

**SYNTHESIS OF COPPER-BASED BIMETALLIC
ELECTROCATALYST FOR EFFICIENT
WATER SPLITTING**

BY

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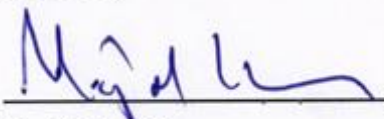
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**Dedicated to myself and
my beloved mother**

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ABSTRACT

Name : Ayu Wahyuni
Title : Synthesis of Copper-Based Bimetallic Electrocatalyst for Efficient Water Splitting
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This study investigates the synthesis and performance of Cu-based bimetallic electrocatalysts (CuCo and CuNi) for water splitting. Both catalysts were synthesized using a facile hydrothermal method. X-ray diffraction (XRD) results confirmed the formation of layered double hydroxides (LDH) and their transformation to mixed bimetallic oxides (CuO-Co₃O₄ and CuO-NiO) after annealing at 600 °C. The catalysts were further modified with highly reduced graphene oxide (HRG). All catalysts were well-characterized using X-ray diffraction (XRD), Scanning Electron Microscopy (SEM), and Transmission Electron Microscopy (TEM). Performance evaluations were conducted on two substrates, FTO and NF. The results indicate that overall, CuCo exhibited better performance than CuNi. Among the catalysts tested on FTO, CuCoOx/HRG demonstrated the best performance, with significantly lower overpotentials (462 mV at 10 mA cm⁻²) and Tafel slopes (76 mV dec⁻¹). CuCoOxHRG/FTO showed a higher electrochemically active surface area (ECSA) of 72.7 cm² and a high turnover frequency of 0.317 s⁻¹ at -0.46 V (vs RHE). While on nickel foam, CuCo-LDH/HRG performed the best among other catalysts. CuCo-LDH/HRG/NF had an overpotential of 275 mV at 10 mA cm⁻², a Tafel slope of 56 mV dec⁻¹, an ECSA of 61.8 cm², and a turnover frequency of 0.063 s⁻¹ at -0.27 V (vs RHE). These findings highlight the potential of Cu-based bimetallic electrocatalysts for efficient water splitting.

The electrochemical oxidation reaction of 5-hydroxymethylfurfural (HMFOR) has also been explored as a strategy to enhance electrochemical water splitting. A significant advantage of HMFOR lies in its lower oxidation potential compared to the oxygen evolution reaction (OER), which enables reduced energy consumption and enhances overall efficiency in hydrogen generation. Additionally, this reaction converts 5-hydroxymethylfurfural (HMF) to 2,5-furandicarboxylic acid (FDCA), presenting a sustainable route for producing bio-based chemicals, with FDCA being a potential replacement for terephthalic acid in plastics. For this purpose, CuCo-LDH, specifically the CuCo-LDH catalyst on nickel foam (NF), was tested. The catalyst was evaluated in an H-type electrochemical cell, separated by a Nafion membrane to ensure efficient product separation. As a result, the developed CuCo-LDH/NF catalyst demonstrated efficient electrochemical performance for HMF oxidation in alkaline media, with a significantly lower onset potential of 1.34 V (vs RHE) and higher current density than the OER. Furthermore, electrochemical impedance spectroscopy (EIS) showed reduced charge transfer resistance for HMF oxidation, further enhancing its catalytic performance. These results confirm the ability of HMFOR to enhance electrochemical water splitting. Additionally, the electrochemical studies confirmed a Faradaic efficiency of 96.82% and an FDCA yield of 97.46%, indicating highly selective HMF oxidation. The CuCo-LDH/NF also exhibited excellent stability over multiple cycles, maintaining high conversion and yield. These results highlight CuCo-LDH/NF as a promising electrocatalyst for green, scalable, and efficient HMF-to-FDCA conversion, offering a viable alternative to conventional chemical methods.

Keywords: CuCo-LDH, CuNi-LDH, bimetallic oxide catalyst, electrochemical water splitting, green hydrogen, HMFOR

الرسالة ملخص

الاسم : واهيوني آيو

العنوان : بكفاءة المياه لتقسيم النحاس على يعتمد المعدن ثنائي كهربائي محفز تخليق

التخصص مجال : الكيمياء

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لتقسيم (CuCo و CuNi) النحاس على القائمة المعدن ثنائية الكهربائية المحفزات وأداء تخليق في الدراسة هذه تبحث تكوين (XRD) السينية الأشعة حيود نتائج أكدت. سهلة مائية طريقة باستخدام المحفزين كلا تخليق تم. المياه عملية بعد (CuO-NiO و CuO-Co₃O₄) ثنائية معدنية أكاسيد إلى وتحولها (LDH) الطبقة مزدوجة هيدروكسيدات توصيف تم. (HRG) المخفض الجرافين أكسيد بإضافة المحفزات تعديل تم. مئوية درجة 600 حرارة درجة عند التلدين الإلكتروني والمجهر (SEM) الماسح الإلكتروني والمجهر (XRD) السينية الأشعة حيود باستخدام المحفزات جميع أفضل أداء قدم CuCo أن إلى النتائج أشارت. NF و FTO، الركائز من نوعين على الأداء تقييم تم. (TEM) النافذ حيث، أداء أفضل CuCoOx/HRG قدم، FTO على اختبارها تم التي المحفزات بين من CuNi. بـ مقارنة عام بشكل أظهر. (عقد/ف.م 76) Tafel ومنحدرات (2/سم.أ.م 10 عند ف.م 462) الزائدة الجهود في كبيراً انخفاضاً أظهر بلغ مرتفع دوران ومعدل 72.7 سم² بلغت أعلى (ECSA) كهروكيميائياً نشطة سطح مساحة CuCoOx/HRG/FTO حيث، الرغوي النيكل على أداء أفضل CuCo-LDH/HRG قدم بينما. (مقابل RHE) فولت -0.46 عند -1 ت 0.317 عقد/ف.م 56 بلغ Tafel ومنحدر (2/سم.أ.م 10 عند ف.م 275) بلغت زائدة جهود CuCo-LDH/HRG/NF سجل (مقابل) فولت -0.27 عند -1 ت 0.063 بلغ دوران ومعدل 61.8 سم² بلغت (ECSA) كهروكيميائياً نشطة سطح ومساحة بكفاءة المياه لتقسيم النحاس على المعتمدة المعدن ثنائية الكهربائية المحفزات إمكانيات النتائج هذه تؤكد. (RHE).

الكهربائي المياه تقسيم لتحسين كاستراتيحية (HMFOR) فورفورال ميثيل الهيدروكسي أكسدة تفاعل استكشاف تم كما استهلاك تقليل في يساهم مما، (OER) الأكسجين تطور بتفاعل مقارنة التأكسدي الجهد انخفاض بميزة HMFOR يتميز (HMF) فورفورال ميثيل الهيدروكسي التفاعل هذا يحول، ذلك إلى بالإضافة. الهيدروجين إنتاج كفاءة وزيادة الطاقة أن يمكن حيث، الحيوية الكيميائية المواد لإنتاج مستداماً طريقاً يوفر مما، (FDCA) الفوراندكاربوكسيليك حمض إلى وبالأخص، CuCo-LDH اختبار تم، الغرض هذا لأجل. البلاستيك في التيريفثاليك لحمض محتملاً بديلاً FDCA يكون

بغشاء مفصولة H النوع من كهروكيميائية خلية في المحفز تقييم تم. (NF) الرغوي النيكل على CuCo-LDH المحفز وسط في HMF لأكسدة فعالاً كهروكيميائياً أداء CuCo-LDH/NF المحفز أظهر. بكفاءة المنتج فصل لضمان نفايون علاوة. OER. بـ مقارنة أعلى تيار وكثافة (RHE مقابل) فولت 1.34 البالغ الأولي الجهد في كبير انخفاض مع، قاعدي HMF، لأكسدة الشحنة انتقال مقاومة في انخفاضاً (EIS) الكهروكيميائية الشحنة نقل مقاومة طيف أظهرت، ذلك على بلغ FDCA وعائد 96.82٪ بلغت فارادية كفاءة أيضاً الكهروكيميائية الدراسات أكدت. التحفيزي أدائه يعزز مما عدة مدار على ممتازاً ثباتاً CuCo-LDH/NF أظهر كما. HMF لـ عالية انتقائية أكسدة إلى يشير مما، 97.46٪ واعداً كهربائياً محفزاً يمثل CuCo-LDH/NF أن النتائج هذه تؤكد. مرتفع وعائد عالي تحويل على الحفاظ مع، دورات للطرق للتطبيق قابلاً بديلاً يوفر مما، وفعالة للتوسيع وقابلة خضراء بطريقة FDCA إلى HMF لتحويل التقليدية الكيميائية.

الهيدروجين، الكهربائي المياه تقسيم، المعدن ثنائي أكسيد محفز، CuCo-LDH، CuNi-LDH، المفتاحية الكلمات

HMFOR، الأخضر.

1 CHAPTER ONE

INTRODUCTION

1.1 Background

The growing population, industrialization, and technological advancements have resulted in an increasing demand for energy. Increasing energy needs are exacerbated by increasing greenhouse gas emissions and the rapid depletion of fossil fuels. Consequently, the pursuit of sustainable and environmentally friendly energy sources has become inevitable. Presently, there is a growing interest in clean and renewable energy resources, with hydrogen generation being the most extensively studied and sought-after option.

Hydrogen is a highly efficient and clean form of energy, boasting an energy density of 150 MJ/kg, which is nearly three times that of petroleum fuels (50 MJ/kg). This high energy density makes hydrogen an attractive option for various energy applications, particularly in the quest for sustainable and environmentally friendly energy sources.

Electrochemical water splitting that involves two main reactions, hydrogen evolution reaction (HER) and oxygen evolution reaction (OER) is the forefront method in generating green hydrogen, particularly when powered by renewable electricity. However, a notable challenge in the efficacy of this process lies in the relatively low efficiency of hydrogen production, primarily attributed to the high energy consumption characteristic of the sluggish anodic oxygen evolution reaction (OER). To mitigate this issue, an innovative alternative has surfaced, which is the exploitation of organic oxidation reactions to supplant

the OER. This approach is particularly advantageous given its favorable thermodynamic properties and economic feasibility.

Among the various anodic oxidation reactions, the oxidation of 5-hydroxymethylfurfural (HMF) is especially noteworthy. This reaction, referred to as the 5-hydroxymethylfurfural oxidation reaction (HMFOR), presents a compelling case for replacing the OER, as it facilitates energy-efficient hydrogen production. A significant advantage of HMFOR lies in its lower oxidation potential compared to the OER, which enables reduced energy consumption and enhances overall efficiency in hydrogen generation.

On the other hand, HMFOR shows great potential for transforming renewable biomass into high-value chemicals, thereby decreasing our reliance on fossil fuels. 5-hydroxymethylfurfural (HMF) is a significant biomass-derived intermediate compound. It plays a crucial role as a precursor in the production of a wide range of valuable products, including plastics, liquid fuels, and pharmaceuticals. One of the most valuable oxidation products of HMF is 2,5-furandicarboxylic acid (FDCA). FDCA is a precursor for synthesizing polyethylene furanoate (PEF) as a bio-substituent for petroleum-derived polyethylene terephthalate (PET), offering a more sustainable alternative. Moreover, FDCA can be further processed into succinic acid, a compound with numerous applications. Succinic acid is valuable in the production of antifungal agents, macrocyclic ligands, fuels, and pharmaceuticals, highlighting its versatility and importance in various industrial processes.

To efficiently drive the HER and OER or HMFOR, it is crucial to have catalysts that are highly effective in minimizing overpotentials. However, the acidic conditions narrow down the range of options for OER electrocatalysts to noble metals and noble metal oxides, which

are known to be quite expensive¹. On the other hand, alkaline electrolysis cells allow for a wider range of non-noble metal or metal oxide electrocatalyst options compared to acidic cells. However, the activity and kinetics of HER in alkaline media is generally much lower than in acidic media². As a result, designing an optimal electrocatalyst that can overcome these challenges remains a significant challenge in the field of renewable energy.

In the past, electrocatalyst studies primarily utilized noble elements such as Pt, Ru, Ir, Pd, and Rh in both acidic and alkaline environments. However, the commercial production of these catalysts faces challenges due to their limited availability and high costs. Pt-based catalysts remain the standard for electrochemical hydrogen evolution, owing to their exceptional catalytic activity, low potential, kinetic performance, and absence of anodic poisoning. However, it is hindered by drawbacks related to the expense and scarcity of Pt. Consequently, there is an urgent need to identify materials suitable for hydrogen production that are easily accessible, possess abundant electrocatalytic properties, and can alter the active surface area of the electrode or enhance electrocatalytic activity through doping. Among the extensively researched elements for this purpose, Copper (Cu) stands out³. Electrodes composed of non-noble metals developed with copper have emerged as readily available catalysts, significantly improving catalytic performance in alkaline environments.

Bimetallic catalysts, composed of two distinct metals, exhibit enhanced catalytic activity and efficiency compared to single metal catalysts used for hydrogen evolution. Bimetallic catalysts give greater options to improve catalytic performance by varying surface element distribution, lattice strain, local coordination environment, and charge transfer between various metals than their monometallic counterparts⁴. These catalysts not only possess the inherent catalytic properties of each metal component, but also benefit from a strong

synergistic effect between the metals. Additionally, bimetallic materials have demonstrated significant promise as catalysts for the hydrogen evolution reaction (HER) owing to their distinctive electronic and geometric properties, which can be customized by adjusting the composition and size of the materials. Notably, the utilization of Cu-based bimetal in the creation of electrocatalysts has proven to be highly effective.

1.2 Objectives and Scope

The primary objective is to synthesize Cu-based bimetallic electrocatalyst (CuCo and CuNi) using facile hydrothermal method and evaluate their performance in electrochemical water splitting. The research also studies the effect of different substrates (fluorine-doped tin oxide and nickel foam) to performance of electrocatalysts. Furthermore, the electrocatalysts also asses for HMFOR as a strategy to enhance water splitting. The resulting electrocatalyst will be characterized using various techniques, including X-ray diffraction, scanning electron microscopy, and transmission electron microscopy. The electrocatalytic activity of the synthesized electrocatalyst will be evaluated using electrochemical techniques: linear sweep voltammetry, electrochemical impedance spectroscopy, and chronoamperometry. The findings will contribute to advancing the understanding and development of cost-effective, non-noble metal catalysts for hydrogen production, water splitting, and electrooxidation of HMF.

2 CHAPTER TWO

LITERATURE REVIEW

2.1 Basic of Hydrogen Evolution Reaction (HER)

When an electric current is passed through one mole of water during the process of electrolysis, it breaks down into its constituent elements – one mole of hydrogen and half a mole of oxygen gases. This process of water splitting is achieved through two half-cell reactions - water reduction and water oxidation. During water reduction, protons from water molecules are reduced at the cathode, leading to the formation of hydrogen gas. This process is referred to as hydrogen evolution reaction (HER). At the same time, during water oxidation, water molecules are oxidized at the anode, leading to the production of oxygen gas. This process is known as oxygen evolution reaction (OER)⁵.

Commercial electrolyzers can split water at 1.8-2.0 V, which is 0.55 to 0.77 V greater than the thermodynamic requirements of 1.23 V. Overpotential refers to the additional potential required for overcoming the energy barrier of a reaction. Overpotential can be caused by electrode, electrolyte, and circuit resistance, as well as activation hindering from kinetic processes in both the cathode and anode. Thus, water splitting requires a larger potential than the thermodynamic potential⁵.

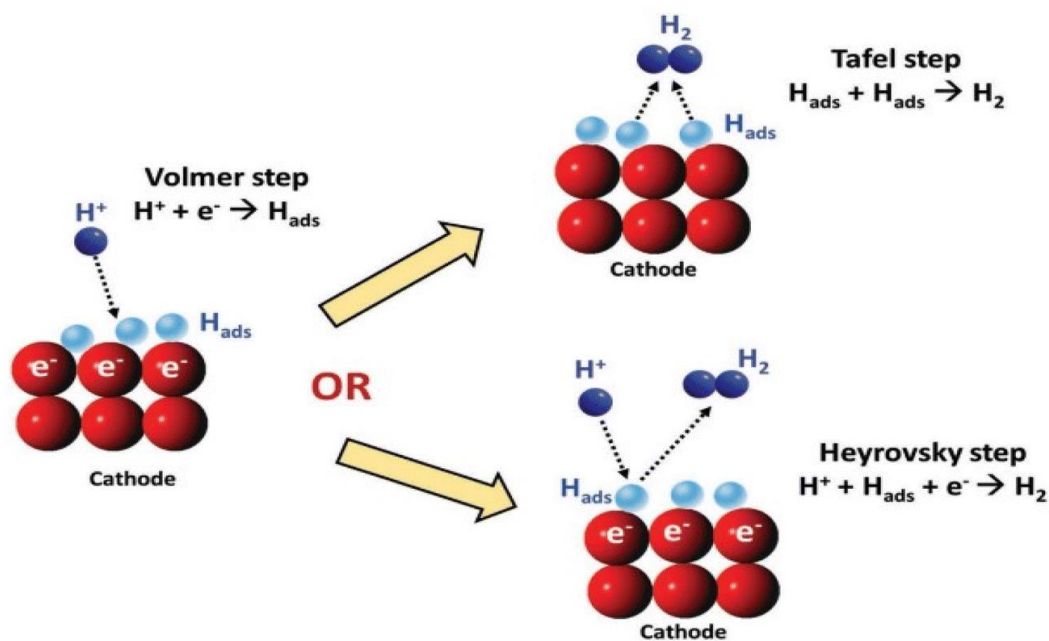


Figure 1. A schematic representation of a possible HER reaction route on the cathode^{6,7}

The hydrogen evolution reaction (HER) is one of the two reactions involved in water-splitting. It occurs in two steps: the first stage involves the adsorption of H_2O or H^+ on the cathode, which is also known as the Volmer step. The second stage involves the desorption of H_2 from the cathode through either a chemical or an electrochemical mechanism, which is known as the Tafel and Heyrovsky steps respectively, as shown in **Figure 1**. For a material to work well as a catalyst for the HER, it should have specific features. These include a large number of active sites with optimal electron density, which can produce moderate bonding strength with adsorbed H atoms, following the Sabatier principle.⁸ Furthermore, it is important that the material exhibits minimal charge transfer resistance at the interface and underlying electrode material. Finally, the material should be stable in electrolyte medium.⁶

2.2 Basic of 5-Hydroxymethylfurfural Oxidation Reaction (HMFOR)

The electrooxidation reaction of 5-hydroxymethylfurfural (HMF) is an electrochemical process that converts HMF into valuable oxidation products, including 2,5-diformylfuran (DFF), 5-hydroxymethyl-2-furancarboxylic acid (HMFA), and 2,5-furandicarboxylic acid (FDCA). This reaction is significant in green chemistry and renewable energy systems, as it enables the production of bio-based chemicals from HMF, which is a platform chemical derived from lignocellulosic biomass.

The mechanism of HMF electrooxidation is complex and involves multiple steps where electrons and protons are removed from HMF. This process often occurs through intermediates that lead to the desired end products. Typically, the reaction takes place on the surface of a catalyst, which may be a noble metal like platinum or palladium, or increasingly, a less expensive metal oxide-based catalyst. These catalysts facilitate the oxidation process by adsorbing HMF onto their surfaces, where the molecule undergoes stepwise oxidation at specific functional groups. Initially, the hydroxymethyl ($-\text{CH}_2\text{OH}$) group is oxidized, forming intermediates like DFF. If the reaction conditions are carefully controlled, this intermediate can be further oxidized to form HMFA or even FDCA, depending on the number of electrons transferred and the applied potential.

Electrooxidation of HMF usually occurs in an aqueous electrolyte solution, which can be either acidic or alkaline based on the type of catalyst and the desired reaction pathway. Alkaline conditions are often preferred because they promote deprotonation steps, making it easier for HMF to oxidize at a lower energy cost. During the reaction, an external power source applies a voltage to the electrode, facilitating electron transfer between the catalyst and HMF, which drives the oxidation process. This not only increases the reaction rate but

also allows for selective tuning of the reaction pathway by adjusting the applied potential and the electrolyte pH. By modulating these parameters, researchers can direct the reaction toward specific products, which is particularly valuable in industrial applications where precise product yields are desired.

The significance of the HMF electrooxidation reaction lies in its ability to produce high-value chemicals through a sustainable and energy-efficient pathway. For example, FDCA is a highly sought-after compound because it serves as a precursor for polyethylene furanoate (PEF), a bio-based plastic that can replace conventional fossil-fuel-derived plastics like polyethylene terephthalate (PET). Furthermore, the electrochemical route to HMF oxidation provides a cleaner alternative to traditional chemical oxidation, which often involves harsh conditions and toxic reagents. In contrast, electrooxidation can be carried out under milder conditions and relies on electricity as the driving force, which can be sourced from renewable energy, thereby reducing the carbon footprint of the process.

2.3 Role of Copper-based Bimetallic Electrocatalyst

Copper, being abundant and relatively inexpensive, has garnered attention as a potential catalyst for HER. The intrinsic electronic properties of Cu enable it to facilitate proton adsorption and hydrogen desorption, though its activity is typically lower than that of the noble metals. Furthermore, Cu-based catalysts often exhibit poor durability due to oxidation and degradation under operational conditions. To enhance catalytic performance of Cu, researchers have explored modifications such as alloying with other transition metals.

Electrocatalytic of Cu-based materials have been widely explored due to their unique properties, which can be tailored to enhance catalytic activity and selectivity^{9–14}. Formation

of Cu-bimetallic^{11–13} materials have been immensely studied. The preference for a core-shell structure in bimetallic nanoparticles is based on how the components separate on the surface of the particle -known as the surface segregation phenomenon.¹⁵ This phenomenon is influenced by various physical properties of the materials, such as atomic radii, surface energy, and electronegativity.¹⁶ Previous research indicates that the cohesive material is usually found in the core, while the component with a larger atomic radius segregates to the surface of the nanoparticle.¹⁵

The presence or absence of a sufficient amount of surface-preferring material has a significant impact on the composition and properties of a surface. In cases where an abundant quantity of the surface-preferring material is present, the surface will primarily comprise this material. In contrast, if the number of atoms is insufficient to form a complete surface layer, the surface will display a heterogeneous mixture of different materials. The extent of surface segregation and the tendency for a core-shell structure were influenced by the availability of the surface-preferring material.¹⁵

In the synthesis of Cu-based particles, heat-induced surface segregation processes are crucial, and high temperatures are typically needed to sustain adequate catalytic activity to predict the equilibrium structures of bimetallic materials. However, in such an environment, the morphological change of bimetallic materials results in a reduction of catalytically active sites. To create bimetallic particles, instability is a significant difficulty.¹⁵

Designing the synthesis of bimetallic materials requires considering several variables, such as size, shape, defects structure, composition, phases, and supports.^{17–19} Another important aspect to consider when evaluating catalytic performance is morphology. Bimetallic particle surfaces are often classified using Miller indices (hkl). The primary surfaces of a

shape-controlled particles with a face-centered-cubic (FCC) lattice are the (100), (111), and (110) planes of a metal catalyst.²⁰ The catalytic event involves adsorption, dissociation, coupling, and interaction of intermediate adsorbates, which are affected by various surfaces, each with a unique coordination number (CN). Additionally, the configuration of exposed surface facets of the atoms has an impact on selectivity.^{21,22}

The oxidation state of metal particles can have a major impact on catalytic activity. As a result of altered electronic interactions occurring between the metal and its substrates, metals in a nanoparticle system are not always neutrally charged, which could affect how reactions turn out. For instance, varying oxidation states alter redox characteristics of nanoparticle, which can either increase or decrease its performance. Furthermore, same metals with different facets exhibit intrinsic structural differences in binding energies due to the different coordination numbers of each facet.²²

2.4 Overview of Bimetallic Electrocatalysts (CuCo, CuNi) for HER and HMFOR

The development of Cu-based bimetallic electrocatalysts has garnered significant attention due to their potential in enhancing the efficiency of electrochemical reactions, particularly in the hydrogen evolution reaction. Among the various combinations, Cu-Co and Cu-Ni bimetallic systems have shown promising results. Bimetallic catalysts combine two metals to create a synergistic effect that can enhance catalytic activity and stability. The interaction between Cu and another metal (e.g., Co or Ni) results in modified electronic structures, altered surface morphologies, and increased active sites, which are favorable for HER. Co and Ni are particularly promising due to their strong hydrogen adsorption capabilities. Recent studies have shown that CuCo and CuNi alloys exhibit improved HER performance

compared to monometallic counterparts due to enhanced electron transfer, charge redistribution, and durability.

