

**Synthesis, Characterization, and
Electrocatalytic Evaluation of Cobalt
Phosphide Nanocrystals in Water Electrolysis**

BY

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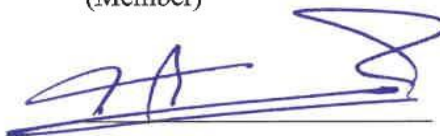
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Dedicated to my Parents & Siblings

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LIST OF ABBREVIATIONS

OER:	Oxygen evolution reaction
HER:	Hydrogen evolution reaction
PEM:	Proton exchange membrane electrolyzers
AEM:	Anion exchange membrane electrolyzers
CoP:	Cobalt phosphides
CoPS:	Cobalt phosphoSulfide
ΔG (kJ mol ⁻¹) :	Gibbs free energy
θ :	The angle at which constructively interfering X-rays leave a crystal
EC:	Electrochemical
RHE :	Reversible hydrogen electrode
DFT :	Density functional theory
FESEM :	Field-emission scanning electron microscope
EDXS :	Energy-dispersive X-ray spectroscopy
XRD :	X-ray diffraction
XPS :	X-ray photoelectron spectrometer

q :	Charge
E_{applied} :	Applied electrode potential
Ag/AgCl :	Silver/ Silver chloride reference electrode
$E^{\circ}Ag/AgCl$:	Standard silver/ silver chloride electrode potential
$E^{\circ}Hg/HgO$:	Standard mercury/ mercury oxide electrode potential
EIS :	Electrochemical impedance spectroscopy
LSV:	Linear sweep voltammetry
CV:	Cyclic voltammetry
CP:	Chronopotentiometry
C_{sc} :	Space charge layer capacitance
C_{dl} :	Double layer capacitance
TOF:	Turn over frequency
ECSA:	Electrochemical surface area
mol :	Moles
FE :	Faradic efficiency
$^{\circ}\text{C}$:	Temperature (degree Celsius)
mV :	milivolt

B.E. :	Binding energy
E_{overall} :	Overall potential
E_{cathode} :	Cathode potential
E_{anode} :	Anode potential
eV :	Electron Volt
At. % :	Atomic percent
VRHE :	Voltage against reversible hydrogen electrode
Im (Z) :	Imaginary component of the impedance
JCPDS :	Joint committee on powder diffraction standards
J:	Current density
ICP:	Inductively coupled Plasma
SEM:	Scanning electron microscopy
FTIR:	Fourier transform infrared spectroscopy
V_{Pt} :	Applied potential against Pt electrode
R_{ct} :	Charge transfer resistance
R_s :	Solution resistance
ΔE :	Binding energy difference

TOP:	Trioctylphosphine
1-OD:	1-Octadecene
IPCC:	Intergovernmental panel on climate change
IEA:	International energy agency
FC:	Fuel cell
η :	Overpotential
NPs:	Nanoparticles
Nc:	Nanocomposite
SHE:	Standard hydrogen electrode

|

ABSTRACT

Full Name : [Wajiha Fatima]

Thesis Title : [Synthesis, Characterization and electrocatalytic evaluation of cobalt phosphides nanocrystals in water electrolysis]

Major Field : [Chemistry]

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The development of effective and durable electrocatalysts for hydrogen production is essential for promoting sustainable energy technologies and diminishing dependence on fossil fuels. Electrochemical water splitting has garnered significant interest, particularly in the development of catalysts for the hydrogen evolution reaction (HER) and the oxygen evolution reaction (OER) for both Proton membrane exchange electrolyzers (PEM) and Anion exchange membrane electrolyzers(AEM). Transition metal phosphides, particularly cobalt phosphides (CoP), have surfaced as attractive options owing to their advantageous electronic structure, elevated conductivity, and catalytic efficacy. Cobalt phosphides (CoP) have emerged as promising candidates due to their favorable electronic structure, high conductivity, and catalytic activity. However, cobalt phosphides still face challenges such as moderate activity and limited active site exposure, which constrain their practical performance. This thesis aims to overcome these constraints by developing cobalt phosphide and cobalt phosphosulfide-based catalysts using a straightforward synthesis technique, with the objective of improving electrocatalytic performance through composition and structure optimization. First, we developed a facile method for synthesizing cobalt phosphide nanoparticles (NPs), namely, Co_2P , CoP, and a CoP/ Co_2P nanocomposite, via the thermal decomposition of cobalt(II) acetate in the presence of oleyl amine (as a reducing agent) and trioctylphosphine (as a phosphorus source). The desired

cobalt phosphide phases were obtained by controlling the P/Co mole ratio and the decomposition temperature. The mechanism of cobalt phosphide formation is best described by the Kirkendall effect. These materials were evaluated as electrocatalysts for HER in 0.5 M H₂SO₄ solution by electrochemical characterization to establish a correlation between phase structure and catalytic activity. The synthesized nanocomposite CoP/Co₂P showed the best activity, achieving 10 mA cm⁻² current density at 152 mV overpotential, and 95% faradic efficiency, making them a viable candidate in PEM electrolyzers. We also tested CoP in alkaline media, but its activity decreased, achieving 10 mA cm⁻² current density at 278 mV overpotential. So, although CoP exhibited good activity in acidic media but their performance in alkaline media was still found to be limited due to insufficient stability and sluggish kinetics under high pH conditions. So, in this thesis, we also addressed these constraints and improved the catalytic activity of CoP in alkaline conditions by synthesizing cobalt phosphosulfide (CoPS) catalysts. Sulfide-based systems provide enhanced stability and inherent conductivity under alkaline circumstances, while the strategic integration of phosphorus into cobalt sulfide further adjusts the electronic environment, enhances charge transfer, and creates new active sites. A similar synthesis route (Thermal decomposition method) was employed to produce CoPS using triphenylphosphine as P precursor, and 1-dodecanethiol was used as sulfur precursor. The synthesized CoPS electrocatalysts have shown improved activity compared to simple CoP in alkaline media, achieving 10 mA cm⁻² current density at 148 mV overpotential. Through this work, a deeper understanding is developed of how material design strategies can be harnessed to develop advanced systems for sustainable energy applications.

ملخص الرسالة

الاسم الكامل: وجيهة فاطمة

عنوان الرسالة: تحضير وتوصيف وتقييم النشاط الكهروحفزي لبلورات نانوية من فوسفيدات الكوبالت في تحليل

الماء كهربائياً

التخصص: الكيمياء

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إن تطوير محفزات كهربائية فعالة ومستدامة لإنتاج الهيدروجين أمراً جوهرياً لدفع تقنيات الطاقة المتجددة وتقليل الاعتماد على الوقود الأحفوري. لقد حظي التحليل الكهربائي للماء باهتمام كبير، خاصةً فيما يتعلق بتصميم محفزات لتفاعل إنتاج الهيدروجين (HER) وتفاعل إنتاج الأكسجين (OER)، لكلاً من أجهزة التحليل الكهربائي ذات غشاء التبادل البروتوني (PEM) وأجهزة التحليل الكهربائي ذات غشاء التبادل الأنيوني (AEM). لقد برزت فوسفيدات المعادن الانتقالية، ولا سيما فوسفيد الكوبالت (CoP)، كخيارات واعدة بسبب بُنيتها الإلكترونية الملائمة، وموصليتها العالية، وكفاءتها التحفيزية. غير أنها لا تزال تواجه تحديات مثل النشاط المعتدل وانكشاف محدود للمواقع النشطة، مما يحدّ من أدائها العملي.

تهدف هذه الرسالة إلى التغلب على هذه القيود من خلال تطوير محفزات قائمة على فوسفيد الكوبالت وفوسفوكبريتيد الكوبالت باستخدام تقنية تحضير بسيطة، بغية تحسين الأداء الكهروحفزي عبر ضبط التركيب والبنية البلورية.

أولاً، تمّ تطوير طريقة سهلة لتحضير جسيمات نانوية من فوسفيد الكوبالت بأنواعه المختلفة (CoP و Co₂P)، بالإضافة إلى مركب نانوي (CoP/Co₂P)، عن طريق التحلل الحراري لأسيتات الكوبالت الثنائي في وجود الأوليل أمين كعامل مختزل وثلاثي أوكثيل الفوسفين كمصدر للفوسفور. أمكن الحصول على الأطوار البلورية المرغوبة بضبط النسبة المولية بين الفوسفور والكوبالت ودرجة حرارة التحلل. وتعزى آلية تكون فوسفيد الكوبالت بشكل رئيس إلى تأثير كيركندال (Kirkendall Effect). تمّ تقييم هذه المواد كمحفزات لتفاعل إنتاج الهيدروجين (HER) في محلول حمضي تركيزه 0.5 مليمول/لتر من H₂SO₄ عن طريق قياسات كهروكيميائية دمجية، وذلك لاستكشاف العلاقة بين البنية البلورية والنشاط التحفيزي. وأظهر المركب النانوي CoP/Co₂P أفضل أداء، إذ سجل كثافة تيار 10 ملي أمبير/سم² عند فرق جهد إضافي مقداره 152 مليمتراً كهربائياً، وبلغت كفاءته الفارادية 95%، مما يجعله مرشحاً عملياً

ومناسباً جداً للاستخدام في أجهزة التحليل الكهربائي من نوع PEM. كما اختبر CoP في وسط قلوي، فأظهر نشاطاً منخفضاً نسبياً، حيث حققت كثافة تيار 10 ملي أمبير/سم² عند فرق جهد إضافي 278 مليمتراً كهربائياً. وعلى الرغم من نشاط CoP الجيد في الوسط الحمضي، إلا أن أدائه في الوسط القلوي ظل محدوداً بسبب الاستقرار غير الكافي وبطء الحركة عند قيم pH العالية.

وانطلاقاً من ذلك، تناولت هذه الرسالة أيضاً هذه القيود وسعت إلى تحسين النشاط الكهروكيميائي لـ CoP في الوسط القلوي من خلال تحضير محفزات فوسفوكبريتيد الكوبالت (CoPS). حيث توفر الأنظمة المبنية على الكبريت استقراراً أفضل وموصلية ذاتية أعلى في الظروف القلوية، كما أن الدمج الاستراتيجي للفوسفور ضمن كبريتيد الكوبالت يضبط البيئة الإلكترونية ويعزز انتقال الشحنة ويخلق مواقع نشطة جديدة. واعتمدنا في ذلك على مسار تحضير مشابه (طريقة التحلل الحراري)، حيث استخدمنا ثلاثي فينيل الفوسفين كمصدر للفوسفور، و 1-دوديكانثيول كمصدر للكبريت، للحصول على فوسفوكبريتيد الكوبالت (CoPS). أظهرت محفزات CoPS المحضرة نشاطاً محسناً مقارنة بـ CoP في الوسط القلوي، إذ تمكنت من تحقيق كثافة تيار 10 ملي أمبير/سم² عند فرق جهد إضافي 148 مليمتراً كهربائياً، مما يدل على جدوى استخدامها في أجهزة التحليل الكهربائي التي تعتمد غشاء التبادل الأنيوني (AEM).

من خلال هذا العمل، تم تحقيق فهم أعمق لكيفية استغلال استراتيجيات تصميم المادة في ابتكار أنظمة متقدمة تلائم المتطلبات الخاصة بتطبيقات الطاقة المستدامة.

CHAPTER 1

INTRODUCTION

1.1 Research Background

Climate change and the energy sector are undeniably interrelated. Industrial improvements and technological progress have improved human comfort, although they have also resulted in increased energy demand. Furthermore, accelerated population expansion persists in propelling this need, leading to a consistent increase in energy consumption over recent decades. The principal concern encompasses not only the quantity of energy utilized but also its origins. Fossil fuels, including petroleum and coal, continue to be the primary energy sources owing to their lower cost relative to alternatives. Nonetheless, their persistent utilization substantially exacerbates global warming, rendering energy transition an imperative urgency[1].

The most recent assessment by the Intergovernmental Panel on Climate Change (IPCC) underscores the fact that worldwide anthropogenic greenhouse gas emissions increased by 70 percent between 1970 and 2004, mostly owing to the consumption of fossil fuels. This has resulted in grave environmental repercussions, such as rising temperatures around the globe, increased melting of ice blankets, and rising sea levels, all of which pose significant challenges to the concept of sustainable development [2]. In the meantime, the demand for energy around the world continues to increase. According to projections made by the International Energy Agency (IEA), the demand for energy would increase by 33 percent between the years 2010 and 2035[3], further highlighting the importance of implementing sustainable energy options. Despite the fact that

renewable sources currently contribute around 89 EJ per year, which is approximately 17% of the overall primary energy supply [4, 5], the majority of this energy still comes from conventional biomass and large-scale hydropower, both of which have their own set of limiting factors. Although the forecasts of the Intergovernmental Panel on Climate Change (IPCC) suggest that the widespread adoption of renewable energy sources might reduce CO₂ emissions by 218 to 561 gigatons between the years 2010 and 2050, this would be a substantial step towards climate mitigation [6]. A significant solution for incorporating renewables into the energy grid is the production of green hydrogen. Hydrogen can be produced via water electrolysis with renewable electricity, offering a clean energy carrier devoid of direct carbon emissions. Currently, more than 90% of hydrogen is generated via methane steam reforming, accounting for roughly 3% of the world's yearly CO₂ emissions [7]. Adopting sustainable hydrogen production techniques such as electrochemical water splitting, photocatalytic and photothermal technologies, and solar thermochemical processes can markedly diminish carbon emissions. Electrochemical water splitting is a promising method that effectively turns electrical energy into hydrogen while maintaining the separation of oxygen and hydrogen to improve safety [8]. The generated hydrogen can be utilized in fuel cells, industrial applications, and ammonia synthesis, substituting fossil fuels across several sectors [9].

With the move to hydrogen energy, there is the potential to drastically reduce reliance on fuels based on carbon. However, in order for a future hydrogen economy to be feasible, the production of clean hydrogen must become more cost-effective, and significant investments will be necessary to support the infrastructure of hydrogen fuel cells [10]

1.2 Challenges of sustainable hydrogen production from water splitting

The unavoidable increase in global energy consumption, propelled by population growth and economic development, has historically been satisfied by fossil fuel sources, especially coal. The changing global energy landscape is intricately connected to environmental issues, requiring a decrease in greenhouse gas emissions. Mitigating the aggregate accumulation of carbon dioxide (CO_2) in the atmosphere necessitates the development and execution of alternative solutions for carbon-neutral production of energy [11]. An innovative and useful way to change energy is to use an electrochemical generator, also known as a fuel cell (FC), to change chemical energy into electrical energy. Molecular hydrogen (H_2) is a popular fuel for fuel cells because it has a very high gravimetric energy density of 122 kJ g^{-3} , which is much higher than the energy densities of organic and inorganic fuels, which are usually between 1 and 9 kWh kg^{-1} [12]. Also, hydrogen combustion only leaves behind clean water, which makes it a very hopeful and long-lasting choice for future energy solutions.

In addition, hydrogen is an indispensable component in industrial uses, particularly in the production of ammonia for use in fertilizers, the refining of petroleum, the production of metals, and other chemical industries. On Earth, hydrogen does not exist in a free state in its natural condition; rather, it is bonded in substances such as water, biomass, and hydrocarbons, which means that it must be extracted before it can be used. At the moment, the bulk of hydrogen production is based on fossil fuels, which results in considerable emissions of greenhouse gases [13]. This highlights the demand for production methods that are both cleaner and more sustainable.

Figure 1.1 depicts the three primary industrial hydrogen (H_2) production techniques: steam methane reforming (SMR), coal gasification, and water electrolysis. An in-depth examination of

these procedures reveals a significant limitation: H₂ production using fossil fuel-based technologies does not mitigate pollution and CO₂ emission issues. Both SMR and coal gasification necessitate high-temperature reactions involving hydrocarbons or coal and water, producing hydrogen, carbon dioxide (CO₂), and additional carbon-based byproducts. These greenhouse gases are then sent into the atmosphere, undermining the primary objective of reducing air pollution and climate change through hydrogen consumption. Thus, these traditional methods not only exhaust fossil fuel sources but also markedly increase global CO₂ emissions [14, 15]. Consequently, the formulation of a cleaner, renewable, and more efficient hydrogen production plan is essential for securing a sustainable energy future.

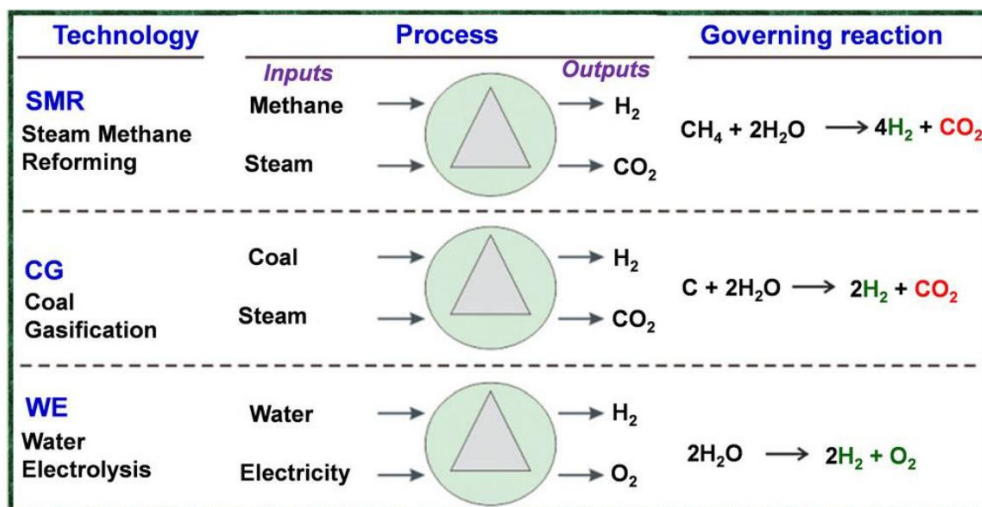


Figure 1.1. Summary of three primary industrial techniques for hydrogen (H₂) production

This issue is increasing public interest in various green energy sources, such as solar, wind, hydro, and other electrolysis methods. Hydrogen may be economically produced by dissociating water through a solar-to-hydrogen conversion system utilizing photochemical and photoelectrochemical techniques [16, 17].

When powered by renewable energy sources like solar and wind, water electrolysis offers a promising pathway for sustainable hydrogen production. A standard electrolyzer consists of three key components: an electrolyte, a cathode, and an anode. When an external voltage is applied, water molecules are split into (H₂) and (O₂). The generated hydrogen can be stored and used as a clean fuel, while the oxygen is either released into the atmosphere or utilized for medical applications. This process involves two main half-reactions: the HER at the cathode and the OER at the anode, as illustrated in Figure 1.2a [18]. The overall water-splitting reaction differs depending on the electrolyte environment, acidic, neutral, or alkaline, each characterized by specific chemical equations. The corresponding electrode potentials are referenced to the SHE. The potential half-reactions are presented in Figure 1.2b based on the reaction conditions [19].

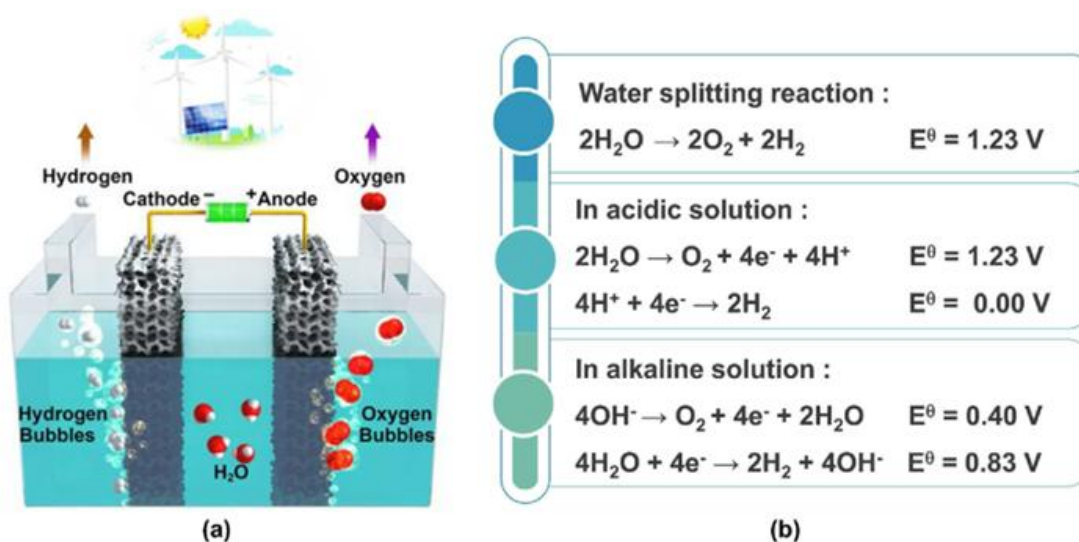


Figure 1.2. A diagram showing (a) water electrolysis and (b) the reactions that occur in basic and acidic solutions. Reprinted from ref. [20]

The water splitting process illustrates that energy input is crucial, irrespective of the medium in which electrolysis occurs. An external voltage is required to facilitate the electrochemical breakdown of water. The lowest energy necessary for this process aligns with the thermodynamic voltage of water oxidation, quantified at 1.23 V under typical conditions (25 °C and 1 bar). This

endothermic reaction exhibits an enthalpy change of 286 kJ per mole and an entropy change of 163 J per mole per Kelvin for hydrogen generation.

This value is dependent on temperature and can be altered accordingly. The thermoneutral voltage, a standard for assessing energy efficiency, is 1.48 V at 25 °C. Nevertheless, the voltage must surpass this theoretical value to facilitate water splitting due to resistive losses in the electrolytic cell. The surplus voltage, referred to as overpotential (η), encompasses many losses, chiefly arising from the inherent activation barriers at the anode (η_a) and cathode (η_c), together with supplementary elements such as electrolyte resistance and contact losses (η_{other}). The practical operating voltage (E_{op}) can thus be expressed as [21]:

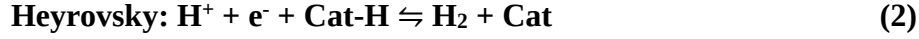
$$E_{\text{op}} = \Delta E^0 + \eta_a + \eta_c + \eta_{\text{other}}$$

To enhance the efficiency of an electrolytic cell, design optimizations can decrease η_{other} , while highly active catalysts are essential to minimize overpotentials at both the anode and cathode [17]. Consequently, developing cost-effective and durable catalysts for the OER and HER is essential for enhancing energy efficiency and economic viability of water electrolysis. This discussion will concentrate on recent improvements in catalysts and electrode designs for the HER and the OER and a fundamental comprehension of these processes, ranging from basic electrolytic solutions to performance evaluation criteria.

1.3 Basics of electrocatalytic HER in aqueous media

The HER is a process that consists of three potential phases, each with two distinct processes, as illustrated in Figure 1.3 [22]:





The initial stage entails the Volmer reaction, which is also referred to as the discharging proton process. H^* is attached to the active site at this stage through adsorption. After producing H^* , two subsequent events occur to generate H_2 molecules. The Heyrovsky reaction occurs when a small quantity of H^* is bonded to the surface. H^* reacts with protons, resulting in the production of hydrogen gas (H_2). When a significant amount of H^* is present on the surface, there is the Tafel reaction, in which two H^* atoms join to produce H_2 .

