

**Design and Development of Droplet-Assisted
Electrocatalytic System for Selective Electro-Organic
Reactions**

BY

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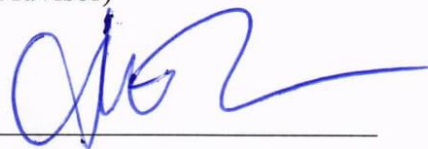


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[This thesis is dedicated to my family for their continuous support and prayers through my journey]

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LIST OF ABBREVIATIONS

°C	: Degree Celsius
μL	: Microliter
CV	: Cyclic voltammetry
EDX	: Energy Dispersive X-ray Spectroscopy
eV	: Electron Volt
FESEM	: Field emission scanning electron microscope
FTIR	: Fourier transform infra-red
GF	: Graphite felt
LSV	: Linear Sweep Voltammetry
TEM	: Transmission Electron Microscopy
XRD	: X-ray powder diffraction
XPS	: X-ray Photoelectrons Spectroscopy
V	: Volt
g	: Gram
s	: Second
mA	: milliamperes

min : Minute (s)

mL : Milliliter

NiF : Nickel foam

UV : Ultraviolet

η : Overpotential

|

ABSTRACT

Full Name : [MOHAMMED ALTAHIR IBRAHIM SULIMAN]

Thesis Title : [Design and Development of Droplet-Assisted Electrocatalytic System for Selective Electro-Organic Reactions]

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Selective electro-organic reactions using electrospray are an emerging research area. At applied potential through droplet chemistry, various selective organic reactions can be achieved on a miniaturized scale. The advanced electrochemical reaction processes are an alternative and advanced technique used for selective oxidation of organic compounds. In this process, the reactions were initiated by electron-transfer reactions that generate radicals via externally applied potentials. This method allows synthesizing the key value-added product under milder reaction conditions, unlike conventional reaction synthesis. However, there are several significant challenges for electrochemical reactions (i) relatively slow kinetics of the processes that require longer processing time, and (ii) the lower selectivity of the catalyst.

A droplet flows electrochemical reactor was investigated for the investigation of the proposed reactions. Recent trends show that droplet chemistry has numerous advantages to speed up the reaction kinetics and for high throughput application. In this work, several composite nanomaterials were functionalized on porous materials. The active catalysts CoB with iron oxide and graphitic carbon nitride was synthesized using sol-gel chemistry. A droplet flow assisted was investigated mechanism to enhance the electrocatalytic oxidation of benzyl alcohol, 2-phenoxyethanol, and hydroxymethylfurfural at room

temperature. The sol-gel coated electrode was characterized using TEM, SEM, EDS, XPS, and XRD spectroscopy, as well as the mechanical stability of the electrodes, which includes roughness and hardness measurements.

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ملخص الرسالة

الاسم الكامل: محمد الطاهر إبراهيم سليمان

عنوان الرسالة: تصميم وتطوير نظام التحفيز الكهربائي بمساعدة القطرات من أجل التفاعلات الكهروضوئية الانتقائية

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تعد التفاعلات الكهروضوئية الانتقائية باستخدام الرش الكهربائي مجال بحث ناشئ. في الإمكانيات المطبقة من خلال كيمياء القطيرات، يمكن تحقيق تفاعلات عضوية انتقائية متنوعة على نطاق مصغر. ان عمليات التفاعل الكهروكيميائية المتقدمة هي تقنية بديلة ومتقدمة تستخدم للأكسدة الانتقائية للمركبات العضوية. في هذه العملية، بدأت التفاعلات عن طريق تفاعلات نقل الإلكترون التي تولد الجذور عبر الإمكانيات المطبقة خارجيا. تسمح هذه الطريقة بتوليف المنتج ذي القيمة المضافة الرئيسية في ظل ظروف تفاعل أكثر اعتدالا، على عكس توليف التفاعل التقليدي. ومع ذلك، هناك العديد من التحديات المهمة للتفاعلات الكهروكيميائية (1) الحركية البطيئة نسبيا للعمليات التي تتطلب وقت معالجة أطول، و (2) الانتقائية الأقل للمحفز.