The combination of copper (Cu) and cobalt (Co) in bimetallic electrocatalysts leverages the unique properties of both metals. Cu is known for its excellent electrical conductivity, while Co provides active sites for HER, leading to improved reaction kinetics. Studies have shown that the incorporation of Co into the Cu matrix can modulate the electronic structure of Cu, thereby enhancing its catalytic properties ²³. Additionally, studies have shown that Cu-Co bimetallic catalysts exhibit higher HER activity compared to their monometallic counterparts. This is attributed to the optimized electronic structure and increased number of active sites ²⁴. The presence of Co helps in reducing the overpotential required for HER, making the process more energy-efficient ²⁵. Cu-Co bimetallic catalysts also demonstrate improved stability and durability under electrochemical conditions. The incorporation of Co into the Cu matrix helps in stabilizing the catalyst structure, preventing degradation over prolonged usage.

Nickel (Ni) is well-known for its catalytic activity in HER, and when combined with Cu, it forms a bimetallic system that benefits from the high conductivity of Cu and the catalytic efficiency of Ni. This combination results in a catalyst with superior performance. The alloying of Ni with Cu leads to the formation of unique surface structures that enhance the adsorption of hydrogen intermediates, facilitating the HER process. The presence of Ni also helps in lowering the activation energy required for the reaction, thereby increasing the reaction rate. Cu-Ni bimetallic catalysts are known for their excellent durability. The interaction between Cu and Ni helps in maintaining the structural integrity of the catalyst during the HER process, ensuring long-term stability ²⁶.

Bimetallic electrocatalysts, such as CuCo and CuNi, have shown significant promise in the electrooxidation of 5-hydroxymethylfurfural (HMF), a key reaction for producing value-added chemicals like 2,5-furandicarboxylic acid (FDCA). These catalysts are particularly effective due to their unique structural and electronic properties, which enhance catalytic activity and stability. CuCo bimetallic catalysts are known for their high efficiency in HMF electrooxidation. The combination of copper and cobalt creates a synergistic effect that improves the adsorption and activation of HMF molecules, resulting in higher conversion rates and selectivity towards FDCA. The presence of cobalt enhances the oxidative capabilities, while copper provides excellent conductivity and stability. Similarly, CuNi bimetallic catalysts exhibit remarkable performance in HMF electrooxidation. The integration of nickel with copper forms a hierarchical structure that increases the number of active sites and improves electron transfer. This structure is beneficial for both the aldehyde and alcohol groups in HMF, leading to efficient oxidation processes. CuNi catalysts have demonstrated high current densities and low overpotentials, making them highly effective for this reaction. Overall, these bimetallic electrocatalysts offer enhanced activity, high stability, increased selectivity, and efficient electron transfer, making them crucial for sustainable chemical production. By efficiently converting HMF to FDCA, these catalysts contribute to the production of bio-based polymers and other valuable chemicals, supporting green chemistry initiatives.

2.5 Hydrothermal Synthesis of Electrocatalysts

Various synthesis methods have been employed to prepare Cu-based bimetallic electrocatalysts. These include hydrothermal synthesis, co-precipitation, electrodeposition, and solvothermal methods. The choice of synthesis technique significantly affects the

structure, particle size, and surface area of the resulting catalysts, which in turn influences their electrochemical properties. Among these, hydrothermal method is particularly suited for producing uniform and well-defined bimetallic nanoparticles with tunable composition and morphology.

A significant technique for producing bimetallic materials is hydrothermal synthesis. This process can be used to easily create highly ordered structures by heating a solution of dissolved metal precursors in an autoclave at autogenic pressure ^{11,12}. Sun et al. synthesized Cu-Co bimetal/HRG via a one-step hydrothermal process, using urea as an in-situ reducing and stabilizing agent.¹¹ They found that the morphology and characteristics of the composite are influenced by the annealing temperatures during the hydrothermal process. They noticed that when the annealing temperature rose, the diffraction peaks became more intense and sharper. That suggests that the material's crystallinity was improved. Additionally, when the temperature of calcination increases, the size and distribution of the Cu-Co bimetallic nanospheres in graphene become more uniform.¹¹

Chen et al. also produced Cu-Co bimetallic by a hydrothermal process. Polyethylene glycol (PEG) and tartaric acid were employed as the capping and the reducing agent, respectively. The composite was employed as a cocatalyst in the process of photocatalytic hydrogen evolution.¹² They discovered that the catalyst's active site is greatly impacted by the ratio of raw materials to synthesis conditions. Their research showed that a composite containing a 1:3 ratio of Cu to Co had the most effective catalytic activity. There were noticeable differences in catalytic activity of cocatalyst even though its structure was comparable at various calcination temperatures.¹²

Xu et al. used a one-step hydrothermal synthesis process that involved the coincident reduction of graphene oxide, copper, and nickel salt to successfully manufacture Ni–Cu bimetallic alloy NPs doped with reduced graphene oxide. This synthetic approach is commended as a accessible, efficient, and environmentally friendly technique to create composites Due to the fact that it does not necessitate the use of surfactants and high temperatures.²⁷

2.6 Modification with Highly Reduced Graphene Oxide

Modifying Cu-based bimetallic electrocatalysts with reduced graphene oxide (rGO) dopants can significantly enhance their performance for the hydrogen evolution reaction (HER). rGO provides a highly conductive network that facilitates efficient electron transfer during the HER process. This reduces the overall resistance and improves the catalytic activity¹³. The incorporation of rGO increases the number of active sites available for the HER. This is due to the large surface area of rGO, which allows for better dispersion of the bimetallic particles². The combination of Cu-based bimetallic materials with rGO can create synergistic effects that enhance the intrinsic catalytic properties. For example, Cu-Co oxides embedded in N-doped rGO have shown improved HER performance due to the synergistic interaction between the metals and the conductive support¹. rGO can improve the stability and durability of the electrocatalyst. It helps in maintaining the structural integrity of the catalyst during prolonged electrochemical reactions, which is crucial for practical applications²⁸. The addition of rGO can lower the overpotential required for HER, making the process more energy-efficient. Studies have shown that Cu-based bimetallic electrocatalysts with rGO exhibit lower overpotentials compared to their non-modified counterparts²⁸.

2.7 Drop-casting Method for Electrode Fabrication

The drop-casting method is a simple and widely used technique for preparing thin films and coatings, particularly in the field of electrochemistry and materials science. Its origins can be traced back to the need for a straightforward and cost-effective way to deposit materials onto substrates. The method has been used for decades, primarily in the preparation of chemically modified electrodes. It gained popularity due to its simplicity and the minimal equipment required ²⁹. Over time, the technique has been refined and adapted for various applications, including the deposition of nanoparticles, metal oxides, and other catalytic materials onto substrates like glass, silicon, and metals ³⁰.

Drop-casting involves depositing a small volume of a solution containing the desired material onto a substrate and allowing it to dry, forming a thin film. It can be used with a wide range of materials and substrates, making it a versatile tool in research and development. The method is inexpensive compared to other deposition techniques, such as chemical vapor deposition or sputtering ³⁰.

Drop-casting is commonly used to prepare electrodes for sensors, enhancing their sensitivity and selectivity ²⁹. It is also used to create catalytic surfaces for reactions like the hydrogen evolution reaction (HER) and oxygen evolution reaction (OER) ³⁰. The method is employed in the fabrication of electrodes for batteries and supercapacitors ³⁰.

2.8 Characterization Methods for Electrocatalysts

Characterization of electrocatalysts is essential for understanding their structure-property relationships and optimizing their performance. Techniques such as X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), and X-ray photoelectron spectroscopy (XPS) are commonly used to analyze the crystal

structure, morphology, and surface composition of electrocatalysts. Additionally, electrochemical characterization techniques like cyclic voltammetry (CV), linear sweep voltammetry (LSV), and electrochemical impedance spectroscopy (EIS) provide insight into the catalytic activity and charge transfer kinetics of the catalysts during HER.

2.8.1 X-ray Diffraction (XRD)

X-ray diffraction is based on Bragg's law ($n\lambda = 2d\sin\theta$). In this technique, a monochromatic beam of X-rays is directed at a sample, and the reflected X-rays are detected by a detector. The resulting X-ray diffraction pattern is specific to the substance being studied. This method is particularly useful for analyzing the percent crystallinity in natural fibers before and after they undergo physical or chemical treatments. Typically, the X-ray diffractogram of a sample is obtained using an X-ray diffractometer operating at known voltages and current, and Cu K α X-rays (with a wavelength of 0.15406 nm) over the 2θ range from 10 to 100 degrees in 0.01 degree increments at room temperature. The sample is placed in open quartz holders. Amorphous regions of the samples produce broad peaks, whereas crystalline regions produce sharp peaks. The degree of crystallinity (X_c) can be determined by calculating the intensities of the crystalline (I_c) and amorphous (I_a) contents in the sample using the formula: $X_c = (I_c / (I_a + I_c)) \times 100$ ³¹.

2.8.2 X-ray Photoelectron Spectroscopy (XPS)

X-ray photoelectron spectroscopy (XPS) involves the irradiation of a sample with X-rays, causing the ejection of electrons with specific energies. These ejected electrons are then detected and their energies are analyzed, generating a plot of electron energy versus relative abundance. By discerning the unique paths followed by electrons of different energies, the spectrometer is able to differentiate them and produce the observed spectra.³²

XPS enables the determination of the composition of a compound through the quantification of atoms present, as expressed by the equation (1):

$$E_{Binding} = E_{Photon} - (E_{Kinetic} + \phi) \quad (1)$$

This involves the consideration of binding energy (the energy of an electron attracted to a nucleus), photon energy (the energy of the X-ray photons used), and the kinetic energy of the ejected electrons. With knowledge of the work function (the minimum energy required to eject an electron from an atom) and photon energy, the measurement of kinetic energy by the detector allows for the determination of binding energy.³²

Moreover, XPS facilitates the identification of chemical shifts by accounting for the influence of the local chemical environment on binding energy. This aspect reflects the nuanced interplay between electron shells and the structural context in which atoms are situated, offering insights into the diverse binding energies exhibited by different chemical entities.³²

2.8.3 Inductively Coupled Plasma - Optical Emission Spectrometry (ICP-OES)

ICP-OES, is widely recognized as the preferred technique for elemental analysis due to its ability to simultaneously measure multiple elements. This method uses inductively coupled plasma to generate excited atoms and ions that emit specific electromagnetic radiation. The plasma, a critical component of any ICP instrument, is an ionized gas containing free electrons and cations at high temperatures and low pressures, typically powered by a free-running radio frequency (RF) generator. Plasma is considered one of the primary states of matter. Induction plasma, or "inductively coupled plasma," refers to the use of a flowing gas under specific pressure and temperature conditions as a plasma source.³³

In an Inductively Coupled Plasma (ICP), each element emits photons with unique wavelengths that can be traced back to specific elements. The brightness of the emitted light is directly linked to the concentration of the element. When in its ground state, an electron occupies the lowest energy orbital available. However, if provided with enough energy, typically from an excitation source such as a plasma, an electron can move to a higher energy level, known as an excited state. Consequently, as the electron returns from the higher energy level to a lower one, it releases photons with a wavelength corresponding to the energy difference between the two levels.³³

2.8.4 Scanning Electron Microscopy (SEM)

Scanning electron microscopy (SEM) is a method for producing surface images of a sample by scanning it with a focused beam of electrons. When the incident electron interacts with the sample, it creates signals that reflect direct images and the atomic composition of the scanned surface. The incident electrons cause the emission of elastically backscattered electrons (BS), secondary inelastically scattered electrons, and characteristic X-rays from the atoms on the sample surface. The most common mode of detection in SEM is to collect the secondary electrons using a special detector to create the sample image³⁴.

2.8.5 Transmission Electron Microscopy (TEM)

Transmission electron microscopy (TEM) is an advanced imaging technique that utilizes a focused electron beam to visualize the transmission of electrons through a material at extremely high magnification. Unlike traditional light-based imaging methods, TEM offers significantly greater resolution by using electrons instead of light to illuminate the sample. The interaction of the electron beam with the sample's thickness and material results in changes to the amplitude and phase of the transmitted beam, which in turn creates contrast

in the resulting images. This allows for the analysis of incredibly detailed high-resolution images with the ability to visualize structures as small as 0.2 nanometers in diameter ³⁵.

In addition to imaging, TEM also employs electron diffraction, which is a valuable technique for identifying the phase of materials, determining their structure and symmetry, measuring lattice parameters, and identifying any disorder or defects present. Furthermore, TEM is particularly advantageous for studying organic materials as it does not require metallic staining, enabling direct visualization of the crystalline lattice and providing detailed information about the shape, size, and 2-dimensional morphology of green synthesized nanoparticles ³⁵.

2.8.6 Linear Sweep Voltammetry (LSV)

Linear sweep voltammetry (LSV) and cyclic voltammetry (CV) are widely utilized voltametric techniques for examining redox reactions of organic and inorganic species. They excel in providing insights into the electrochemical process steps with minimal time and effort required for data acquisition and interpretation. These electroanalytical methods necessitate uncomplicated and cost-effective instrumentation and offer information not only on typical electrochemical quantities of a redox process, but also on chemical reactions coupled with charge transfer steps. The electrode serves as a tool for generating reactive species in a small solution layer surrounding its surface and concurrently monitoring chemical reactions involving these products. Furthermore, given that the relevant responses can be obtained within a few milliseconds after the electrode stimulation, they can be used to study mechanisms involving rapid reactions, facilitating the detection of short-lived transient intermediates. The LSV and CV techniques were introduced in the early 1950s, but during that time, only a few theoretical approaches capable of rationalizing the simplest

responses were developed. The extensive utilization of these electroanalytical methods gained momentum later, in the 1970s and 1980s, owing to the enhanced understanding of more nuanced criteria for interpreting the relevant responses and the greater availability of theoretical tools for processing experimental data ³⁶.

2.8.7 Electrochemical Impedance Spectroscopy (EIS)

Electrochemical Impedance Spectroscopy (EIS) is used to characterize the interface between an electrode and conductive solution. EIS is very useful in evaluation of coatings, analysis of electrochemical mechanism and rates, and evaluation of battery performance. Electrochemical Impedance Spectroscopy (EIS) provides detailed information on the kinetics and mechanisms of different electrochemical systems. It is widely used in corrosion research, semiconductor science, energy conversion and storage technologies, chemical sensing, biosensing, and noninvasive diagnostics. EIS involves disturbing a stable electrochemical system by applying a sinusoidal signal, either as alternating current or voltage, across a wide range of frequencies. The system's response to this disturbance, measured as the sinusoidal current or voltage, is then monitored. Since the system being examined is linear and time-invariant, EIS is a technique that models the relationship between the output signal (sinusoidal current or voltage) and the input signal (sinusoidal voltage or current) across a wide range of frequencies.

Compared to other electrochemical methods, the significance of EIS lies in its ability to differentiate and provide a wealth of information on various electrical, electrochemical, and physical processes occurring in an actual electrochemical system. This technique is challenging due to the diverse range of processes, each with distinct time characteristics that vary from very quick to very slow. These processes include the resistance of a liquid

electrolyte, the conductivities in the bulk and at the grain boundaries when using a solid polycrystalline electrolyte, the charging and discharging of the electric double layer at the interface between electrolytes, the influence of the electrode surface morphology and electrolyte composition on the capacitive behavior of the electric double layer, the kinetics of charge transfer reactions at the electrode, reactions occurring uniformly and adsorption/desorption phenomena associated with charge transfer reactions, and mass transfer phenomena such as species diffusion to the electrode surface, all exhibiting distinct time constants (τ), which measure the time behavior of each process.

2.8.8 Double-Layer Capacitance (C_{dl})

The electrochemically active surface area (ECSA) is determined from double-layer capacitance (C_{dl}) is a valuable electrochemical technique used to quantify the accessible electrode surface area. ECSA plays a key role in comparing the performance of electrocatalyst, especially where the differences between geometrical and active surface area are expected to be important. ECSA allows to draw a connection between the active catalytic sites of the material and its activity, supporting catalysts comparison and benchmarking. ECSA plays a pivotal role in understanding the electrochemical performance of electrocatalyst, particularly in HER and OER process. The basis of such method lies in the relationship between the ECSA and C_{dl} of the electrode. The C_{dl} is an electrochemical parameter that reflects the ability of the electrode's electrical double layer to store charges, which is inherently linked to electrocatalyst surface area.

3 CHAPTER THREE

RESEARCH METHODOLOGY

3.1 Chemicals

All chemicals used are analytical grade. $\text{Cu}(\text{CH}_3\text{COO})_2$, $\text{Co}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$, $\text{Ni}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$, graphite powder, H_2SO_4 , NaNO_3 , KMnO_4 , H_2O_2 , hydrazine hydrate, urea, absolute ethanol. All reagents were utilized as received without subsequent purification. Deionized water was employed in all experimental procedures.

3.2 Synthesis Methodologies

3.2.1 Synthesis of Bimetallic CuCo and CuNi

Initially, 2 mmol of $\text{Cu}(\text{CH}_3\text{COO})_2$ and 4 mmol of $\text{Co}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ were accurately weighed and dissolved in 20 mL of deionized water. Subsequently, 16 mmol of urea in 10 mL was added dropwise with continuous stirring until homogeneous. The resulting mixture was then transferred to a hydrothermal kettle equipped with a polytetrafluoroethylene liner (100 mL) and maintained at 150 °C for 4 hours. Following cooling to room temperature, the residues were subjected to filtration, washed three times with distilled water and ethanol, and subsequently dried at 60 °C for 2 hours. Ultimately, the brownish powders were obtained, denoted as CuCo. Meanwhile, the synthesis route of CuNi same as CuCo excepts the precursor of cobalt replaced with nickel precursor, $\text{Ni}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$. The synthesis route depicting in **Figure 3**.

3.2.2 Synthesis of HRG

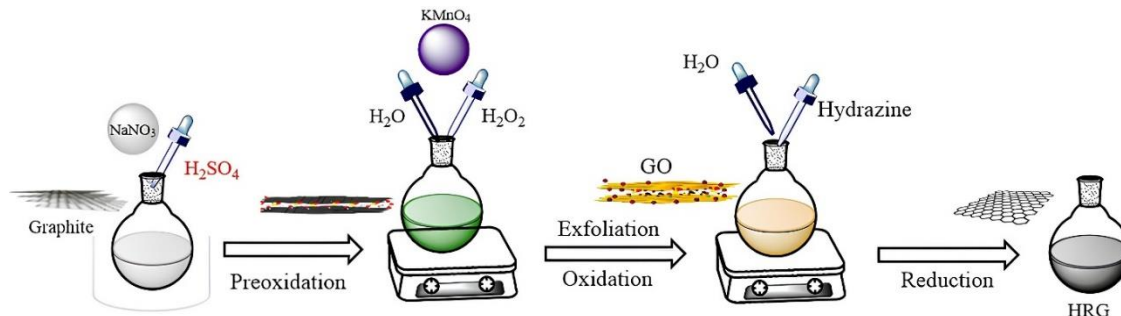


Figure 2. Schematic illustration of synthesis of HRG

The synthesis of graphene oxide is accomplished through a modified Hummer's method, and the resulting graphene oxide is reduced using hydrazine hydrate, as shown in **Figure 2**. Firstly, 0.125 g of graphite fine powder and 0.125 g of sodium nitrate are mixed, followed by the addition of 5.75 ml of concentrated sulphuric acid under constant stirring for 10 minutes (in an ice bath). After that, 0.775 g of potassium permanganate is gradually added to the mixture (in an ice bath) and stirred for another 10 minutes - the color of the mixture changes to dark green. The reaction mixture is then transferred to a pre-heated oil bath and stirred at 35 °C for an hour. The resulting mixture is diluted by the addition of 10 ml of DI water, then heated up to 90 °C for 30 minutes. Further, 25 ml of DI water is added, and after that, 1 ml of H₂O₂ is added to terminate the reaction - the mixture turns to earthy yellow. Then the product is washed with distilled water and dried in an oven at 60 °C for 24 hours - the resulting product is a sticky black solid (graphene oxide paste). Lastly, the graphene oxide paste is dissolved in DI water and reduced with hydrazine hydrate to produce HRG.

3.3 Fabrication of electrodes

The electrodes were prepared using drop-casting method on two different substrates, which are FTO and nickel foam. First, the FTO electrode was cleaned by sonication with DI water,

ethanol, and acetone for 10 minutes of each. After that, the FTO was dried at 60°C in an oven. Meanwhile, nickel foam was subjected to cleaning via sonication with 3 M HCl to eliminate the oxide layer, followed by rinsing with acetone, ethanol, and deionized water for 5 minutes each. The nickel foam was then dried at ambient temperature.

As illustrating in **Figure 3**, the ink formulation involved dispersing 10 mg of synthesized bimetallic catalysts in a 2 mL solvent mixture comprising deionized water, ethanol, and 5% Nafion as a binder. The mixture subsequently sonicated for 30 minutes to form homogenous ink. After that 30 μ L ink was drop casted onto nickel foam and conductive side of FTO substrate for each. The fabricated electrode was dried at 60°C in an oven and annealed at 100°C for 30 minutes.