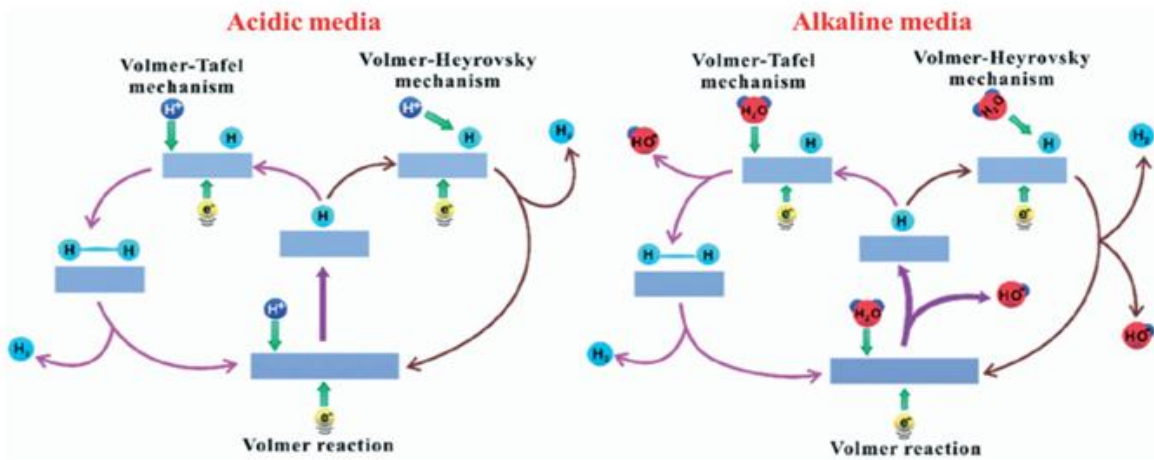


Figure 1.3. Mechanism of HER in acidic and alkaline media. Reprinted from ref. [23]

In general, HER pathways can be explained using either the V-H or V-T mechanisms. HER with a Tafel slope of around 40 mV dec^{-1} operates according to the V-H mechanism, where the electrochemical desorption step limits the reaction rate. Whereas HER with a Tafel slope of around 30 mV dec^{-1} operates according to the V-T mechanism, where the chemical desorption step limits the reaction rate. On the other hand, a Tafel slope of around 120 mV dec^{-1} indicates that the Volmer step, the electrochemical adsorption of hydrogen step, is the rate-controlling step [23, 24]. Since

the Tafel reaction happens more frequently than the Heyrovsky reaction, particularly in acidic environments, the V-T reaction is the perfect HER process [25] [26]. A successful HER catalyst should form a compatible bond with the adsorbed hydrogen species (H^*). Unnecessary adsorption will limit the process of breaking bonds and releasing gaseous H_2 , while insufficient adsorption will impede the proton-electron transfer mechanism necessary for the creation of H_2 . An ideal catalyst should effectively catalyze hydrogen's combination and liberation while preserving phase equilibrium. The optimal value for ΔG_H^* would ideally be zero. ΔG_H^* is a vital factor in evaluating the efficiency of the HER and plays a key role in directing the advancement of electrocatalysts for HER [27].

1.4 Techniques for evaluating, characterizing, and verifying HER electrocatalysts

This part addresses a basic question: "How can I find if the material I just synthesized suits HER?" Several important parameters have to be systematically evaluated and examined if one is to reach this. These consist of:

1. Overpotential, Onset Potential, and Electrode Activity
2. Tafel Plot Analysis
3. Faradaic Performance
4. Turnover Frequency and Turnover Number
5. Durability and Stability

Evaluating the catalytic performance of the material for hydrogen evolution depends critically on each parameter.

1.4.1 Overpotential, onset potential, and electrode activity

Electrochemical HER tests are generally performed using a three-electrode configuration, comprising a working electrode (where the catalytic ink is applied), a reference electrode (which regulates the potential of the working electrode), and a counter or auxiliary electrode (which enables current flow). The predominant method for evaluating HER activity is LSV, although CV can also yield valuable information regarding electrode performance. In LSV experiments, the working electrode's potential varies from a higher value, marginally above 0 V vs. RHE, to a lower value determined by the catalyst and electrolyte employed. Scan rates typically vary from 1 to 50 mV s^{-1} . According to the International Union of Pure and Applied Chemistry (IUPAC) convention, the current during the HER is negative, indicating a reduction process. The measured current is adjusted by the geometric surface area of the electrode to derive the current density (j). Sometimes, the current may also be normalized by the sample mass to ascertain the catalytic activity per unit mass. To compare the activities of the samples, two specific overpotentials in the HER are typically presented intentionally [17]. One is the onset potential, a critical characteristic for assessing electrocatalysts in HER. This word lacks a precise definition and may differ among various studies. To maintain clarity and uniformity in research articles, it is advisable to include an accurate current density value when describing the onset overpotential, often within the range of 0.5 to 2 mA cm^{-2} . Second is overpotential, a vital metric to assess the activity to attain a current density of 10 mA cm^{-2} , which is commonly acknowledged as a standard benchmark for HER activity [28, 29].

Many gas bubbles accumulate on the electrode surface during the hydrogen evolution reaction or water electrolysis. Certain bubbles do not detach promptly, diminishing the electrode's active area and elevating the overpotential (η). Moreover, the existence of entrapped bubbles might generate

noise in polarization curves, which must not be disregarded. An excellent method to mitigate this issue is using a spinning electrode, which enhances the removal of H₂ bubbles. Another significant form of overpotential is resistance overpotential, often referred to as junction overpotential, which occurs due to the material's morphology. The material structure's internal resistance (R) induces an extra voltage drop, resulting in a measured overpotential that exceeds the true value. To achieve precise findings, this overpotential is rectified by iR compensation, which considers resistance and modifies the polarization curves correspondingly. In a standard three-electrode configuration, the principal source of resistance lies between the reference electrode and the surface of the working electrode. Many modern electrochemical workstations can directly quantify this resistance and adjust the polarization data autonomously. Electrochemical impedance spectroscopy (EIS) can also determine R by examining the Nyquist plot.

1.4.2 Analysis of Tafel slope

The Tafel slope is a critical parameter for assessing the reaction kinetics of an electrocatalyst and can be determined through LSV data. The Tafel equation ($\eta = b \log j + a$) indicates that the slope, represented by b, can be derived from the graph of overpotential versus log(current density), where η denotes the overpotential and j signifies the current density. A reduced Tafel slope signifies enhanced reaction kinetics, indicating that the catalyst promotes electron transfer more effectively and demonstrates increased electrocatalytic activity.

Obtaining the Tafel slope from polarization curves presents certain limitations. The calculated value may fluctuate based on the chosen overpotential range and the applied ohmic drop compensation, introducing a degree of subjectivity influenced by the experimenter's decisions [30]. Additionally, isolating the contribution of catalyst resistance in non-conductive catalysts poses challenges that may compromise the accuracy of the results [31].

In 2013, Hu's group introduced an alternative method utilizing electrochemical impedance spectroscopy (EIS) to determine the Tafel slope, addressing existing challenges more reliably. Impedance was measured at various overpotentials, and a plot of $\log(1/R_{ct})$ versus η was generated, resulting in a Tafel slope that accurately represents charge-transfer kinetics while excluding resistive contributions. This method offers a more accurate and foundational comprehension of the electrochemical behavior of the catalyst [31].

1.4.3 Hydrogen bonding energy

An optimal HER electrocatalyst should possess a balanced hydrogen adsorption-free energy that is neither excessively weak nor overly strong [32]. Weak adsorption complicates proton attachment to the catalyst, hence impeding the process. If hydrogen binds excessively (H_{ads}), desorption becomes challenging, resulting in catalyst poisoning due to the occupation of active sites. Given that the standard hydrogen electrode potential is established at zero, an ideal hydrogen evolution reaction electrocatalyst should possess a Gibbs free energy of hydrogen adsorption approximating zero. This value is generally ascertained via density functional theory (DFT) computations. A Sabatier volcano plot is generated by graphing the exchange current density against the Gibbs free hydrogen adsorption energy. Catalysts positioned nearer to the summit of this volcano exhibit enhanced hydrogen evolution reaction (HER) activity [33].

1.4.4 Faradic performance

Faradaic efficiency, referred to as Faradaic yield, coulombic efficiency, or current efficiency, quantifies the effectiveness of charge (electrons) transfer in an electrochemical system to facilitate oxidation or reduction reactions. This measures the fraction of electrons the external circuit provides that participate in the desired Faradaic reaction, while considering losses due to heat or unintended byproducts. Measuring both theoretical and experimental quantities of hydrogen

produced is essential to assess Faradaic efficiency. The theoretical production of H₂ is determined by integrating data obtained from galvanostatic (constant current) or potentiostatic (constant potential) electrolysis methods. The experimental measurement of H₂ production is conducted using gas chromatography or the water-gas displacement method. Faradaic efficiency is determined by calculating the experimental to theoretical hydrogen production ratio. An approach of 100% efficiency is preferred, signifying minimal energy loss and optimal catalytic performance.

1.4.5 Turnover frequency and turnover number

Turnover frequency (TOF, s⁻¹) and turnover number (TON, unitless) are fundamental concepts in catalysis research, frequently employed to assess catalyst efficiency. Nonetheless, their definitions are somewhat ambiguous, resulting in ongoing debate and inconsistencies within the literature [34, 35]. TOF is defined as the quantity of reactant molecules transformed into the desired product per active catalytic site per unit time, providing insight into the intrinsic activity of each site. TON denotes the cumulative number of catalytic cycles a site experiences over a specified duration, calculated using the formula.

$$\text{TON} = \text{TOF} \times \text{reaction time}$$

TOF quantifies the number of protons reduced to hydrogen per second per active surface atom for HER catalysis [36, 37]. It is expressed electrochemically as:

$$\text{TOF} = \frac{j \times N_A}{n \times F \times N_s}$$

TOF (turnover frequency) refers to the number of molecules converted per active site per second (molecules per active site s⁻¹). Here, **j** is the current density (mA cm⁻²), **n** is the number of electrons involved in the reaction - typically 2 electrons for reducing H⁺ in acidic media or H₂O in alkaline

media to produce H_2 . N_A stands for Avogadro's constant ($6.02 \times 10^{23} \text{ mol}^{-1}$), F is the Faraday constant (96485 C mol^{-1}), and N_s represents the surface density of active sites (sites cm^{-2}).

Both TOF and TON exhibit dependence on potential, indicating that they vary with the applied voltage. TOF is typically assessed at $j = -10 \text{ mA cm}^{-2}$, corresponding to the overpotential observed at this current density. Accurately determining the turnover frequency (TOF) for solid-state catalysts presents significant challenges, despite its importance. The presence of readily accessible surface atoms and inaccessible internal catalytic species in HER catalysts complicates the accurate quantification of active sites. Certain calculations focus solely on surface atoms, resulting in potential overestimations, whereas others account for all catalytic species, which may lead to underestimations of actual activity. The activity and accessibility of atoms in a nanomaterial are not uniform, leading to significant variations in reported TOF values based on the methodology employed [17]. As a result, the absence of a universal standard for TOF determination complicates direct comparisons across studies.

1.4.6 Durability and stability

Besides catalytic activity, stability is essential in assessing a material's suitability for practical hydrogen production through water electrolysis. A catalyst must sustain its efficacy over prolonged durations without considerable deterioration; otherwise, its practical utility is constrained. To assess electrochemical stability, various essential methodologies are utilized:

Chronoamperometry (CA): It measures current over time at a fixed voltage to evaluate the catalyst's activity retention throughout prolonged operation.

Chronopotentiometry (CP): It monitors potential variations at a constant current, offering insights regarding catalyst longevity and possible deterioration.

Cyclic voltammetry (CV): It entails repetitive potential cycling to detect alterations in electrochemical behavior, potentially signifying material instability or surface modifications.

These stability assessments are crucial for evaluating a catalyst's long-term dependability and efficacy, confirming its viability for extensive hydrogen production.

|

CHAPTER 2

LITERATURE REVIEW

2.1 A thorough review of the elements involved in the development of HER electrocatalysts

The HER is a crucial step in water splitting, and the choice of elements in electrocatalyst design greatly affects its efficiency. The components utilized in HER catalysts can be categorized based on their physical and chemical characteristics into noble metals, transition metals, and nonmetals, as shown in Figure 2.1.

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
H	Periodic Table of Elements																He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn

	Pt-containing noble metal HER catalysts
	Metals that are used for constructing noble metal-free HER catalysts
	Nonmetals that are used for constructing noble metal-free HER catalysts

Figure 2.1. Elements used for the development of HER electrocatalysts. Reprinted from ref. [17]

Platinum (Pt) is the standard catalyst among noble metals, characterized by its small overpotential, elevated exchange current density, and exceptional durability. The d-band electrical structure facilitates excellent hydrogen adsorption and desorption, making it very efficient. Platinum is exceedingly rare in the Earth's crust, with an abundance of around 3.7×10^{-6} wt%, making it one of the most costly elements [38, 39]. The elevated expense has prompted significant investigation into alternatives devoid of noble metals, including alloying techniques with transition metals like nickel (Ni) and cobalt (Co), as well as the creation of nanostructured materials to optimize catalytic surface area. Transition metals have surfaced as viable candidates for hydrogen evolution reaction electrocatalysis to address the cost limitation of platinum-based catalysts. First-row transition metals such as Fe, Co, Ni, and Cu are widely studied owing to their natural abundance and low cost, as illustrated in Figure 2.2 [27, 40].

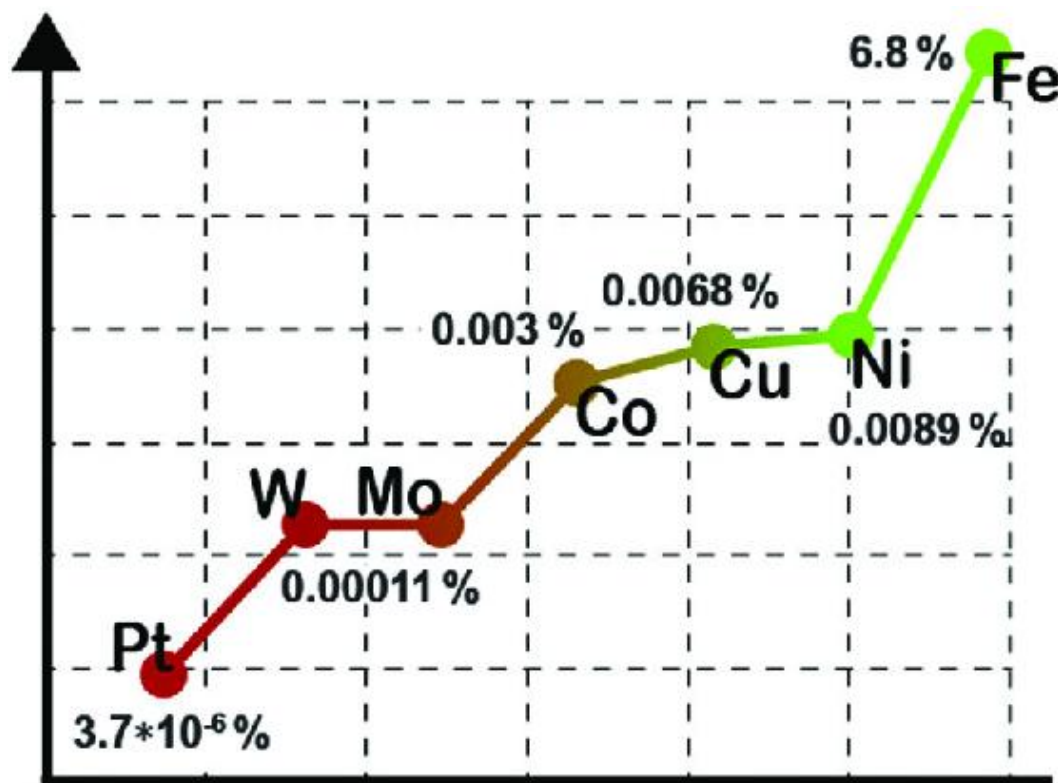


Figure 2.2. The abundance Chart of first-row transition metals. Reprinted from ref. [17]

Iron, one of the most prevalent and cost-effective elements, is an essential constituent in HER catalysts, including iron phosphides, sulfides, and carbides. Cobalt-based catalysts, such as cobalt phosphides and selenides, demonstrate significant stability and moderate to high HER activity, especially in alkaline conditions. Nickel, widely utilized in commercial alkaline electrolyzers, produces extremely active hydrogen evolution reaction catalysts like Ni_2P , Ni_3S_2 , NiSe_2 , and NiMo alloys. Copper, although less reactive than iron, cobalt, and nickel, has been utilized in electrocatalysts such as Cu_2S and CuP_2 , and is frequently alloyed with other transition metals to improve catalytic efficacy. Molybdenum (Mo) and tungsten (W) are essential in HER electrocatalysis beyond the first-row transition metals. Molybdenum-based catalysts, such as MoS and MoP , are among the most extensively researched nonprecious metal materials for HER. Tungsten-based catalysts, including WS_2 , WP , and tungsten carbides (WC), exhibit hydrogen evolution reaction (HER) activity similar to molybdenum-based materials, however, with marginally reduced catalytic efficiency [17]. Carbon-based materials, including graphene, carbon nanotubes (CNTs), and carbon nitrides ($\text{g-C}_3\text{N}_4$), are commonly employed as conductive substrates to improve HER performance. Doping carbon materials with heteroatoms like N, P, S, and Se can impart catalytic activity, providing a metal-free hydrogen evolution reaction (HER) electrocatalysis method. Doped carbon materials may proficiently regulate charge distribution and enhance hydrogen adsorption energies, offering a viable approach for developing efficient and economical HER electrocatalysts. The increasing demand for sustainable hydrogen production necessitates the development of non-precious metals catalysts for HER utilizing transition metals and nonmetals to ensure economic feasibility and large-scale application.

2.2 Cobalt-supported heterogeneous catalysts for water splitting

Cobalt (Co) has emerged as a prominent non-noble metal due to its catalytic efficacy in water splitting. Cobalt (Co)-based electrocatalysts are viable alternatives to noble metal catalysts owing to their cost-effectiveness, low toxicity, exceptional durability, and outstanding catalytic efficacy [41-43]. Cobalt demonstrates moderate Gibbs free energy for hydrogen adsorption (ΔG_{H^*}), rendering Co-based materials such as cobalt oxides, phosphides, selenides, sulfides, and cobalt-layered double hydroxides (Co-LDHs) particularly appropriate for the HER. These materials provide specific benefits for HER. Cobalt oxides contain numerous defect sites that promote the dissociation of water molecules, thereby improving catalytic efficiency. In contrast, cobalt phosphides, selenides, sulfides, and Co-LDHs exhibit varied compositions, crystalline structures, and adjustable morphologies, facilitating the creation of highly effective electrocatalysts for water-splitting applications [27]. Here, we will demonstrate a potential approach for developing cobalt-based electrocatalysts in water electrolysis.

2.2.1 Cobalt phosphides as heterogeneous electrocatalysts for HER

TMPs, especially cobalt phosphide nanocatalysts, have attracted considerable interest in electrocatalysis owing to their numerous advantages, such as natural abundance, high electrical conductivity, exceptional catalytic activity, and outstanding stability [44-47]. Cobalt phosphides possess a trigonal prismatic structure, distinguished by a blend of metallic and covalent bonding, alongside semiconducting characteristics that enhance their intrinsic activity and longevity. The remarkable properties of cobalt phosphide nanoparticles render them highly interesting candidates for water-splitting applications [48-50].

a) Role of phosphorus in HER electrocatalysis

Phosphorus is not just a spectator in transition metal phosphides; it plays a significant role as given below.

Essential role of P: Density functional theory (DFT) studies have shown that phosphorus (P) atoms significantly enhance the HER activity of TMPs [32, 51-56]. Owing to their elevated electronegativity, phosphorus atoms extract electrons from metal atoms, resulting in negatively charged phosphorus sites that function as bases to sequester positively charged protons during the electrochemical HER. As a result, increasing the atomic percentage of P in metal phosphides can effectively improve their catalytic performance. For example, monodispersed nickel phosphide nanocrystals with various phases were produced by changing the precursor ratio. Of Ni_2P , Ni_5P_4 , and Ni_{12}P_5 , Ni_5P_4 , possessing the highest phosphorus concentration (44 at% P), demonstrated superior hydrogen evolution reaction (HER) activity [57]. A comparable trend was noted in morphologically analogous Co_2P and CoP hollow nanoparticles, produced by modulating the reaction temperature. The results showed that CoP nanoparticles required a significantly lower overpotential than Co_2P to achieve the same current density [58]. This conclusion was corroborated by comparisons between MoP and Mo_3P , even in their bulk forms [32]. These studies indicate that TMPs with elevated phosphorus content consistently demonstrate enhanced HER performance.

Conductivity: As phosphorus (P) is gradually introduced into metals, the resultant metal phosphides shift from electrical conductivity to semiconductivity or insulation. The elevated electronegativity of phosphorus atoms markedly constrains electron delocalization in the metal, resulting in diminished conductivity [59]. Transition metal phosphides (TMPs) can maintain metallic characteristics or even demonstrate superconductivity, especially in metal-rich phosphides, when there is an appropriate electronegativity and atomic ratio balance between the metal and phosphorus. Research conducted by Mar and associates revealed that di-metal and tri-metal phosphides have electronic structures akin to their respective pure metals, affirming their

superior conductivity [60]. The remarkable electrical conductivity of some TMPs significantly enhances electrocatalytic processes by promoting efficient charge transfer.

Gibbs free energy of H adsorption: As previously said, an efficient hydrogen evolution reaction (HER) electrocatalyst must have a moderate hydrogen adsorption free energy. In 2005, density functional theory (DFT) simulations by Liu et al. indicated that surface phosphorus (P) atoms in metal phosphides had a tiny negative charge, attracting protons and promoting H₂ dissociation. This mitigates deactivation resulting from high hydrogen coverage, a prevalent problem associated with pure nickel [51]. Wang's group has conducted a comprehensive investigation of the Gibbs free energy of hydrogen adsorption (ΔG_{H}^0) on P-terminated (001)-MoP surfaces. At low hydrogen coverage, ΔG_{H}^0 was marginally negative. As the coverage escalated from 1/4 monolayer (ML, with one hydrogen adsorbed per 2×2 slab) to complete coverage, ΔG_{H}^0 progressively turned positive. This suggests that phosphorus atoms on the P-terminated (001) MoP surface can efficiently adsorb hydrogen at low coverage and promote its desorption at elevated coverage, functioning as a "hydrogen transporter." This behavior closely mirrors the S-edge sites in MoS₂, recognized for producing a high density of active edge sites for HER [61]. These attributes further support metal phosphides as promising electrocatalysts for HER.

Corrosion resistance: The corrosion resistance of transition metal phosphides (TMPs) in acidic conditions is closely associated with their phosphorus (P) concentration. Kucernak et al. suggested that alloying metals with phosphorus diminishes the thermodynamic propensity for metal breakdown. The creation of a protective phosphate layer on the surface by oxidation further augments the stability of TMPs by inhibiting dissolution [62]. The experimental findings corroborate this notion, Ni₃P₄, which had the greatest phosphorus content among the evaluated nickel phosphides, demonstrated the least rise in overpotential necessary to achieve the same

current density, indicating enhanced hydrogen evolution reaction (HER) stability. A comparable trend is evident in cobalt phosphides, where CoP, with a larger phosphorus content, has superior hydrogen evolution reaction activity and enhanced stability. The results validate that elevated phosphorus content improves the corrosion resistance of phosphides during electrolysis in acidic environments. Various phases of the same metal phosphide occur naturally with differing phosphorus content, including CoP and Co₂P, WP and WP₂, FeP and Fe₂P, Ni₂P, Ni₅P₄, and Ni₁₂P₅. As previously mentioned, increased phosphorus concentration offers additional active sites for proton adsorption, enhancing corrosion resistance and improving hydrogen evolution reaction efficacy. Excessive phosphorus doping can impede electron delocalization, diminish conductivity, and impair hydrogen evolution reaction activity. Consequently, an ideal equilibrium is necessary. In this equilibrium, augmenting the phosphorus content, without significantly undermining conductivity, generally enhances hydrogen evolution reaction activity and stability.

b) Synthetic methods of cobalt phosphides

Cobalt phosphides have attracted significant attention as effective electrocatalysts for water splitting due to their inherent catalytic activity and distinctive structural and compositional characteristics. Various synthesis approaches have been developed to enhance performance, and these diverse synthesis methods facilitate the advancement of sophisticated cobalt phosphide electrocatalysts, augmenting their utility in water splitting technologies.

Solid-phase reaction: The solid-phase process is a widely utilized method for developing cobalt phosphides. This procedure combines a cobalt-containing precursor with a phosphorus source, followed by heat processing in an inert atmosphere or vacuum. Cobalt metal and red phosphorus were initially combined in stoichiometric ratios, sealed in an evacuated silica tube, and subjected to elevated temperatures (about 900 °C) for prolonged periods, typically lasting up to eight days,

to facilitate the synthesis of cobalt phosphide. To improve efficiency, researchers have investigated other cobalt precursors, including cobalt oxides, hydroxides, and other cobalt-based compounds, enabling considerably lower reaction temperatures, generally around 300°C, and a substantial decrease in reaction duration to approximately two hours [49, 63, 64]. For example, Wang et al. [65] They successfully developed nitrogen-doped carbon-supported Au/CoP heterostructure nanoparticles using a straightforward solid-state synthesis method. Initially, gold nanoparticles were embedded into a ZIF-67 metal-organic framework to form the Au@ZIF-67 precursor. The final material, Au/CoP@NC-3, was then obtained by carbonization followed by low-temperature phosphidation of the precursor using NaH_2PO_2 as the phosphorus source.[65] . Consequently, the synthesized Au/CoP@NC-3 exhibited excellent electrocatalytic activity for the HER.