تم فحص مفاعل كهروكيميائي يتدفق قطيرات للتحقيق في التفاعلات المقترحة. تظهر الاتجاهات الحديثة أن كيمياء القطرات لها مزايا عديدة لتسريع حركية التفاعل ولتطبيق الإنتاجية العالية. في هذا العمل، تم توظيف العديد من المواد النانوية المركبة على مواد مسامية. تم تصنيع المحفزات الفعالة CoB مع أكسيد الحديد ونيتريد الكربون الغرافيتي باستخدام كيمياء هلام محلول غرواني. تم فحص آلية تدفق القطرات المساعدة لتعزيز أكسدة التحفيز الكهربائي لكحول البنزيل، 2-فينوكسي إيثانول، وهيدروكسي ميثيل فورفورال في درجة حرارة الغرفة. تم تمييز القطب الكهربائي المطلي بـ sol-gel باستخدام التحليل الطيفي TEM ومجهر إلكتروني ماسح ومطيافية تشتت الطاقة بالأشعة السينية ومطيافية الأشعة السينية بالإلكترونات الضوئي ودراسة البلورات بالأشعة السينية، بالإضافة إلى الاستقرار الميكانيكي للأقطاب الكهربائية، والذي يتضمن قياسات الخشونة والصلابة.

CHAPTER 1

INTRODUCTION

Introduction

1.1 History and introduction of organic electrochemistry

Alessandro Volta established the first electric battery using zinc and copper electrodes in the year 1800, which is regarded as the first electrochemical cell [1]. After studying the disintegration of water into hydrogen and oxygen in the same year, William Nicholson and Anthony Carlisle identified electrolysis as a chemical process. However, the first organic electrosynthesis experiments date back to the mid-nineteenth century, when Faraday reported the formation of carbon dioxide and a hydrocarbon after the electrolysis of potassium acetate [2]. The field's long history is packed with fascinating and enabling discoveries. The legendary Kolbe electrolysis (1847) is one of the first C-C bond formation reactions [3]; the Tafel rearrangement is a potent way to access different hydrocarbons [3]. Between the 1940s and the 1960s, the Monsanto adiponitrile reaction [4] and the Simons fluorination reaction [5] demonstrated electrolysis' inherent capacity to perform difficult chemical transformations in scalable patterns. In the 1970s and 1980s, the uses of electrogenerated acids/bases [6][7] and chiral electrodes [8] opened up new horizons in organic chemistry that are worth exploring. The development of mediators alleviated issues related to heterogeneous electron transmission at electrode surfaces, such as kinetic barriers and electrode passivation.

Current social media reveals a growing knowledge of 21st-century concerns. Discussions concerning climate change, the constraints of fossil fuels and finite resources, and the need for significant changes are gradually getting popular, accompanied by increased news of worldwide catastrophic disasters [9]. Such concerns have previously been noticed by the scientific community, which has been reviewing chemical synthesis and seeking to build sustainable procedures to contribute to the reduction of carbon emissions [9].

Electro-organic synthesis is one of the numerous innovative processes that is steadily growing. Because the most fundamental forces in chemistry are the electrostatic interactions between electrons and nuclei, electrochemistry is one of the most direct and near methods for chemists to deal with molecules [10]. Electrochemistry is redox chemistry, as it involves the addition or removal of electrons from such interactions by the direct application of an electrical potential. After being pushed aside for several decades, this essentially sustainable methodology has re-emerged for synthetic organic chemists, despite the fact that it was already frequently adapted for inorganic conversions such as industrial-scale basic chemical production using the Hall–Héroult process for chloralkali electrolysis and aluminum production [10]. Batch electrochemistry [11], photo-electrocatalysis [12], metallo-electrocatalysis [13], organo-electrocatalysis [14], and other techniques are used for electrochemical synthesis transformations. All electrochemical processes are based on simple electron transport from the electrode to the substrate or vice versa, which reduces the usage of expensive chemicals while increasing efficacy and productivity. The electron transport from the electrode to the substrate can occur in three different ways (see Fig. 1) [15].