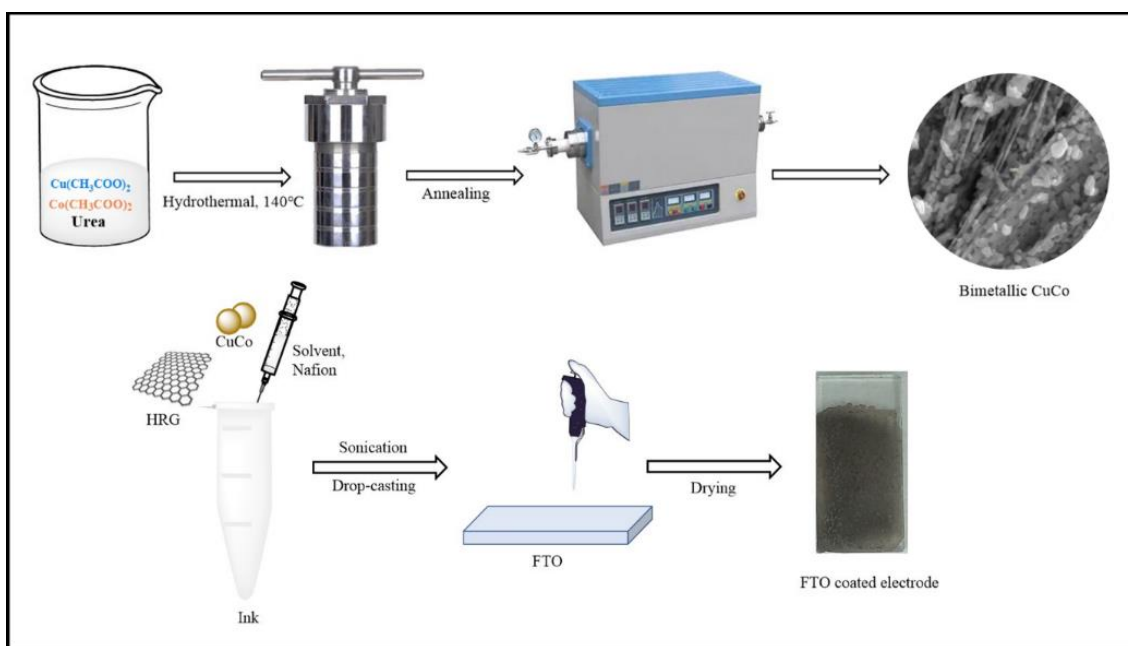


Figure 3. Schematic representation of the synthesis route for CuCo catalyst, illustrating the key steps involved in the hydrothermal synthesis process (top). Diagram of the

electrode fabrication, showing the deposition of CuCo onto FTO substrate, highlighting the preparation and assembly steps for constructing the working electrode.

3.4 Structural Characterization

X-Ray Diffraction (XRD) analysis of powder material as well as fabricated electrodes were obtained on Rigaku Ultima IV X-Ray Diffractometer using Cu K α radiation ($\lambda=1.540$ Å) at 40 kV and a tube current of 40 mA. The samples were scanned at $2\theta = 8-80^\circ$ with a scan rate $1.2^\circ \text{ min}^{-1}$. The morphology was investigated by using Field-Emission Scanning Microscope Spectroscopy (FE-SEM) Thermo Scientific instrument Quattro S at an accelerating voltage of 10 kV and current 92 pA. Transmission Electron Spectroscopy (TEM) was carried out on a JEOL JEM-2100F at 300 kV accelerating voltage. The TEM image was analyzed using a manual image processing methodology with ImageJ software to determine the lattice fringe. The d-spacing values were calculated from the inverted FFT image by measuring the distance using the Plot Profile option. X-Ray Photoelectron Spectroscopy (XPS) was performed with the C 1s peak at 284.8 eV as the standard for evaluating the surface characteristics and identifying the oxidation state of the elements.

3.5 Electrochemical Characterizations

Electrochemical measurement will be conducted in a three-electrode system on electrochemical set up. The catalyst-coated electrode will serve as the working electrode, the Ag/AgCl electrode will be used as the reference electrode, and the platinum electrode will serve as the counter electrode. The tests will take place at ambient temperature, with a KOH 1.0 M (pH=13.6) solution as the electrolyte. To construct the working electrode for electrochemical analysis, the catalyst inks will be prepared and drop-cast onto a fluorine doped tin oxide (FTO) electrode. Cyclic voltammetry was performed prior to HER

investigations between -0.52 to +0.52 V at scan rate 50 mV s⁻¹ for 40 scan to stabilize and precondition of working electrodes.

Linear sweep voltammetry (LSV) measurements were performed at a scan rate 10 mV s⁻¹, and all the potential values were converted to the RHE scale using eq 1 given below:

$$E_{RHE} = E_{Ag/AgCl} + 0.059 \times pH + 0.197 \quad (1)$$

Electrochemical impedance spectroscopy (EIS) was performed at -0.6 V in the frequency range of 10 MHz–10 mHz. The double-layer capacitance (C_{dl}) of the fabricated electrodes was estimated by cycling the working electrode in the non-Faradaic regions at different scan rates (10–60 mV s⁻¹), and the CV data were collected. The current density (j) increased linearly with the scan rate, and the electrical double-layer capacitance was determined from the slope of the plot of current versus the scan rate. The ECSA was obtained by dividing the double-layer capacitance by the specific capacitance ($C_s = 0.022 \text{ mF cm}^{-2}$) of the electrode as presented in eq 2.

$$ECSA = \frac{C_{dl}}{C_s} \quad (2)$$

4 CHAPTER FOUR

RESULTS AND DISCUSSIONS

4.1 Structural and Morphological Analysis

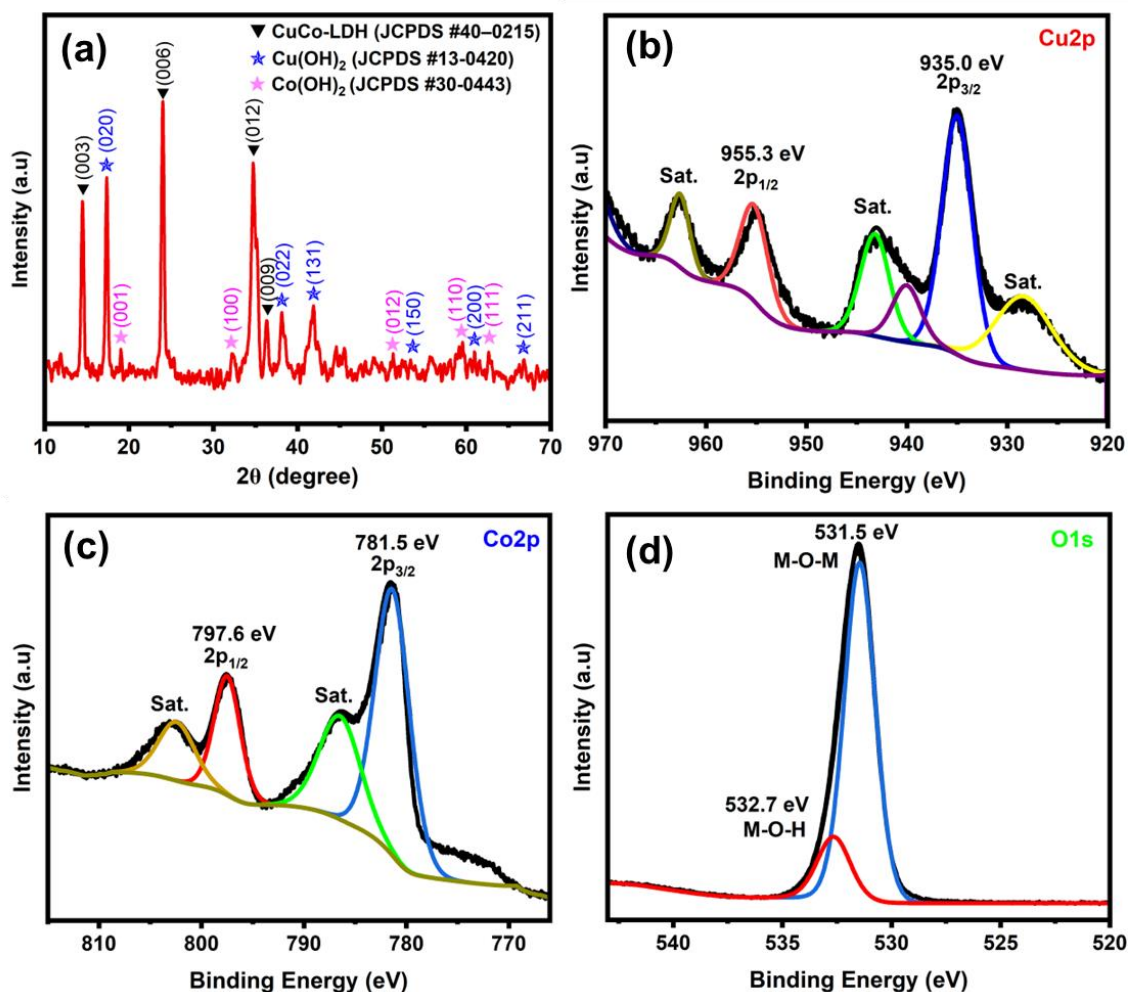


Figure 4. (a) XRD pattern of CuCo as synthesized (CuCo-LDH), XPS spectra of CuCo as synthesized (b) Cu₂p spectrum, (c) Co₂p spectrum, (d) O1s spectrum, indicating the oxidation states and chemical environment of Cu, Co, and O species presents on the surface of CuCo-LDH

The composition and crystal structure of CuCo as synthesized was determined by XRD pattern (**Figure 4a**). The diffraction peaks at $2\theta = 14.4^\circ$, 23.9° , 34.7° , and 36.3° representing the characteristics of (003), (006), (012), and (009) basal plane of LDH, respectively (JCPDS #40-0215)^{37,38}. Utilizing the Braggs equation ($n\lambda = 2d\sin\theta$), the primary interlayer spacing of CuCo-LDH was determined to be 0.61 nm from (003) position. Additionally, set diffraction peaks at $2\theta = 17.3^\circ$, 38.1° , 41.7° , 53.4° , 61.0° , and 66.8° associated to $\text{Cu}(\text{OH})_2$ (JCPDS #13-0420)³⁹. The other diffraction peaks at $2\theta = 19.1^\circ$, 32.2° , 51.3° , 59.5° , and 62.6° aligned to $\text{Co}(\text{OH})_2$ (JCPDS #30-0443)⁴⁰. The results confirmed the successful synthesis of CuCo-LDH.

XPS was conducted to analyze the surface chemistry of the CuCo as synthesized (CuCo-LDH) catalyst. The full XPS spectrum revealed the presence of Cu, Co, and O elements on the surface of the CuCo-LDH catalyst. **Figure 4b** shows the high-resolution spectrum of Cu2p. A couple of peaks at 955.3 and 935.0 eV correspond to Cu $2p_{1/2}$ and $2p_{3/2}$, respectively, with a spin-orbit splitting value of 20.3 eV, which is the characteristic of Cu^{2+} species³⁹. Similarly, the Co 2p spectrum recorded in **Figure 4c** demonstrates two peaks of Co $2p_{3/2}$ and Co $2p_{1/2}$ at 781.5 and 797.6 eV, along with satellites associated with Co^{2+} in $\text{Co}(\text{OH})_2$ ⁴¹. Moreover, the observed spin-orbit splitting value of 15.7 eV for $2p_{1/2}$ and $2p_{3/2}$ is consistent with $\text{Co}(\text{OH})_2$ ⁴². The O 1s spectrum (**Figure 4d**), the peaks located at 531.5 and 532.7 eV corresponded to the O^{2-} (in O-M) and OH^- , in alignment with prior findings⁴². The XPS analysis further confirmed the formation of CuCo-LDH, in line with the XRD results.

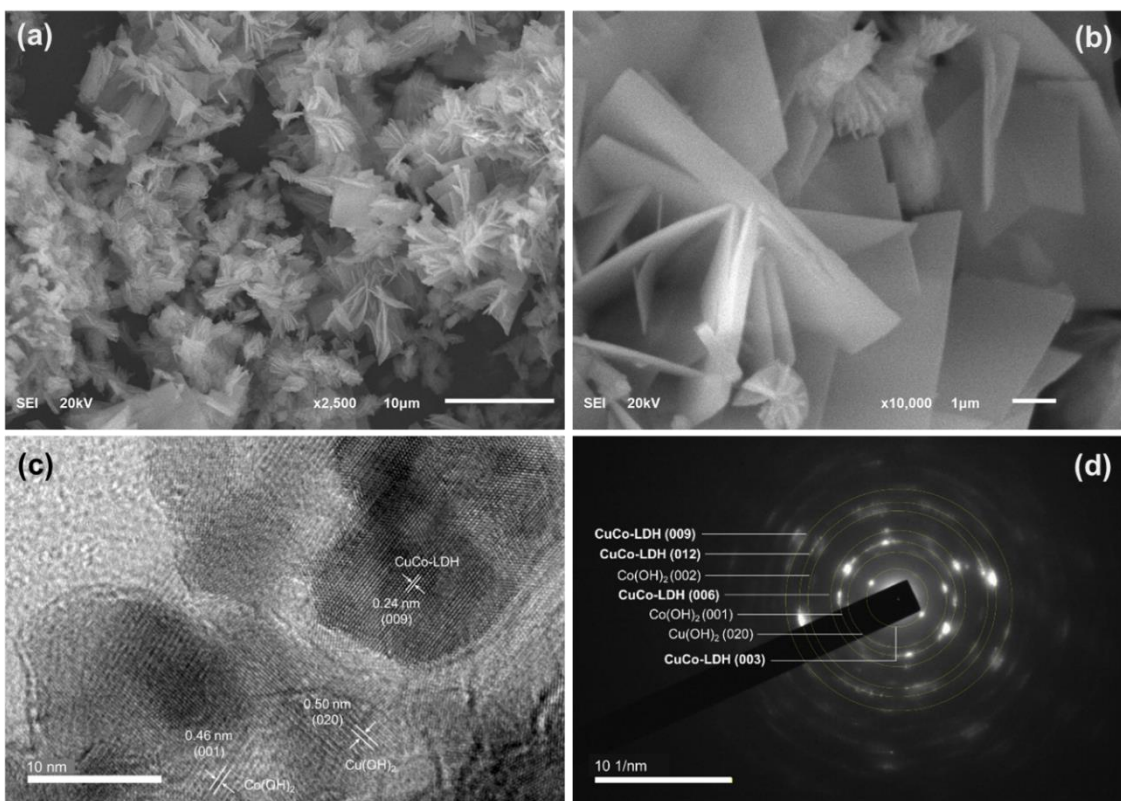


Figure 5. (a-b) Scanning Electron Microscopy (SEM) images showing the surface morphology of CuCo as synthesized (CuCo-LDH), revealing its layered structure and uniform distribution. (c) Transmission Electron Microscopy (TEM) image displaying the nanoscale features of the CuCo-LDH, highlighting the layered arrangement. (d) Selected Area Electron Diffraction (SAED) pattern confirming the crystalline nature of the CuCo as synthesized (CuCo-LDH), showing distinct diffraction spots.

The SEM image of the CuCo-LDH catalyst depicts a distinct stacked micro-sheets structure as shown in **Figure 5a-b**. These micro-sheets indicate a high surface area, which could be advantageous for catalysis applications where surface activity plays a crucial role. The uniformity in the structure observed in the SEM images implies a controlled synthesis process, potentially leading to homogeneity in functional properties of the material.

TEM images (**Figure 5c**) shows distinct $\text{Co}(\text{OH})_2$ lattice fringe with spacing value of 0.46 nm which corresponds to (001) plane. The lattice fringe of 0.50 nm corresponds to interdistance of $\text{Cu}(\text{OH})_2$ (020) plane. Meanwhile, the lattice fringe of CuCo-LDH observed with interlayer spacing of 0.24 nm. This spacing corresponds to higher-order reflection plane of (009), which is a multiple of the primary interlayer spacing. The higher-order reflection plane of (009) confirming a well-ordered layered structure of CuCo-LDH. The selected area electron diffraction (SAED) image of CuCo-LDH presented in **Figure 5d** reveals polycrystalline feature. The form rings excellently match with the (003), (006), (009), (012) basal plane of CuCo-LDH, (020) plane of $\text{Cu}(\text{OH})_2$, and (001), (002) planes of $\text{Co}(\text{OH})_2$. The results in line with the XRD pattern.

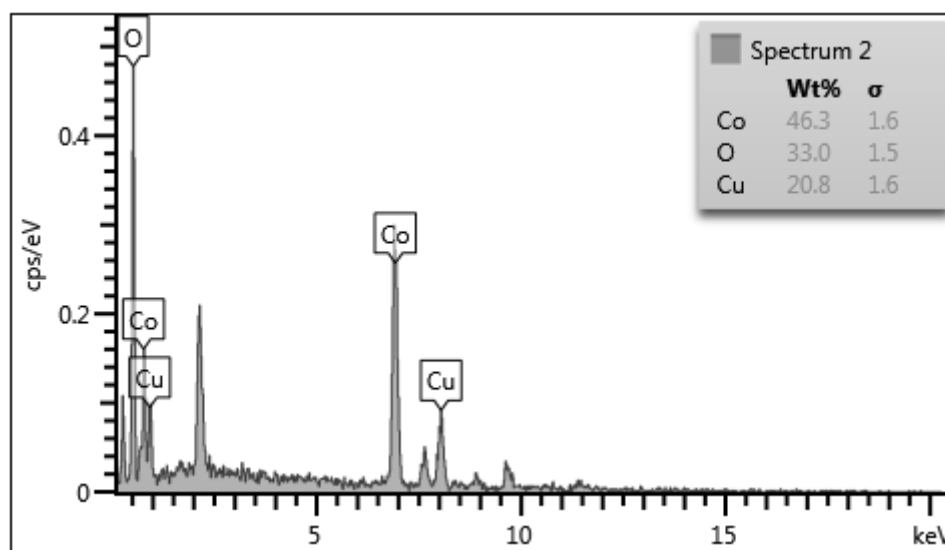


Figure 6. Energy Dispersive X-ray (EDX) analysis spectrum of CuCo as synthesized (CuCo-LDH)

The EDX presents the elemental composition of the CuCo-LDH (**Figure 6**). The elemental analysis reveals the following composition: Co 46.3%, Cu 20.8%, and O 33.0%. The relatively high cobalt content indicates that the sample is cobalt-rich, consistent with ICP

results. Furthermore, the presence of oxygen (33.0%) suggests the likely formation of oxides or hydroxides, commonly observed in such systems.

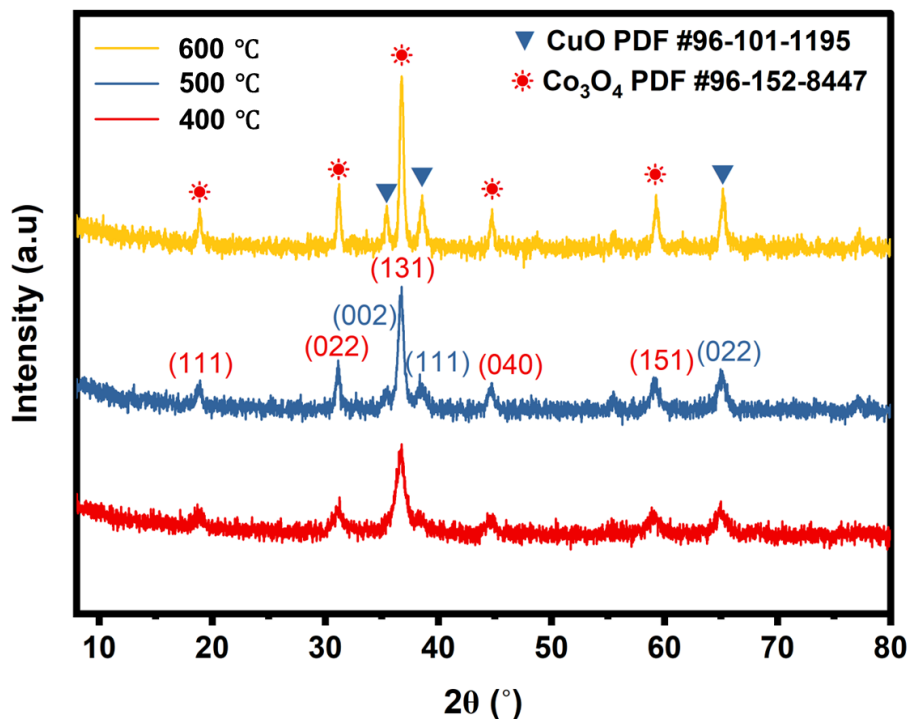


Figure 7. XRD patterns of CuCo-LDH after annealed at 400 °C, 500 °C, and 600 °C confirming the formation of CuO- Co_3O_4 (CuCoOx)

Meanwhile, the XRD pattern of annealed CuCo-LDH at 400°C, 500°C, and 600°C depicting in **Figure 7**, demonstrates distinct reflections centered at $2\theta = 35.4^\circ$, 38.6° , and 65.2° related to the miller indices (002), (111), and (022) crystal planes of the monoclinic tenorite CuO⁴³. In addition, the reflections were clearly observed at $2\theta = 18.9^\circ$, 31.2° , 36.8° , 44.7° , and 59.3° , corresponding to (111), (022), (131), (040), and (151) crystal planes of cubic Co_3O_4 ,⁴⁴ respectively. The XRD data exhibit excellent alignment with CuO standard (PDF #96-101-1195, marked with blue indices) and Co_3O_4 (PDF #96-152-8447, marked with red indices). It means that the bimetallic oxide CuO- Co_3O_4 compounds are successfully formed,

further named as CuCoOx. The XRD patterns clearly show that annealing temperature affects the crystallinity of CuCoOx which is beneficial to the control of the catalytic property of the material.