Wet Chemistry Method : Wet chemistry is a versatile approach for synthesizing cobalt phosphide nanoparticles (NPs) using organic solvents such as oleic acid, oleylamine (OAm), and 1-octadecene (ODE) as the reaction medium[66-68]. This method allows precise control over the size and structure of cobalt phosphides by adjusting key factors such as reaction temperature, pH, Co/P molar ratio, surfactants, and stabilizers. Lin et al. [68] developed a simple organic ligand-assisted synthesis to produce CoP/NiCoP with a nanotadpole (NT)-like morphology. They used $\text{Ni}(\text{acac})_2$ as the metal precursor and trioctylphosphine (TOP) as the phosphorus source, along with oleyl amine (OAm) and octadecene (ODE). The formation of heterointerfaces in this structure improves proton chemisorption and H_2O dissociation by stabilizing a specific phosphide polymorph at the interface. This optimization accelerates HER kinetics, producing exceptional catalytic performance across a wide pH range.

Metal organic precursor decomposition: The breakdown of metal-organic precursors is a prevalent technique for generating cobalt phosphides. This procedure is performed at moderate temperatures and addresses issues related to traditional phosphidation techniques, including eliminating leftover phosphine gas. In this procedure, metal-organic compounds and organic phosphorus sources are combined to create an organometallic complex, which is subsequently thermally destroyed at a regulated temperature to produce cobalt phosphides. Trioctylphosphine (TOP) and tributylphosphine are frequently utilized as phosphorus sources. Li et al.[69] synthesized highly monodispersed CoP and Co₂P nanocrystals were successfully synthesized by reacting (Co(acac)₃) with TOP at temperatures of 320°C and 280°C, respectively. In this process, Co(acac)₃ acted as the cobalt precursor, while TOP was the phosphorus source and solvent. The resulting CoP nanocrystals displayed prominently exposed (211) facets and a phosphorus-enriched surface, significantly enhancing their electrocatalytic performance for the HER.

Electrodeposition: In addition to the methods previously mentioned, other techniques for fabricating cobalt phosphides include direct electrodeposition and deposition followed by phosphidation. Co-P films have been produced directly onto copper foil through potentiodynamic electrodeposition.[70] . Similarly, Pu et al.[71] fabricated CoP nanosheet arrays supported on Ti plates by first electrodepositing α -Co(OH)₂ nanosheet arrays onto a Ti plate. The samples were then phosphidated using NaH₂PO₂ in a porcelain boat, heated at 300°C for 60 minutes in an argon atmosphere.

The electrocatalytic performance of cobalt phosphides is affected by their composition and several parameters, including shape, electrical structure, and crystalline phase. Extensive research efforts have been dedicated to creating advanced ways to reconcile their catalytic properties with standard criteria. These Include

- Improving Conductivity
- Expanding the specific surface area
- Elevating intrinsic activity,
- Interface Engineering
- Exploiting synergistic effects.

Improving Conductivity: Enhancing electrical conductivity is crucial for electrochemical reactions, as it directly affects the efficiency of proton and electron transfer[72, 73]. Enhancing the inherent conductivity of cobalt phosphide is a direct and efficient approach to augment its electrocatalytic efficacy[73]. Transition metal phosphides (TMPs) exhibit notable electrical conductivity, contingent upon their crystalline structure and stoichiometric composition. Research indicates that metal-rich phosphides exhibit enhanced metallic characteristics and reduced ionic properties, resulting in higher electrocatalytic performance than phosphorus-rich phosphides. Jin et al. noted this phenomenon in cobalt phosphides, where Co_2P , possessing a greater metal concentration, demonstrated enhanced electrical conductivity and electrocatalytic activity relative to CoP [74]. In addition to adjusting the metal-to-phosphorus ratio, another useful method for improving the electrical conductivity of cobalt phosphides is incorporating conductive substrates. Carbon-derived materials, including carbon nanotubes, carbon black, and graphene, are extensively utilized for this application[75, 76]. Chen et al.[77] successfully produced a CoP nanoparticle/defective graphene composite, wherein the defects in graphene markedly enhanced the electrical conductivity of CoP and altered its local electronic structure. This alteration resulted in a significant improvement in electrocatalytic efficacy for the hydrogen evolution reaction (HER).

Expanding the specific area: Besides electrical conductivity, electrocatalytic efficacy is strongly associated with the catalyst's specific surface area. Catalysts possessing greater surface areas typically demonstrate improved electrocatalytic activity, as they offer more active sites for reactions[78]. Consequently, substantial studies have focused on enhancing the surface area of cobalt phosphides through morphological optimization. An increased specific surface area enhances the contact between the catalyst and the electrolyte, while also promoting efficient charge and mass transport, hence improving electrocatalytic performance[79]. Motivated by this approach, Pan et al[80]. created an innovative hybrid nanostructure comprising CoP nanoparticles integrated into a nitrogen-doped carbon nanotube hollow polyhedron (NCNHP). The hollow polyhedral configuration markedly enhanced the catalyst's surface area and had well-defined internal channels that facilitated charge and mass movement during electrocatalysis. The work further illustrated that effective electron transfer from NCNHP to CoP might alter the electronic states of cobalt's d-orbital adjacent to the Fermi level. Electronic modification enhanced hydrogen bonding contact, resulting in greater electrocatalytic activity and increased durability.

Elevating intrinsic activity: The electrocatalytic performance of a catalyst is predominantly determined by the quantity of surface-active sites and the inherent activity of each site. Enhancing the catalyst's shape to maximize surface area is one of the most effective methods for increasing the number of active sites. Moreover, the inherent activity of these locations can be augmented by selectively exposing highly active crystal facets[81]. Prior research has demonstrated that the catalytic efficacy of noble metal-based nanomaterials can be markedly enhanced by augmenting the exposure of high-index facets. By applying this technique to cobalt phosphides, strategically exposing their highly active phase facets can significantly improve their electrocatalytic activity.[82, 83]. Cao et al[84]. Effectively constructed three-dimensional (3D) flower-like micro

balls made of nanowires featuring exposed (002) facets. These aspects substantially enhanced the intrinsic activity of active sites, resulting in superior electrocatalytic performance. Furthermore, the organized nanowire architecture promoted effective vectorial electron transport, thereby augmenting the catalytic performance for the HER and OER.

Interface Engineering : Fabricating cobalt phosphides with distinctive heterostructures offers a viable approach to augmenting their electrocatalytic efficacy by facilitating the amalgamation of the benefits of individual constituents[86]. The robust synergistic and electrical interactions among several phases enhance catalytic efficiency. Motivated by this hypothesis, much research has focused on creating heterostructures with precisely defined interfaces to optimize these effects. Lin et al.[68] utilized the disparities in surface energy between the (111) facets of CoP and NiCoP to construct an innovative CoP/NiCoP heterojunction featuring a nanotube-like shape. The intentional design of the interface in these CoP/NiCoP nanotubes resulted in electronic disorder and modified coordination conditions at the interface, which markedly improved their hydrogen evolution reaction (HER) performance[87]. Moreover, prior research has shown that heterostructures with superior interfaces may efficiently generate interfacial charge redistribution, essential for enhancing electrocatalytic activity. Expanding on this idea, Lin et al[88] created faulty carbon/CoP nanoparticles (NPs), wherein the charge redistribution at the interface between defective carbon and CoP markedly improved oxygen evolution reaction (OER) performance. The flawed carbon/CoP NP hybrid necessitated a minimal overpotential of 320 mV to attain a current density of 10 mA cm⁻² in a 1 M KOH solution.

Exploiting Synergistic Effect: The synthesis of multicomponent cobalt phosphides is an efficient approach to improve their electrocatalytic efficacy in water splitting. This method provides two primary benefits: firstly, the charge transfer among various components generates electronic effects that augment intrinsic catalytic activity, and secondly, the robust synergistic interactions between the components substantially enhance both electrocatalytic efficiency and durability. This approach has devoted significant efforts to the systematic design and synthesis of multicomponent cobalt phosphides. Li et al. described a dodecahedral CoP/CN@MoS₂ composite generated from ZIF-67, wherein CoP nanoparticles were encapsulated within nitrogen-doped carbon matrices. This distinctive architecture demonstrated outstanding hydrogen evolution reaction (HER) activity in both acidic and alkaline environments and impressive oxygen evolution reaction (OER) performance. Mechanistic investigations showed that the highly conductive CoP, in conjunction with porous carbon nitride (CN), improved overall conductivity and expedited electron transport during electrochemical reactions. Furthermore, the porous dodecahedral architecture enhanced the accessibility of numerous active sites, while the carbon matrix proficiently inhibited the aggregation of CoP nanoparticles and MoS₂ nanosheets. The robust synergistic interaction between CoP and MoS₂, a key factor in achieving exceptional electrocatalytic performance for HER and OER, is a significant finding of this research.

2.2.2 Cobalt sulfides as heterogeneous electrocatalysts for HER

Transition metal sulfides (TMS) have arisen as a promising category of catalysts for water splitting owing to their unique physical and chemical characteristics. In contrast to metal oxides, TMS-based materials typically have enhanced electrical conductivity due to their narrow bandgap, enabling them to operate as semiconductors. Two-dimensional (2D) layered TMS structures provide a substantial surface area, remarkable stability, and several accessible active sites for

hydrogen adsorption. These attributes enhance their remarkable electrocatalytic efficacy in the HER[89, 90]. Furthermore, the synthesis of TMS materials is very gentle compared to other transition metal-based catalysts. In contrast to metal carbides and nitrides, which often necessitate multi-step, high-temperature processes, or metal phosphides, whose synthesis generates poisonous gases, TMS materials can be synthesized under more regulated conditions. Numerous TMS compounds, including MoS_2 , Co_3S_4 , and FeS_2 , have been thoroughly investigated and exhibit considerable promise as catalysts for HER and OER. The catalytic activity of some TMS materials has been improved through intrinsic and extrinsic alterations, such as surface engineering, phase and structural control, and compositional tuning, nearing the performance of platinum-group catalysts[91].

Considering the success of transition metal sulfides (TMS) in electrocatalysis, researchers are currently investigating cobalt sulfides as a viable alternative. Cobalt sulfides, characterized by their distinctive electronic structure, adjustable composition, and robust metal-sulfur interactions, have exceptional catalytic efficacy for the hydrogen evolution reaction (HER) and oxygen evolution reaction (OER). Enhancing their shape, doping techniques, and heterostructure design can further improve their performance, positioning them as a strong contender for next-generation water-splitting catalysts.

a) Synthesis Methods of Cobalt Sulfides

Hydrothermal method: Hydrothermal synthesis is extensively utilized to fabricate transition metal sulfides (TMS) owing to its advantages, such as simplicity, adaptability, and meticulous control over composition and shape. This technique has been effectively employed to manufacture a wide array of TMS materials.[92]. Typical sulfur sources for TMS synthesis comprise thioacetamide, carbon disulfide, sodium sulfide, L-cysteine, and thiourea. Through the meticulous

selection of metal precursors and sulfur sources, alongside the precise adjustment of reaction parameters including time, pH, temperature, and reactant concentration, diverse TMS-based nanostructures can be synthesized. A biomolecule-assisted hydrothermal method has been employed to manufacture several nanostructured cobalt sulfide (CoS) forms, including nanospheres and nanowires. Notably, only modifying the polarity of the aqueous solvent with an ethanol co-solvent can result in varied morphologies. Proposed formation mechanisms suggest that these morphological variations significantly influence the capacitive behavior of the resulting materials. [93].

Template-directed growth of TMS: Templating techniques, such as hard and sacrificial templates, are dependable for synthesizing transition metal sulfides (TMS) with precisely defined nanoarchitectures[94]. In the hard templating process, TMS materials are synthesized on the surfaces of diverse substrates, including carbon nanotubes (CNTs), graphene, nickel foam (NF), and carbon fiber paper[95]. The distinctive interfacial interactions and synergistic effects between the TMS and the template frequently provide hybrid materials with markedly improved electrocatalytic performance relative to their pure equivalents. Han et al. synthesized a $\text{Co}_{0.1x}\text{Ni}_x\text{S}_2$ graphene composite by affixing Co–Ni–S nanoparticles (CNS) onto an N-doped reduced graphene aerogel (NGA) template, resulting in the CNS–NGA hybrid. Electrochemical study indicated that this hybrid necessitated a much reduced overpotential of 330 mV to attain a current density of 10 mA cm^{-2} , surpassing its components CNS (440 mV) and NGA (>570 mV)[96].

Gas Sulfidation Method: The gas sulfidation method typically involves preparing metal precursors, which are then subjected to a sulfidation process in a hydrogen sulfide (H_2S) or sulfur atmosphere at high temperatures to anneal the samples. This approach is a simple and efficient technique for producing transition metal sulfides (TMS), particularly for creating unique structures

that are challenging to achieve with other methods. One of the difficulties in synthesizing TMS with interconnected, continuous-pore structures is the substantial volume contraction and weak interactions between the metal and sulfur. Yonemoto et al. introduced a comprehensive oxide-to-sulfide approach for synthesizing ordered mesoporous metal sulfides to address this challenge.[99]. This approach begins with forming a metal oxide within a mesoporous silica template, which is then transformed into a metal sulfide through sulfidation in a hydrogen sulfide (H_2S) or sulfur vapor environment. This gas sulfidation method has successfully synthesized a range of ordered mesoporous metal sulfides, including cobalt sulfide, iron sulfide, and nickel sulfide.

b) Modification of cobalt sulfides

In recent years, significant attempts have been undertaken to investigate the catalytically active sites, reaction constraints, and exact chemical and structural controls of transition metal sulfides, presenting prospects to improve their catalytic efficacy.[100]. The methodologies encompass phase control, defect engineering, size optimization, chemical doping, and the creation of heterostructures. Enhancing the edge activity of transition metal sulfide nanoparticles can directly improve their catalytic capabilities; nevertheless, their total performance is constrained by inadequate electron modulation within the multilayer frameworks.

Recently, amorphous transition metal sulfides have exhibited superior catalytic activity, which is attributed to improved charge transport rates and a heightened density of active sites, akin to the newly produced 2D transition metal sulfides. Nonetheless, their inadequate durability and amorphous structure continue to pose issues that require solutions.[101] Furthermore, two preparation techniques for transition metal sulfides, including edge alignment and three-

dimensional structures, have been shown to improve their catalytic efficacy. These approaches have been enhanced by augmenting layer spacing and incorporating strain into the lattice; yet, the performance continues to be poor. The primary technical obstacles constraining these methodologies encompass the inactive planes within the three-dimensional channels and the charge transfer complications between the edge-aligned layers. Conversely, 2D materials exhibit enhanced activity attributable to superior charge transport efficiency, an increased exposed surface area, and more complex surface chemistry. Nonetheless, they continue to encounter limitations, including reduced central active sites and low usage efficiency, which require a solution.[102].

Regulating electronic structure: Modifying the electrical structure of a catalyst is a straightforward and effective approach to improving its catalytic performance. Nevertheless, attaining exact control over the electronic structure continues to pose difficulties. Prevalent methods for electronic modulation encompass chemical doping and the formation of heterogeneous structures.[103]. Luo's group[104] Developed a 3D, dandelion flower-like N-doped CoS₂ self-supporting electrode for the hydrogen evolution reaction (HER), exhibiting enhanced catalytic performance relative to most TMS-based electrocatalysts. The electrode attained a remarkable overpotential of merely 28 mV to yield a current density of 10 mA cm⁻². DFT studies indicated that N-doping enhances the adsorption-free energies of hydrogen (ΔG_{H^*}) and water molecules by modifying the d-band center of CoS₂, facilitating the HER process in alkaline electrolytes. Concurrently, Zhang et al.[105] Produced phosphorus-doped CoS₂ using a simple hydrothermal technique. This material demonstrated exceptional electrocatalytic activity, featuring an ultra-low overpotential of just 53 mV at 10 mA cm⁻². P-doping did not modify the metallic characteristics of CoS₂ but augmented the quantity of reactive sites. The formation of a

P–H bond weakens the ΔG_{H^*} of the nearby Co atom, hence improving HER performance. The contact between the catalyst and the electrolyte significantly impacts catalyst performance.

Heteroatom doping: Heteroatom doping is an effective technique for altering the composition of transition metal sulfides (TMS) to create efficient electrocatalysts for water splitting. Incorporating heteroatoms can enhance the adsorption energies of reactive species by modifying the electronic structure, augmenting the density of active sites, and generating lattice faults and distortions. These adjustments jointly augment catalytic performance, facilitating enhanced bifunctionality for water splitting reactions [106].

Engineering advanced heterostructures: Heterostructure engineering frequently utilizes synergistic interactions among several components to develop effective catalysts for the hydrogen evolution process (HER). The robust interactions at the heterointerface can modify charge distribution and electron transport rates, influencing intermediate species' adsorption strength. Li et al. [107] Effectively engineered FeS₂ and CoS₂ heterointerfaces rich in defects, illustrating that the two-dimensional structure reveals an increased number of edge-active sites, while the defective sites at the interface enhance the adsorption of reactive species. The FeS₂/CoS₂ nanosheets demonstrated a hydrogen evolution reaction overpotential of 78.2 mV at 10 mA cm⁻² and shown remarkable stability, cycling over 80 hours in a 1 M KOH solution. Moreover, the OER overpotential was 302 mV at 100 mA cm⁻², exhibiting merely a 1% voltage decline after 70 hours of cycling. The catalyst exhibited stability across prolonged water electrolysis, with only the cobalt and sulfur constituents near the interface undergoing oxidation during OER cycling, while the HER reaction remained unaltered. In a separate instance, Song et al.[108] Engineered a 3D nanomaterial by in-situ synthesizing MoS₂/CoS₂ heterostructure nanosheets on one-dimensional nanorods, establishing a heterointerface. The robust interaction between MoS₂ and CoS₂ prompted

a phase transition in MoS₂ (from 2H to 1T phase), resulting in increased active centers and improved conductivity. The 1T-MoS₂/CoS₂ heterostructure catalyst exhibited exceptionally low overpotentials of 71 mV and 26 mV in basic and acidic environments at 10 mA cm⁻², respectively. DFT simulations further validated that the Gibbs free energy (ΔG_H) at the heterojunction surface is approximately zero.

2.3 Challenges & Objectives of Work

Traditional combustion engines fueled by carbon sources provide a considerable environmental hazard due to their emissions, prompting the shift towards low- or zero-carbon-emission technologies such as fuel cells. Nonetheless, hydrogen (H₂) generated during coal reforming contains CO, which can contaminate fuel cell cathodes by forming carbonyl compounds with platinum atoms, diminishing active sites and obstructing electrochemical reactions. Consequently, there has been an increasing interest in water electrolysis for producing pure H₂. Although electrolysis shows potential, it encounters thermodynamic and kinetic obstacles, resulting in elevated overpotentials for both the HER and the OER, necessitating efficient catalysts. Traditionally, platinum (Pt) has been utilized for HER, while iridium (Ir) or ruthenium (Ru) has been employed for OER; however, these precious metals are costly and limited in availability. In response, research has transitioned to 3D-transition-metal sulfides and phosphides, which are more economical and plentiful. Recent investigations indicate that the sulfides and phosphides of 3d transition metals, specifically iron (Fe), cobalt (Co), and nickel (Ni), may effectively catalyze both the HER and the OER over a broad pH spectrum with comparable kinetics. These materials are plentiful, cost-effective, and adaptable, as they may be customized into diverse shapes and structures to improve electrolysis efficiency.

This thesis will concentrate on synthesizing cobalt phosphide (CoP) and cobalt phosphosulfide (CoPS) by a thermal decomposition approach. The existing literature for these materials has not thoroughly investigated this technique. Although the synthesis of these compounds has been extensively researched, we will focus on optimizing the reaction parameters, including temperature, duration, and precursor concentrations, to enhance their structural and electrochemical properties. We intend to juxtapose these results with other catalysts documented in the literature, including transition metal sulfides and phosphides, while examining the impact of our specific synthesis methods on the catalytic properties. The distinctive aspect of our research will be optimizing the thermal decomposition approach for CoP and CoPS, an area that remains underexplored in the current literature. Furthermore, our research will concentrate on the comparative analysis of cobalt-based phosphides and sulfides, examining their efficacy in both acidic and alkaline environments, which are essential for their utilization in water electrolysis systems. So, This thesis aims to synthesize cobalt phosphide and cobalt phosphosulfide nanocrystals with tunable composition and crystal structure for electrochemical hydrogen production. The specific objectives are as follows:

1. Synthesis and characterization of CoP and CoPS nanocrystals by thermal decomposition and hot-injection method.
2. Characterization of different synthesized catalysts of CoP and CoPS nanoparticles by XRD, SEM, TEM, and XPS analysis to determine the structural, morphological, and compositional properties.
3. Make stable electrocatalytic ink and assess the electrocatalytic performance of the synthesized CoP and CoPS catalysts in water electrolysis using LSV, CV, and EIS.

4. Measure important performance measures, including overpotential, Tafel slope, and stability.
5. Measure the rate of H₂ production and the Faradaic efficiency.

CHAPTER 3

MATERIALS AND CHARACTERIZATION

This chapter provides a detailed account of the materials and experimental methods utilized in this study, covering the following aspects:

1. The synthesis and surface modification of cobalt phosphide (CoP) and cobalt phosphosulfide (CoPS) electrocatalysts via a thermal decomposition method, optimizing reaction parameters to enhance their structural and electrochemical properties.
2. The primary characterization techniques employed to analyze the physicochemical properties of the synthesized materials include X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), energy-dispersive X-ray spectroscopy (EDS), and X-ray photoelectron spectroscopy (XPS).
3. The electrochemical methods used to investigate the catalytic performance of CoP and CoPS for water electrolysis include cyclic voltammetry (CV), linear sweep voltammetry (LSV), electrochemical impedance spectroscopy (EIS), and chronoamperometry to assess their activity, stability, and charge transfer dynamics in HER.

3.1 Chemicals

Cobalt (II) acetate tetrahydrate ($(\text{CH}_3\text{COOH})_2\text{Co}\cdot 4\text{H}_2\text{O}$, $\geq 98\%$), trioctylphosphine (TOP, 90%), oleylamine (OAm, 70% technical grade), 1-octadecene (ODE, 90%), 1-Dodecanethiol, Nafion solution (5% in a blend of lower aliphatic alcohols and water), 20 wt.% Pt/C catalyst, hexane (99.5%), ethanol (99.7%), and isopropyl alcohol (99.5%) were acquired from Sigma Aldrich and used as received without further purification. All reactions were performed under nitrogen, utilizing standard air-free methodologies.

3.2 Synthesis Methodologies

3.2.1 Synthesis of cobalt phosphides via a thermal decomposition method

Synthesis of Co_2P nanoparticles (Co_2P NPs): In a typical synthesis procedure, a solution of cobalt acetate tetrahydrate (249 mg, 1.0 mmol) was prepared by dissolving it in oleylamine (10 mL, 30.4 mmol) and 1-octadecene (5 mL, 15.6 mmol) in a three-necked round-bottom flask containing a glass-encapsulated magnet stirring bar. The flask was then securely fixed to a heating mantle and equipped with a thermometer adapter, a condenser, and a gas intake adapter (Scheme 1). The reaction mixture was heated at 120 °C for 1 hour under vacuum to remove water and other volatile impurities, turning the solution dark purple. Subsequently, a solution of trioctylphosphine (TOP) (2.5 mL, six mmol, P/Co ratio = 6) was introduced into the mixture, and the temperature was raised to 300 °C, where it was maintained for 1 hour. The solution turned black. The flask was removed from the heating mantle and cooled to room temperature. After cooling, the resulting product was isolated by centrifugation at 7000 rpm for 5 minutes using a hexane/ethanol (1:3) solvent blend. This step was repeated 3–4 times to remove any by-products. Finally, the obtained Co_2P NPs were dried in a vacuum oven at 60 °C for 24 hours.