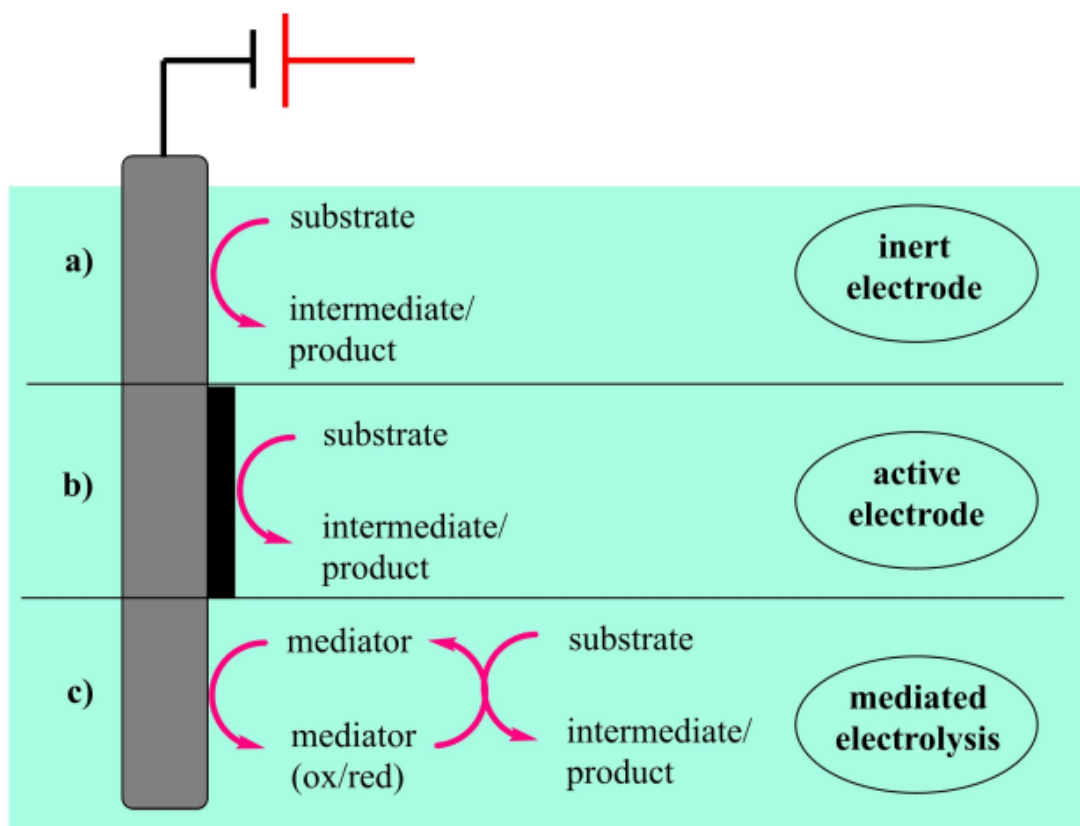


Figure 1: Electrode operation modes in electro synthetic applications.

The addition or removal of electrons in an electrochemical reaction activates the molecules. In a simple electrolysis cell, a solid anode (positive) and cathode (negative) are immersed in a solution comprising the substrate and a supporting electrolyte to transport current through the cell. To complete the circuit, an electrical current, measured in amperes, flows through the solution from the cathode to the anode (Fig. 2). The substrate might be oxidized (electrified) at the anode or reduced at the cathode (gaining electrons). Because this activity occurs at the electrode's surface, it is a heterogeneous process. The electrode that causes the desired response is known as the "working" electrode, while the other is known as the "counter" or "auxiliary" electrode [16]. The species that are electrically charged are known as radicals.