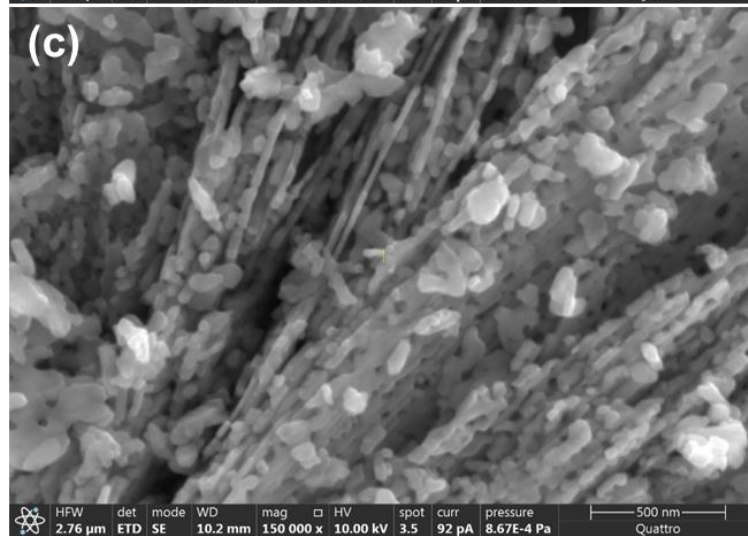
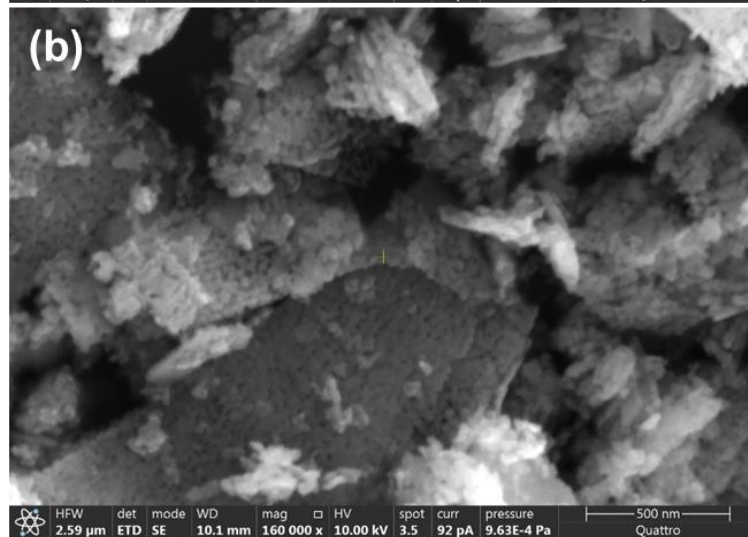
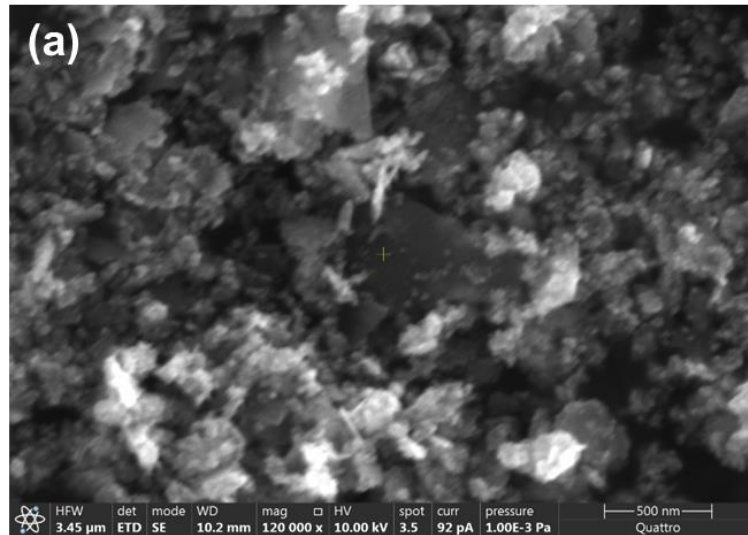


Figure 8. SEM image of CuCoOx annealed at (a) 400 °C, (b) 500 °C, (c) 600 °C showing the morphology structure of the catalysts

The structural characteristics of the annealed CuCo catalysts were investigated using field-emission scanning electron microscopy (FESEM). The impact of varying the annealing temperature on the morphological evolution can be observed in the high-resolution FESEM images depicted in **Figure 8**. Initially, the sample treated at 400°C (CuCoOx400) displayed a heterogeneous sheet-globular morphology (**Figure 8a**), showing significant change in morphological structure from CuCo-LDH which has stacked micro-sheets structure (**Figure 5a-b**). Detailed examination revealed that the sample annealed at 500°C (CuCoOx500) featured interconnected small globular structures, forming a continuous sheet-like pattern (**Figure 8b**). Finally, the sample processed at 600°C (CuCoOx600) exhibited a network of rod-like features formed by the merging of nano-globules (**Figure 8c**). This underscores one of the key advantages of the hydrothermal method, wherein precise control over the sintering temperature enables facile modulation of sample morphology and the rapid preparation of diverse nanomaterial designs.

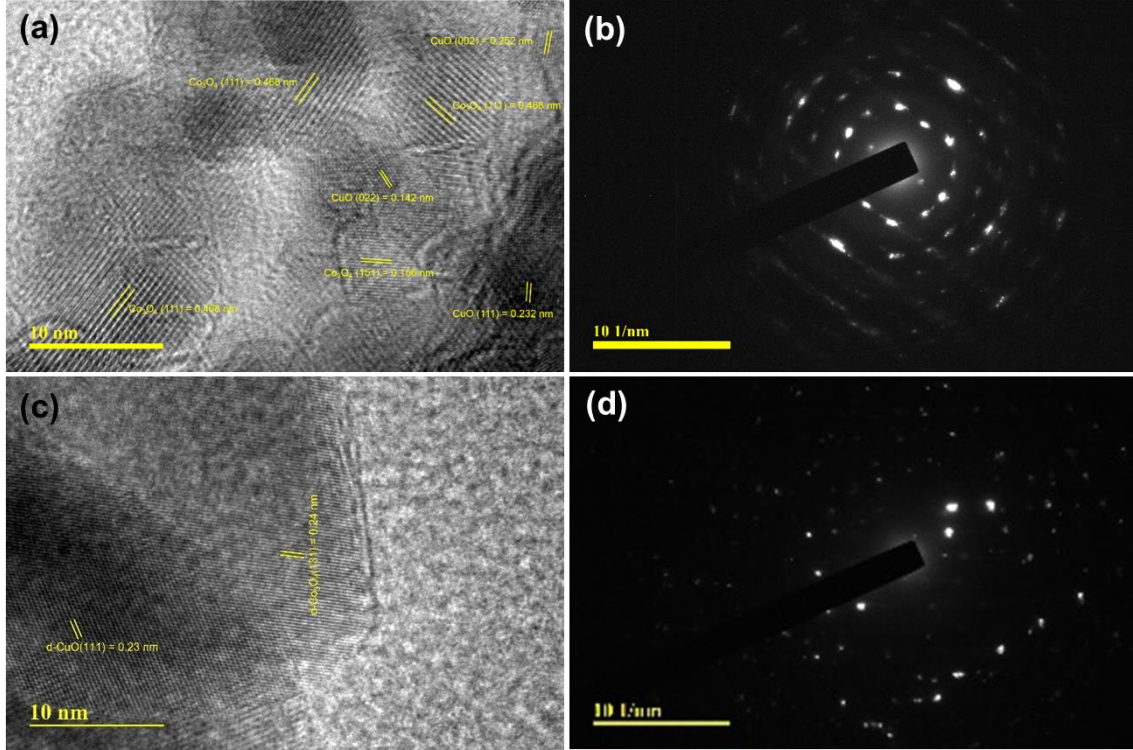


Figure 9. TEM image and SAED pattern of CuCoOx annealed at (a-b) 400 °C, (c-d) 600 °C

The TEM images of CuCoOx annealed at 400 °C and 600 °C are depicted in **Figure 9a** and **9c**, respectively. Set of measured lattice fringes of CuCoOx400 depicting in **Figure 9a** related to CuO and Co₃O₄ planes. **Figure 9c** shows the corresponding lattice fringe of CuCoOx600 shows the (111) plane of CuO, which measures 0.23 nm, and the (131) plane of Co₃O₄, measuring 0.24 nm, consistent with the XRD reflections. The selected area of electron diffraction (SAED) pattern of both CuCoOx400 and CuCoOx600 (**Figure 9b** and **9d**) displays distinct dots, indicating polycrystalline features.

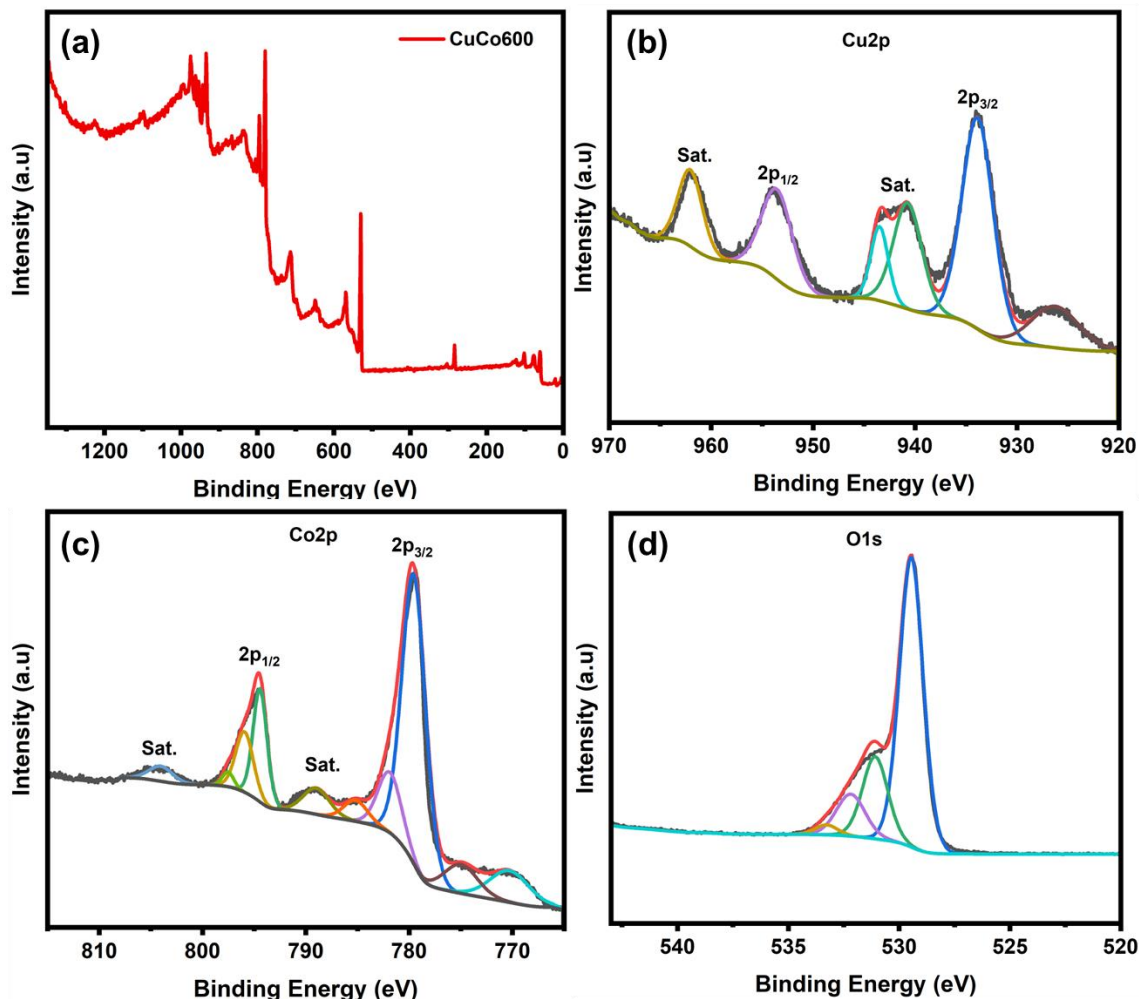


Figure 10. (a) XPS survey spectra of CuCoOx600, (b) high resolution spectra of Cu2p, (c) high resolution spectra of Co2p, (d) high resolution spectra of O1s, indicating the electronic structure and chemical environment of CuCoOx600

XPS survey spectra of CuCoOx600 in **Figure 10a**, confirming the presence of Cu, Co, and O. **Figure 10b** presents several key peaks of Cu2p spectra indicating the presence of copper in the +2-oxidation state. The peak at 933.86 eV corresponds to the Cu2p_{3/2} binding energy, confirming predominantly oxidized Cu²⁺, which is commonly associated with copper oxides like CuO. This peak distinguishes Cu²⁺ from metallic copper, which appears around 932.5 eV. Additionally, satellite peaks at 940.73 eV and 943.48 eV, associated with Cu²⁺,

highlight electron-electron interactions typical of Cu^{2+} and further confirm its oxidized state, absent in Cu^0 or Cu^{1+} . The peak at 953.53 eV represents the $\text{Cu}2p_{1/2}$ binding energy, consistent with spin-orbit splitting for Cu^{2+} ; its detection alongside the $\text{Cu}2p_{3/2}$ peak reinforces the interpretation of copper in an oxidized form within an oxide or mixed-metal oxide framework. Another shake-up peak at 962.03 eV provides additional evidence of Cu^{2+} , indicating strong electronic interactions with oxygen. Lastly, a less common peak at 926.23 eV could suggest minor components or complex interactions within mixed-metal oxides. Overall, the $\text{Cu}2p$ spectra strongly indicate that the copper in the sample predominantly exists in the +2 oxidation state, reflecting significant interactions with oxygen. It confirmed the formation of CuO in line with XRD result.

The analysis of the $\text{Co}2p$ spectra (**Figure 10c**) reveals several key peaks that elucidate the oxidation states of cobalt within the sample. The most prominent peak at 779.5 eV corresponds to the $\text{Co}2p_{3/2}$ binding energy, which is primarily indicative of Co^{3+} . It is important to note that this peak can also imply the presence of Co^{2+} in certain contexts, particularly within mixed cobalt oxides such as Co_3O_4 . Furthermore, a notable peak at 781.8 eV suggests the existence of Co^{2+} , indicating a coexistence of Co^{3+} and Co^{2+} in the sample. This mixed oxidation state is characteristic of cobalt oxides and is significant for their catalytic and electronic properties.

Additionally, the observation of the $\text{Co}2p_{1/2}$ peak at 794.43 eV, aligning with Co^{3+} , reinforces the presence of this oxidation state alongside Co^{2+} , which is confirmed by another peak at 795.9 eV. The weak shake-up satellite peaks detected at 785.2 eV and 788.9 eV, as well as at 804.03 eV in the $\text{Co}2p_{1/2}$ region, further affirm the presence of Co^{2+} and highlight the oxidation of cobalt in the context of an oxide lattice. Together, these findings provide

robust evidence for the mixed oxidation states of cobalt in the sample, consistent with the recognized characteristics of cobalt-containing oxides, such as Co_3O_4 .

The O 1s spectra typically display distinct peaks at binding energies of 529.5 eV and 531.2 eV, which are indicative of varying bonding environments of oxygen within different compounds (**Figure 10d**). The peak observed at 529.5 eV is generally associated with oxygen in metal oxides, wherein oxygen is integrated within a lattice structure, signifying a robust bond to transition metals. This finding suggests the possible presence of oxide phases within the sample. In contrast, the peak at 531.2 eV corresponds to more loosely bound oxygen species, such as surface-adsorbed hydroxyl groups or water molecules, indicating a distinct chemical environment. The observed variation in binding energy may also be attributed to non-stoichiometric oxides or defects within complex structures, thereby reflecting the intricate role of oxygen in these materials.

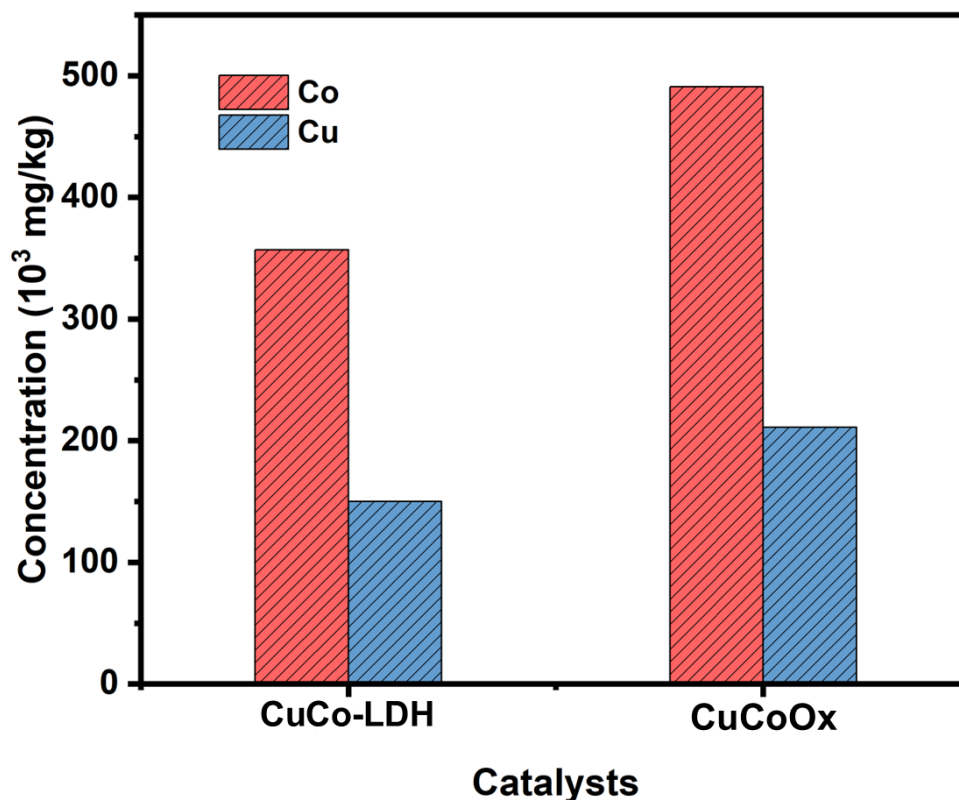


Figure 11. ICP results of CuCo-LDH and CuCoOx600, showing the metal composition of the catalysts

The ICP-OES analysis conducted on CuCo-LDH unveils a cobalt concentration of 357,967.6 mg/kg and a copper concentration of 150,365.8 mg/kg, indicating a significantly higher presence of cobalt compared to copper (**Figure 11**). To elucidate the metal composition further, the mole ratio of Co to Cu was determined. The mole ratio of Co to Cu approximates 2.56:1, highlighting the significance of cobalt within the complete composition. Comparatively, CuCoOx600 contains 1.37 times more cobalt and 1.41 times more copper than CuCo-LDH. This makes CuCoOx600 more cobalt-rich, suggesting enhanced HER catalytic property where higher cobalt content is desirable ^{45,46}.

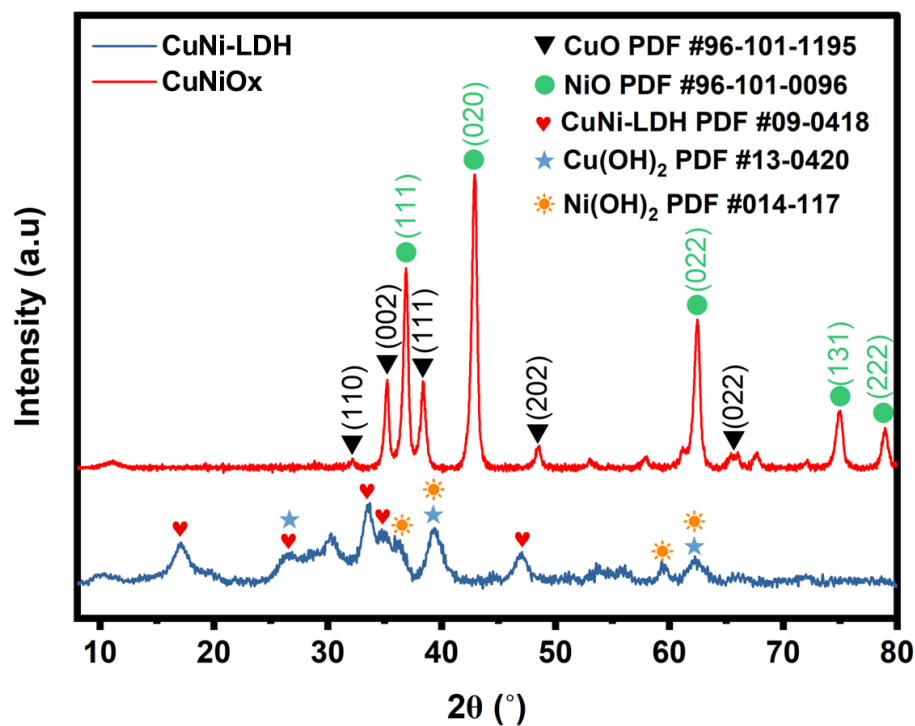


Figure 12. XRD pattern of CuNi-LDH and CuNiOx, illustrating the crystalline structure and phase compound

The XRD pattern of CuNi-LDH in **Figure 12**, shows set of diffraction peaks that aligned with CuNi-LDH (JCPDS 09-0418). While the rest of diffraction peaks excellently match with Cu(OH)₂ and Ni(OH)₂. The XRD analysis of CuNiOx reveals a series of peaks corresponding to both CuO and NiO, confirming the successful formation of a bimetallic CuNi oxide (CuO-NiO). The observed diffraction peaks match the monoclinic phase of CuO, with characteristic peaks at $2\theta \approx 32.5^\circ$, 35.5° , 38.7° , and 48.7° , which correspond to the (110), (002), (111), and (202) planes, respectively. These values align well with the reference data from the Crystallography Open Database (COD) with PDF #96-101-1195. The diffraction pattern also exhibits peaks consistent with the cubic phase of NiO, with key peaks observed at $2\theta \approx 37.3^\circ$, 43.3° , 62.9° , and 75.4° , corresponding to the (111), (200), (220), and (311) planes, respectively. These peaks match the reference pattern from the

PDF #96-101-0096, indicating the formation of crystalline NiO. Additionally, the morphological structure of both CuNi-LDH and CuNiOx displayed a sea urchin-like structure, as illustrated in **Figure 13**. However, CuNiOx (**Figure 13b**) demonstrates greater porosity, confirming that thermal treatment has increased the porosity.

