the elemental composition and chemical states of the electrode surface.

3.3. Electrochemical Measurements

A traditional three-electrode setup in 0.5 M of H₂SO₄ with an overall volume of 10 mL was used to conduct the HER experiments. A number of electrochemical techniques (LSV, OCP, EIS, etc.) were used to examine the catalysts' stability and electrocatalytic performance. Particularly, to observe relative electrocatalytic HER performance, different electrodes were scanned between −0.2 and −0.8 V at a scan rate of 0.1 V s^{−1} several times until reproducible i-E responses were obtained. The Sigma Plot v.10 software was used to analyze gathered data from electrochemical measurements.

4. Conclusions

This study presents the optimization of the in situ development and comprehensive evaluation of a CuO-TiO₂/Ti catalyst, highlighting its potential as an efficient electrocatalyst for hydrogen evolution reaction in acidic environments. The nanocomposite exhibited excellent electrocatalytic activity, achieving a low overpotential of 543.7 mV at a current density of 10 mA cm^{−2}, along with a comparatively small Tafel slope of 101.09 mV dec^{−1} and a high exchange current density of 0.35 mA cm^{−2}. The findings underscore the productive collaboration between CuO and TiO₂/Ti, which collectively improve the catalytic efficiency of the electrode. The elevated electrochemical active surface area and TOF provide additional validation of its inherent activity. During a 25 h chronoamperometric evaluation, the catalyst maintained stable operation and exhibited a 36% increase in current

density, demonstrating excellent long-term durability and sustained HER performance. The outstanding performance of CuO-TiO₂/Ti powers it as a viable option for energy conversion technologies. Future research should aim to further improve its long-term stability and efficiency, optimize its composition and morphology, and develop more scalable synthesis routes. In addition, evaluating its activity under different pH conditions, including neutral and alkaline media, will broaden its relevance for hydrogen generation. The development of stable and economically viable catalysts such as CuO-TiO₂/Ti is crucial for the progress of sustainable hydrogen-based energy technologies.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/catal16070591/s1>. Figure S1 Experimental Nyquist plots and corresponding fitted EIS spectra. Figure S2 Bode plots. Figure S3 LSV curves recorded for Ex-situ CuO-TiO₂/Ti. Figure S4 CV curves of (A) Ti, (B) TiO₂, (C) COT, obtained at varying scan rates (0.01, 0.02, 0.03, and 0.04 V s⁻¹) (D) Graph of current density versus scan rate. Figure S5 Schematic illustration of fabrication of CuO/TiO₂/Ti electrode.

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Data Availability Statement: The data can be made available upon request to the corresponding authors.

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