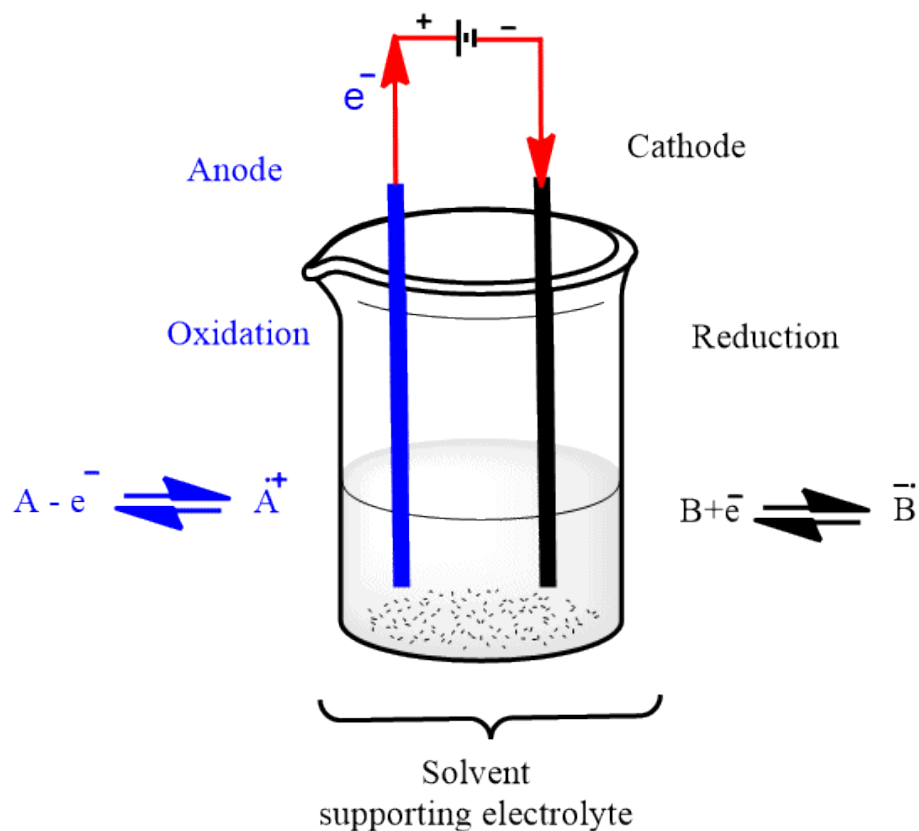


Figure 2: Electrolysis cell

1.2 Methods of electrolysis

In electrochemistry, the quantity of electricity consumed in a process may be regulated in two ways: constant current or constant potential.

1.2.1 Controlled potential electrosynthesis

Constant potential electrosynthesis is less common than constant current electrolysis. However, with a constant potential, better selectivity or mechanistic details can be acquired. When doing constant potential electrolysis, the oxidation or reduction potential of the

substrate of interest must be known ahead of time, therefore it must be measured before the reaction is carried out [16]. This way, the reactivity may be regulated. For example, if a substrate that has been oxidized or reduced can be subjected to additional oxidation or reduction, the voltage applied can be used to control whether or not this second transformation occurs. The same idea may be applied to molecules having two or more functional groups that are prone to reacting; precisely controlling the potential can regulate the desired reaction. Constant potential electrolysis necessitates the use of a third electrode, known as the reference electrode. The current is passed through the working and counter electrodes in this three-electrode setup, while the potential is measured with respect to the reference electrode, which is currentless. This reference electrode can be omitted in some cases.

1.2.2 Controlled current electrosynthesis

The current is kept constant in controlled current electrosynthesis, but the voltage varies to retain the current at the required constant value. Because there is no feedback from the reference electrode to the power source, this approach is more often utilized because the electrolytic system and instruments are simpler than in controlled potential electrolysis. Product selectivity may occasionally be regulated in this type of setup by varying the current density (amperes per square decimeter) and the quantity of power delivered through the cell.

Electrocatalytic synthesis is recognized as an environmental friendly methodology for oxidation and the reduction of organic compounds, since highly reactive and toxic redox reagents are replaced by electric current, and the overall energy is reduced [17] [18], While the electrochemical step is normally only one part of a multi-step sequence, it is a key process

for a variety of reactive intermediates to be produced. It also provides a means by which unstable or hazardous reagents can be produced in situ and allows for mild conditions.

1.3 Organic electrochemistry in a continuous flow

Flow electrochemistry is described as a well-established methodology in the synthetic organic laboratory, with numerous advantages over other conventional batch electrochemistry, including a short residence time, an extremely high electrode surface-to-reactor volume ratio, and no or low concentration of supporting electrolyte, and easier scale-up. When compared to traditional cells, the electrode gap in flow electrochemical reactors is very tiny, often less than 500 μm , which reduces ohmic resistance and eliminates the existence of high current gradients, resulting in a uniform current distribution.

The use of electrochemical flow [19], [20] which often has a small gap separating the electrodes, can eliminate some of the drawbacks of traditional electrosynthesis [21]. As a result, lower supporting electrolyte concentrations are achievable, or possibly the absence of an external supporting electrolyte completely. A variety of microfluidic electrochemical cells have been successfully developed [22]–[25].