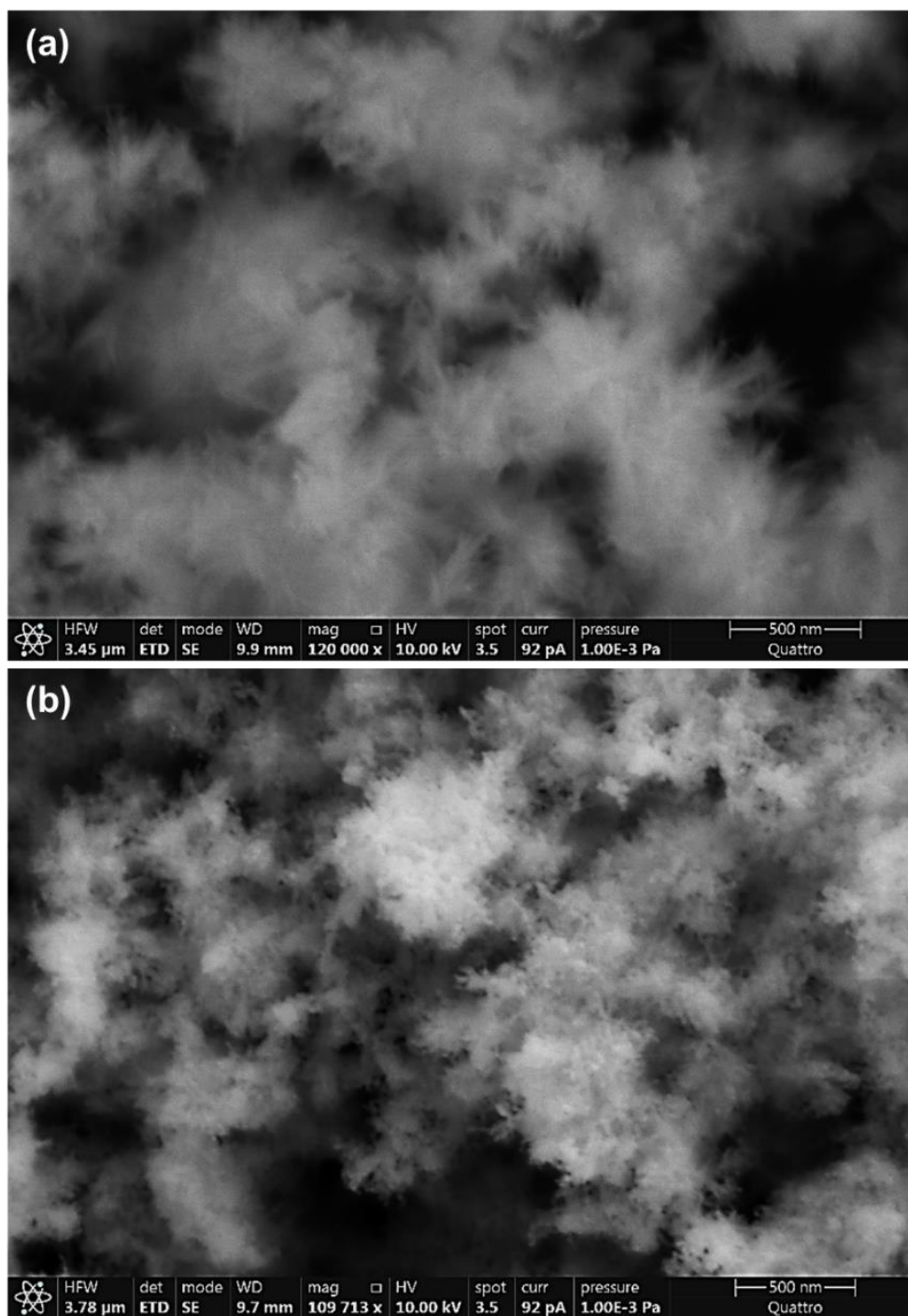


Figure 13. SEM image of (a) CuNi-LDH, (b) CuNiOx, confirming the morphology structure of the catalysts

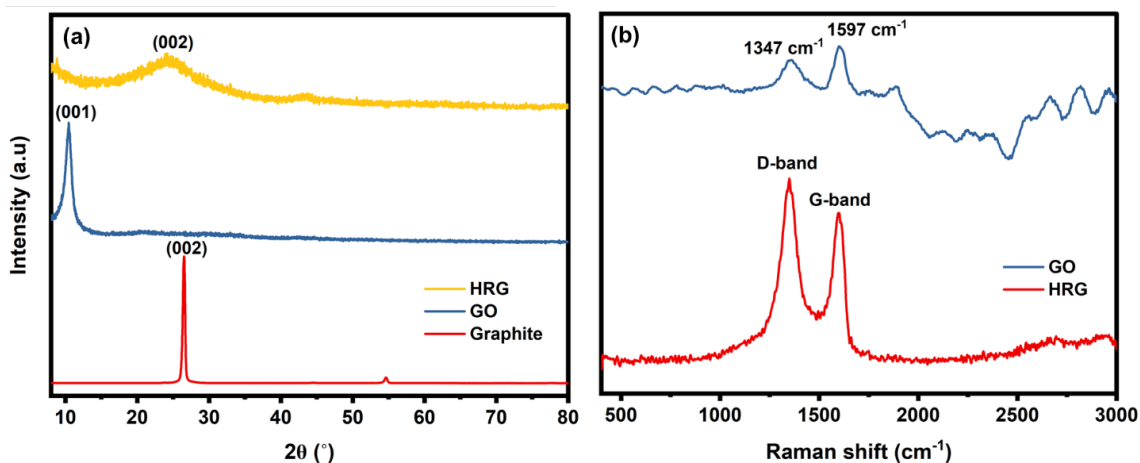


Figure 14. (a) XRD patterns of HRG, (b) Raman spectra of HRG

Furthermore, all catalysts modified with 1% HRG to enhanced the performance. Graphite powder was used to produced graphene oxide (GO) using Hummer's method then further reduced using hydrazine hydrate to produce HRG. The XRD pattern (**Figure 14a**) of GO shows a strong and sharp peak at $2\theta = 10.46^\circ$, which corresponds to an interlayer distance of $8.4 \text{ \AA}$ for the (001) plane. In contrast, the HRG exhibits a well-defined diffraction peak at $2\theta = 24.6^\circ$, indicating a lattice spacing of 0.36 nm . This is slightly larger than the lattice spacing of crystalline graphite, which has a value of 0.34 nm at $2\theta = 26.5^\circ$ (002), suggesting the presence of oxygen-containing functional groups in the HRG structure. The broad diffraction peak observed in HRG indicates the presence of a few layers of graphene sheets. Additionally, a small peak at $2\theta = 43.1^\circ$ corresponds to the (102) plane of the HRG structure. These XRD results confirm the exfoliation and reduction processes of GO, as well as the removal of intercalated water molecules and oxide groups during the transformation to HRG.

The quality of the resulting HRG was evaluated using Raman spectroscopy (**Figure 14b**), which serves as a straightforward and non-invasive technique for characterizing carbon

structures. The Raman spectra of both GO and HRG exhibit the characteristic G and D bands commonly observed in carbon nanomaterials. The G-band, appearing at 1597 cm^{-1} , corresponds to the in-plane vibrational motion of sp^2 -bonded carbon atoms within the hexagonal lattice structure⁴⁷. In contrast, the D-band, located at a lower wavenumber of 1347 cm^{-1} , is associated with the presence of sp^3 -hybridized carbon atoms that introduce disorder into the hexagonal lattice⁴⁷. The higher intensity of the D-band relative to the G-band in HRG suggests a significant level of reduction, indicating a substantial removal of oxygen-containing groups.

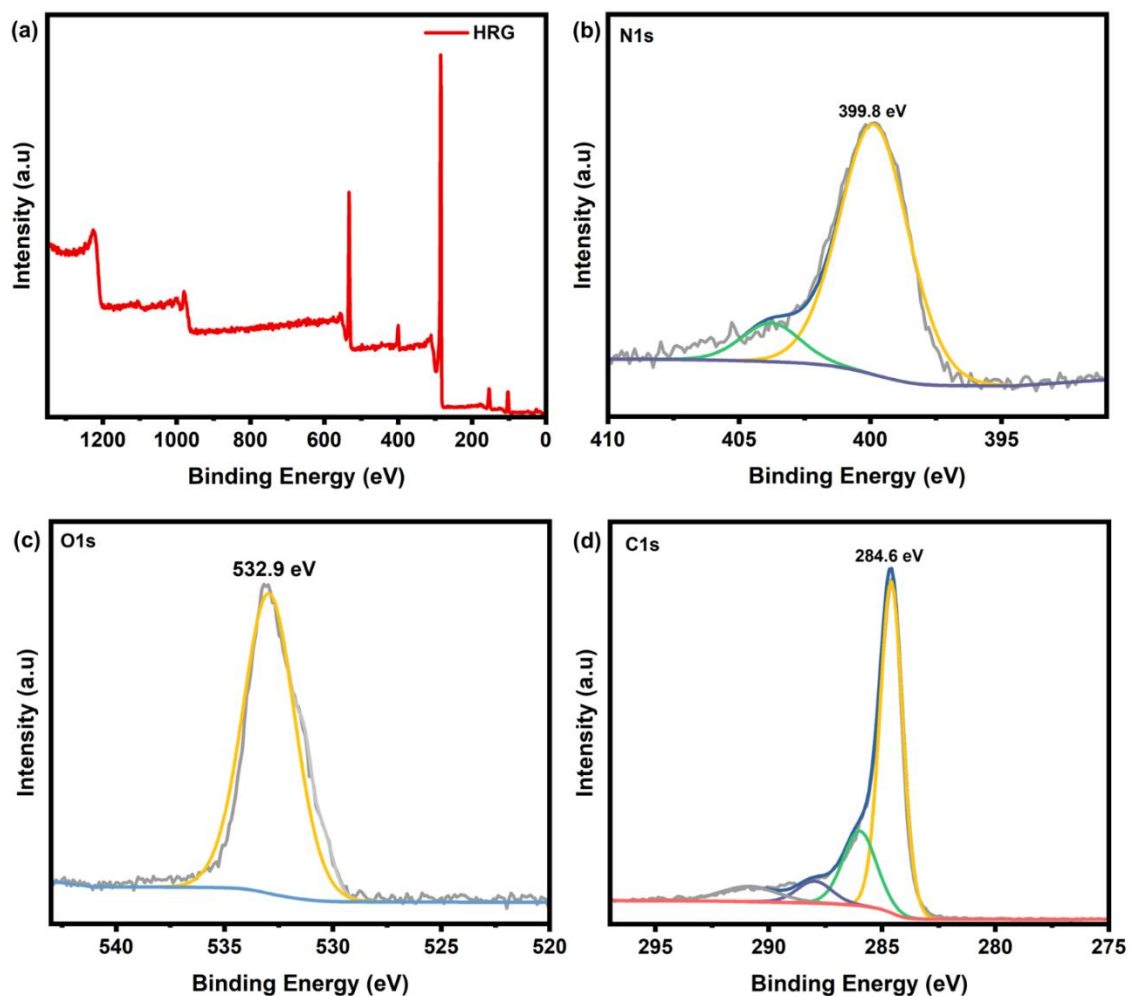


Figure 15. XPS spectra of HRG

The X-ray photoelectron spectroscopy (XPS) analysis of HRG shown in **Figure 15**, indicates the presence of carbon, oxygen, and nitrogen. The N1s peak observed at 399.8 eV is likely attributed to an excess of hydrazine, which functions as a reducing agent. Hydrazine introduces nitrogen-containing functional groups that bind to the surface of graphene oxide during the reduction process. This incorporation results in the formation of nitrogen-doped sites, as evidenced by the observed XPS peak, and contributes to the modification of the electronic properties and chemical reactivity of HRG. The deconvoluted C1s peak reveals a binding energy of 284.6 eV, corresponding to the C-C bond, indicating the reduction of exfoliated graphene oxide ⁴⁷. The O1s peak at 532.9 eV corresponds to oxygen species, primarily associated with C=O groups, suggesting the presence of residual carbonyl groups on the surface.

4.2 Electrocatalytic Performance of CuCo and CuNi for HER

4.2.1 Electrochemical Performance of CuCo Electrocatalyst

a. CuCo on FTO Substrate

The initial assessment of electrochemical performance of synthesized catalyst was conducted using cyclic voltammetry (CV) analysis. During this process, the working electrode surface was activated by performing 40 consecutive CV scans. The enhancement of electroactive sites on the catalyst surface during the activation phase can be attributed to the formation of electroactive forms from metal throughout CV process.

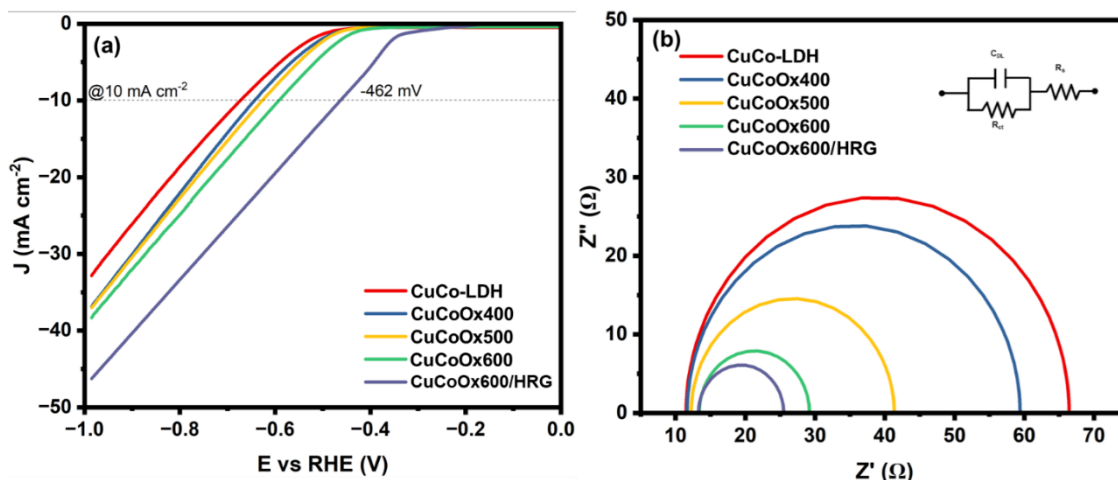


Figure 16. (a) HER polarization curve, (b) Nyquist plot illustrating the impedance behavior of CuCo-LDH and CuCoOx electrocatalyst

After completing the activation process, a Linear Sweep Voltammetry (LSV) analysis was conducted to evaluate the HER performance of the fabricated electrodes. **Figure 16a** presents comparative polarization curves, which reveal significant insights. Notably, an increase in annealing temperature results in a clear shift of the onset potential towards lower values, accompanied by an enhancement in current density. The electrode fabricated using materials calcined at 600°C (CuCoOx600) demonstrates superior HER performance compared to other samples calcined at different temperatures. Consequently, to augment the HER performance, HRG 1% is introduced into the ink formulation, alongside CuCoOx600, and subsequently drop-cast onto FTO electrodes, named as CuCoOx600/HRG. The addition of 1% HRG leads to a reduction in the overpotential (-462 mV at 10 mA cm⁻²) and an increase in current density.

Electrical conductivity is another important aspect to consider when evaluating the effectiveness of an electrocatalyst for water splitting catalysis. In this study, the EIS was examined for all electrodes that were created. A comparative Nyquist plot for the

synthesized electrodes is depicted in **Figure 16b**. The simplified Randles circuit (inset Figure 16b) is widely utilized as a foundational model for electrochemical cells. It comprises a solution resistance, double layer capacitance, and either a charge transfer or a polarization resistance⁴⁸. The double layer capacitance (C_{dl}) runs in parallel with the charge transfer resistance (R_{ct}), and this parallel combination is in series with the ohmic resistance (R_s). This configuration is analogous to a metal electrode immersed in an electrolyte. The corresponding Nyquist plot features a semi-circular arc intersecting the real axis (Z') at two points, as illustrated in Figure 4b. The intercept closest to the origin provides the value of the solution resistance (R_s), while the intercept farthest from the origin yields the total resistance value ($R_s + R_{ct}$)⁴⁸.

The charge transfer resistance (R_{ct}) values for CuCo-LDH, CuCoOx400, CuCoOx500, and CuCoOx600 were determined. The lowest R_{ct} value of CuCo600 indicates the highest electrical conductivity, which can result in faster charge transfer and enhanced HER performance across the electrode surface. The addition of 1% of HRG increased the conductivity and decreased the charge resistance to 12 Ohm. The high charge transfer rate of the CuCoOx600/HRG electrode may be attributed to its large surface area. Additionally, the presence of HRG creates an electron pathway, and the uniform dispersion of particles on the FTO substrate, facilitates efficient electron transfer at the surfaces.

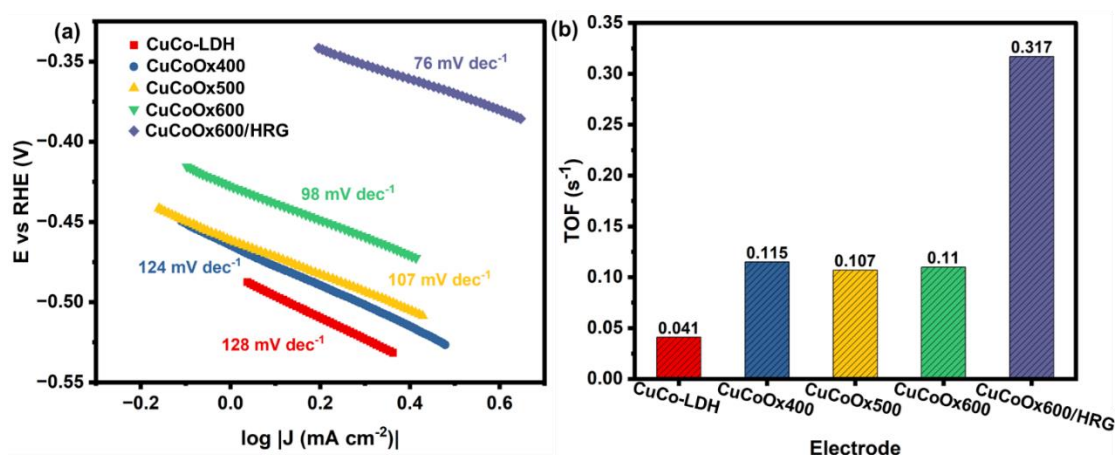


Figure 17. (a) Tafel slope providing insights to the kinetic of electrochemical reaction, (b) Bar graph depicting TOF value illustrating the intrinsic activity of catalysts

The Tafel slope serves as a vital parameter in the assessment of electrocatalysts. This parameter elucidates the kinetics of electrochemical processes, providing insight into the rate-determining steps as well as the efficiency of electron transfer at the electrode interface. Typically, a lower Tafel slope is preferred, as it indicates a more efficient electrocatalytic reaction characterized by accelerated kinetics, thereby enabling higher current densities at reduced overpotentials.

Tafel slopes were systematically measured for various CuCo electrocatalysts as shown in the **Figure 17a**. The CuCo-LDH exhibited a Tafel slope of 128 mV/dec. In contrast, the Tafel slopes for the annealed samples showed notable reductions: CuCoOx400 presented a slope of 124 mV/dec, CuCoOx500 achieved a slope of 107 mV/dec, and CuCoOx600 exhibited the lowest Tafel slope of 98 mV/dec. This progressive decrease in Tafel slope with increasing annealing temperature suggests a significant enhancement in the catalytic activity of the electrocatalyst. Specifically, the lowest Tafel slope observed for CuCoOx600 indicates that the optimal thermal treatment at 600°C produces structural or compositional

modifications beneficial to electrocatalysis, potentially augmenting the active surface area or improving the electronic properties of the material, thereby facilitating a more efficient electron transfer process.

Further enhancements in catalytic performance were achieved by integrating CuCoOx600 with HRG, resulting in an even lower Tafel slope of 76 mV/dec. This considerable reduction implies a synergistic interaction between the CuCo600 catalyst and HRG, whereby the conductive properties of HRG likely enhance charge transfer and contribute to an optimized electrochemical environment. The observed lower Tafel slope for the CuCoOx600/HRG composite suggests that this combination offers superior electrocatalytic efficiency, positioning it as a promising candidate for practical applications that require high catalytic performance.

The hydrogen evolution reaction (HER) commences with the Volmer step, where an adsorbed hydrogen atom (H^*) is generated on the electrode surface through the reaction: $M-H^* + H_2O + e^- \rightarrow M + H_2 + OH^-$. This step is subsequently followed by the Heyrovsky step, which is characterized by electrochemical desorption, leading to the formation of hydrogen gas through the same initial reaction, $M-H^* + H_2O + e^- \rightarrow M + H_2 + OH^-$. Alternatively, the Volmer step can lead to the Tafel step, involving chemical desorption, occurring when two adsorbed hydrogen atoms combine to produce hydrogen gas as described by the reaction $2M-H^* \rightarrow 2M + H_2$.

Based on the characteristics of hydrogen desorption, the overall mechanism for the hydrogen evolution reaction (HER) can be categorized as either Volmer–Tafel or Volmer–Heyrovsky. A Tafel slope value below 30 mV/dec suggests a Volmer–Tafel mechanism,

where the Tafel step is the rate-determining step (RDS). Conversely, slope values around 40 mV dec^{-1} and 120 mV dec^{-1} are indicative of the Volmer–Heyrovsky mechanism, with the Heyrovsky and Volmer steps acting as the RDS, respectively.

The observed Tafel slope value suggest that the CuCoOx600/HRG electrocatalysts likely operate under a Volmer-Heyrovsky mechanism, where the initial adsorption step is followed by electrochemical desorption in a basic medium. This mechanism underscores the significance of both electron transfer and hydrogen desorption processes in enhancing the HER performance of these catalysts.

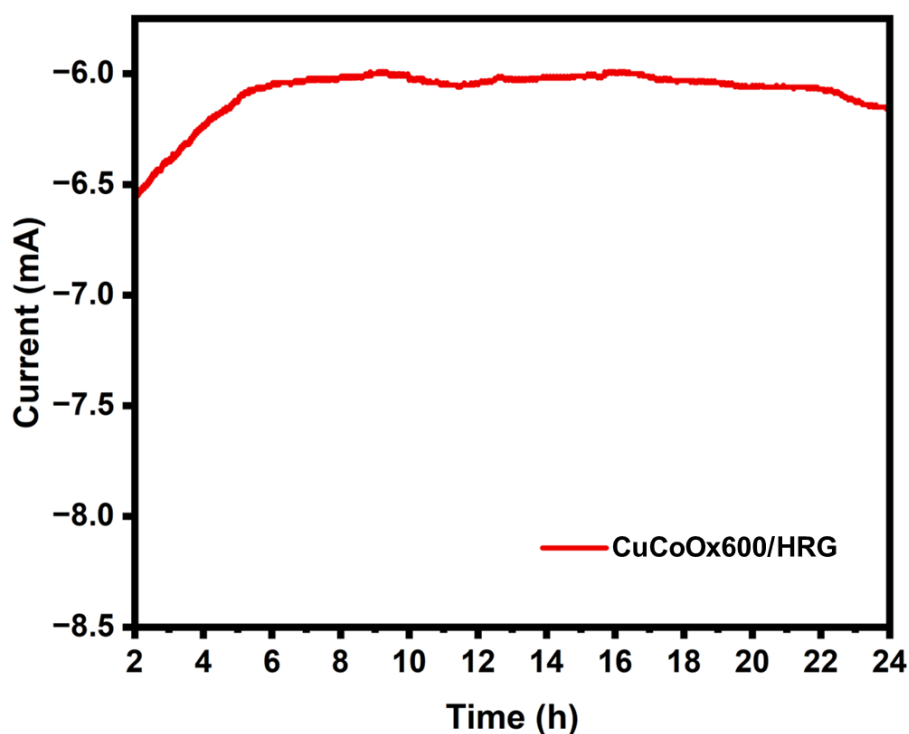


Figure 18. Chronoamperometry curve showing the stability of CuCoOx600/HRG for 24 hours continuous operation

Turnover frequency (TOF) depicted in **Figure 17b** reflects the intrinsic activity of active sites in an electrocatalyst, with higher values indicating superior performance. In this study,

TOF was measured at overpotential -0.46 V, TOF values for CuCo catalysts demonstrate the effects of thermal treatment and the incorporation of highly reduced graphene oxide (HRG) on electrocatalytic activity. The CuCo-LDH catalyst exhibits the lowest TOF at 0.041 s^{-1} , suggesting limited efficient active sites. Thermal treatment at 400°C (CuCoOx400) enhances the TOF to 0.115 s^{-1} , indicating significant improvement in catalyst efficiency likely due to favorable structural changes. At 500°C (CuCoOx500), the TOF slightly decreases to 0.107 s^{-1} , reflecting a potential plateau in intrinsic activity as structural improvements and sintering effects balance. An increase to 0.110 s^{-1} for CuCoOx600 indicates optimal structural enhancement without excessive sintering. The combination of CuCoOx600 with HRG (CuCoOx600/HRG) yields the highest TOF of 0.317 s^{-1} , highlighting a strong synergistic effect. The conductivity of HRG facilitates enhanced charge transfer, improving reaction kinetics and the effective utilization of active sites.

These findings illustrate that thermal treatment significantly optimizes TOF, while the addition of HRG substantially elevates catalytic performance, underscoring the importance of structural optimization and composite formation in achieving high efficiency in electrocatalysis.

The stability of the CuCoOx600/HRG electrocatalyst was evaluated at a constant potential of -0.48 V over a 24-hour period, shown in **Figure 18**. The results demonstrate that the current remained consistently around 6.25 mA, indicating excellent stability and sustained catalytic activity throughout the duration of the test.