Synthesis of CoP/Co₂P nanocomposite (CoP/Co₂P NC): For the synthesis of CoP/Co₂P NC, the same steps as for the synthesis of Co₂P NPs were followed, with modifications in phosphorus content and reaction temperature. Specifically, an increased amount of trioctylphosphine (TOP) (5 mL, 11 mmol; P/Co ratio = 11) was introduced into the reaction mixture. The temperature was then ramped to 330 °C over 30 minutes and maintained at this temperature for 1 hour. The solution turned black, indicating successful reaction progression. The isolation, purification, and drying procedures were identical to those for Co₂P NPs.

Synthesis of CoP nanoparticles (CoP NPs): For the synthesis of CoP NPs, a higher P/Co ratio and a higher temperature were required relative to Co₂P NPs and CoP/Co₂P NC. In a typical synthesis procedure, the same steps as for the synthesis of Co₂P nanoparticles were conducted except that the amount of trioctylphosphine solution was increased to 8 mL (8 mL, 18 mmol, P/Co ratio 18) and the final temperature was increased to 350 °C. The isolation, washing, and drying steps were the same as for the Co₂P NPs.

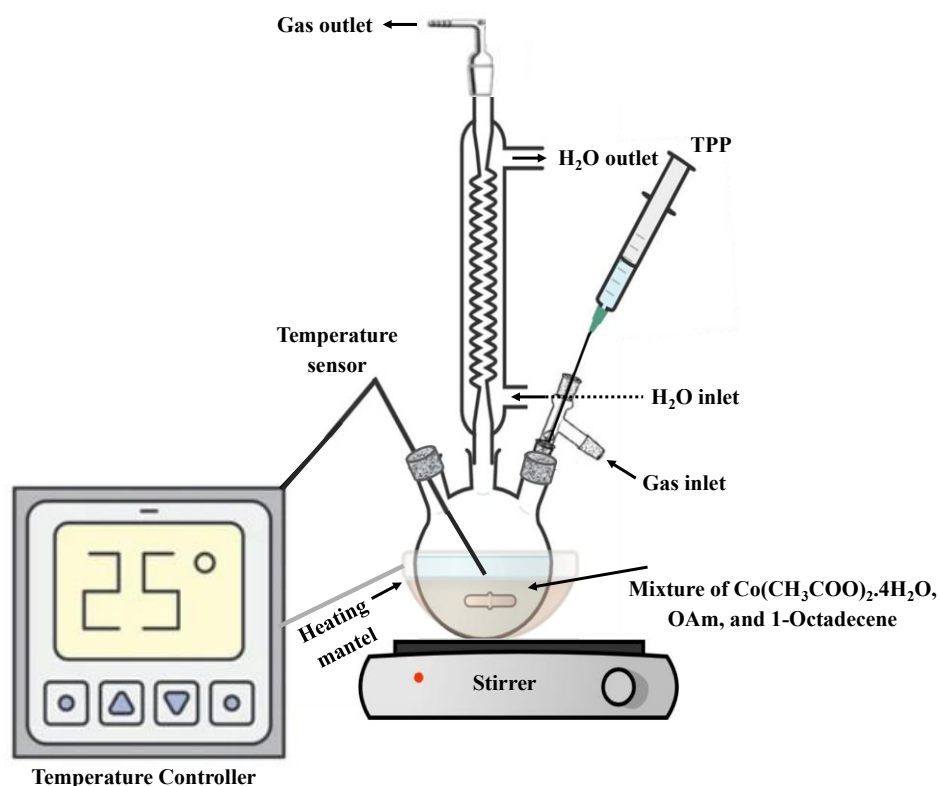


Figure 3.1. Synthesis scheme of Co₂P Nps, CoP Nps, and CoP / Co₂P nanocomposite via a Thermal Decomposition method

3.2.2 Synthesis of cobalt phosphosulfides via a thermal decomposition method

Synthesis of Cobalt Sulfide (Co₃S₄): In a typical synthesis procedure, a solution of cobalt acetate tetrahydrate (372 mg, 1.5 mmol) was prepared by dissolving it in oleyl amine (7 mL, 21.5 mmol) and 1-dodecanethiol (0.9 mL, 3.756 mmol) in a three-necked round-bottom flask containing a glass-encapsulated magnet stirring bar. The flask was then securely fixed to a heating mantle and equipped with a thermometer adapter, a condenser, and a gas intake adapter (Scheme 3.1). The reaction mixture was heated at 120 °C for 30 minutes under vacuum conditions to remove water and other volatile impurities. The temperature was raised to 300 °C and maintained for 5 hours. The solution turned black. The flask was removed from the heating mantle and cooled to room

temperature. After cooling, the resulting product was isolated by centrifugation at 7000 rpm for 5 minutes using a hexane/ethanol (1:3) solvent blend. This step was repeated 3–4 times to remove any by-products. Finally, the obtained Co_3S_4 NPs were dried in a vacuum oven at 60 °C for 24 hours.

Synthesis of Phosphorus Doped Cobalt Sulfide (P-CoS): For the synthesis of different phosphorus doped CoS, ($\text{P}_{(1\text{mmole})}$ -CoS), a solution of cobalt acetate tetrahydrate (372 mg, 1.5 mmol) was prepared by dissolving it in oleyl amine (7mL, 21.5 mmol) and 1-Dodecanethiol (0.9mL, 3.756 mmol) and Triphenylphosphine (262.29mg 1mmole) in a three-necked round bottom flask containing a glass-encapsulated magnet stirring bar. The flask was then securely fixed to a heating mantle and equipped with a thermometer adapter, a condenser, and a gas intake adapter. The reaction mixture was heated at 120 °C for 30 minutes under vacuum conditions to remove water and other volatile impurities. The temperature was raised to 300 °C and maintained for 5 hours. The solution turned black. Similarly, three different catalysts ($\text{P}_{(2\text{ mmole})}$ -CoS), ($\text{P}_{(3\text{ mmole})}$ -CoS), ($\text{P}_{(6\text{ mmole})}$ -CoS), to 524.6 mg, 1049.2 mg, 1573.7 mg, respectively, were prepared just by changing the amount of Triphenylphosphine. The isolation, purification, and drying procedures were identical to those for Co_3S_4 NPs.

3.2.3 Fabrication of CoP /GC electrodes

The Fabrication of cobalt phosphide (CoP) electrodes on glassy carbon (GC) involved the formulation of a catalyst ink, which was subsequently applied to the electrode surface via drop casting. Before catalyst application, the GC electrode was rigorously cleaned using sequential polishing with alumina slurry, followed by extensive rinsing with deionized water and sonication in ethanol and deionized water to eliminate surface contaminants. Subsequently, uniformly dispersed ink was made by ultrasonically blending a designated quantity of CoP powder with a

combination of isopropanol, deionized water, and Nafion as a binder to improve adhesion. The produced ink was subsequently drop-cast onto the cleaned GC electrode and permitted to dry at ambient temperature to guarantee uniform catalyst loading. The electrode was subsequently dried under vacuum or mild heating to enhance conductivity and catalyst-substrate interaction. The synthesized CoP/GC electrodes were subsequently employed for electrochemical evaluation to assess their performance in water electrolysis, as shown in Scheme 2.

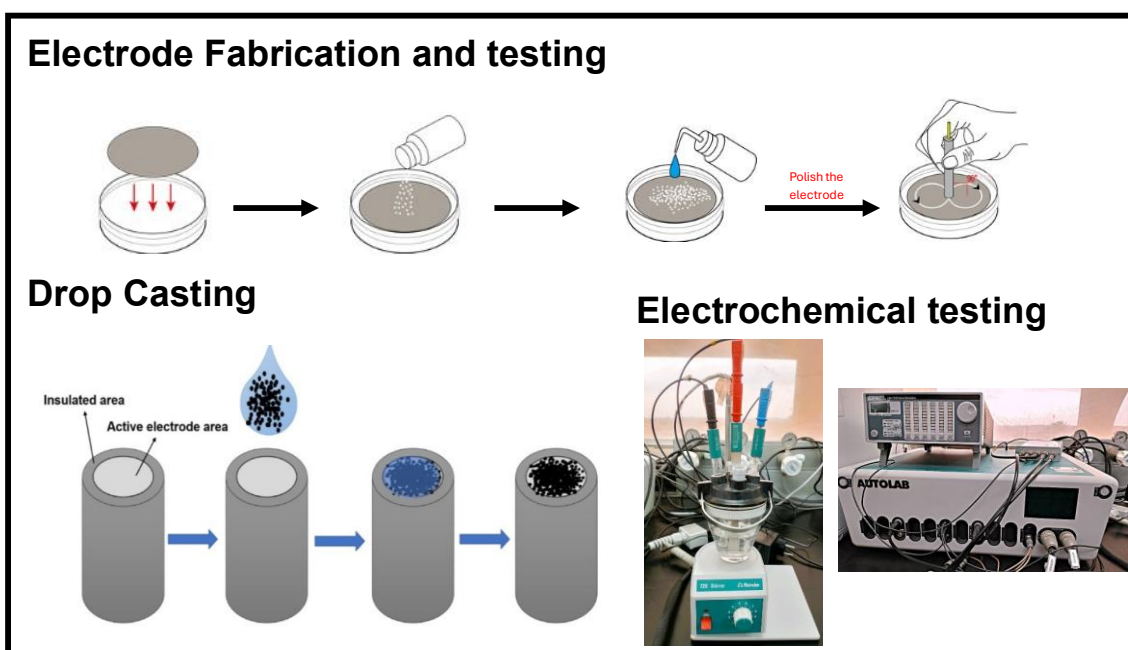


Figure 3.2. Cleaning of GCE and Fabrication of CoP/GC electrodes.

3.2.4 Fabrication of CoPS/CP electrodes

The fabrication of cobalt sulfide (CoS) and phosphorus-doped Cobalt Sulfide (P-CoS) electrodes on carbon paper (CP) entailed the formulation of a catalyst ink followed by its application onto the substrate. Before coating, the CP underwent sonication in acetone, ethanol, and deionized water to eliminate impurities and enhance surface wettability. The catalyst ink was made by dispersing CoS

powder in a blend of isopropanol, deionized water, and Nafion as a binder, and then subjected to ultrasonication to achieve uniform dispersion. The ink was deposited onto the cleaned CP and allowed to dry at ambient temperature to guarantee robust adherence. The manufactured CoS/CP electrodes were further analyzed electrochemically to evaluate their efficacy in water electrolysis.

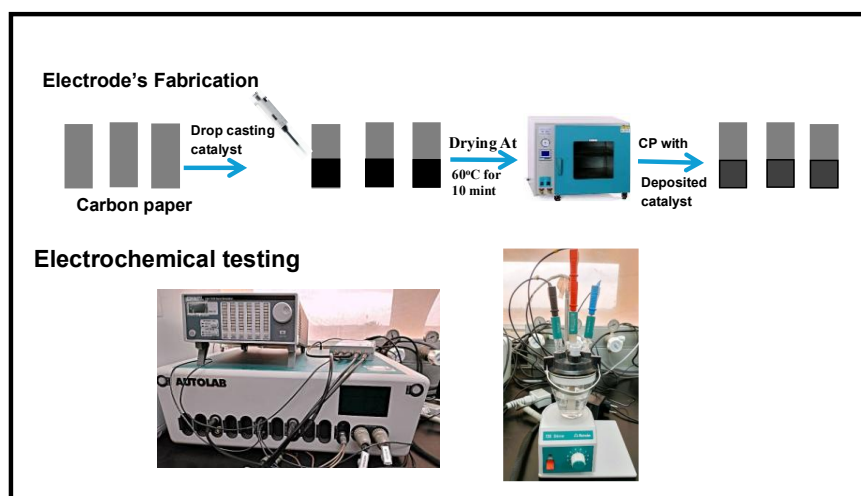


Figure 3.3. Fabrication of CoPS/Cp electrodes

3.3 Characterizations

3.3.1 X-ray diffraction (XRD)

The Rigaku X-ray diffractometer with Cu $K\alpha$ ($\lambda=1.54 \text{ \AA}$) X-ray radiation source was used for XRD measurements. The XRD pattern of all samples was recorded from $2\theta = 10^\circ - 70^\circ$ with a scan rate of $1^\circ/\text{min}$. The XRD spectrum obtained gives the relationship between light intensities vs. detector angle. The distance between the sample, the detector, and the X-ray focal point is the same during XRD measurements. The sample position is fixed, and the X-ray and detector are moved simultaneously at an angle θ . The peak obtained during XRD measurements is due to the constructive interference of the diffracted wave from the sample. The intensity of the XRD peaks only depends on the number and type of scattering points in each plane.

3.3.2 Field emission scanning electron microscope (FE-SEM)

FE-SEM measurements were carried out by the TESCAN field emission microscope operating at an accelerating voltage of 15 kV. The focused beam of high-energy electrons is utilized for high-resolution images of the surface of the materials. In FE-SEM, a high-energy beam of electrons is generated and accelerated by the high voltage (1-30 kV). When this high-energy electron beam strikes the sample, it penetrates it for a few microns to produce different signals. The secondary and backscattered electrons are collected by the detector and combined to create high-resolution images on the screen. For EDS measurements, the LINKINCA program system was attached to the FE-SEM to find out the sample's elemental composition. The X-ray detector is positioned so that X-rays emitted by the sample are intercepted. This generates a small current, which is further changed into the voltage pulse, and the size of this pulse is proportional to the frequency of the X-rays.

3.3.3 X-ray photoelectron spectroscopy (XPS)

The X-ray photoelectron spectroscopy (XPS) examination was conducted using the ESCALAB™ Xi+ X-ray photoelectron spectrometer manufactured by Thermo Scientific. This spectrometer utilized a monochromatic micro-focused Al K α X-ray source for the XPS investigation. The calibration of the XPS spectra was performed using the C 1s peak at 284.8 eV as a reference standard

3.3.4 Transmission electron microscopy (TEM)

Transmission Electron Microscopy (TEM) is a powerful characterization technique employed to examine materials' shape, dimensions, and structural attributes at the nanoscale. In Transmission Electron Microscopy (TEM), a high-energy electron beam is sent through an exceedingly thin

specimen, and the transmitted electrons are gathered to create a picture—the image's contrast results from variations in atomic composition and sample thickness. TEM offers comprehensive insights into the internal architecture, crystal lattice, and imperfections present in the material. The materials were reduced to nanoscale thickness for TEM investigation to facilitate adequate electron transmission. For samples sensitive to damage from the electron beam, careful consideration was paid to the electron dose and exposure duration. Transmission Electron Microscopy (TEM) is vital for acquiring high-resolution pictures, facilitating the examination of intricate details such as particle size, morphology, and crystalline structure, which are crucial for comprehending the material's characteristics and functionality.

3.3.5 Inductively coupled plasma mass spectrometry (ICP-MS)

Inductively Coupled Plasma Mass Spectrometry (ICP-MS) was utilized as a very sensitive analytical method for elemental analysis, specifically for determining the composition of cobalt phosphides (CoP) and cobalt sulfides (CoS). This approach involved introducing the sample into an inductively coupled plasma, which ionized the sample, and the resultant ions were quantified using a mass spectrometer. ICP-MS facilitated the identification of trace concentrations of diverse elements, ensuring precise and accurate quantification of the elemental composition of the samples. ICP-MS was employed to quantify the concentrations of cobalt, phosphorus, sulfur, and other elements in cobalt phosphides and cobalt sulfides. The analysis of ions generated from the sample via ICP-MS facilitated the assessment of the stoichiometry and purity of the synthesized cobalt-based products. This characterization was essential for comprehending the materials' composition, uniformity, and quality, which markedly affected their electrocatalytic activity and stability.

3.4 Electrochemical measurements

3.4.1 Linear sweep voltammetry (LSV)

In a three-electrode arrangement, linear sweep voltammetry (LSV) is an electrochemical method where the voltage provided to the working electrode is altered at a constant rate, referred to as the "scan rate." The voltage is regulated between the working and reference electrodes, guaranteeing the stability of the reference electrode within the electrochemical environment. The resultant current between the working and counter electrodes is quantified and graphed as a function of the applied voltage. In an electrolyzer configuration without a reference electrode, the regulated variable in linear sweep voltammetry (LSV) measurements is the voltage difference between the anode and cathode. LSV is highly effective for determining onset potentials, reaction kinetics, and overpotentials in electrocatalytic reactions.

3.4.2 Cyclic voltammetry (CV)

Cyclic voltammetry (CV) is an electrochemical technique where the potential is varied between two thresholds at a constant scan rate; however, in contrast to linear sweep voltammetry (LSV), the direction of the potential sweep is inverted upon reaching the designated potential limit. This repetitive forward and reverse sweeping enhances the understanding of electrochemical processes. CV facilitates the differentiation between capacitive and faradaic processes, assesses reaction reversibility, and identifies redox couples. This approach is essential in electrochemical research, providing critical insights into charge storage, reaction kinetics, and electrode stability.

3.4.3 Electrochemical impedance spectroscopy(EIS)

In electrochemical impedance spectroscopy (EIS), a small amplitude sinusoidal potential or current is supplied to the working electrode, and the resultant current or potential (the uncontrolled

variable) is measured. A spectrum of frequencies is employed for the sinusoidal signal. The fundamental objective of this technique is to examine the correlation between potential and current in the frequency domain. The subsequent equation obtains the impedance value for each frequency:

$$Z(f) = E/I$$

In which:

- $Z(f)$ corresponds to the impedance value and depends on the frequency.
- E is the potential applied/measured.
- I is the current applied/measured.

Consequently, impedance is determined by the ratio of amplitudes and the phase difference between voltage and current. The transfer function relating the independent variable (E) to the dependent variable (I) can be established by acquiring a sequence of impedance values at different frequencies. A detailed investigation of this data can disclose vital information regarding the electrochemical system, including capacitances, resistances, diffusion coefficients, and reaction rates. Although EIS is an effective method for comprehending electrochemical systems, specific parameters must be satisfied to guarantee precise outcomes. The system must be stable, as any extraneous time-dependent changes could result in erroneous impedance estimations. Secondly, the perturbation must stay linear, necessitating modest amplitude signals. This can be corroborated by the Lissajous diagram. Finally, a causal relationship must exist between the potential and current, indicating that the observed variations in the variable must exclusively stem from the controlled variable, devoid of external influences.

3.4.4 Chronopotentiometry (CP)

Chronopotentiometry (CP) is an electrochemical method wherein a continuous current is administered to the working electrode, and the resultant potential is documented as a function of time. In contrast to voltametric methods, chronoamperometry (CA) is a step-current approach, wherein a constant current is delivered, resulting in a dynamic alteration of the electrode potential in response to electrochemical reactions. During the initial phase of the experiment, double-layer charging and transient phenomena transpire before system stabilization. Temporal variations in electrode potential yield insights into reaction kinetics, mass transport constraints, and the stability of the electrode material. CP is especially valuable for assessing catalyst deterioration, electrode passivation, and long-term performance in electrochemical applications, such as water electrolysis.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Phase and composition-dependent electrocatalytic activity of cobalt phosphides in Acidic media

The phase-selective synthesis of cobalt phosphides, including pure Co_2P NPs, CoP NPs, and a $\text{CoP}/\text{Co}_2\text{P}$ nanocomposite, was accomplished through the thermal decomposition of cobalt(II) acetate tetrahydrate as the cobalt source, with trioctylphosphine serving as the phosphorus source, oleylamine as complex and reducing agent, and 1-octadecene as solvent. By precisely tuning the ratio of trioctylphosphine to cobalt(II) acetate tetrahydrate, along with carefully controlling the reaction temperature and duration, the phase structure of the synthesized cobalt phosphides was effectively tailored, enabling the targeted formation of CoP and Co_2P phases and a composite of them. To confirm the crystalline phase structures of the synthesized cobalt phosphide catalysts, X-ray diffraction (XRD) analysis was conducted. Figure 4.1a illustrates the XRD patterns of CoP , $\text{CoP}/\text{Co}_2\text{P}$, and Co_2P nanoparticles (NPs). Figure 4.1a-I presents the XRD pattern of pure CoP NPs, with characteristic diffraction peaks matching the orthorhombic CoP phase (PDF# 00-029-0497). The observed peaks located at $2\theta = 31.7^\circ, 38.9^\circ, 46.2^\circ, 48.1^\circ, 52.6^\circ$, and 56.5° align well with the (011), (111), (112), (211), (103), and (020) crystallographic planes, confirming the successful synthesis of phase-pure CoP NPs. Figure 4.1a- II displays the XRD pattern of the Co_2P NPs, exhibiting diffraction peaks corresponding to the hexagonal Co_2P structure (PDF# 00-054-0413). The observed peaks at $40.9^\circ, 49^\circ, 52.6^\circ$, and 55.6° can be indexed to the (111), (120), (002),

and (030) planes, confirming the formation of crystalline Co₂P pure phase. Figure 4.1a- III presents the XRD pattern of the CoP/Co₂P nanocomposite, revealing diffraction peaks at $2\theta = 31.7^\circ$, 38.9° , 46.2° , and 48.1° , indicative of the orthorhombic CoP phase (PDF# 00-029-0497), assigned to the (011), (111), (112), and (211) planes. Additionally, peaks observed at $2\theta = 40.9^\circ$ and 52.6° correspond to the hexagonal Co₂P phase (PDF# 00-054-0413), associated with the (111) and (002) crystallographic planes. The absence of extraneous peaks confirms the high purity of the CoP/Co₂P nanocomposite, comprising both phases without significant impurities. Figures 4.1b and 4.1c further illustrate the crystal structures of CoP and Co₂P, respectively, visually representing their atomic arrangements. These structural models reinforce the distinct crystallographic features observed in the XRD patterns. The CoP/Co₂P nanocomposite, incorporating both structures, is expected to leverage the advantages of each phase, offering a synergistic enhancement in catalytic performance. Overall, the XRD analysis confirms the successful phase-selective synthesis of CoP, Co₂P, and CoP/Co₂P composite, demonstrating precise control over phase structure and composition through systematic variations in reaction conditions.

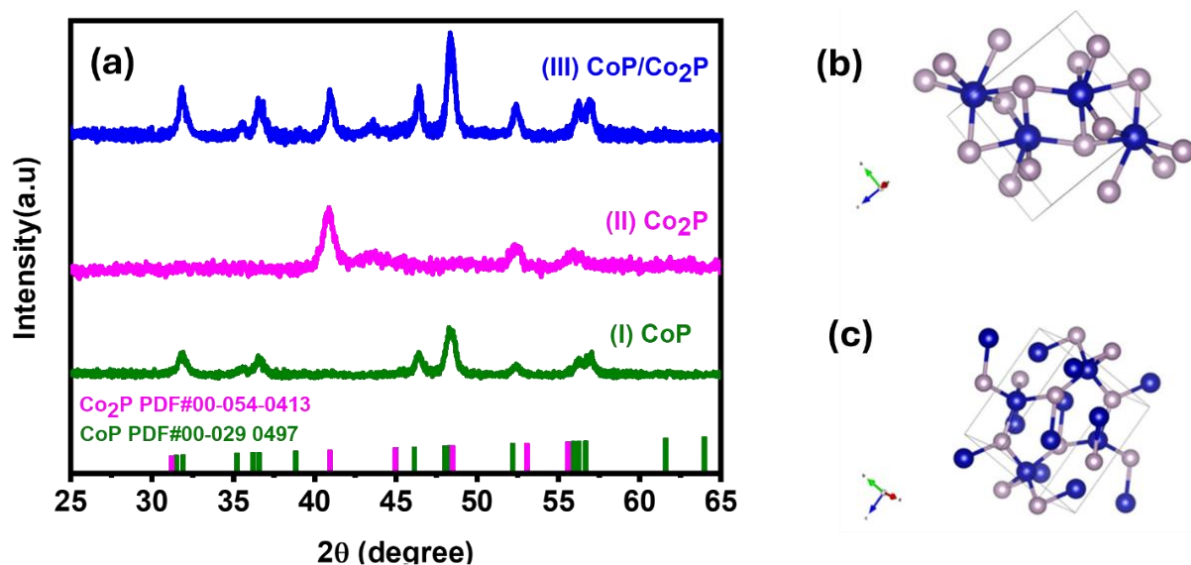


Figure 4.1. (a) XRD patterns of CoP, Co₂P, and CoP/Co₂P nanocomposite; (b and c) Crystal structures of CoP and Co₂P, respectively, where Co is represented by the blue ball and P by the gray ball.