Organic electrochemistry thus also provides interesting and useful alternatives to traditional chemical approaches and is a useful tool for the organic chemist. With numerous laboratory-scale applications in addition to several industrial applications, organic electrosynthesis can be considered a very flexible and mature field of organic synthesis. This methodology offers some clear advantages over alternative methods [26], such as reaction selectivity, which can be adjusted by the type of the electrode, the potential applied at the working electrode, or the composition of the electrolyte utilized. The degree of change of a molecule can also be

regulated, such as in classical organic chemistry, by modulating electron consumption. In general, the reaction conditions for an electrochemical transition are classified as mild since they are normally conducted at atmospheric pressure and ambient temperature. However, electrosynthesis has several limitations. Because the reaction only occurs at the electrode surface, the region for electron transport is restricted. The scale-up can also be troublesome, since controlling a big cell might be more difficult and cause overheating issues owing to the increasing electrical consumption.

CHAPTER 2

LITERATURE REVIEW

2.1 Electrosynthesis

Synthesis of organic compounds using applied potential in presence of light in continuous flow microreactors is considered an efficient and alternative approach to conventional organic synthesis. There is growing interest in flow-assisted synthesis due to its simplicity [27]. The microreactors offer many advantages, for example, the reaction kinetics increases with high heat- and mass-transfer ratios, with inherent safety. Only small quantities of reagents are used in flow channels thus the capillary microreactors are suitable for highly exothermic, explosive, or toxic reactions. The reaction products are controlled using over residence (reaction) time. Recently, several researchers demonstrated that flow-assisted capillary flow reactors can be used in large-scale reactions. By connecting several devices in parallel mode, reaction yield will be increased due to the high surface-to-volume ratio, this enables automation. Additionally, the microreactors allow the integration of several reaction steps, which help to study the reaction engineering of the process in a shorter time compared to traditional batch processes.

Recently, advanced oxidation processes (AOP) were used to obtain an alternative pathway to produce fine chemicals. AOP depends on electrochemical techniques, and it is also called the electrochemical advanced oxidation reaction (EOR). These techniques depend on the production of oxidizing agents, such as hydroxyl radical ($\bullet$ OH). EOR involves anodic

oxidation and photoelectron catalyzed processes as a heterogeneous method, in which adsorbed hydroxyl radicals ($\bullet\text{OH}$) are generated at the anode surface (M) via electrochemical or photochemical processes.

On other hand, a homogeneous method like electro-Fenton, and photo-electro-Fenton, in which adsorbed hydroxyl radicals are produced in a bulk solution [28]. The electrochemical oxidation process has been used as a modern technique in pollution removal due to its environmental friendliness, high energy efficiency, and strong controllability [29]. Advantages of electrochemical oxidation reactions (EORs) include easy operating because of the simple equipment needed, conformability to automation, and it can operate under room temperature and pressure [30].

Electrodes are by far the most important components of an electrochemical cell, as they often influence the result of electrochemical synthesis. Pletcher [31] has written a comprehensive analysis of several electrode materials and their reactivity. The chosen electrode must satisfy the following requirements:

- Electrical conductivity is required for current to flow across the circuit.
- Chemical stability, as well as inertness to the solvent, substrates, and intermediates produced during the reaction.
- Physical stability is required to avoid breakage during the construction and usage of the electrolytic system.
- Durability /Cost, having a long-life span to minimize process cost increases.
- Electrocatalytic activity is selective to promote the desired reaction.

Carbon electrodes are utilized in electrochemical applications such as sensing and electrocatalysis. This type of electrode has various advantages like low-cost, high conductivity, electrochemical stability, easy-to-surface modifications, having a wide current window, and good electrocatalytic activity towards some of the redox reactions [32].

Several types of carbon nanomaterials such as carbon nanotube, graphene, and graphite have been reported by various techniques [33]. Graphite is the most utilized material in electrochemistry because it has a wide range of potential and less background of current [34]. A graphite electrode has different advantages such as high sensitivity, low cost, utilized for the detection of a redox reaction, and easy fabrication. In addition, a graphite electrode is utilized as a working electrode in electrochemical measurements [10].