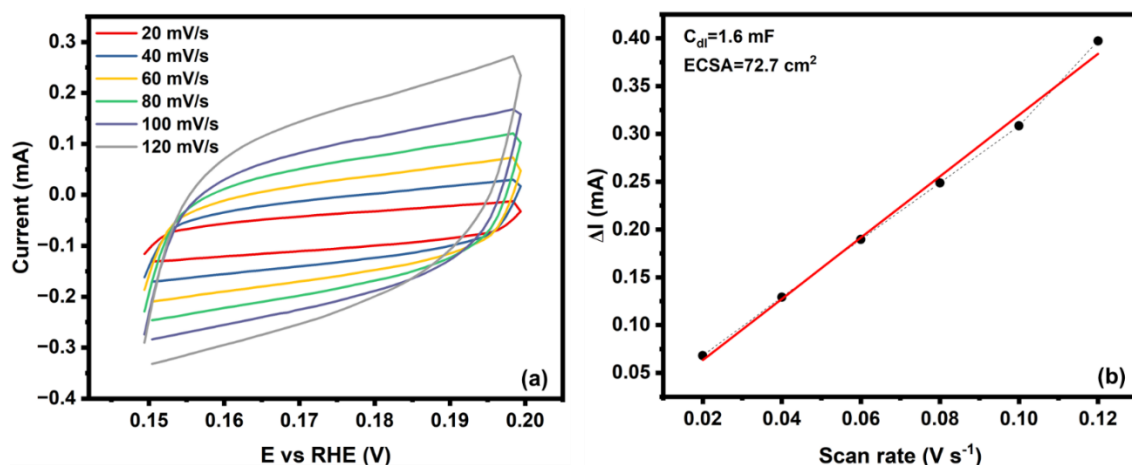


Figure 19. (a) CV at different scan rate, (b) ECSA of CuCoOxHRG

By monitoring CV curves in the non-Faradaic region at various scan rate (**Figure 19a**), the electrochemically active surface area (ECSA) was determined using double-layer capacitance (Cdl). The double-layer capacitance (Cdl) is determined by plotting ΔI ($I_a - I_c$) against the scan rate and analyzing the slope of the linear fit of the data (**Figure 19b**). CuCoOx600/HRG, the best electrocatalyst that was fabricated, had a Cdl value of 1.6 mF and ECSA of 72.7 cm^2 . By dividing the Cdl by the electrode's specific capacitance, ECSA is calculated. Utilizing the reported particular capacitance of metallic surfaces in 1.0 M KOH, 0.022 mFcm^{-2} ⁴⁹, the ECSA is determined. The ECSA value shows that the actual surface area contributing to HER for an electrode submerged in 1 cm^2 is 72.7 cm^2 , indicates high active site of electrocatalyst.

b. CuCo on NF Substrate

The performance of CuCo catalysts were evaluated nickel foam substrate, comparing it to previous results obtained on an FTO (fluorine-doped tin oxide) substrate. The same electrochemical techniques are used, including linear sweep voltammetry (LSV) and

electrochemical impedance spectroscopy (EIS). The analysis aimed to investigate the impact of substrate selection on electrocatalyst performance.

The results demonstrated significant differences in electrocatalyst affinity for each substrate. On the FTO substrate, thermally treated CuCoOx600 showed markedly improved performance compared to the CuCo-LDH catalyst, indicating CuCoOx600 has higher affinity with FTO. Conversely, on the nickel foam substrate, CuCo-LDH catalyst outperformed CuCoOx600, suggesting CuCo-LDH has more favorable interaction linked to the structural or electronic properties of the nickel foam.

These findings underscore the importance of substrate selection in electrocatalytic applications, as substrate affinity significantly influences catalyst efficiency. This study highlights the need to optimize both catalyst designs and supporting materials to enhance catalytic performance across various applications.

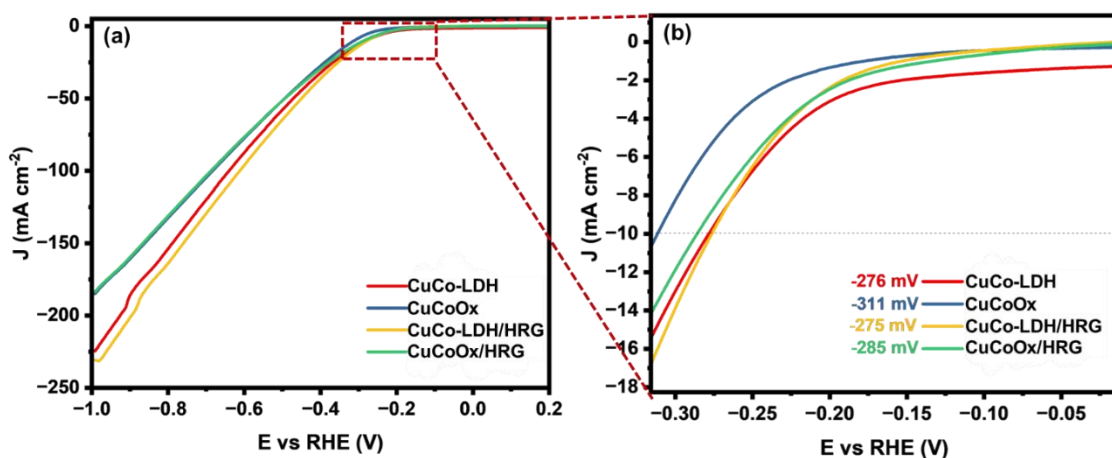


Figure 20. (a) LSV curve of CuCo-NF in 1.0 M KOH with constant scan rate 5 mV s⁻¹, (b) enlarged LSV curve with corresponding overpotential value at 10 mA cm⁻²

The LSV measurements of electrocatalysts on nickel foam in 1.0 M KOH, conducted at a scan rate of 5 mV/s, are illustrated in **Figure 20a**. The enlarged image (**Figure 20b**) clarifies the performance of each electrocatalyst in terms of hydrogen evolution reaction (HER) activity at various applied potentials.

The LSV results indicate that CuCo-LDH catalyst exhibits superior HER activity compared to the thermally treated CuCoOx, possibly due to a higher density of electrochemically active sites or an advantageous surface structure. Both catalysts benefit from the addition of highly reduced graphene oxide (HRG), which enhances electron conductivity and facilitates charge transfer.

Specifically, CuCo-LDH/HRG demonstrates the highest HER activity, requiring an overpotential of only 275 mV to achieve a current density of 10 mA cm⁻², a standard benchmark for HER performance. In contrast, CuCoOxHRG requires a slightly greater overpotential of 285 mV for the same current density. These findings suggest that CuCo-LDH/HRG possesses the most efficient HER catalytic performance among the tested samples, highlighting a synergistic effect between CuCo-LDH and HRG that optimizes electron transfer and maximizes active site availability.

The observed differences in overpotential further emphasize the influence of substrate choice and composite formation on catalytic efficiency. The lower overpotential of CuCo-LDH/HRG indicates its high intrinsic activity and enhanced conductivity, positioning it as a promising candidate for HER applications.

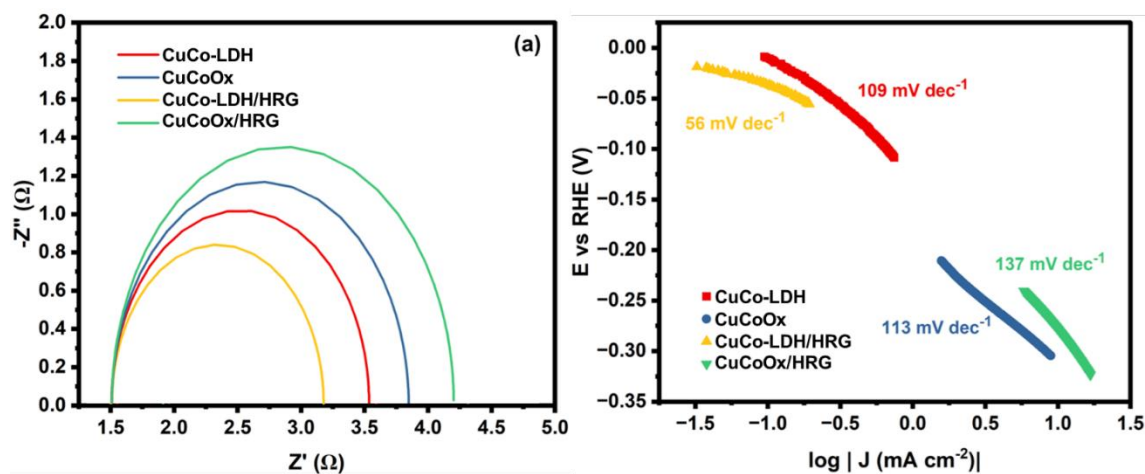


Figure 21. (a) Nyquist plots illustrating the impedance behavior of CuCo-NF catalysts, (b) Tafel slopes representing the kinetics

Based on the Nyquist plots for each electrocatalyst presented in **Figure 21a**, the CuCo-LDH/HRG composite exhibits the smallest semicircle, corresponding to the lowest charge transfer resistance (R_{ct}) of 1.67Ω . This indicates superior electron transfer efficiency at the catalyst interface. Following CuCo-LDH/HRG, the order of increasing R_{ct} is observed as CuCo-LDH, CuCoOx/HRG, and finally CuCoOx, suggesting that the CuCo-LDH/HRG composite benefits from an optimal combination of active sites and enhanced conductivity due to the addition of HRG.

The Tafel slope is a crucial measure of the reaction kinetics associated with the HER mechanism. A lower Tafel slope signifies improved reaction dynamics and more efficient electron transfer. As illustrated in **Figure 21b**, among the CuCo catalysts studied, significant differences in Tafel slopes were observed: CuCo-LDH has a slope of 109 mV/dec, while CuCo-LDH/HRG shows a notably lower slope of 56 mV/dec. These results suggest that adding highly reduced graphene oxide (HRG) greatly enhances the kinetics of HER. Conversely, calcined samples like CuCoOx (113 mV/dec) and CuCoOx/HRG (137

mV/dec) revealed suppressed kinetics, likely due to transformations in surface morphology and conductivity induced by high-temperature processing.

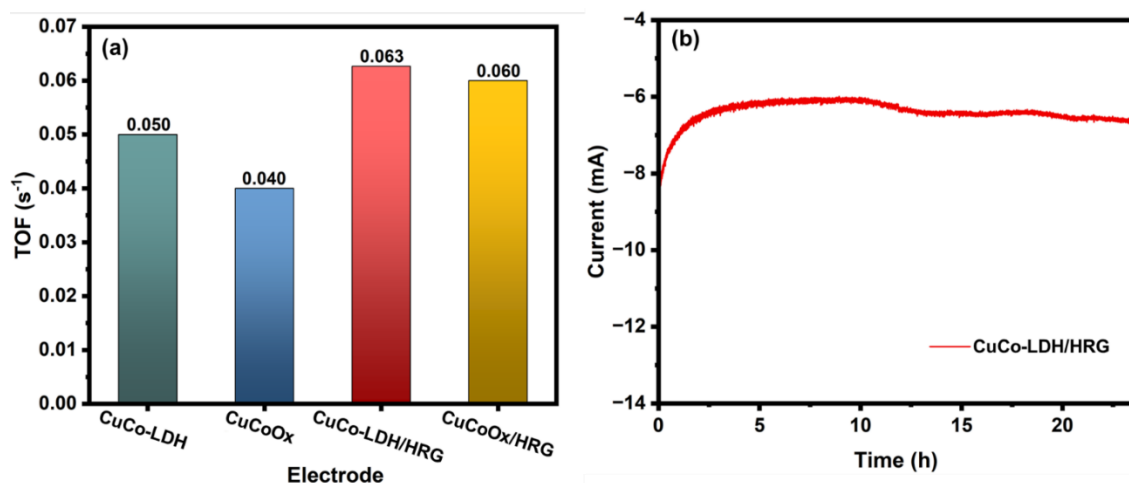


Figure 22. (a) TOF bar graph depicting intrinsic catalytic activity of CuCo-NF catalysts, (b) chronoamperometry curve of CuCo-LDH/HRG on nickel foam

TOF quantifies the intrinsic activity of the catalyst by determining the number of reactant molecules converted to products per active site per second, with higher TOF values reflecting better catalytic performance. As depicted in **Figure 22a**, the CuCo-LDH/HRG (0.063 s^{-1}) and CuCoOxHRG (0.06 s^{-1}) samples significantly exceed the performance of CuCo-LDH (0.05 s^{-1}) and CuCoOx (0.04 s^{-1}). This trend emphasizes the important role of HRG in enhancing catalytic activity through improved electronic conductivity and accessibility of active sites. Nevertheless, it should be noted that calcination may reduce TOF, possibly due to a decrease in the number of accessible active sites.

The CuCo-LDH/HRG demonstrates the most advantageous overall performance among the catalyst samples evaluated, characterized by both a low Tafel slope and a high TOF. This indicates a synergistic effect between CuCo=LDH and HRG that optimizes their kinetic and

intrinsic catalytic properties. While calcination at 600°C enhances crystallinity, it appears to adversely affect surface characteristics and electron mobility, as indicated by the elevated Tafel slope and lower TOF observed in CuCoOx/HRG.

These findings support earlier research by Zhao et al. (2021), which showed that the addition of conductive materials like graphene oxide can improve HER performance through enhanced charge transfer dynamics and increased surface area. Such results underscore the importance of carefully balancing synthesis parameters, including calcination, to achieve optimal catalytic performance.

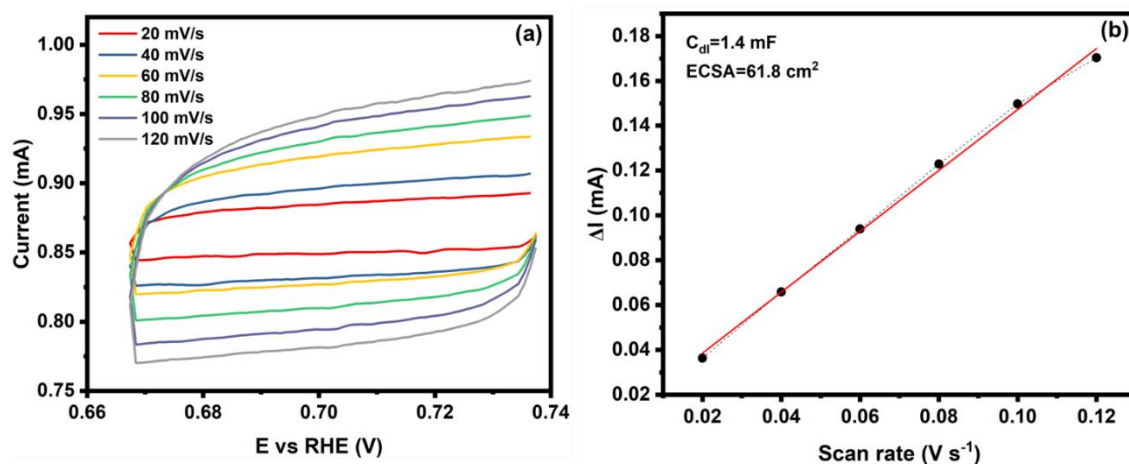


Figure 23. (a) CV at different scan rates 20 – 120 mV s⁻¹, (b) Plot of current density vs scan rate of CuCo-LDH/HRG on nickel foam

The electrochemical surface area (ECSA) of CuCo-LDH/HRG is assessed by observing the current response in the non-Faradaic region of the cyclic voltammetry (CV) at various scan rates, ranging from 20 to 120 mV (Figure 23a). By plotting the scan rate against the current change, the slope is determined, yielding a double-layer capacitance (C_{dl}) of 1.4 mF (Figure 23b). Using the reported specific capacitance of metallic surfaces in a 1.0 M KOH

solution, which is 0.022 mF/cm², the ECSA is calculated by dividing C_{dl} by C_s, resulting in an ECSA of 61.8 cm².

Figure 22b shows the stability observed in chronoamperometry, marked by a steady current density of around 7 mA maintained over 24 hours, underscores the structural integrity and operational reliability of CuCo-LDH/HRG. Such a high level of stability is crucial for practical applications that require consistent performance over extended periods. The robust stability of this electrocatalyst indicates a strong structural integration between CuCo and highly reduced graphene oxide (HRG), which significantly boosts both electron conductivity and mechanical durability in alkaline environments.

4.2.2 Electrochemical Performance of CuNi Electrocatalyst

a. CuNi on FTO Substrate

The electrochemical performance of cuprous nickel (CuNi) catalysts, supported on fluorine-doped tin oxide (FTO), in the hydrogen evolution reaction (HER) was rigorously investigated through a series of electrochemical assessments, including linear sweep voltammetry (LSV), electrochemical impedance spectroscopy (EIS, illustrated via Nyquist plots), turnover frequency (TOF), and Tafel slope analysis. These electrochemical parameters are essential for providing a comprehensive understanding of the catalytic activity, electron transfer kinetics, and intrinsic efficiency exhibited by the CuNi catalysts under examination.

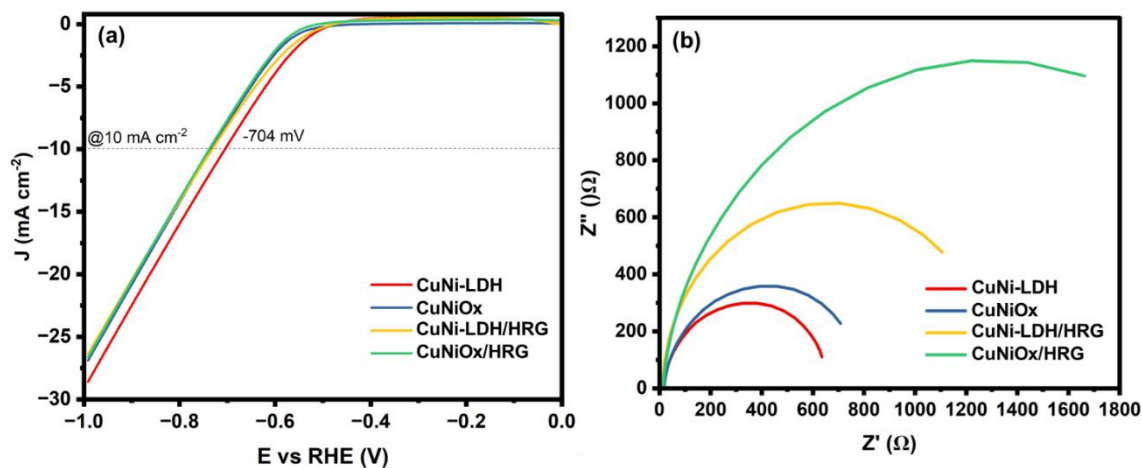


Figure 24. (a) LSV curves of CuNi on FTO catalysts in 1.0 M KOH with fixed scan rate 5 mV s⁻¹, (b) Nyquist plots

Figure 24a displays the Linear Sweep Voltammetry (LSV) curves, which are crucial for assessing the overpotential required to achieve specific current densities. This analysis offers valuable insights into the catalytic efficiency of various materials. Among the CuNi catalysts tested on FTO, CuNi-LDH catalyst stood out, demonstrating the lowest overpotential. This notable feature highlights its high catalytic performance in promoting the hydrogen evolution reaction (HER) compared to CuNiOx, CuNi-LDH/HRG, and CuNiOx/HRG.

Interestingly, the addition of highly reduced graphene oxide (HRG) to the catalyst matrix did not lead to the expected decrease in overpotential. This finding contradicts the common belief that the conductive and synergistic qualities of HRG should enhance catalytic performance. The unexpected behavior of the CuNi-LDH/HRG system might be due to potential adverse interactions between HRG and the CuNi-LDH catalyst matrix. Such interactions could limit access to active catalytic sites or alter the electronic structure, hindering the HER process. Additionally, the incorporation of HRG may create extra

interfaces or resistive pathways that counteract its anticipated benefits, possibly resulting in a neutral or even negative impact on overall catalytic efficiency.

The Nyquist plot presented in **Figure 24b**, derived from EIS measurements, offers additional insights into the electron transfer dynamics occurring at the electrode interface. Notably, the CuNi-LDH exhibited the smallest semicircle radius, which is indicative of reduced charge transfer resistance (R_{ct}). This characteristic underscores the capability of electrocatalysts to efficiently facilitate electron transfer processes, a vital element in optimizing HER performance. The enhanced electron transfer efficiency associated with CuNi-LDH can be attributed to its advantageous structural and electronic attributes.

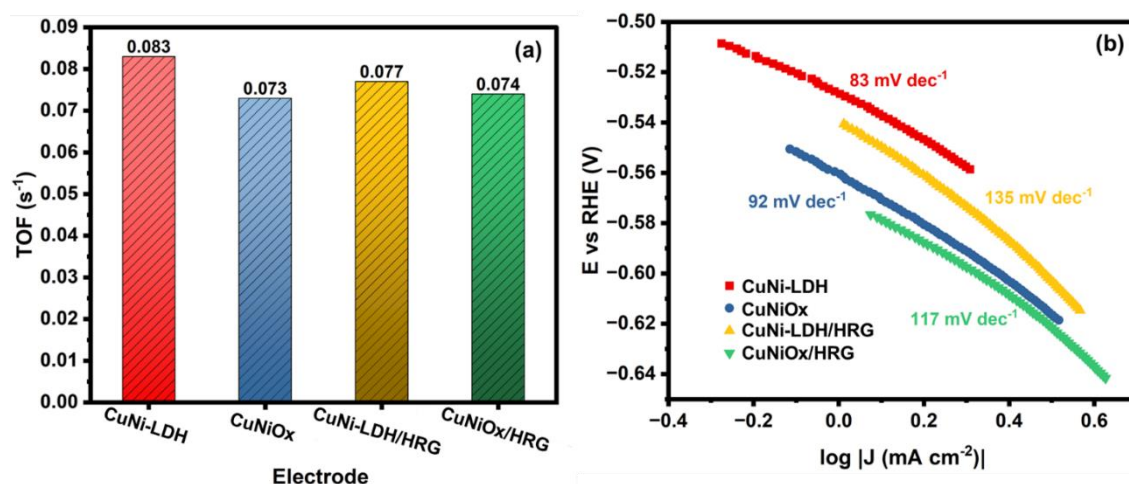


Figure 25. (a) TOF graph depicting intrinsic catalytic activity of CuNi on FTO, (b) Tafel slopes of CuNi on FTO catalysts representing the kinetics of electrochemical reactions

Further elucidation of the intrinsic activity of electrocatalysts is provided by the turnover frequency (TOF) values depicted in **Figure 25a**. Among the variants, CuNi-LDH demonstrated the highest TOF at $0.083\ s^{-1}$, followed by CuNi-LDH/HRG ($0.077\ s^{-1}$), CuNiOx/HRG ($0.074\ s^{-1}$), and CuNiOx ($0.073\ s^{-1}$). The elevated TOF for CuNi-LDH

signifies its superior capability to facilitate a greater quantity of hydrogen evolution reactions per active site per second. This finding is consistent with the observations made through LSV and Nyquist analyses, reinforcing the superior catalytic performance of CuNi-LDH.