The synthesized cobalt phosphide nanoparticles' surface elemental composition and chemical states were systematically analyzed using X-ray photoelectron spectroscopy (XPS). Figure 4.2a presents the high-resolution XPS spectrum of Co 2p in Co₂P. According to reported literature [109-111], the two distinct peaks observed at 781.38 eV and 797.38 eV correspond to Co 2p_{3/2} and Co 2p_{1/2}, respectively, associated with Co–P bonds in the Co₂P nanoparticles. The binding energy difference between the Co 2p_{3/2} and Co 2p_{1/2} peaks in Co₂P is 15.9 eV, which aligns well with previously reported values for cobalt phosphide [112]. Additionally, two satellite peaks were detected at 787.5 eV and 803 eV, corresponding to Co 2p_{3/2} and Co 2p_{1/2} of oxidized cobalt species [113]. Figure 4.2b depicts the high-resolution XPS spectrum of the P 2p region for Co₂P, revealing two distinct peaks: one at 128.5 eV, attributed to cobalt phosphides, and another at 133.0 eV, which is associated with the oxidation of phosphorus to phosphate [114]. Figures 4.2c and 4.2d present the XPS results for CoP. In Figure 4.2c, the 778.8 eV and 793.8 eV peaks are attributed to Co 2p_{3/2} and Co 2p_{1/2}, respectively, corresponding to Co–P bonds in the CoP phase. Additionally, two

peaks were observed at 781.1 eV and 797.9 eV, representing oxidized cobalt species, along with two broad peaks at 783.3 eV and 803.3 eV, which are associated with satellite features [115]. Cobalt oxidation is likely due to the superficial oxidation of CoP nanoparticles upon exposure to air [116]. Figure 4.2d depicts the P 2p signal, revealing two prominent peaks at 129.5 eV and 133.1 eV, corresponding to cobalt phosphides and cobalt phosphate, respectively [117]. The peak at 133.1 eV is attributed to oxidized phosphate (PO_4^{3-}) species on the sample's surface, which likely formed due to oxidation upon air exposure [118]. Figures 4.2e and 4.2f present the XPS results for the CoP/Co₂P nanocomposite. In Figure 4.2e, the Co 2p XPS spectrum reveals Co 2p_{3/2} peaks at 779 eV and 781.9 eV, accompanied by a satellite peak at 786.2 eV, while the Co 2p_{1/2} peaks are located at 795 eV and 798.7 eV, with an additional satellite peak at 802.7 eV [109]. The peaks at 779 eV and 795 eV are attributed to cobalt in Co–P bonds within the CoP/Co₂P nanocomposite, whereas the peaks at 781.9 eV and 798.7 eV correspond to cobalt species in Co–O bonds, arising from the oxidation of CoP/Co₂P nanocomposite [109]. Figure 4.2f illustrates the high-resolution P 2p spectrum, which exhibits three distinct peaks at 129.4 eV, 130.5 eV, and 133.6 eV, corresponding to P 2p_{3/2}, P 2p_{1/2}, and P–O species, respectively [119, 120]. In all cases-CoP, Co₂P, and CoP/Co₂P-the binding energy of Co 2p_{3/2} is higher than that of metallic Co (778.1–778.2 eV), while the binding energy of P 2p is lower than that of elemental phosphorus (130.2 eV). This indicates that cobalt in CoP carries a partial positive charge (δ^+), whereas phosphorus carries a partial negative charge (δ^-), suggesting an electron density transfer from Co to P [121, 122]. In HER catalysis, it is proposed that the negatively charged P sites and positively charged Co sites work synergistically to form catalyst-hydrogen complexes. Molecular hydrogen is subsequently released through the combined effect of these oppositely charged sites, thereby enhancing the hydrogen evolution reaction (HER) process [53, 123].

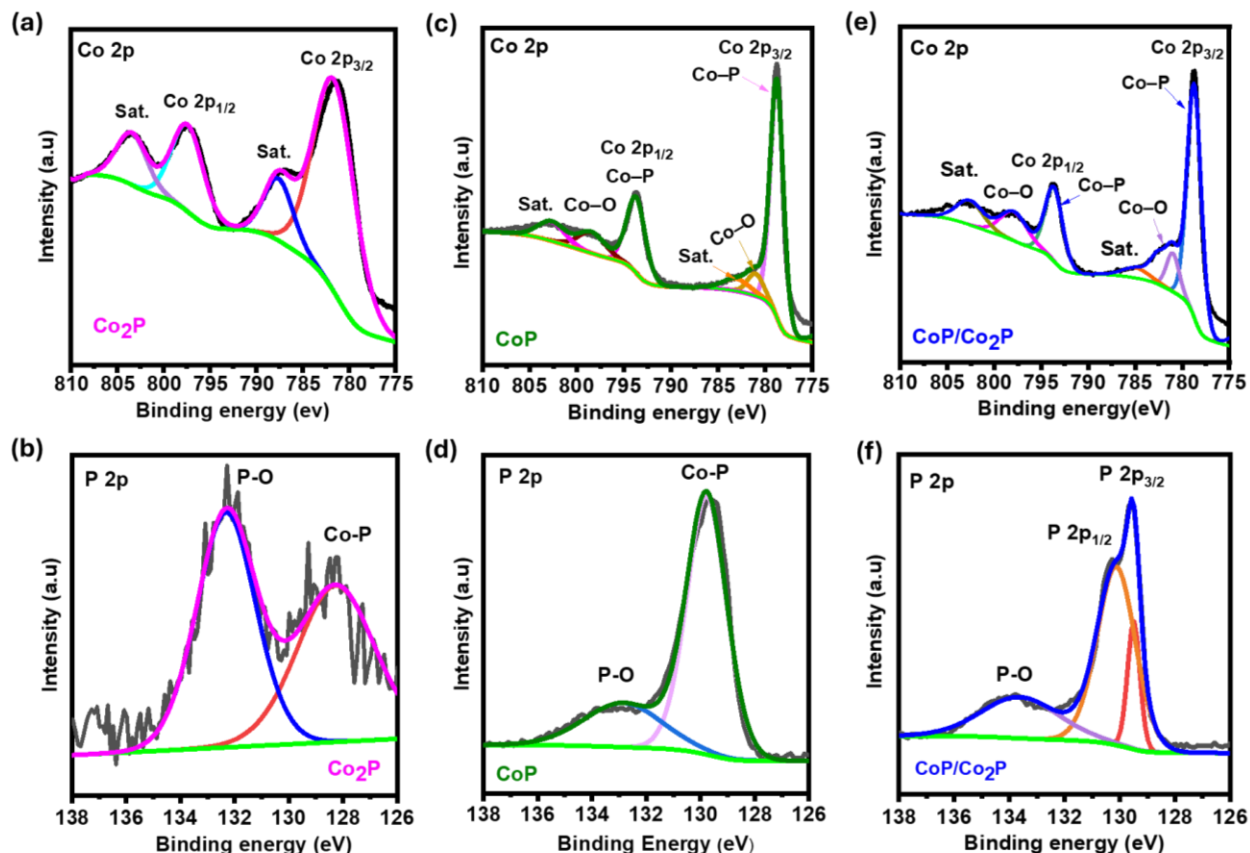


Figure 4.2. High-resolution XPS spectra of the Co 2p and P 2p regions for (a, b) Co₂P, (c, d) CoP, and (e, f) the CoP/Co₂P composite

The morphologies of the as-synthesized Co₂P NPs, CoP NPs, and CoP/Co₂P nanocomposite were characterized by scanning electron microscopy (SEM) and transmission electron microscopy (TEM), as shown in Figure 4.3. Figures 4.3a-c present the SEM images of Co₂P NPs, CoP NPs, and CoP/Co₂P nanocomposites. The SEM images reveal distinct morphological differences among the Co₂P NPs, CoP NPs, and CoP/Co₂P nanocomposite samples. The Co₂P sample (Figure 4.3a) consists of uniformly aggregated particles with an average diameter of 32 nm, as shown in the histogram of particle size distribution in Figure 4.4a. In comparison, the CoP sample (Figure 4.3b) has larger particles with the same morphology but a bigger size (average diameter of 72 nm, Figure

4.4b). The CoP/Co₂P nanocomposite (Figure 4.3c) has the largest average particle size (130 nm, Figure 4.4c) and exhibits obvious irregular morphology. Energy-dispersive X-ray (EDX) analysis confirmed the presence of cobalt and phosphorus in all synthesized samples, and elemental mapping data demonstrated the homogeneous distribution of Co and P in the as-prepared nanoparticles, as shown in Figure 4.5. Furthermore, the TEM images revealed notable morphological differences between Co₂P NPs, CoP NPs, and CoP/Co₂P composite. The Co₂P sample (Figure 4.3d, g) exhibited pseudospherical and hollow nanoparticles. The hollow regions in the Co₂P particles were marked with a circular line. The CoP sample (Figure 4.3e), on the other hand, displayed larger pseudospherical solid nanoparticles. Figure 4.3f illustrates the distinctive hierarchical structure of the CoP/Co₂P composite, characterized by pseudospherical core particles surrounded by radial and showing a dendritic nanostructure. This unique architecture is expected to increase significantly the surface area compared to the simpler morphologies of Co₂P and CoP. The effective synthesis of different cobalt phosphide phases (Co₂P and CoP) and their composite is confirmed by calculating the d-spacing from the high-resolution transmission electron microscopy (HRTEM) images (Figure 4.3 g-i). Lattice fringes with an interplanar spacing of $d = 0.221$ nm, corresponding to the (111) plane of Co₂P, are observed in Figure 4.3g. The crystalline structure of CoP is further demonstrated in Figure 4.3h, where lattice fringes indexed to the (111) plane ($d = 0.247$ nm) are visible. The Co₂P/CoP heterostructure is depicted in Figure 4.3i, showing Co₂P with the (111) plane ($d = 0.221$ nm) and CoP with the (111) plane ($d = 0.247$ nm). Due to the possible synergy between the two phases, the formed heterostructure might enhance electrocatalytic performance by providing dual catalytic sites and improved electron transport.

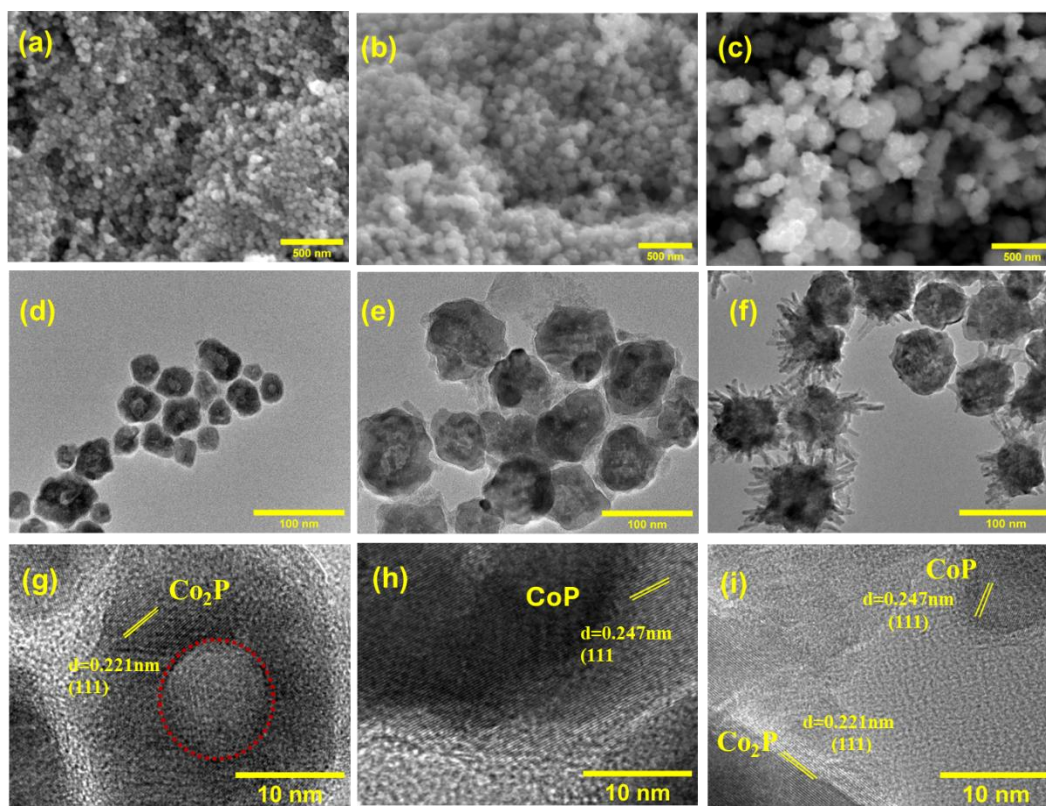


Figure 4.3. Morphology (a-c) SEM images, (d-f) low-resolution TEM images, and (g-i) high-resolution TEM images of Co_2P , CoP , and $\text{CoP}/\text{Co}_2\text{P}$ NPs.

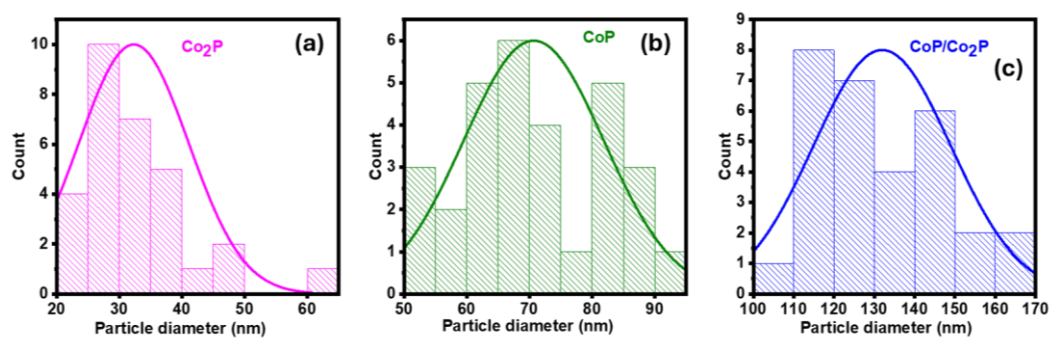
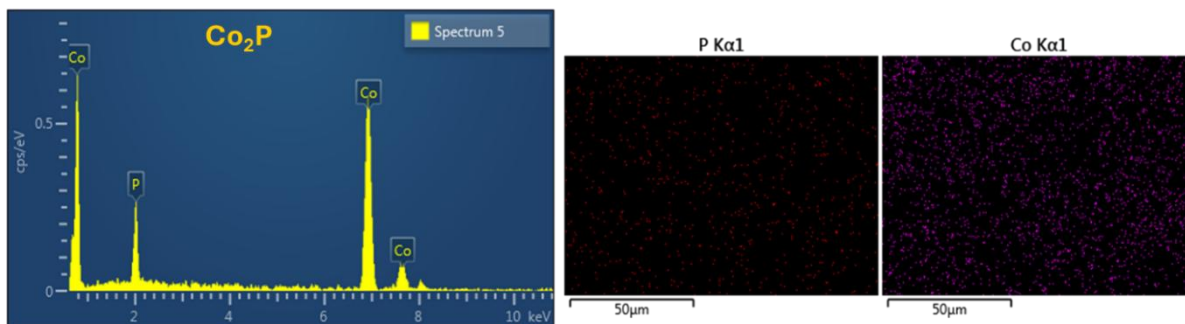
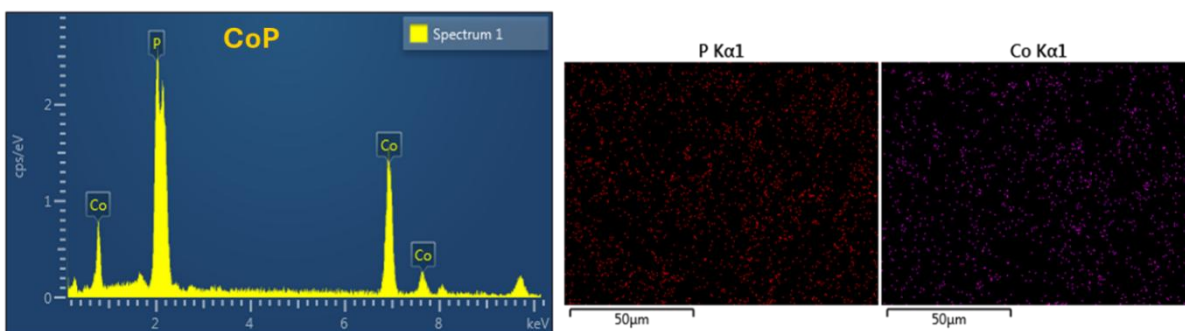


Figure 4.4. Particle diameter histogram calculated from the TEM images of Co_2P (a), CoP (b), and $\text{CoP}/\text{Co}_2\text{P}$ (c).

(a) Co₂P NPs



(b) CoP NPs



(c) Co₂P NPs

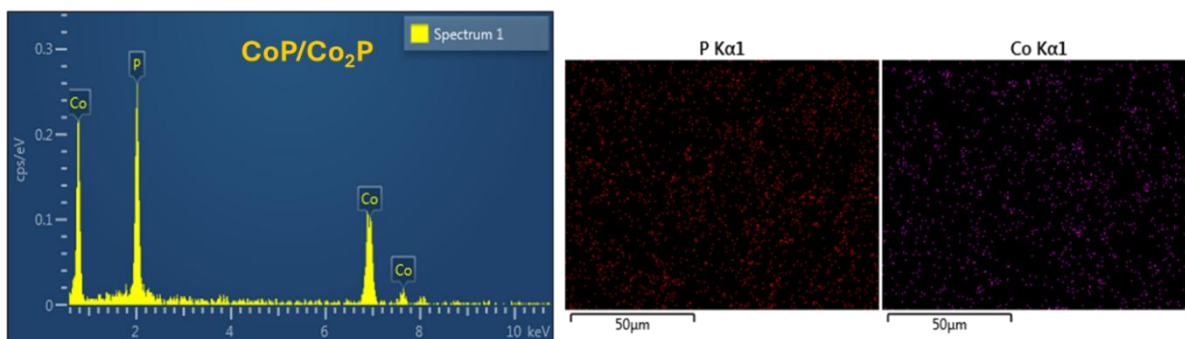


Figure 4.5. EDX analysis and elemental Mapping of Co₂P (a), CoP (b), and CoP/Co₂P (c).

FT-IR spectroscopy was employed to examine the surface states of the cobalt phosphides (Co_2P , CoP , and $\text{CoP}/\text{Co}_2\text{P}$), as depicted in Figure 4.6. The organic capping ligands, such as TOP and OAm, were effectively removed during the synthesis process, as evidenced by the absence of peaks at 2926 cm^{-1} and 2855 cm^{-1} , which are typically associated with the stretching vibrations of C–H bonds in methyl and methylene groups. Furthermore, the absence of a signal at 1630 cm^{-1} is often attributed to the stretching vibration of C=C bonds in oleylamine. The OAm seems to act as a complex and reducing agent rather than a capping agent. This has been evidenced by the separation of metallic cobalt (See Figure S1). The decomposition of TOP leads to the formation of reactive P that reacts with the reduced cobalt ions, forming cobalt phosphides with minimal or no residue on the surface. These findings demonstrated that cobalt phosphides have been successfully synthesized with very little organic contamination, offering electrocatalysis surfaces that are both clean and active without the need for the ligand exchange step.

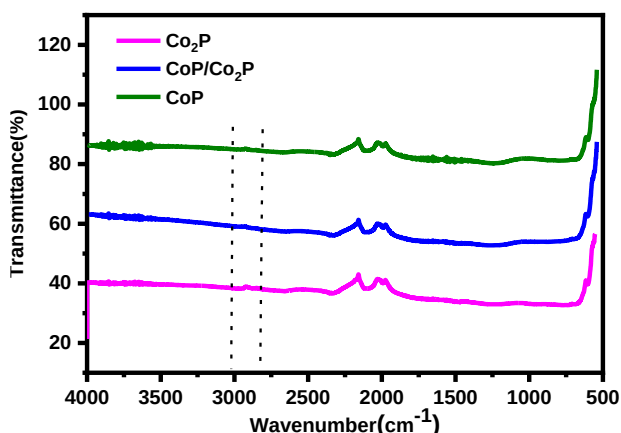


Figure 4.6. FTIR analysis of Co_2P , CoP , and $\text{CoP}/\text{Co}_2\text{P}$ NPs.

Possible mechanism for CoP , Co_2P , and $\text{CoP}/\text{Co}_2\text{P}$ NPs formation. : The XRD results indicated that the synthesis of Co_2P , CoP , and $\text{CoP}/\text{Co}_2\text{P}$ nanocomposites can be controlled by adjusting the P/Co precursor ratio. The TEM results showed that the morphology of cobalt phosphide NPs can

also be regulated by altering the P/Co precursor ratio. The Co₂P showed pseudospherical and hollow nanoparticles, CoP exhibited solid pseudospherical and pseudospherical core particles with dendritic morphology, characterizing the CoP/Co₂P nanocomposite. Considering the diffusion dynamics of cobalt and phosphorus atoms during the synthesis process, the formation of hollow Co₂P NPs can be explained by considering the Kirkendall effect [124]. During the early stages of the synthesis, oleylamine (OAm) serves as a reductant, reducing cobalt ions (Co²⁺) into cobalt nanoclusters upon reaching a reaction temperature of approximately 220 °C. This fact was confirmed by the XRD analysis of the cobalt nanoclusters isolated at 220 °C and presented in Figure 4.7. Then, trioctylphosphine (TOP), a potent ligand, adheres to the surface of cobalt nanoclusters [125], which assists in stabilizing the cobalt nanoparticles and inhibiting premature aggregation as the reaction temperature rises to approximately 300 °C; the P–C bonds in the TOP break, releasing phosphorus atoms. These phosphorus atoms begin to diffuse into the cobalt nanoclusters, a process governed by the Kirkendall effect. The Kirkendall mechanism involves the relative rates of outward diffusion of cobalt atoms and inward diffusion of phosphorus atoms. At a low P/Co mole ratio (6:1) and temperature of 300 °C, limited phosphorus availability leads to rapid outward diffusion of cobalt atoms and reduced inward diffusion of phosphorus atoms, creating a diffusion imbalance that results in the formation of hollow Co₂P nanoparticles. Similar behavior was reported for the synthesis of nickel phosphides [57]. At a high P/Co mole ratio (18:1) and high temperature (350 °C), phosphorus atoms become more abundant and diffuse more efficiently into the cobalt nanoclusters, leading to the formation of CoP with solid pseudospherical NPs morphology and larger size. At a moderate P/Co mole ratio (11:1) and temperature (330 °C), a balance between inward phosphorus diffusion and outward cobalt diffusion—combined with the temperature required for the phase transformation from Co₂P to CoP—results in the formation of a

CoP/Co₂P nanocomposite featuring pseudospherical core particles surrounded by radial (dendritic nanostructure). The proposed Kirkendall mechanism for synthesizing Co₂P, CoP, and CoP/Co₂P nanocomposite is schematically shown in Figure 4.8.