Graphite electrodes are used as a good active anode with modified surface functional nanomaterials for catalyzing the oxidation reaction. Assortment of carbon substrate kinds such as graphite rod, graphite felt, carbon felt, and carbon sponge has been utilized as an electrode in laboratory-scale and EORs [11]. The solid carbon conducting materials were produced by using sol-gel methods. The utilization of this method to increase the advantages of these materials involves; high conductivity, wide potential range, better mechanical properties, easy surface renewability, easy to able chemical modification, and increase stability in different solvents [12]. Electrochemical reactions occur at the electrodes and are hence heterogeneous processes. Because they often occur at the interface between an electrode (which is restricted in area and mobility) and the electrolyte, they can be slower than homogeneous reactions. High surface area electrodes (e.g., felt or sponge type electrodes) are employed to improve this situation. Moving electrodes also provide more mass-transport characteristics. In other circumstances, mediators that function as electron

carriers between the electrode and the substrate (i.e., indirect electrolysis) can be used to boost the reaction rate. The reaction of interest is thus carried out in a homogenous phase [26].

It is often essential to separate the cell's separate compartments, the anodic and cathodic chambers, because the electrode reaction or products at the counter electrode may interfere or compete with the desired product or reaction at the working electrode. Normally, diaphragms or porous materials are used for this purpose. This allows current to pass through the anodic and cathodic compartments while preventing catholyte and anolyte mixing. This type of cell is known as "divided cells" [35].

Suga et al.[36][37] developed a cation flow method involving the continuous generation of a carbocation in the absence of nucleophiles via low-temperature electrolysis, which is a fascinating method for achieving direct oxidative C–C bond formation. The reactor had a diflone and stainless-steel body. A polytetrafluoroethylene (PTFE) membrane separates two compartments in the cell. (Fig. 3).

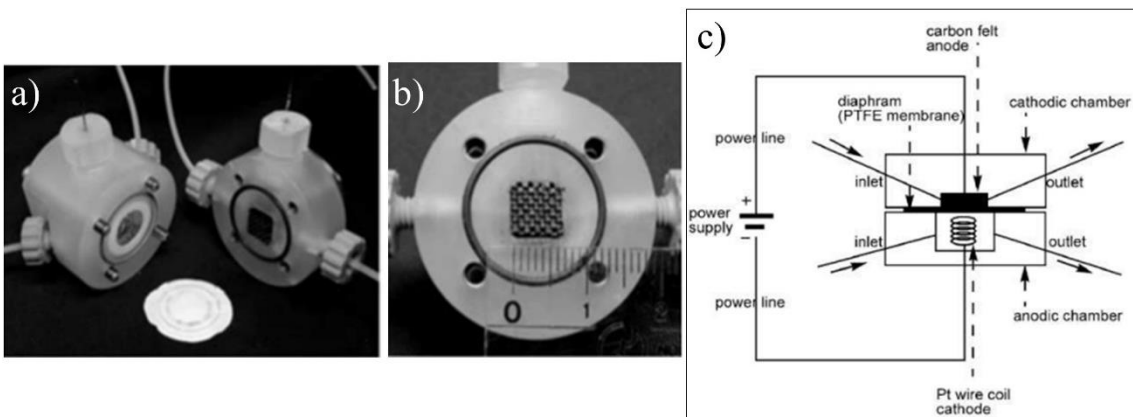


Figure 3: Electrochemical microflow reactor used for cation flow method. (a) inside (b) outside, (c) diagram of the flow electrochemical cell [36]

The utilization of electro-organic reactions has been taken more attention as a green process, especially to avoid the utilization of a conventional method of oxidation. The electrochemical reaction parameters are important in the electrochemical synthesis such as the electrolysis voltage and the concentration. Electro-organic synthesis needs an organic matter such as an organic solvent and electrolyte [13].

Recent research has explained the attractive potential of electrochemical techniques to offer promising alternative routes for the conversion of organic materials [14]. The major advantages are simplicity, ease of control, increased efficiency, and the possibility of building compact bipolar electrochemical reactors. The transformation of organic compounds is facilitated by both reduction and oxidation routes. Electrochemical reactions can be attained through two mechanisms: direct and indirect via electro-generated intermediates formed at the anode surface [6].