The Tafel slope analysis, illustrated in **Figure 25b** provides further insights into the reaction kinetics associated with the HER. A lower Tafel slope is indicative of a more rapid catalytic reaction mechanism. In this context, CuNi-LDH exhibited the lowest Tafel slope at 83 mV/dec, in comparison to CuNiOx (92 mV/dec), CuNiOx/HRG (117 mV/dec), and CuNi-LDH/HRG (135 mV/dec). The higher Tafel slopes observed for the latter catalysts imply the existence of additional kinetic barriers, which may arise from variations in morphology or surface properties induced by thermal treatments or the incorporation of HRG.

When comparing the CuNi catalyst to the previously examined CuCo system, it becomes clear that the CuNi catalyst may fall short in catalytic effectiveness for the HER. This difference can be attributed to the distinct electronic and structural properties inherent to the two bimetallic systems. Copper-cobalt combinations are well-known for demonstrating more favorable synergistic effects for HER due to optimal electronic configurations and enhanced hydrogen adsorption-desorption dynamics. In contrast, the CuNi system may face significant limitations in striking a balance among these essential factors, leading to a less efficient catalytic process. Furthermore, variations in the formation of active sites may further explain the relatively modest performance of the CuNi catalyst in comparison to the CuCo system.

b. CuNi on NF Substrate

The electrochemical hydrogen evolution reaction (HER) performance of the CuNi electrocatalysts on nickel foam was systematically evaluated using linear sweep voltammetry (LSV), electrochemical impedance spectroscopy (EIS), turnover frequency (TOF), and Tafel slope analysis. These parameters collectively provide insight into the catalytic efficiency, electron transfer dynamics, and intrinsic activity of the catalysts.

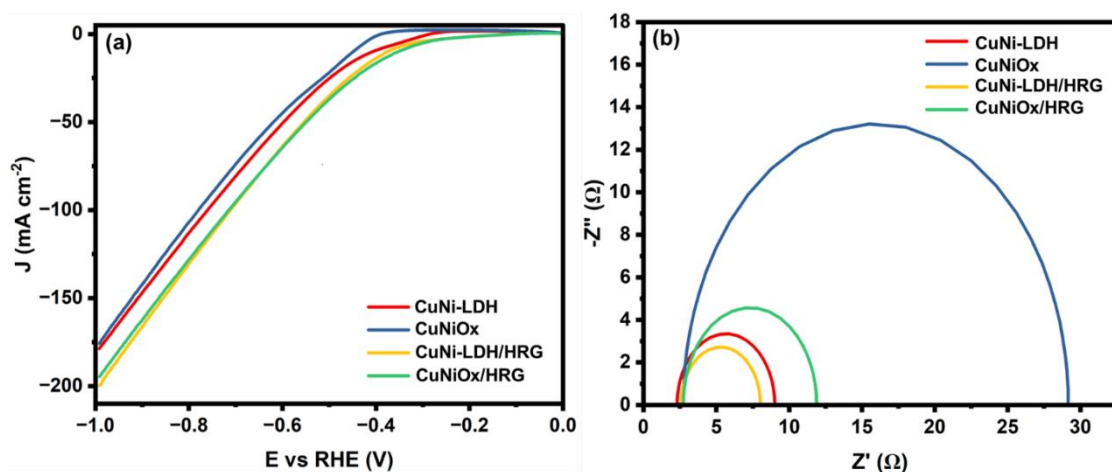


Figure 26. (a) LSV curves in 1.0 M KOH with constant scan rate 5 mV s⁻¹, (b) Nyquist plots of CuNi catalyst on nickel foam

The overpotential required to achieve a current density of 10 mA cm⁻², derived from the LSV measurements (**Figure 26a**), is a critical indicator of the catalytic activity of HER electrocatalysts. Among the tested samples, CuNiOx/HRG exhibited the lowest overpotential of 352 mV, followed by CuNi-LDH/HRG (376 mV), CuNi-LDH (406 mV), and CuNiOx (449 mV). This trend highlights the enhanced catalytic activity of CuNiOx/HRG, which can be attributed to the synergistic effects between the highly reduced

graphene oxide (HRG) and CuNiOx. The HRG likely improves charge transport, while the annealing process promotes the formation of more active catalytic sites.

EIS analysis, represented through Nyquist plots (**Figure 26b**), was conducted to assess the charge transfer resistance (R_{ct}) of the catalysts. Smaller semicircles in the Nyquist plots indicate lower R_{ct} and better charge transfer kinetics. The catalysts ranked in the following order of increasing R_{ct} : CuNi-LDH/HRG, CuNi-LDH, CuNiOx/HRG, and CuNiOx. Notably, CuNi-LDH/HRG exhibited the smallest semicircle, implying superior conductivity and lower resistance to electron flow during the HER process. This observation underscores the effectiveness of HRG in facilitating efficient charge transport.

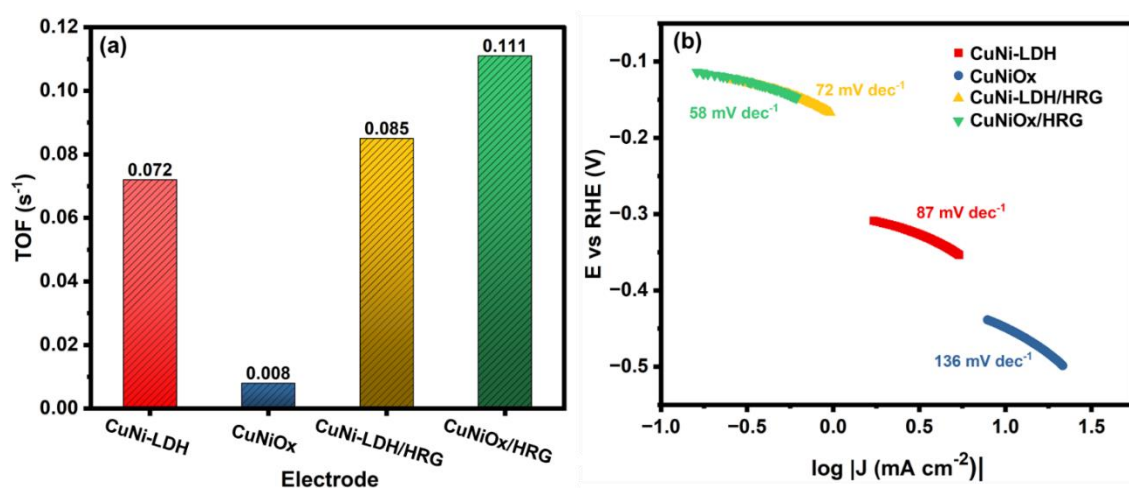


Figure 27. (a) TOF graphs illustrating the intrinsic catalytic activity, (b) Tafel slopes representing the kinetics of CuNi on nickel foam catalysts

The turnover frequency (TOF) as represented in **Figure 27a** further provides a measure of the intrinsic catalytic activity by estimating the number of hydrogen molecules generated per active site per second. CuNiOx/HRG displayed the highest TOF value of $0.111 s^{-1}$, indicating its excellent intrinsic activity. The TOF values for the other catalysts followed

the order: CuNi-LDH/HRG (0.085 s^{-1}), CuNi-LDH (0.072 s^{-1}), and CuNiOx (0.008 s^{-1}). The significantly lower TOF value of CuNiOx suggests that the annealing process without HRG incorporation adversely affects the catalytic activity, likely due to the loss of accessible active sites or changes in structural composition.

The Tafel slope is another crucial parameter, as it reflects the reaction kinetics and provides insight into the HER mechanism. A lower Tafel slope indicates faster reaction kinetics. Among the samples, CuNiOx/HRG demonstrated the lowest Tafel slope of 58 mV dec^{-1} , followed by CuNi-LDH/HRG (72 mV dec^{-1}), CuNi-LDH (87 mV dec^{-1}), and CuNiOx (136 mV dec^{-1}), as shown in **Figure 27b**. These results highlight the superior kinetics of CuNiOx/HRG, which can be attributed to its optimized electronic structure and improved proton adsorption capabilities.

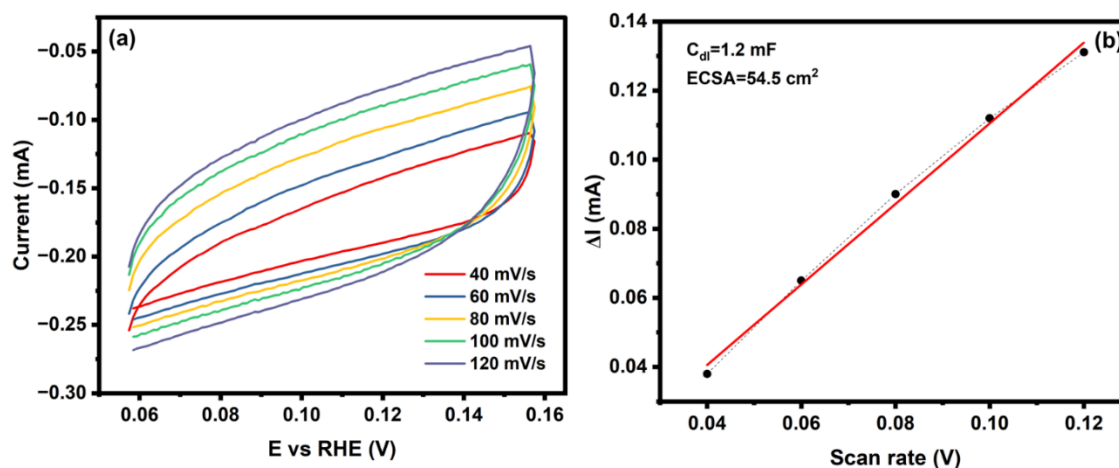


Figure 28. (a) CV curves at varying scan rates $40 - 120\text{ mV s}^{-1}$, (b) Plot of current density versus scan rate of CuNi600HRG/NF

The electrochemical performance of CuNiOx/HRG as a HER electrocatalyst was further examined by determining its electrochemically active surface area (ECSA), double-layer capacitance (Cdl), and stability under prolonged operation. The ECSA was estimated using

cyclic voltammetry (CV) conducted in the non-faradaic region at various scan rates (**Figure 28a**). The relationship between the current and the scan rate was plotted, yielding a Cdl value of 1.2 mF. Based on this, the ECSA was calculated to be 54.5 cm² (**Figure 28b**). This enhancement highlights the effective integration of highly reduced graphene oxide (HRG) with the CuNi, providing an increased number of active sites accessible for the hydrogen evolution reaction.

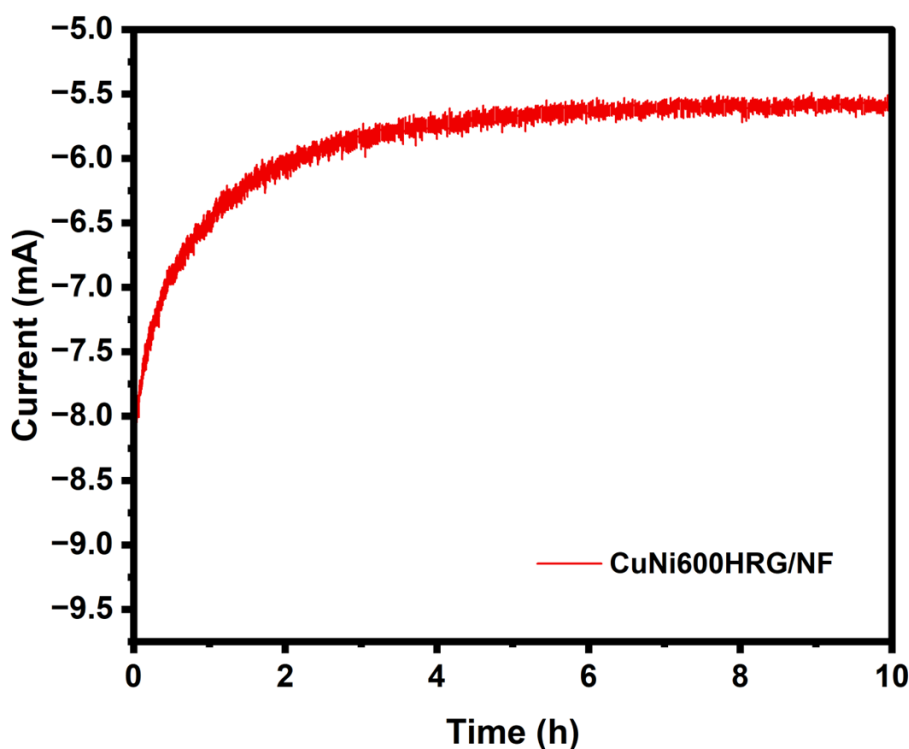


Figure 29. Chronoamperometry curve of CuNi600HRG/NF

Figure 29 illustrates the stability observed in chronoamperometry, showcasing a consistent current density of approximately 5 mA sustained over a period of 10 hours. This underscores the structural integrity and operational reliability of CuNiOx/HRG on nickel foam. The remarkable stability of this electrocatalyst indicates a robust integration between

CuNiOx and highly reduced graphene oxide (HRG), which significantly enhances both electron conductivity and mechanical durability in alkaline environments.

Table 1. HER performance of synthesized catalysts in this work

Bimetal	Substrate	Catalysts	Overpotential (mV) at 10 mA cm ⁻²	Tafel slope (mV dec ⁻¹)
CuCo	FTO	CuCo-LDH	591	128
		CuCoOx400	626	124
		CuCoOx500	643	107
		CuCoOx600	672	98
		CuCoOx600/HRG	462	76
	NF	CuCo-LDH	276	109
		CuCoOx	311	113
		CuCo-LDH/HRG	275	56
		CuCoOx/HRG	285	137
CuNi	FTO	CuNi-LDH	704	83
		CuNiOx	734	92
		CuNi-LDH/HRG	731	135
		CuNiOx/HRG	738	117
	NF	CuNi-LDH	406	87
		CuNiOx	449	136
		CuNi-LDH/HRG	376	72
		CuNiOx/HRG	352	58

4.3 Water Splitting Enhancement with HMFOR

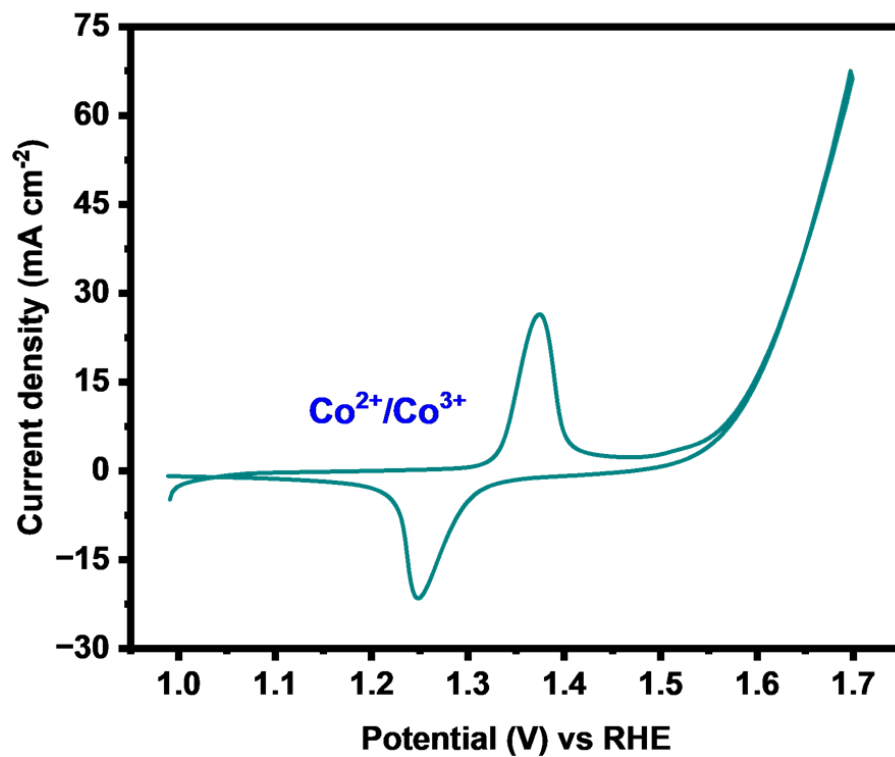


Figure 30. Cyclic voltammetry (CV) of as-prepared CuCo-Layered Double Hydroxide (CuCo-LDH) in 1.0 M KOH with a potential window from 1.0 V to 1.7 V vs. RHE at a scan rate of 5 mV s⁻¹

The synthesized CuCo-Layered Double Hydroxide (CuCo-LDH) was thoroughly analyzed using cyclic voltammetry (CV) in a 1.0 M KOH electrolyte solution, spanning a potential range from 1.0 V to 1.7 V versus the reversible hydrogen electrode (RHE) at a scan rate of 5 mV s⁻¹ (**Figure 30**). A distinct and sharp oxidation peak was observed at 1.37 V vs. RHE, indicating the oxidation of Co²⁺ ions to Co³⁺. The rapid increase in current following the oxidation peak suggests the initiation of the oxygen evolution reaction (OER), highlighting the significant role of Co³⁺ species in facilitating water oxidation. During the subsequent reduction scan, a corresponding peak at 1.24 V vs. RHE was detected, confirming the

reversible reduction of Co^{3+} back to Co^{2+} , and demonstrating the dynamic electrochemical behavior of the catalyst.

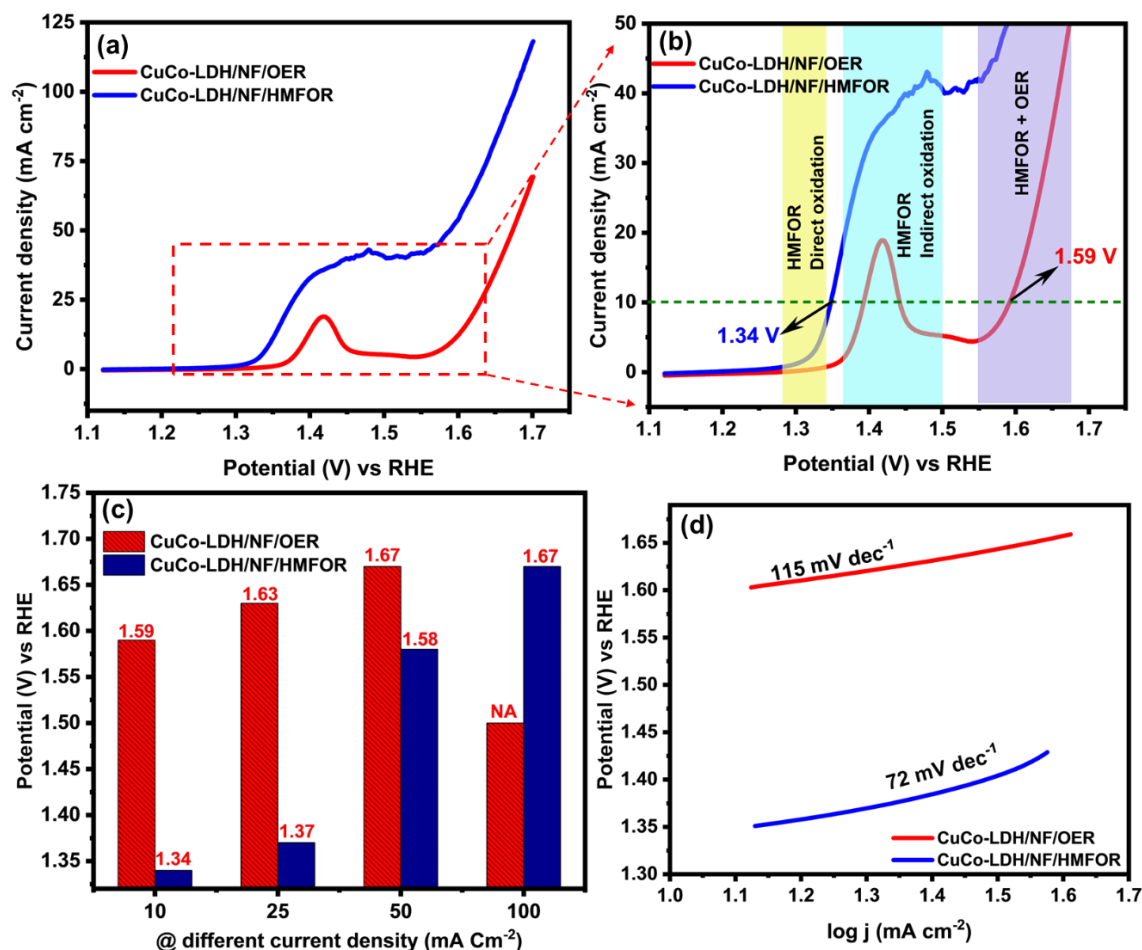
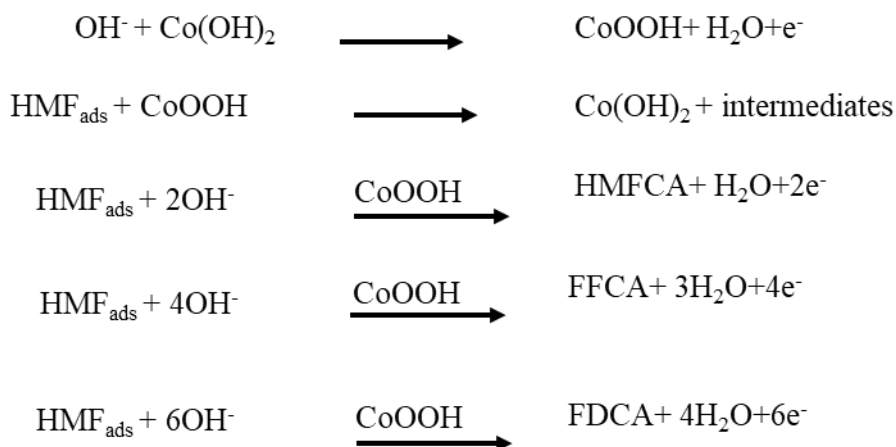


Figure 31. (a) LSV curves of the CuCo-LDH/NF in presence and absence of 10mM HMF in 1.0 M KOH, with a fixed scan rate of 5 mVs^{-1} . (b) Magnified view of the LSV curves to better illustrate the oxidation peaks associated with the catalyst performance. (c) Bar graph depicting the potential versus current densities of the CuCo-LDH/NF catalyst for both OER and HMFOR. (d) Tafel slopes for the OER and HMFOR of CuCo-LDH/NF, providing insights into the kinetics of the electrochemical reactions.

Furthermore, **Figure 31a** illustrates the linear sweep voltammetry (LSV) curves of the CuCo-LDH catalyst in a 1.0 M KOH solution, comparing the results both with and without the presence of 10 mM hydroxymethylfurfural (HMF) at a uniform scan rate of 5 mV s⁻¹. **Figure 31b** provides an enlarged view of the LSV curve, allowing for a clearer presentation of the observed oxidation peaks. In the absence of HMF, a distinct unimodal peak appears at approximately 1.38 V vs. RHE, corresponding to the oxidation of Co²⁺ to Co³⁺. Following this peak, the onset of the oxygen evolution reaction (OER) occurs around 1.55 V vs. RHE, with the catalyst reaching a current density of 10 mA cm⁻² at 1.59 V vs. RHE, demonstrating its catalytic efficiency.