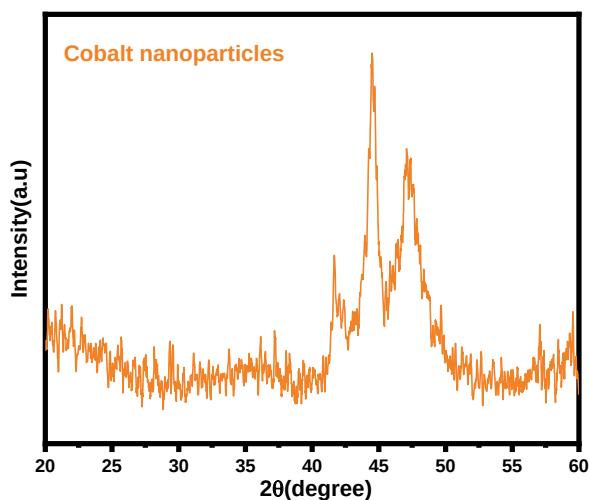


Figure 4.7. XRD of cobalt nanoparticles

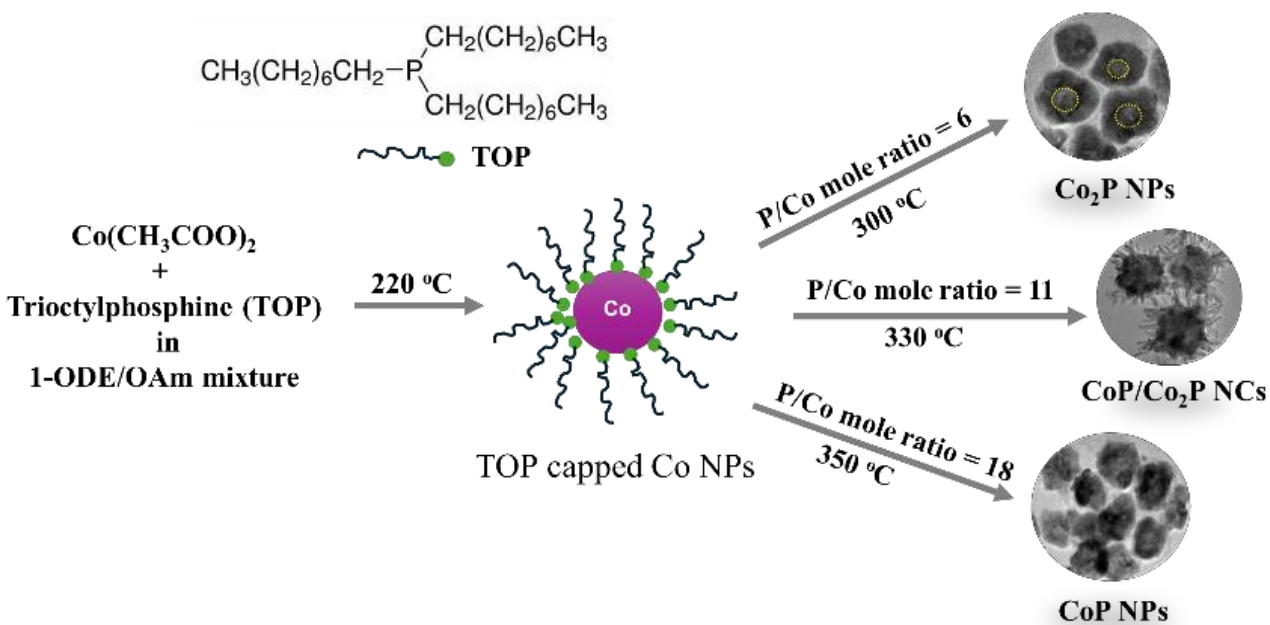


Figure 4.8. Possible formation mechanism of the as-synthesized cobalt phosphide NPs with different phases and morphologies.

Electrochemical measurements: At room temperature, the electrochemical experiments were conducted in 0.5 M H₂SO₄ (pH = 0.5, purged with N₂ gas). All reported potentials are without iR correction and are given versus the reversible hydrogen electrode (RHE) according to the Nernst equation:

$$E_{\text{RHE}} = E_{\text{applied}} + 0.0591 \text{ pH} + E^{\circ}_{\text{ref}} (0.198\text{V})$$

All linear sweep voltammograms (LSV) were recorded within a potential range of -0.5 V to 0.1 V vs. RHE at a scan rate of 5 mV s⁻¹. Electrochemical impedance spectroscopy (EIS) measurements were performed at an applied potential of 0.15 V vs. RHE, with scanning frequencies ranging from 10⁵ Hz to 0.01 Hz. The EIS data were then fitted using a suitable equivalent circuit model to determine the charge transfer resistance accurately, providing critical insights into the system's electrochemical behavior. The double-layer capacitance (*C*_{dl}) was determined from cyclic voltammograms (CV) recorded in the non-faradaic region (0.1 to 0.2 V vs. RHE) at various scan rates (20 to 220 mV s⁻¹). A chronopotentiometry test was conducted to evaluate the catalyst's stability at a constant current density of 10 mA cm⁻² for 24 hours.

We examined the phase-dependent electrocatalytic activity of synthesized cobalt phosphide NPs (CoP and Co₂P) and their nanocomposite (CoP/Co₂P NC) for HER using a standard Metrohm three-electrode cell in 0.5 M H₂SO₄ at ambient temperature. The linear sweep voltammetry (LSV) test was performed at a scan rate of 5 mV s⁻¹ within the potential range of -0.5 to 0.1 V vs RHE. Figure 4.9a illustrates the LSV curves for bare GCE, CoP NPs, Co₂P NPs, CoP/Co₂P nanocomposite, and 20 wt% % Pt/C electrocatalysts. Bare GCE exhibits minimal HER activity, while CoP/Co₂P demonstrates superior HER performance, achieving a low overpotential of 152 mV at a current density of 10 mA cm⁻². This overpotential is significantly lower than that of bare GCE, CoP (192 mV), and Co₂P (242 mV) recorded under the same conditions (refer to Figures 6a and b)—the 20

wt.% Pt/C catalyst exhibits the highest HER activity, achieving an overpotential of 32 mV at 10 mA cm⁻²; however, the scarcity and high cost of noble metals hinder their widespread utilization. The electrochemical data indicate that both CoP and Co₂P phases of cobalt phosphide serve as active catalysts for HER, with the CoP/Co₂P nanocomposite requiring a lower overpotential compared to CoP and Co₂P individually. The enhanced HER activity exhibited by the CoP/Co₂P nanocomposite can be attributed to its unique dendritic nanostructure, which increases its surface area and available active sites.

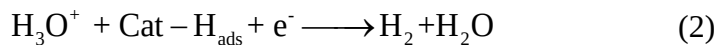
The HER reaction mechanism can be explained by using Tafel analysis. Figure 4.9c shows Tafel plots for 20 wt.% Pt/C, CoP, Co₂P and CoP/Co₂P derived from polarization curves using the following equation:

$$\eta = a + b \log(j)$$

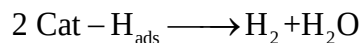
Where b is the Tafel slope and j is the current density. The Tafel slopes for the CoP/Co₂P nanocomposite, CoP, and Co₂P are 56 mV dec⁻¹, 76 mV dec⁻¹, and 92 mV dec⁻¹, respectively, as shown in Figure 6c. These values indicate that the HER rate of CoP/Co₂P is faster than that of Co₂P and CoP. The small Tafel slope of CoP/Co₂P nanocomposite indicates that its catalytic performance is superior to that of Co₂P NPs and CoP NPs. Generally, three possible reaction steps have been proposed for the HER in acidic solutions. [22], commonly named, the Volmer reaction (Eq. 1), where the H₃O⁺ ions are electrochemically adsorbed onto the surface of the electrocatalyst (Cat):



The Heyrovsky reaction (Eq. 2), which represents the electrochemical desorption step:



The Tafel reaction (Eq. 3) represents the electrochemical desorption step:



When equation (1) is the rate-determining step (RDS) of the HER, the Tafel slope measures 120 mV dec⁻¹. When equation (1) is quick, either equation (2) or (3) serves as RDS, and the Tafel slope is 40 or 30 mV dec⁻¹, respectively [126]. The adsorption of H⁺ ions is expected to occur at the negatively charged P sites and, therefore, depends on the number of exposed P atoms in contact with the electrolyte. The ensemble of P atoms at the surface is known to influence HER activity. [127]. ICP analysis (Figure 4.10) showed that the phosphorus content in the CoP/Co₂P composite (47.5 at.%) is comparable to that in CoP (49.5 at.%) and significantly higher than that in Co₂P (37.6 at.%), which exhibits the lowest HER activity and the highest Tafel slope. This suggests that the elevated P content in CoP/Co₂P facilitates proton adsorption (Volmer step), indicating that HER is primarily governed by the desorption of hydrogen gas, either via the Heyrovsky step (electrochemical desorption) or the Tafel step (chemical desorption). The Tafel slope of CoP/Co₂P is 56 mV dec⁻¹ (closer to the theoretical value for the Heyrovsky mechanism), suggesting that electrochemical desorption is likely the RDS. In contrast, Co₂P, with the lowest P content, exhibits a Tafel slope of 92 mV dec⁻¹ (closer to the theoretical value for the Volmer mechanism), indicating that the electrochemical adsorption of H₃O⁺ is the RDS. Although CoP has a P content similar to the CoP/Co₂P composite, it shows a higher Tafel slope (92 mV dec⁻¹), implying that the synergy between CoP and Co₂P contributes significantly to the enhanced HER performance.

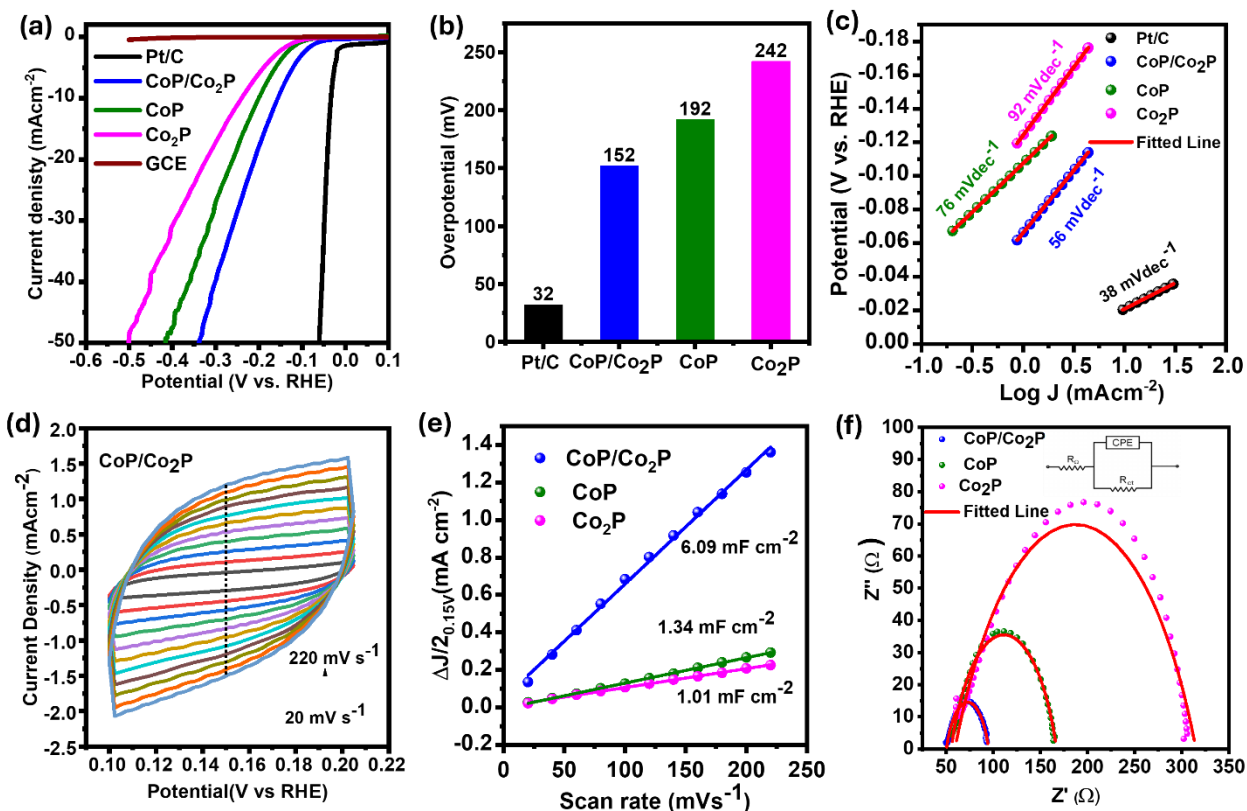


Figure 4.9. The electrochemical performance of CoP, Co₂P, CoP/Co₂P, and the benchmark 20 wt.% Pt/C electrodes: (a) LSV curves (without IR correction) recorded in 0.5 M H₂SO₄ solution at a scan rate of 5 mV s^{-1} , (b) Comparison of overpotentials at a current density of 10 mA cm^{-2} , and (c) Corresponding Tafel plots with linear fittings (d) Nyquist plots of these catalysts measured at 0.15 V vs. RHE (e) Cyclic voltammetry curves of CoP/Co₂P NPs at varying scan rates. (f) The linear fitting of average capacitive currents versus scan rates to estimate the double-layer capacitance (C_{dl}).

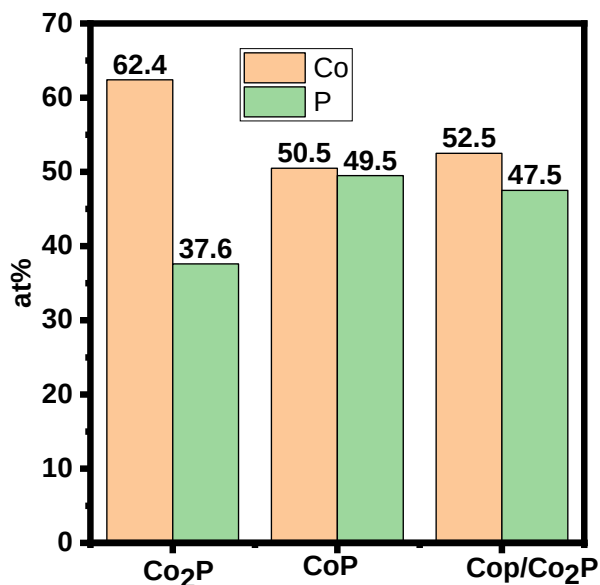


Figure 4.10. ICP analysis of synthesized cobalt phosphide nanoparticles

To evaluate the intrinsic HER activity of the synthesized catalyst, cyclic voltammetry (CV) was conducted to determine the double-layer capacitance (C_{dl}), which serves as an indicator of the electrochemically active surface area (ECSA) of the samples [128]. The CV measurements were performed at varying scan rates (20–220 mV/s) within the potential window of 0.1 to 0.2 V vs. RHE in 0.5 M H₂SO₄ (Figures 4.9d, 4.11a, 4.11b). Since the hydrogen evolution reaction (HER) is predominantly surface-dependent, catalysts with a larger electrochemical surface area (ECSA) typically exhibit superior catalytic performance. This enhancement is attributed to the increased number of active sites available for the reaction, which ultimately boosts the overall efficiency of the HER process. As illustrated in Figure 4.9e, the CoP/Co₂P nanocomposite exhibits a C_{dl} of approximately 6.06 mF cm⁻², which is sixfold higher than that of CoP (1.34 mF cm⁻²) and Co₂P (1.01 mF cm⁻²) in 0.5 M H₂SO₄. This significant increase in C_{dl} indicates that CoP/Co₂P

nanocomposite possesses the largest ECSA, underscoring their exceptional HER activity in acidic media. The ECSA is a vital parameter for assessing catalytic performance as it quantifies the electrode surface area accessible for electron transfer or charge storage. The ECSA was calculated using the equation $ECSA = (C_{dl}/Cs) \times A$, as detailed in the Supplementary Information [129]. Here, Cs represents the specific capacitance per unit area of a smooth planar surface of the material. In this study, a typical specific capacitance value of $Cs = 0.035 \text{ mF cm}^{-2}$ was employed for acidic media [129]. By substituting the measured values of C_{dl} and the specific capacitance, the ECSA values for CoP/Co₂P NCs, CoP, and Co₂P were calculated to be 12.29 cm^2 , 2.7 cm^2 and 2.03 cm^2 , respectively shown in 4.12. The substantial enhancement in electrochemically active surface area (ECSA) observed for the CoP/Co₂P electrode is primarily attributed to its distinctive dendritic nanostructure, coupled with the synergistic interplay between the CoP and Co₂P phases, which collectively promote the formation of a higher density of active sites. Leveraging the ECSA data, the intrinsic HER activities of CoP/Co₂P, CoP, and Co₂P were evaluated by normalizing the current densities to their respective ECSAs (Figure 4.13). As shown in Figure 4.13, the CoP phase demonstrates higher intrinsic activity than Co₂P, consistent with the trend in geometric HER activity. Interestingly, despite exhibiting the highest geometric HER activity, the CoP/Co₂P composite shows the lowest intrinsic activity among the three, suggesting that its superior overall performance is primarily governed by the significantly enlarged ECSA rather than enhanced activity per site. This observation underscores the critical role of the dendritic nanostructure in exposing a greater number of catalytic sites. Furthermore, the work function of CoP (3.82 eV) is notably lower than that of Co₂P (4.43 eV), and upon interfacial contact, electron transfer from CoP to Co₂P becomes thermodynamically favorable. This electronic redistribution enhances the nucleophilicity of Co₂P, facilitating the adsorption of H_3O^+ ions and further contributing to the

generation of active sites [130, 131]. While this synergistic mechanism effectively boosts the geometric HER activity of the composite, CoP alone still exhibits the highest activity per catalytic site.

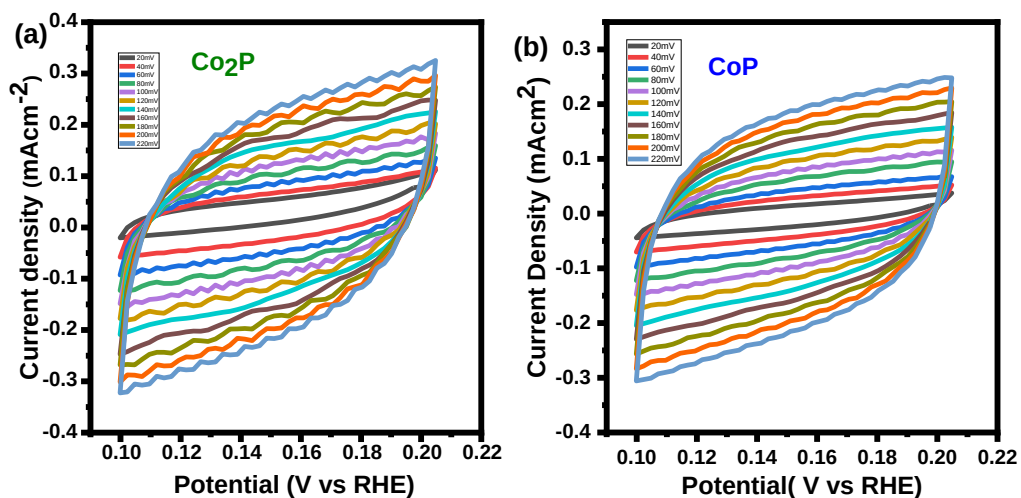


Figure 4.11. CV profiles measured in the double-layer region for (a) Co₂P, and (b) CoP catalysts at various scan rates (from 20 to 220 mV s⁻¹).

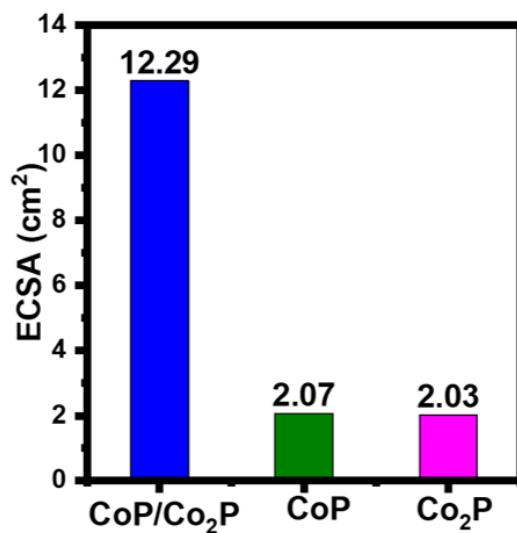


Figure 4.12. Comparison of the calculated ECSA of Synthesized electrocatalysts

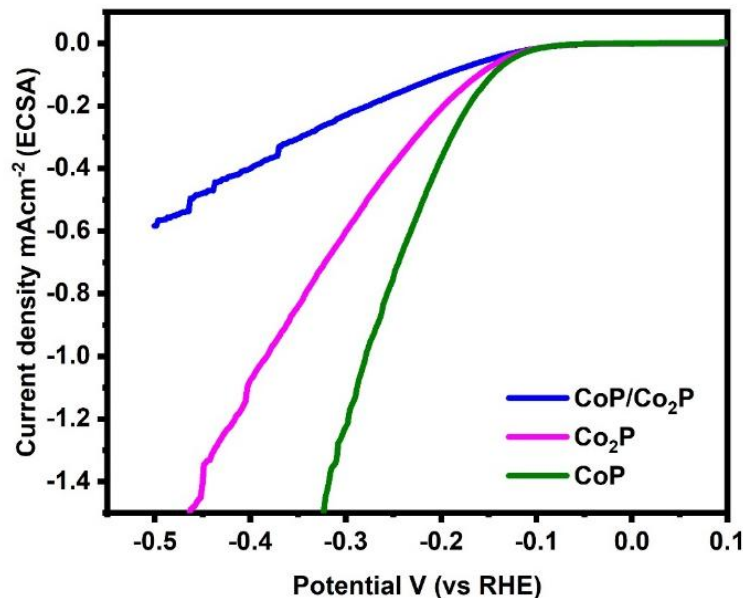


Figure 4.13. LSV polarization curves normalized by the ECSA

To further investigate the kinetics of the hydrogen evolution reaction (HER) on the synthesized CoP, Co₂P, and CoP/Co₂P catalysts, electrochemical impedance spectroscopy (EIS) was conducted at a potential of -150 mV vs. RHE over a frequency range of 100 kHz to 0.1 Hz (Figure 6f). The analysis was based on the equivalent circuit model shown in the inset of Figure 6f, where R_s represents the ohmic resistance arising from the electrolyte and all contacts. In contrast, the constant phase element (CPE) and charge transfer resistance (R_{ct}) correspond to the double-layer capacitance and charge transfer resistance at the electrolyte/electrode interface. These parameters are crucial for evaluating the electrode's kinetic behavior. The Nyquist plots at -150 mV vs. RHE in 0.5 M H₂SO₄ (Figure 4.9f), along with the fitted data presented in Table 4.1, reveal a significantly reduced charge transfer resistance (R_{ct}) for the CoP/Co₂P nanocomposite (44.74 Ω) compared to CoP (111.9 Ω) and Co₂P (255.7 Ω). Generally, a lower R_{ct} value indicates enhanced reaction kinetics [132]. The observed decreasing trend in R_{ct} correlates well with the previously reported catalytic activities from the linear sweep voltammetry (LSV) results (CoP/Co₂P > CoP >

Co₂P), further confirming the superior HER performance of the CoP/Co₂P nanocomposite compared to the other synthesized catalysts.

Table 1. Fitting charge resistance (R) values and constant phase element (CPE) at -150 mV overpotential.

Catalysts	R _s (Ω)	R _{ct} (Ω)	C _{dl} (F)
Co ₂ P	59.19	255.7	6.504×10^{-6}
CoP	55.15	111.9	83.65×10^{-6}
CoP/Co ₂ P	50.27	44.74	0.3892×10^{-3}

To further evaluate the stability of the synthesized CoP, Co₂P, and CoP/Co₂P catalysts - an essential criterion for practical applications - a chronopotentiometry test was conducted in 0.5 M H₂SO₄ at a constant current density of -10 mA cm⁻² over a duration of 25 hours. This assessment provides valuable insights into the catalysts' long-term durability and operational reliability under continuous HER conditions. Figure 4.14a shows the chronopotentiometry curves for all prepared catalysts. It can be seen clearly that all catalysts have shown excellent stability for 25 hours. It was found that, after 25 hours, the overpotential of CoP/Co₂P required to reach a current density of -10 mAcm⁻² was increased only by 5 mV while for CoP NPs it was increased from 192 mV to 205 mV. Whereas for Co₂P NPs, the overpotential was increased from 242 mV to 252 mV. This drop in the overpotential is more likely due to the formation of bubbles that induce the blocking of active sites due to the formation of hydrogen on the surface of the GCE. After conducting the chronopotentiometry test, we again took LSV measurements to further justify our results. The plotted LSV results before and after the chronopotentiometry test are presented in Figure 4.14b. As observed from the LSV curves, the CoP/Co₂P nanocomposite catalyst exhibited negligible change before and after the 25-hour chronopotentiometry test, demonstrating remarkable stability and an excellent life cycle in an acidic environment. In contrast, the LSV curves for CoP Nps and

Co₂P Nps showed a slight decline in potential of approximately -10 mV from their initial values. These results indicate that all cobalt phosphide-based catalysts possess outstanding catalytic stability for HER, with only minor differences in performance.