2.2 Statement of the problem

Since the electron is not bound to a chemical compound it is inherently pollution-free, reducing the waste produced by electrosynthesis. These properties make electrosynthesis a viable alternative production method based on green chemistry. In conventional heterogeneous catalytic processes, oxidation of most substrates is conducted using stoichiometric oxidants, such as permanganate, nitric acid, or chromic acid. The use of strong and toxic oxidants makes it difficult to control the reaction pathway, thus leading to an unsatisfactory selectivity towards desired products. Platinum and noble metals are well known as the best electrocatalyst for electrochemical conversion, however, the occurrence of these noble metals in nature is very rare. The development of abundant and efficient non-

noble transition metal-based electrocatalysts for electrochemical conversion is in utmost need.

Since electricity will be the prime vitality of things to come being given by regenerative assets, for example, wind control and photovoltaics, its immediate use in synthetic transformation represents a reappearing field in a compound blend. Electro-organic synthesis as an approach is innately sheltered and remarkably feasible in light of the fact that reagent squander is evaded. Novel ideas for electrolytes, methodologies for response screening, and terminal materials make ready a problematic engineered strategy that may be a distinct advantage for future chemistry.

Developing Fe and Co-based catalysts is a very attractive approach. CoB/g-C₃N₄ has shown promising activity for Oxygen evolution reaction. It is a promising electrocatalyst for electro conversion. However, its activity is limited by its poor dispersion of supports. An attempt was made to establish and create experimental conditions for improved activity and selectivity, including catalyst loading, supporting electrolyte, and electrochemical cell design.

2.3 Research Objectives

Most of the previous studies on the electrochemical oxidation or reduction of even coupling reaction were focused on the use of noble metal catalyst electrodes such as Gold, platinum and due to high catalytical activity and efficacy in conversion. Due to the limited availability and excessive cost of precious metal catalysts, cheap and readily available catalysts derived from earth-abundant elements are unquestionably more appealing. Our objective on design and synthesis CoB g-C₃N₄ nanosheet, CoP, and Fe₂O₃ potential active solid support. Our

work focused on dispersing or loading the synthesized catalyst on the surface of the highly conductive porous support, such as nickel foam and graphite felts.

- Characterize as-prepared nanostructured electrode materials by standard techniques.
- Development of a droplet flow reactor for selective organic reactions.
- Development and optimize functionalized electrocatalysts for proposed reactions and improvement of activity and the stability of the catalyst.
- Characterize the functionalized electrocatalysts on the electrode substrate.
- Identification of the reaction pathways using liquid chromatography.

The specific objectives of the work completed in this thesis are listed under each chapter. The thesis is divided into three chapters, the third of which focuses on the development of cobalt boride on the surface of graphitic carbon nitrile and the use of this electrocatalyst in the electrochemical oxidation of 5-Hydroxymethylfurfural to 2,5-Furandicarboxylic Acid. The synthesis of cobalt phosphide by electrodeposition method of droplets assisted electrocatalytic oxidation of selected alcohol compounds is investigated in chapter four. The electrocatalytic reduction of nitrogen to ammonia under ambient conditions and droplet flow assisted electrocatalytic oxidation utilizing C-Fe₂O₃ electrocatalysts are also discussed in Chapter 5.

CHAPTER 3

Cobalt Boride/g-C₃N₄ Nanosheets-Assisted Electrocatalytic

Oxidation of 5-Hydroxymethylfurfural into 2,5-

Furandicarboxylic Acid

Abstract

The electrochemical production of 2,5-furandicarboxylic acid (FDCA) from 5-(hydroxymethyl)furfural (HMF) is receiving growing attention. The FDCA-based polyethylene 2,5-furan dicarboxylate (PEF) polymer is a green candidate for substituting polyethylene terephthalate. This work demonstrated a highly efficient CoB/g-C₃N₄ nanosheet on the surface of the nickel foam as an electrode for the HMF electrooxidation reaction. Electrolysis at a constant potential combined with liquid chromatography showed the formation of FDCA with a yield of 97% with an excellent faradaic efficiency of near 95%. CoB/g-C₃N₄ achieved a current density of 20 mA cm⁻² for HMF oxidation in 1.0 M KOH with 10 mM HMF at 1.37 V vs. RHE before the competing oxygen evolution reaction. The electrocatalyst was effectively reused up to three times without compromising efficiency. This work demonstrates a cheap and active electrocatalyst material for the electrochemical formation of FDCA from HMF and gives a perception of the reaction mechanism