In contrast, the addition of 10 mM HMF to the system initiates hydroxymethylfurfural oxidation (HMFOR) at a significantly lower potential of 1.27 V vs. RHE, signifying the direct oxidation of HMF. Notably, the Co³⁺ oxidation peak remains evident in the presence of HMF, indicating that HMF undergoes an indirect oxidation process. In this scenario, the active Co³⁺ species, CoOOH, is initially generated electrochemically, subsequently facilitating the oxidation of HMF. The detailed electrochemical oxidation mechanism of HMFOR on the CuCo-LDH/NF system is further described in mechanism 1.



Mechanism 1. Proposed electrochemical pathway for the oxidation of HMF to FDCA on CuCo-LDH/NF.

The integrated HMFOR (hydrogenation of 5-hydroxymethylfurfural) and OER (oxygen evolution reaction) process becomes particularly noteworthy at a potential of 1.57 V vs. RHE (reversible hydrogen electrode). Remarkably, HMFOR reaches a current density of 10 mA cm⁻² at a significantly lower potential of 1.34 V vs. RHE, showcasing a marked improvement in efficiency over the OER process alone. In **Figure 31c**, a bar graph illustrating the relationship between potential and current density vividly captures this comparative performance, demonstrating that HMFOR consistently operates at lower potentials across a range of current densities. Furthermore, the results reveal that HMFOR not only takes place at a reduced overpotential compared to OER but also enhances the OER process itself by facilitating a more effective transfer of electrons at the electrode surface. This interplay indicates that the CuCo-LDH (Copper-Cobalt Layered Double Hydroxide) catalyst significantly boosts overall catalytic performance when working in tandem with HMF (5-hydroxymethylfurfural).

Additionally, the Tafel slopes gleaned from these experiments provide profound insights into the reaction kinetics and the overall efficiency of the catalytic processes involved. As illustrated in **Figure 31d**, the Tafel slope value for OER was measured at 115 mV dec⁻¹, signaling relatively sluggish reaction kinetics. This elevated Tafel slope for OER suggests that the reaction proceeds through multiple steps characterized by substantial energy barriers, a reflection of the inherent complexity involved in water oxidation, which requires the transfer of four electrons. On the other hand, the Tafel slope for HMFOR is considerably lower at 72 mV dec⁻¹, indicating that the CuCo-LDH electrode operates much more

efficiently in facilitating the oxidation of HMF in comparison to OER. This lower Tafel slope conveys more favorable reaction kinetics and a decreased energy requirement for each decade of current increase, suggesting that the electrooxidation of HMF occurs with greater ease and responsiveness on the catalyst surface.

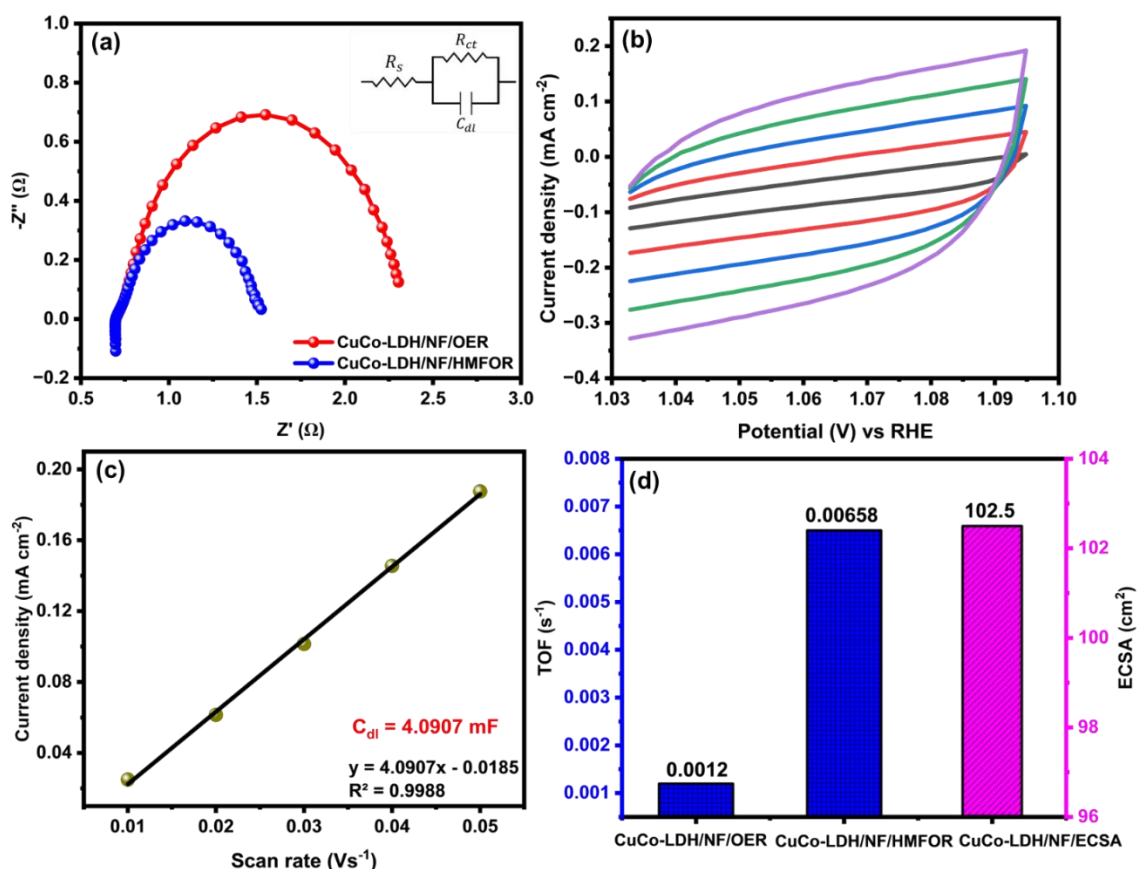


Figure 32. (a) Nyquist plots illustrating the electrochemical impedance behavior of CuCo-LDH/NF in the presence and absence of 10 mM HMF, highlighting differences in charge transfer resistance. (b) CV curves obtained at varying scan rates 10–50 mV s^{-1} , demonstrating the catalyst electrochemical activity. (c) Plot of current density versus scan rate. (d) Bar graph representing the TOF of CuCo-LDH/NF in the presence and absence of HMF, alongside the ECSA of CuCo-LDH.

In addition, EIS was performed to gain insights into the charge transfer kinetics and electrochemical interface characteristics of the CuCo-LDH catalyst during both OER and HMFOR, using 1 M KOH as the electrolyte. The Nyquist plots were fitted using a Randles-type equivalent circuit model (inlet **Figure 32a**). A simple Randles cell model equivalent circuit was used to analyze the impedance spectra, which include the charge transfer resistance (R_{ct}), solution/series resistance (R_s), and the capacitance of the electrochemical double-layer (C_{dl}). From **Figure 32a**, the Nyquist plots showed a larger semicircle for OER compared to HMFOR, indicating that the charge transfer resistance (R_{ct}) is significantly higher for OER. Conversely, the Nyquist plot for HMFOR exhibited a smaller semicircle, reflecting a lower charge transfer resistance. This suggests that the electrochemical oxidation of HMF on the CuCo-LDH catalyst is more facile. Moreover, the lower resistance also highlights the favorable interaction between the catalyst surface and HMF, enabling faster adsorption, electron transfer, and oxidation processes.

To determine the Electrochemically Active Surface Area (ECSA) of the CuCo-LDH catalyst, CV was performed in the non-faradaic region using various scan rates ranging from 10 to 50 mV s^{-1} . The CV curves, displayed in **Figure 32b**, exhibit a linear increase in current density with increasing scan rate, indicating that the observed current is primarily associated with the charging of the electrical double layer. The double-layer capacitance (C_{dl}) was determined from the slope of the linear fit of the plot of current density versus scan rate (**Figure 32c**), which was found to be $4.0907 \text{ mF cm}^{-2}$. The linear relationship between current density and scan rate, coupled with the high C_{dl} highlights the extensive electrochemical surface area and accessibility of the active sites on the catalyst. Furthermore, the ECSA were calculated using the equation (2),

$$\text{ECSA} = C_{\text{dl}}/C_s \quad (2)$$

where C_s is the specific capacitance (0.04 mF cm^{-2}) in 1 M KOH is adopted from previous reports, as the result the ECSA of the CuCo-LDH catalyst was measured to be 102.5 cm^2 . The high ECSA value indicates that the layered structure of the CuCo-LDH material effectively exposes more active sites, promoting better interaction between the catalyst and the electrolyte. This is particularly beneficial for enhancing the reaction kinetics and improving the efficiency of the catalyst in both oxygen evolution and organic oxidation processes.

The turnover frequency (TOF) is a crucial parameter for evaluating the intrinsic activity of electrocatalysts, representing the number of reactant molecules converted per active site per unit of time. The TOF values for both OER and HMFOR were measured, with detailed calculation procedures provided in the supporting information S6. The TOF for OER was found to be 0.0012 s^{-1} , whereas the TOF for HMFOR was 0.00658 s^{-1} . These values are illustrated in **Figure 32d** as a bar graph for a clear comparison. The TOF for HMFOR is significantly higher compared to that for OER, suggesting that the CuCo-LDH catalyst is more efficient at facilitating the oxidation of HMF than it is at promoting the oxygen evolution reaction. The higher TOF for HMFOR indicates that the catalyst possesses a greater number of active sites available for HMF oxidation, or that the catalytic pathway for HMFOR is more favorable in terms of energy requirements and electron transfer kinetics compared to OER. This aligns well with the observations from other electrochemical characterizations, such as EIS and Tafel slope analyses, where HMFOR consistently exhibited lower resistance and more favorable kinetics compared to OER.

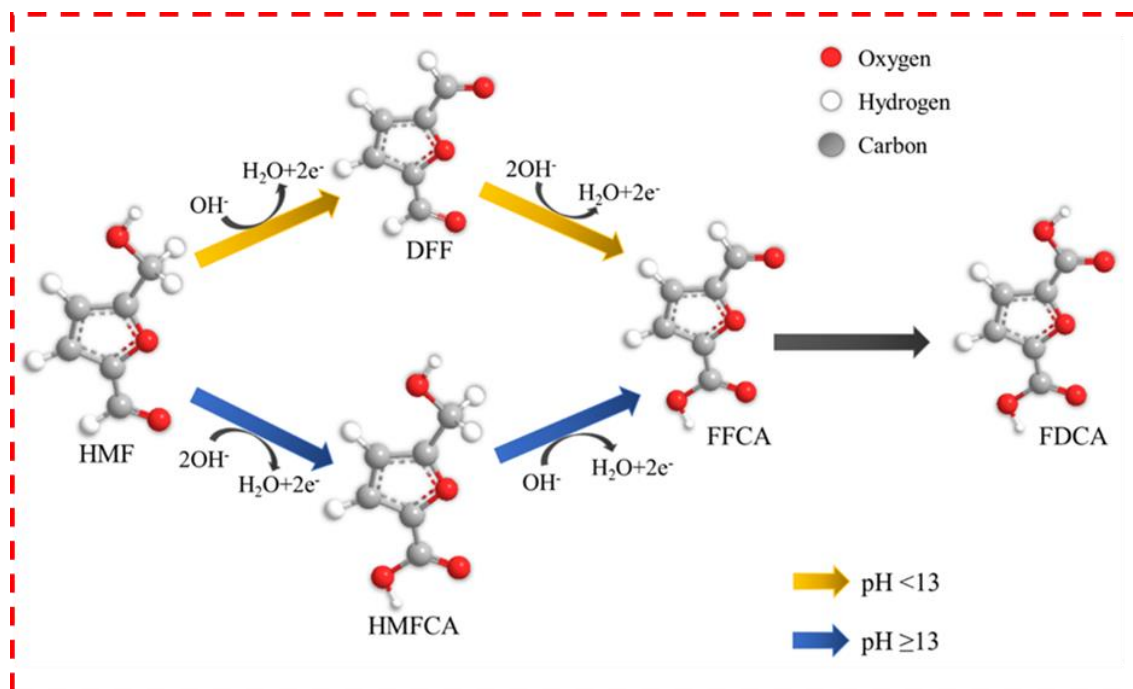


Figure 33. The possible electrochemical mechanism of electrochemical oxidation of HMF into FDCA

To evaluate the oxidation products and Faradaic efficiency (FE) of the CuCo-LDH catalyst during HMF oxidation, the experiment was carried out at an applied potential of 1.42 V vs. RHE in an H-cell separated by a Nafion membrane. A theoretical charge of 102.5 C was passed during the reaction, and the results are shown in **Figure 34a**. The mechanism of HMF oxidation on CuCo-LDH is also illustrated in **Figure 33**. **Figure 34a** displays the chronoamperometric response during the HMFOR, which shows a gradual decrease in current density, indicating the continuous consumption of HMF over time. The HMF oxidation to FDCA involves two possible pathways due to the presence of both hydroxyl and aldehyde groups. In the first pathway, the aldehyde group is preferentially oxidized, forming 5-hydroxymethyl-2-furancarboxylic acid (HMFCFA). Alternatively, in the second pathway, the hydroxyl group is initially oxidized, resulting in 2,5-diformylfuran (DFF).

Both intermediates, HMFCFA and DFF, further oxidize to 5-formyl-2-furancarboxylic acid (FFCA) before ultimately forming FDCA (mechanism 1).

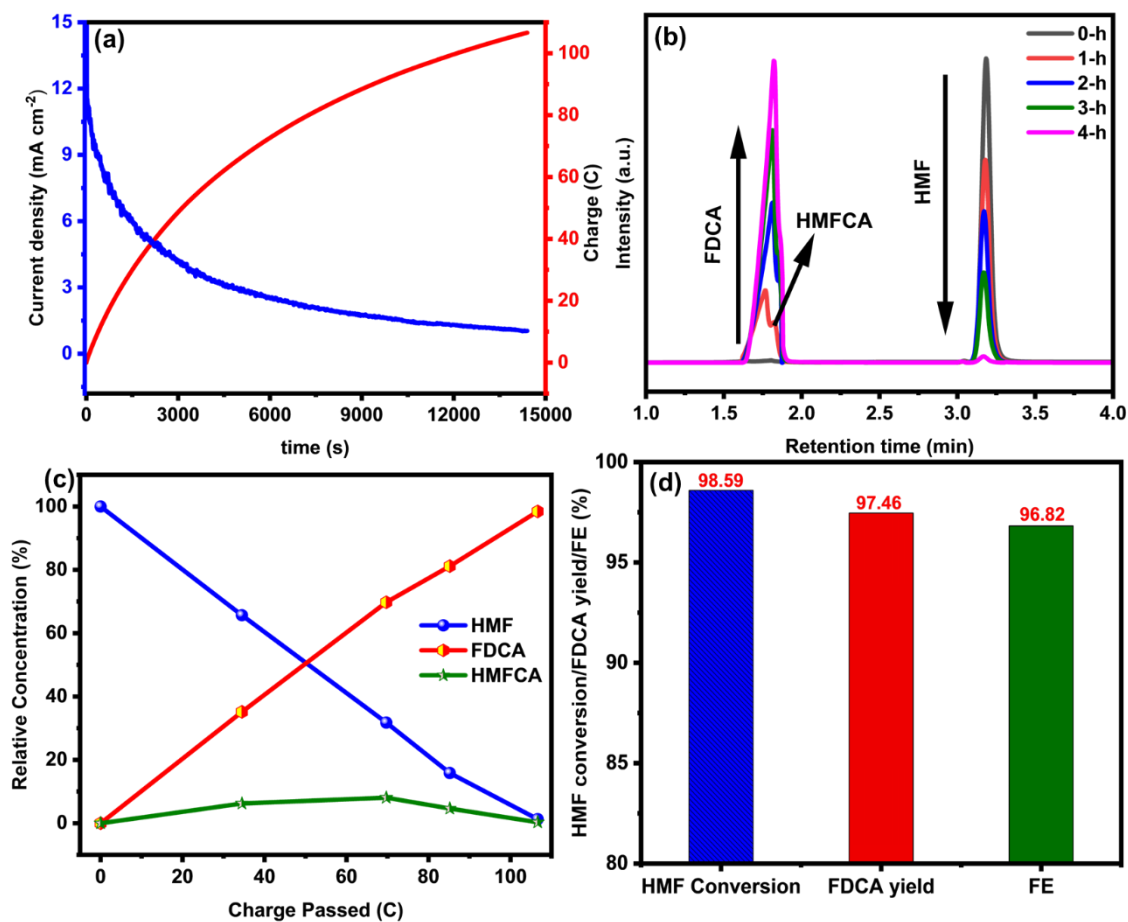


Figure 34. (a) Chronoamperometry curve measured at CuCo-LDH/NF in the presence of 10 mM HMF, showing the current response and the total charge passed over 4 h. (b) HPLC chromatogram of electrolyte samples collected at different time intervals. (c) Corresponding concentration changes of HMF, HMFCFA, and FDCA over time, indicating the progression of the electrochemical conversion. (d) Bar graph representing HMF conversion, FDCA yield, and Faradaic efficiency (FE) of the CuCo-LDH catalyst for HMFOR.

Table 2. Comparative parameters of HMFOR catalysts

Electrocatalyst	HMF		Oxidation			Ref.
	Concentration (mM)	Electrolyte	Potential (V) vs RHE	FDCA yield	Faradic Efficiency	
CuCo-LDH/NF	10	1.0 M KOH	1.27	97.46	96.82	This work
Pd/Ni(OH) ₂	50	1.0 M KOH	0.6	97.3	~80	50
CoAl-LDH	10	1.0 M KOH	1.52	--	99.4	51
Cu(OH) ₂ @Ni ₃ Co ₁ -LDH	10	1.0 M KOH	1.0	93.65	--	52
NiSe@NiO _x /NF	10	1.0 M KOH	1.42	99	99	53
CuxS@NiCo-LDH	10	1.0 M KOH	1.30	99	100	54
NiCo ₂ O ₄	10	1.0 M KOH	1.35	94.3	89.6	55
CuNi(OH) ₂ /C	5	1.0 M KOH	1.45	93.3	95	56
MoO ₂ -FeP	10	1.0 M KOH	1.45	--	97.8	57
NiCo-MOFs	10	pH 13	1.55	99	78.8	58

Cu(OH) ₂ NWs/	5	0.1 M KOH	1.69	80.3	80.5	59
CuF						

To track the concentrations of HMF and its oxidation products over time, high-performance liquid chromatography (HPLC) was used, with electrolyte samples taken at different time points (**Figure 34b**). As shown in **Figure 34c**, the concentrations of HMF and intermediates decrease with increasing charge, while the FDCA concentration increases, indicating effective conversion of HMF to FDCA. The absence of DFF supports the preference for aldehyde group oxidation under the given experimental conditions. As the results, the CuCo-LDH catalyst demonstrated a high performance with 98.59% conversion of HMF, a product yield of 97.46%, and a Faradaic efficiency of 96.82%. These results indicate that CuCo-LDH is highly effective at catalyzing the electrochemical conversion of HMF to FDCA, showing high selectivity and efficiency. The elevated Faradaic efficiency confirms that most of the applied charge directly contributes to FDCA formation, emphasizing the suitability of CuCo-LDH as an efficient electrocatalyst for biomass valorization.

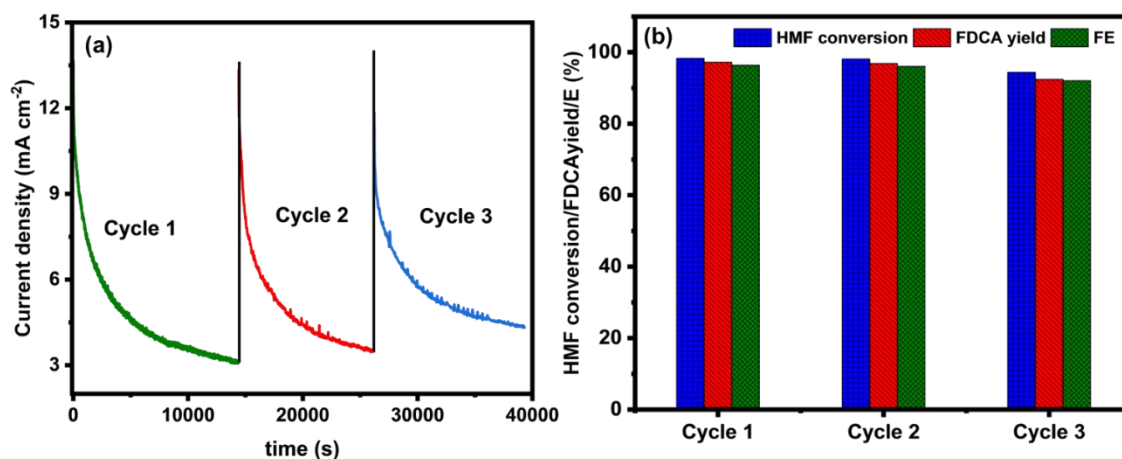


Figure 35. (a) Chronoamperometry curves illustrating the current response over three consecutive cycles in the presence of 10 mM HMF, demonstrating the catalyst's stability and reproducibility. (b) Bar graph representing HMF conversion, FDCA yield, and FE for each cycle, highlighting the performance and efficiency of the CuCo-LDH catalyst across multiple cycles.

To evaluate the cyclic stability of the CuCo-LDH electrode, repeated electrochemical tests were conducted in the presence of 10 mM HMF in 1 M KOH over three successive cycles, with fresh electrolyte introduced after each cycle (**Figure 35a**). The bar graph in **Figure 35b** summarizes the HMF conversion, FDCA yield, and Faradaic efficiency (FE) for each cycle. The CuCo-LDH electrode demonstrated impressive stability, with 94.42% HMF conversion, 92.2% FDCA yield, and 91.89% FE even after three consecutive cycles. This indicates that the catalytic activity of CuCo-LDH remains effectively intact, suggesting minimal loss in activity or selectivity over multiple uses. The stable performance of the electrode in terms of HMF conversion and FDCA yield emphasizes the robustness of the catalyst structure under repeated electrochemical conditions. Furthermore, the Faradaic efficiency remaining above 90% across all cycles indicates that most of the applied charge was consistently utilized for the targeted oxidation reaction, reinforcing the stability and efficiency of CuCo-LDH as a promising electrocatalyst for biomass conversion.

5 CHAPTER FIVE

CONCLUSION

In conclusion, this study successfully synthesized and characterized Cu-based bimetallic electrocatalysts (CuCo and CuNi) for water splitting, demonstrating that CuCo catalysts, particularly those modified with highly reduced graphene oxide (HRG), exhibited superior performance for the splitting of water molecule into hydrogen and oxygen. The CuCoOx600/HRG catalyst showed the best performance on FTO substrates, while CuCo-LDH/HRG excelled on nickel foam. Additionally, the study explored the electrochemical oxidation of 5-hydroxymethylfurfural (HMF) as a strategy to enhance water splitting efficiency. The CuCo-LDH/NF catalyst proved highly effective for HMF oxidation, achieving high Faradaic efficiency and FDCA yield, and demonstrating excellent stability. These findings highlight the potential of Cu-based bimetallic electrocatalysts for efficient and sustainable water splitting and HMF-to-FDCA conversion.

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- Developing a bimetallic CuO/Co₃O₄ catalyst for electro-oxidation of 5-hydroxymethylfurfural into 2,5-furandicarboxylic acid. (*Submission in process*)
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