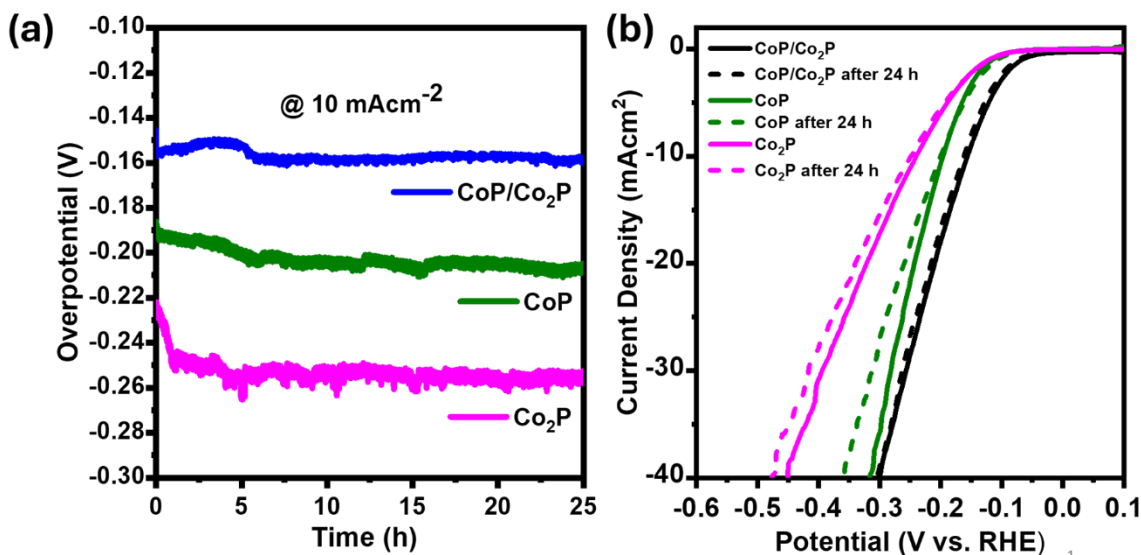


Figure 4.14. (a) Chronopotentiometry (CP) curves of Co₂P, CoP, and CoP/Co₂P (b) Polarization curves of the as-obtained Co₂P, CoP, and CoP/Co₂P catalysts before and after Chronopotentiometry (CP); conditions were performed in 0.5 M H₂SO₄ with scan rate 5 mVs⁻¹.

To further assess the efficiency of synthesized cobalt phosphide-based electrocatalyst, we measured the faradic efficiency (FE) for our best catalyst (CoP/Co₂P). Theoretical gas evolution was calculated using Faraday's law, and the experimental results were analyzed to estimate the Faradaic Efficiency (FE) employing the following formulas:

$$\text{Rate of } H_2 \text{ Evolution } (\mu\text{mol} \cdot s^{-1}) = \frac{P \text{ (atm)} \cdot \text{Flow rate (Ls}^{-1})}{\text{Slope} \cdot R \cdot T}$$

$$\text{Rate of } e \text{ generation } (\mu\text{mol} \cdot s^{-1} \text{cm}^{-2}) = \frac{\text{Current Density (mAcm}^{-2}) \cdot 1000}{n \cdot F \text{ (C mol } e^{-})}$$

The comparison of theoretical moles to experimental moles is calculated. After calculating moles, the following formula was used to calculate Faradic efficiency:

$$\text{FE (\%)} = (n_{\text{experimental}} / n_{\text{theoretical}}) \times 100$$

The FE of HER was determined using a three-electrode electrochemical setup in 0.5 M H₂SO₄. The system included a CoP/Co₂P modified glassy carbon electrode as the working electrode, a saturated Ag/AgCl reference electrode, and a platinum counter electrode. The produced H₂ and O₂ gases were determined using gas chromatography. As illustrated in Figure 4.15, the rate of H₂ evolution closely matches the theoretical rate calculated from the charge passed throughout the working electrode, demonstrating high stability and efficient gas production. The rate of O₂ evolution was also measured and compared with the theoretical rate calculated assuming that the current passing through the working electrode is equivalent to that passing through the counter electrode. Inset Figure 8 showed that the CoP/Co₂P catalyst has a Faradaic efficiency of 95% for the HER over a period of 16 hours, indicating that the majority of the charge was used for the H₂ evolution. These findings highlight the higher catalytic activity and stability of CoP/Co₂P for water reduction.

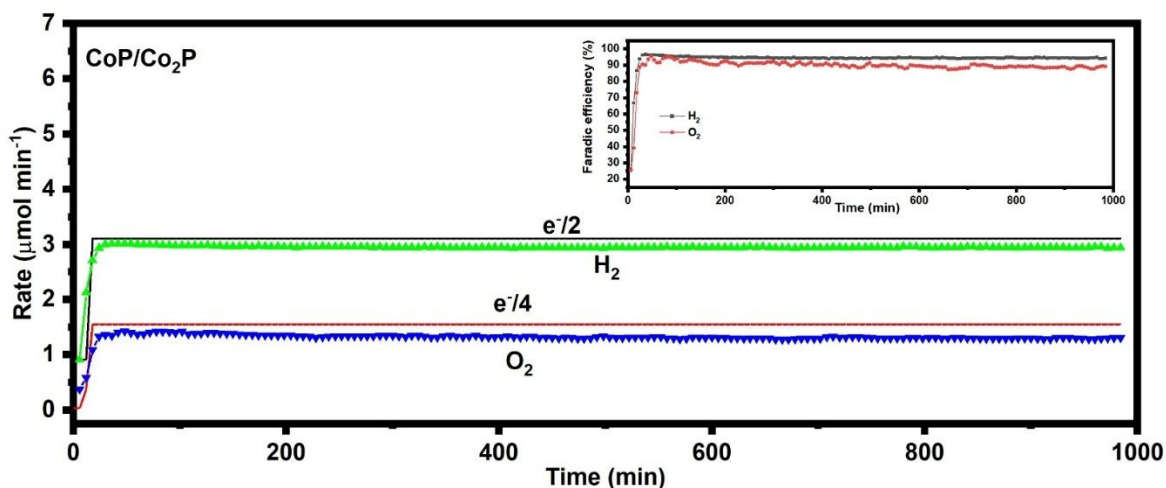


Figure 4.15. Rates of H₂ and O₂ evolution at a current density of 10 mA cm⁻², along with the corresponding theoretical rates. The Inset Figure shows the Faradaic efficiencies.

4.2 Cobalt phosphosulfide (CoPS) electrocatalysts for Hydrogen Evolution Reaction in Alkaline media

X-ray diffraction was employed to investigate the phase evolution of pristine and phosphorus-doped cobalt sulfide nanomaterials, as shown in Figure 4.16(a-f). Figure 4.16(b) demonstrates that the cobalt sulfide sample exhibits distinct peaks at $2\theta \approx 31.3^\circ$, 38.1° , and 55.1° , that can be assigned to (3 1 1), (4 0 0) and (4 4 0) crystal faces confirming the presence of a pure Co₃S₄ phase which is consistent with the reference JCPSC card No. 00-047-1738. Phosphorus doping at 1, 2, and 4 mmol concentrations leads to a progressive shift in diffraction peaks relative to the undoped material, as shown in Figure 4.16(c-e). The consistent peak displacements demonstrate the successful incorporation of phosphorus atoms into the cobalt sulfide lattice, leading to local lattice distortion attributed to the variations in size and electronegativity between sulfur and phosphorus. Despite these changes, the overall pattern closely resembles that of Co₃S₄, indicating that phosphorus doping at these concentrations primarily results in lattice-level substitution rather than

a complete structural transformation. At the maximum phosphorus loading of 6 mmol, the XRD pattern shows a notable change, marked by distinct and sharper peaks. The observed peak shifts indicate the successful formation of a new crystalline phase at high doping concentrations, as shown in Figure 4.16 (f).

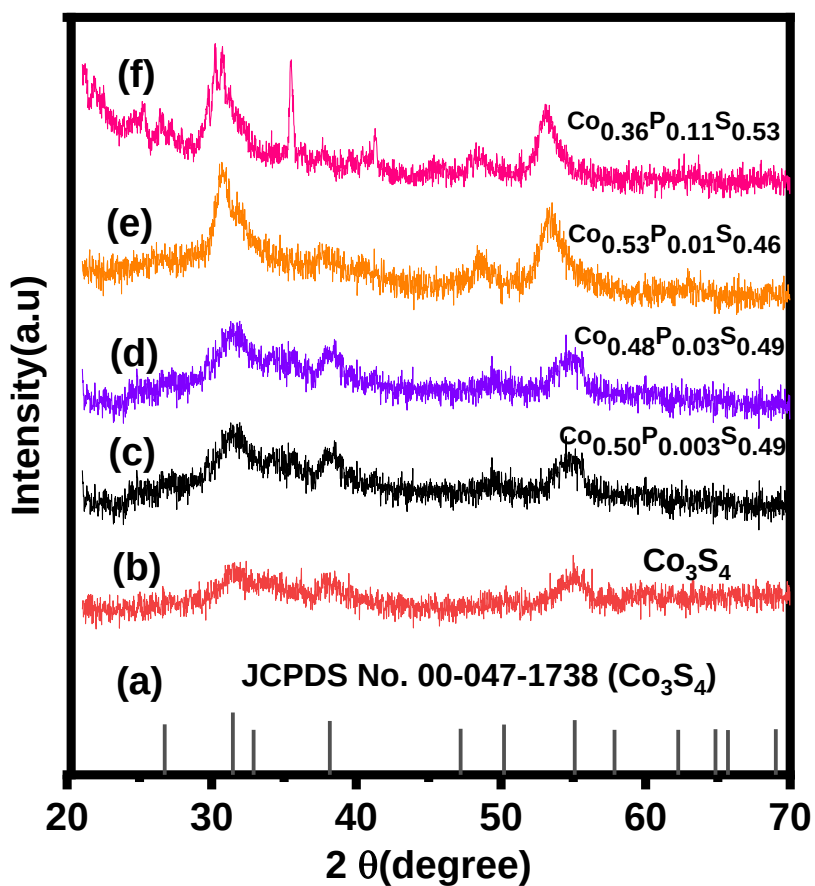


Figure 4.16. (a–f) illustrates the XRD pattern of cobalt sulfide and Cobalt phosphosulfide samples.

As the dopant concentration increases, a significant morphological alteration is observed by the TEM analysis, which is also reflected in the trend of catalytic activity. The TEM image of the pristine cobalt sulfide sample shown in Figure 4.17a indicates the formation of a thin layered structure with a loosely stacked nanosheet shape. These sheets possess exposed active sites and a substantial surface area, which are advantageous for catalytic activities. Introducing one mmol of the dopant resulted in a distinct thickening of the sheets and the emergence of rod-like or platelet structures (Figure 4.17b). Although nanosheet characteristics are largely retained, morphology becomes more compressed, likely reducing surface accessibility. Doping at 2 mmol of phosphorus precursor makes the nanosheets increasingly crumpled and interconnected, forming a porous, web-like architecture (Figure 4.17c). This form is optimal for catalytic activity, providing substantial surface exposure and efficient charge transfer pathways. Indeed, this sample exhibits the highest catalytic activity among the series. Despite increased stacking and localized densification, the nanosheet structure remains distinct with 4 mmol doping (Figure 4.17d). Although it may considerably diminish surface access, this signifies robust activity aligned with its performance. At a concentration of 6 mmol, morphology undergoes a significant transformation. The nanosheet architecture collapses to yield compact, aggregated nanoparticles as shown in Figure 4.17e. The agglomeration leads to diminished catalytic efficacy by significantly reducing the effective surface area and accessibility of active sites. This morphological alteration is followed by additional peaks in the X-ray diffraction (XRD) patterns, suggesting the probable formation of secondary phases or structural transitions at elevated dopant concentrations. Altering the material's electrical configuration or crystallinity may reduce activity through these phase transitions.

To determine the elemental composition of the synthesized catalysts, Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) was conducted on Co_3S_4 and phosphorus-modified

cobalt sulfides (P–CoS) with varying phosphorus precursor concentrations (1, 2, 4, and 6 mmol). The atomic percentages (at%) of cobalt (Co), phosphorus (P), and sulfur (S) are summarized in Table 4.2. Inductively coupled plasma analysis reveals that the Co/P/S ratio of the product is very close to $(\text{Co}_{0.50}\text{P}_{0.003}\text{S}_{0.49})$, $(\text{Co}_{0.48}\text{P}_{0.03}\text{S}_{0.49})$, $(\text{Co}_{0.53}\text{P}_{0.01}\text{S}_{0.46})$, and $(\text{Co}_{0.36}\text{P}_{0.11}\text{S}_{0.53})$ for one mmole, two mmole, four mmole, and 6 mmole of phosphorus precursor, respectively.

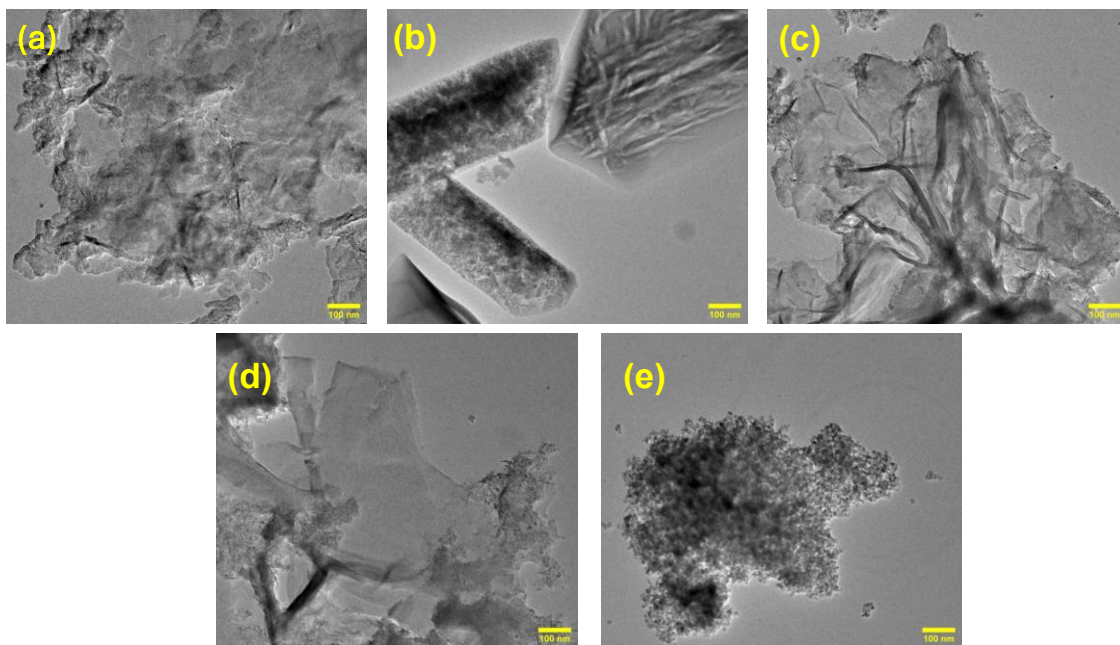


Figure 4.17.(a-e) TEM images of Co_3S_4 , $(\text{Co}_{0.50}\text{P}_{0.003}\text{S}_{0.49})$, $(\text{Co}_{0.48}\text{P}_{0.03}\text{S}_{0.49})$, $(\text{Co}_{0.53}\text{P}_{0.01}\text{S}_{0.46})$ and $(\text{Co}_{0.36}\text{P}_{0.11}\text{S}_{0.53})$

Table 2. ICP-OES elemental Co, P, and S analysis in P–CoS samples.

Co/TPP/1-DDT mole ratio	Co (at.%)	P (at.%)	S (at.%)
1.5/3.75	53.31	-	46.69
1.5/1/3.75	50.37	0.29	49.33
1.5/2/3.75	48.09	3.33	48.58
1.5/4/3.75	52.79	1.21	45.99
1.5/6/3.75	36.19	11.36	52.45

Electrochemical Measurements: The electrocatalytic activity of the prepared catalysts was evaluated in 1M KOH solution. The measurements were performed at ambient temperature with the Autolab PGSTAT302N electrochemical station. The reference electrode in a standard Metrohm three-electrode setup consists of Hg/HgO, the counter electrode was a Pt wire, and the working electrode was carbon paper. The potentials were calibrated relative to a reversible hydrogen electrode (RHE) by applying the equation.

$$E_{\text{RHE}} = E_{\text{applied}} + 0.0591 \text{ pH} + E^{\circ}_{\text{ref}} (0.118\text{V})$$

The experiment consisted of conducting linear sweep voltammetry (LSV) measurements in the voltage range of -0.5 to 0.1 V concerning the reversible hydrogen electrode (RHE), employing a scan rate of 5 mVs⁻¹. Using the same electrochemical workstation and FRA32M, impedance

module the EIS studies were performed, covering a frequency range from 10^5 Hz to 0.01 Hz, with an alternating current (AC) amplitude of 10 mV. The EIS data were standardized by leveling it to the geometric area of the working electrode. The double layer capacitance (C_{dl}) was obtained using cyclic voltammetry (CV) scanning from 0.1 to 0.2 V vs. RHE with different scan rates from 100 to 200 mV s^{-1} . A chronopotentiometry test was performed to check the stability of the catalyst for 24 hours.

The HER activity of the synthesized catalysts was evaluated using linear sweep voltammetry (LSV) and Tafel slope analysis, as presented in Figure 4.18a-d. The progression in catalytic performance was studied from bare carbon paper (CP), pristine Co_3S_4 and cobalt phosphosulfide samples ($\text{Co}_{0.50}\text{P}_{0.003}\text{S}_{0.49}$), ($\text{Co}_{0.48}\text{P}_{0.03}\text{S}_{0.49}$), ($\text{Co}_{0.53}\text{P}_{0.01}\text{S}_{0.46}$), ($\text{Co}_{0.36}\text{P}_{0.11}\text{S}_{0.53}$). As shown in Figure 4.18a-b, the bare CP electrode exhibited minimal HER activity with negligible current density, reflecting its inert nature. Upon deposition of pristine Co_3S_4 , the performance improved considerably, achieving a current density of -10 mA cm^{-2} at an overpotential of 325 mV. Doping with phosphorus further boosted the HER activity. The $\text{Co}_{0.48}\text{P}_{0.03}\text{S}_{0.49}$ sample showed a reduced overpotential of 148 mV, which is 177 mV lower than that of pure Co_3S_4 indicating more favorable reaction kinetics. Similarly, other doped samples $\text{Co}_{0.50}\text{P}_{0.003}\text{S}_{0.49}$ and $\text{Co}_{0.53}\text{P}_{0.01}\text{S}_{0.46}$ have an overpotential of 261 mV, and 233 mV, respectively, which is still lower than pure Co_3S_4 . Finally, the $\text{Co}_{0.36}\text{P}_{0.11}\text{S}_{0.53}$ sample showed the poorest performance among the doped variants, exhibiting a high overpotential of 378 mV and the highest Tafel slope of 210 mV dec^{-1} , indicating sluggish HER kinetics. The trend in HER activity can be rationalized based on structural and electronic considerations introduced by phosphorus doping. Phosphorus doping at lower to moderate concentrations leads to electronic structure modulation of the Co-S matrix, improving electrical conductivity and facilitating better adsorption/desorption of hydrogen intermediates (H^*) [133-

135]. The improved HER performance of $\text{Co}_{0.48}\text{P}_{0.03}\text{S}_{0.49}$, characterized by a high P/S ratio, is attributed to the modulation of the electronic structure by replacing sulfur with the more electron-donating phosphorus, hence promoting the HER process. Furthermore, the progressively generated sulfur vacancies can be dynamically filled by hydrogen atoms owing to the reduced energy barrier, which is crucial in preventing the aggregation of active sites over time, enhancing hydrogen evolution reaction (HER) activities [136-138].

At higher phosphorus content, however, the formation of agglomerated structures and possible phase changes suggested by additional peaks in XRD patterns can impair the accessibility of active sites and hinder electron transport. This structural deterioration leads to a significant drop in catalytic efficiency.

The inherent HER activity of the catalyst was assessed using reaction kinetics, illustrated by Tafel plots as shown in Figure 4.18c-d. $\text{Co}_{0.48}\text{P}_{0.03}\text{S}_{0.49}$ had the lowest Tafel slope of 95 mV dec^{-1} among the evaluated samples, surpassing $\text{Co}_{0.50}\text{P}_{0.003}\text{S}_{0.49}$ (137 mV dec^{-1}), $\text{Co}_{0.53}\text{P}_{0.01}\text{S}_{0.46}$ (121 mV dec^{-1}), $\text{Co}_{0.36}\text{P}_{0.11}\text{S}_{0.53}$ (210 mV dec^{-1}), and pure Co_3S_4 (147 mV dec^{-1}), as illustrated in Fig. 4(c). In alkaline conditions, the hydrogen evolution reaction (HER) generally occurs through three primary stages: (1) electrochemical adsorption of protons onto the catalyst surface (Volmer step), (2) electrochemical desorption of adsorbed hydrogen atoms (Heyrovsky step), and (3) chemical desorption through recombination to produce hydrogen gas (Tafel step). Co_3S_4 initially exhibited a high Tafel slope of 147 mV dec^{-1} , indicating that the Volmer step, which involves the electrochemical adsorption of hydrogen ($\text{H}^+ + \text{e}^- \rightarrow \text{H}_{\text{ads}}$), is the rate-determining step (RDS) during HER. This steep slope reflects sluggish reaction kinetics and significant energy barriers associated with the initial proton-electron transfer. After phosphorus (P) doping, the Tafel slope decreased notably to 95 mV dec^{-1} , suggesting an improvement in the HER kinetics. The

incorporation of phosphorus likely enhanced the electrical conductivity and modified the electronic structure of CoS, resulting in a more favorable hydrogen adsorption energy. Despite this improvement, the Volmer step is still the RDS, although with reduced kinetic limitations. This demonstrates that P doping effectively accelerates the HER process by lowering the activation energy of the initial adsorption step without changing the fundamental reaction pathway [139-141].

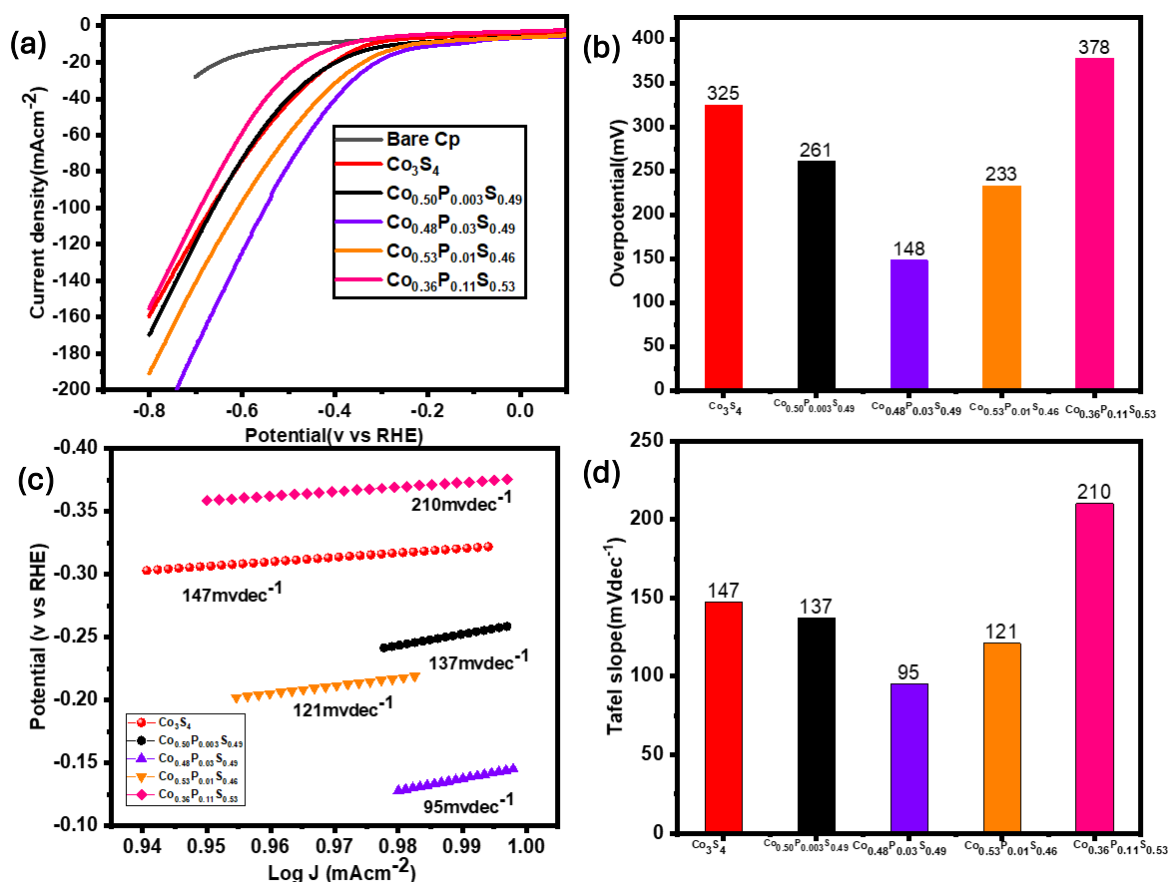


Figure 4.18. The electrochemical performance of Co₃S₄ and CoPS (Co_{0.50}P_{0.003}S_{0.49}), (Co_{0.48}P_{0.03}S_{0.49}), (Co_{0.53}P_{0.01}S_{0.46}), (Co_{0.36}P_{0.11}S_{0.53}) and bare carbon paper: (a) LSV curves (without IR correction) recorded in 1 M KOH solution at a scan rate of 5 mV s⁻¹, (b) Comparison of overpotentials at a current density of 10 mA cm⁻², and (c) Corresponding Tafel plots with linear fittings (d) Comparison of Tafel slopes of all catalysts.

Electrochemical impedance spectroscopy (EIS) was further employed to complement the LSV and Tafel analyses and provide deeper insight into the interfacial charge-transfer behavior of Co₃S₄ and phosphorus-doped CoPS catalysts. As shown in the Nyquist plots (Figure 4.19a), R_{ct} represents the charge-transfer resistance, which reflects the ease of electron transfer at the electrode–electrolyte interface and has close relation with HER activity [142]. The bare Co₃S₄ sample exhibited the largest semicircle, corresponding to a high R_{ct} value of approximately 199 Ω , indicative of poor charge-transfer kinetics and limited catalytic efficiency. With phosphorus incorporation, a progressive reduction in R_{ct} was observed [142, 143]. Among the various P-doped samples Co_{0.48}P_{0.03}S_{0.49} demonstrated significantly reduced R_{ct} value 47.8 Ω , which is lower than all other doped samples Co_{0.50}P_{0.003}S_{0.49} (137 Ω), Co_{0.53}P_{0.01}S_{0.46} (55 Ω), Co_{0.36}P_{0.11}S_{0.53} (229 Ω) respectively as compared in 4.19b, suggesting enhanced conductivity and accelerated electron transport for Co_{0.48}P_{0.03}S_{0.49} that are in excellent agreement with its superior HER performance in the LSV and Tafel slope data. The EIS data confirms moderate phosphorus doping effectively promotes charge-transfer processes and improves catalytic behavior. These EIS results further validate the earlier electrochemical trends, emphasizing that controlled phosphorus doping enhances HER activity by improving electrical conductivity and charge-transfer efficiency. In contrast, over-doping can be detrimental to catalytic performance.

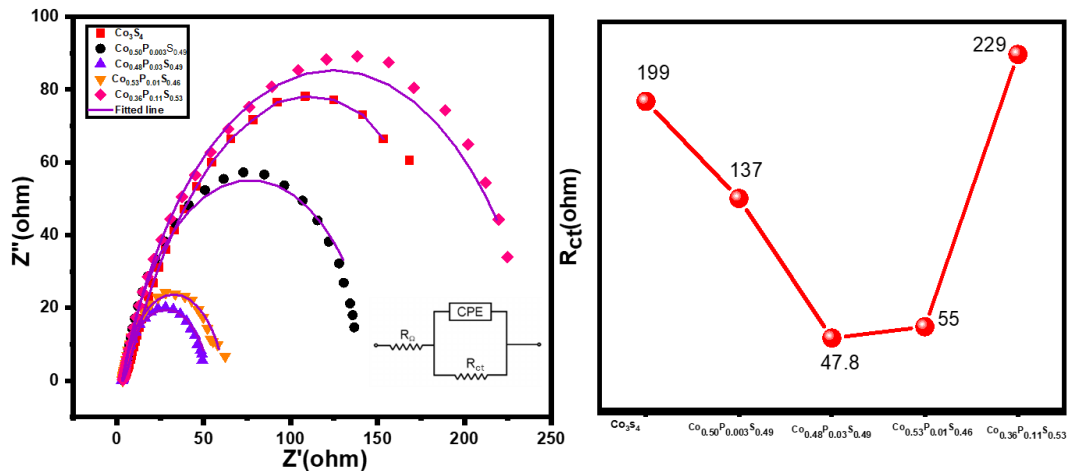


Figure 4.19. (a) Nyquist plots of these catalysts measured at 0.2 V vs. RHE (b) Comparison of Charge transfer resistance of all catalysts

To better understand the HER performance of the synthesized catalysts, a systematic investigation was conducted by examining their double-layer capacitance (C_{dl}), electrochemically active surface area (ECSA), and intrinsic activity normalized to ECSA. The results are summarized in Figures 4.20 and 4.21. In electrochemical systems, the double-layer capacitance (C_{dl}) is often used as a proxy to estimate the electrochemically active surface area (ECSA), which reflects how many catalytic sites are accessible for the reaction [144, 145]. Cyclic voltammetry (CV) was performed in a non-faradaic potential region, where no redox reactions occur. This allows for measuring only the capacitive current (i.e., due to the electrical double layer at the electrode–electrolyte interface). CV scans were recorded at various scan rates (e.g., 100–200 mV/s as shown in Figure 4.20(a-e)). The current density difference ($\Delta j = j_a - j_c$) was plotted against the scan rate for each catalyst. The slope of the resulting linear fit corresponds to (C_{dl}) as shown in Figure 4.21a. A higher (C_{dl}) indicates a larger surface area accessible to the electrolyte, implying more active catalytic sites. Among the catalysts, $Co_{0.48}P_{0.03}S_{0.49}$ highest C_{dl} , suggesting it has the largest electrochemically active surface as shown in figure 4.21b. Using the relation:

$$ECSA = C_{dl}/C_s \cdot A$$

where C_s is the specific capacitance of a flat surface (typically $\sim 0.04 \text{ mF cm}^{-2}$ for metal oxides or sulfides in acidic media)[129], the ECSA values were calculated and compared $\text{Co}_{0.48}\text{P}_{0.03}\text{S}_{0.49}$ displays the highest ECSA among the samples, followed closely by $(\text{Co}_{0.53}\text{P}_{0.01}\text{S}_{0.46})$. The parent compound Co_3S_4 , $(\text{Co}_{0.50}\text{P}_{0.003}\text{S}_{0.49})$, and $\text{Co}_{0.36}\text{P}_{0.11}\text{S}_{0.53}$ has shown significantly lower ECSA. This indicates that phosphorus doping (especially at the 2 mmol level) effectively increases surface roughness or introduces porosity, thus exposing more catalytic sites as shown in Figure 4.21c.

The goal here is to determine intrinsic catalytic activity, independent of how large or small the surface area is. This is crucial for distinguishing whether a material performs well because of more active sites or because each site is intrinsically better at catalyzing HER. The original linear sweep voltammetry (LSV) data (current density vs. potential) were divided by the ECSA of each catalyst, so the resulting plot reflects current density per unit ECSA. This means we are now comparing how efficient each square centimeter of catalyst surface is, regardless of total surface area. Even after normalization, $\text{Co}_{0.48}\text{P}_{0.03}\text{S}_{0.49}$ outperforms Co_3S_4 as shown in Figure 4.21d. This indicates that the phosphorus-doped material is larger in surface area and has higher intrinsic activity at each site. Therefore, the enhancement in HER activity is not solely due to surface effects but also due to favorable electronic and structural modifications induced by phosphorus incorporation.

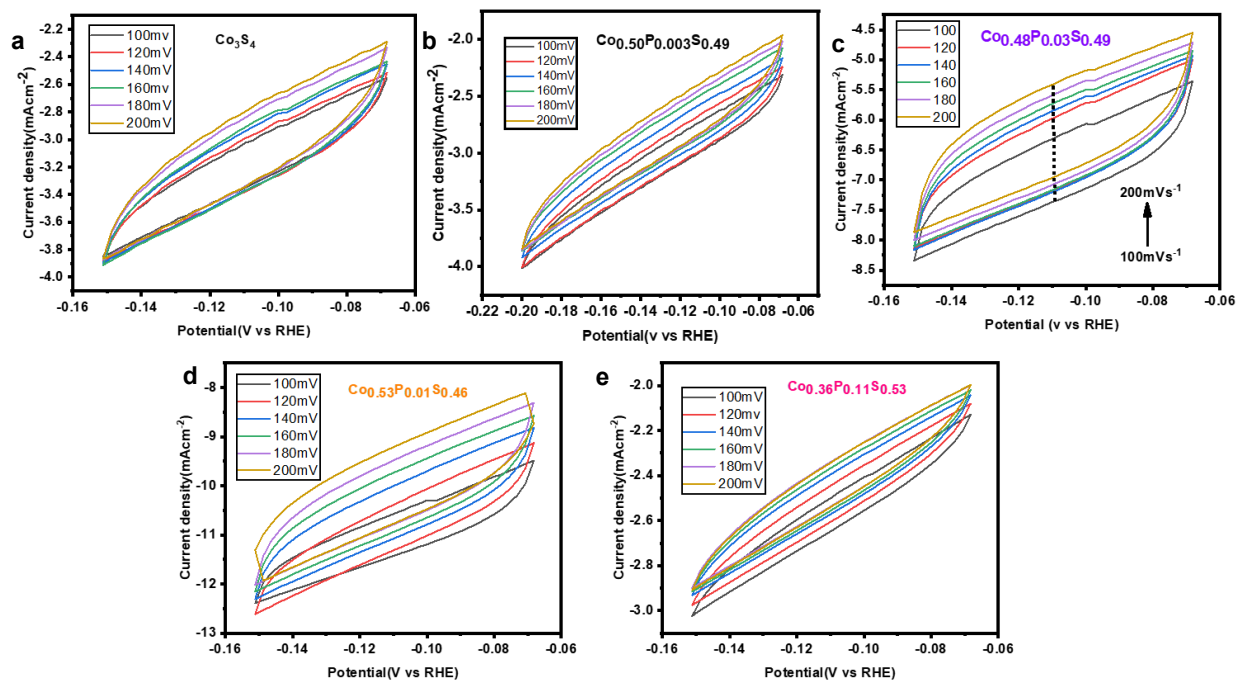


Figure 4.20. (a-e) Cyclic voltammetry curves of Co_3S_4 and CoPS ($\text{Co}_{0.50}\text{P}_{0.003}\text{S}_{0.49}$), ($\text{Co}_{0.48}\text{P}_{0.03}\text{S}_{0.49}$), ($\text{Co}_{0.53}\text{P}_{0.01}\text{S}_{0.46}$), ($\text{Co}_{0.36}\text{P}_{0.11}\text{S}_{0.53}$) at varying scan rates.

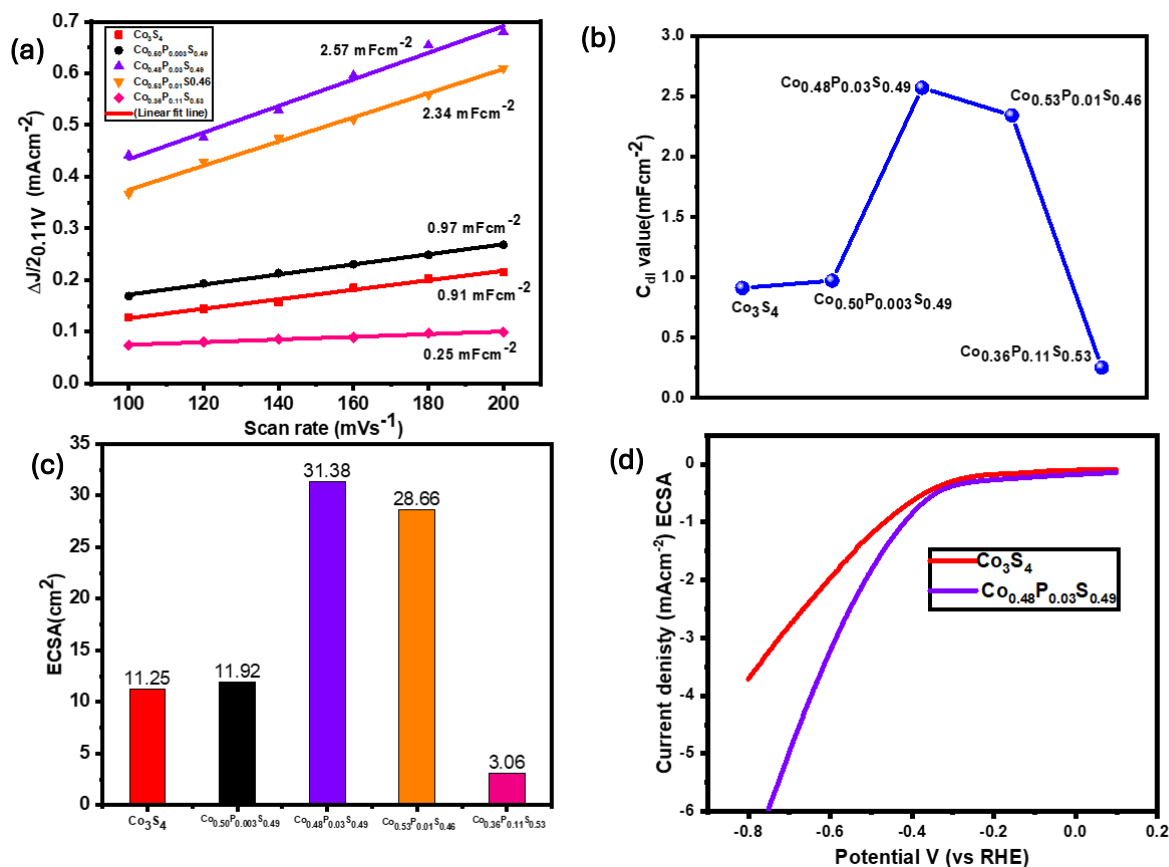


Figure 4.21. Fitting of the capacitive current density versus scan rate for Co₃S₄, CoPS (Co_{0.50}P_{0.003}S_{0.49}), (Co_{0.48}P_{0.03}S_{0.49}), (Co_{0.53}P_{0.01}S_{0.46}), (Co_{0.36}P_{0.11}S_{0.53}) to estimate the double-layer capacitance (C_{dl}). (b) Comparison of measured C_{dl} values (c) Electrochemically active surface area (ECSA) of all catalysts, calculated from their respective C_{dl} values. (d) ECSA-normalized linear sweep voltammetry (LSV) curves of Co₃S₄ and (Co_{0.48}P_{0.03}S_{0.49}), highlighting intrinsic catalytic activity for HER in 1 M KOH

This study conducted a chronopotentiometry test using the optimized **Co_{0.48}P_{0.03}S_{0.49}** in 1 M KOH to evaluate its long-term electrochemical stability and degradation behavior. During the test, a stable potential of 148 mV was consistently maintained at a constant current of 10 mA cm⁻², indicating excellent catalytic durability with minimal performance loss over time as shown in figure 4.22. Using the optimized catalyst formulation in an alkaline medium further demonstrates its robustness and sustained activity. These results confirm the reliability and long-term

applicability of the CoPS catalyst, supporting its potential for use in both industrial and research environments

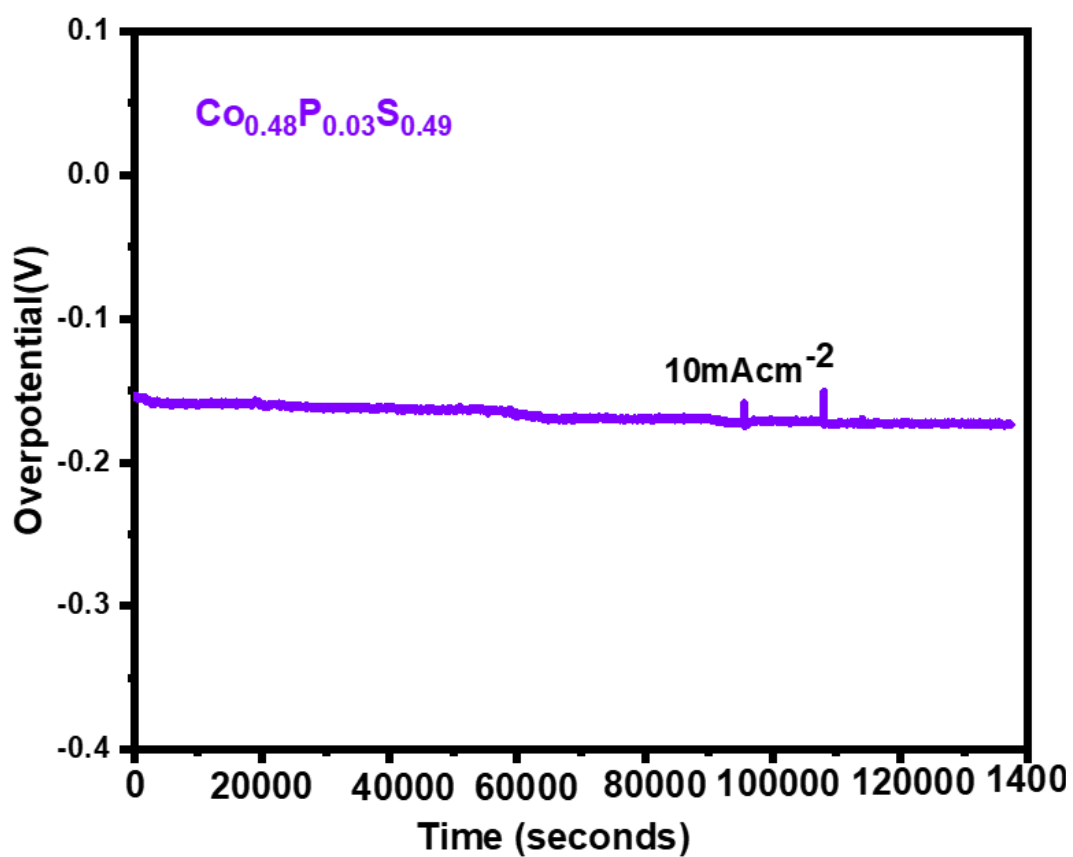


Figure 4.22. Chronopotentiometry (CP) curve of $\text{Co}_{0.48}\text{P}_{0.03}\text{S}_{0.49}$, at 10 mAcm^{-2} Current density

CHAPTER 5

CONCLUSION

In this thesis, we presented a systematic investigation into the synthesis of cobalt phosphide nanoparticles with varied phases, compositions, and morphologies, along with evaluating their electrocatalytic performance for the hydrogen evolution reaction (HER) in an acidic medium. By modulating key synthesis parameters—specifically, the mole ratio of trioctylphosphine (TOP) to cobalt acetate and the thermal decomposition temperature—pure CoP, Co₂P, and a CoP/Co₂P composite were successfully synthesized. The Kirkendall effect best describes the formation mechanism of these materials. Initially, cobalt metal nanoparticles capped with TOP form at 220 °C; subsequently, at 300 °C and above, the P–C bonds in TOP decompose, releasing phosphorus atoms that diffuse into the cobalt nanoclusters. Due to differing diffusion rates—outward for cobalt atoms and inward for phosphorus atoms—cobalt phosphides with distinct structures and morphologies are produced. Specifically, pseudospherical hollow Co₂P NPs with a hexagonal crystal structure, solid CoP NPs with an orthorhombic crystal structure, and dendritic CoP/Co₂P NCs were obtained. The synthesized materials' geometric and intrinsic HER activities were evaluated in 0.5 M H₂SO₄ to establish correlations between phase structure and catalytic performance. The results revealed that Co₂P nanoparticles achieved a geometric cathodic current density of 10 mA cm⁻² at an overpotential of 242 mV. In contrast, CoP nanoparticles required only 192 mV to reach the same current density. The CoP/Co₂P nanocomposite exhibited superior performance, achieving 10 mA cm⁻² at a significantly lower overpotential of 152 mV. While the CoP phase displayed higher intrinsic activity than Co₂P, consistent with its better geometric HER

performance, the CoP/Co₂P composite, despite having the highest geometric activity, showed the lowest intrinsic activity among the three. This indicates that the composite's enhanced overall performance is primarily due to its significantly increased ECSA, attributed to its unique dendritic nanostructure and high density of accessible active sites. Furthermore, upon interfacial contact between CoP and Co₂P in the nanocomposite, electron transfer from CoP to Co₂P is thermodynamically favorable due to their differing work functions. This electronic redistribution increases the nucleophilicity of Co₂P, facilitating H₃O⁺ ion adsorption and promoting the formation of additional active sites. Although this synergistic mechanism effectively enhances the geometric HER activity of the composite, CoP alone still exhibits the highest activity per catalytic site. These findings demonstrate that CoP is a viable candidate for HER catalysis, while the CoP/Co₂P composite benefits from synergistic effects and morphological advantages that further enhance its electrocatalytic performance.

We also explored the cobalt phosphosulfide nanosheets for HER in alkaline media using the same synthesis method. We have successfully synthesized different P-doped cobalt sulfide samples. The synthesized catalysts were characterized using XRD, TEM and ICP, confirming successful incorporation of P into Co-S Structure and revealing nanosheet structure for synthesized CoPS. We also investigated their electrochemical performance in 1M KOH using a three-electrode cell. The observed results indicated that Co_{0.48}P_{0.03}S_{0.49} electrocatalyst has shown excellent electrocatalytic performance among all doped sample and demonstrated excellent stability in alkaline media. We explored that the enhanced performance of the Co_{0.48}P_{0.03}S_{0.49} catalyst is attributed to the following main reasons. (1) Phosphorus doping at lower to moderate concentrations leads to electronic structure modulation of the Co-S matrix, improving electrical conductivity and facilitating better adsorption/desorption of hydrogen intermediates (H*); (2)

Substitution of (S) with (P), which is more electron-donating than sulfur, tends to push more electron density toward nearby cobalt. This change in electron distribution modifies the electronic structure of the catalyst; (3) When (P) replaces (S) in the lattice, it causes lattice strain (because P is greater than S) and electronic imbalance. This makes the nearby sulfur atoms less tightly bound and makes it easier to leave the lattice, creating S vacancies; and (4) Filling vacancies with H^+ stabilizes the surface and prevents the catalyst from degrading, keeping the active sites well-distributed and effective. So all these factors contributed to an overall increase in the HER performance of cobalt phosphosulfide.

By developing cobalt phosphide and phosphorus-doped cobalt sulfide catalysts, this work successfully enhances catalytic performance in both acidic and alkaline media. The former showed promising activity under acidic conditions, while the latter exhibited excellent stability and efficiency in alkaline environments. These results highlight the practical potential of these materials for real-world hydrogen production and sustainable energy technologies. |

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Research Interests: Electrocatalysis, Water Splitting, Energy Storage, and Production

Publications

1. **Jahangir, T. N.;** Kandiel, T. A.; Fatima, W.; Abdalmawla, A. M.; Ahmed, A. A.; Ahmed, Y.A. Insights into the Role of Co₃O₄/Ti₃C₂ MXene Hybrid Material in Photoelectrochemical Water Oxidation over BiVO₄ Photoanode, **Elsevier: Journal of Environmental Chemical Engineering**, 113058 (2024) DOI: 10.1016/j.jece.2024.113058
2. Unveiling the Phase-Dependent Electrocatalytic Activity of Cobalt Phosphide Nanoparticles for Hydrogen Evolution Reaction. Authors: **Fatima, Wajiha ;** Alhakemy, Ahmed; Al-Betar, Abdul-Rahman; Kandiel, Tarek
Manuscript Status: under review

3. Cobalt phosphosulfide nanosheets with tailored electronic properties for enhanced hydrogen evolution performance in alkaline media. Authors: **Fatima, Wajiha, Kandiel, Tarek (in preparation)**

Conferences:

1:Exploring Phase specific electrocatalytic behavior of cobalt phosphide for Hydrogen Evolution Reaction, Comparative analysis of Nanostructured phases synthesized via a thermal decomposition method .(**ACS Qatar RCS Regional MENA Conference**)

2: Unveiling the Phase-Dependent Electrocatalytic Activity of Cobalt Phosphide Nanoparticles for Hydrogen Evolution Reaction (**33rd Annual Saudi Japan Symposium**)