3.1 Introduction

Recently, value-added product manufacturing from [38], [39] The generated 5-hydroxymethylfurfural (HMF) by C6 carbohydrates dehydration has been recognized as one of the top 12 value-added chemicals reported by the United States Department of Energy, obtained from biomass [40]. Through the different catalytic processes, various high-value products and their derivatives have been produced from HMF [41][42]. 2,5-furandicarboxylic acid (FDCA) is a known essential monomer alternative to terephthalic acid.

The transformation of HMF to FDCA can occur in heterogeneous or homogenous catalysts [43]–[46]. However, HMF conversion using homogenous catalysis suffers from poor selectivity and low FDCA yields. Furthermore, it is worth mentioning that using the acidic media reaction would give side reactions that suppress the efficiency of producing FDCA [47].

Electrocatalysis offers an alternative, environmentally friendly route to avoid high pressure and temperature [48][49]. The significant expense of the commonly utilized heterogeneous noble metal catalysts, for example, Ru [50], [51]–[54] Au [55]–[57], and Pt [58]–[62] warrants efforts to succeed them with transition-metal-based catalysts and to discover practical techniques for HMF oxidation. Conventional HMF oxidation to FDCA usually depends on noble metals in high-temperature substances or chemical oxidants and an O₂ pressure reaction [50], [62]–[64]. Electrochemical oxidation in the aqueous medium is an excellent approach. The applied potential drives the response, removing the need for high pressures of O₂ as an oxidant and the demand for wasteful stoichiometric chemical oxidants. Moreover, the half-reaction of HMF oxidation to FDCA can be combined with value-added products in an electrochemical system, for example, the production of H₂ from water, expanding the general payback and value of the system [47].

High temperatures (80–150 °C) are currently used in the conventional performance for selective HMF oxidation to FDCA utilizing a novel metal base catalyst [65]. One of the challenging tasks is to propose a route for selective HMF oxidation into FDCA under mild conditions.

Masa's group described cobalt boride (Ni_xB) as a prospective electrocatalyst for electrochemical HMF oxidation [66]. In addition, Jonas et al.[67] studied the use of various cobalt metalloid alloys (CoX ; $\text{X} = \text{As}, \text{Te}, \text{P}, \text{Si}, \text{B}$) as potential electrolytes for HMF oxidation, concluding that CoB is the most active electrocatalyst. Furthermore, the use of a Co-based electrocatalyst for HMF oxidation has been investigated [68][69]. Luo et al. [70] presented evidence that the dynamic valence states of Co are determining factors in the selective oxidation of HMF under alkaline conditions.

Graphitic carbon nitride ($\text{g-C}_3\text{N}_4$) is a metal-free polymer semiconductor and has advantages of high stability, nontoxicity, low cost, and earth-abundant elemental composition [71]. Several attempts are made to modify the surface of $\text{g-C}_3\text{N}_4$ by co-catalysts. Undoubtedly, Au, Ag, and Pt [72] have a positive impact but are less recommended due to their high price. Surface modification of $\text{g-C}_3\text{N}_4$ with cost-effective co-catalysts, such as Ni, Mo, Co, etc., is more promising from an application viewpoint. Furthermore, many research focus on the using phosphorus-doped- $\text{g-C}_3\text{N}_4$, $\text{MoS}_2/\text{Graphene/g-C}_3\text{N}_4$, CoP , and NiP as cocatalyst on the $\text{g-C}_3\text{N}_4$ has been reported [73]. The $\text{g-C}_3\text{N}_4$ is an example of a metal-free photocatalyst that combines the benefits of nontoxicity, high stability, and easy availability [74]. Various methods have been used for $\text{g-C}_3\text{N}_4$ modification, and the best choice is decorated with a co-catalyst. The $\text{g-C}_3\text{N}_4$ bears a π -conjugated system and excellent electron transferability, and high conductivity material.

In this work, g-C₃N₄ was utilized to support cobalt boride (CoB) to form a hybrid catalyst for selective HMF oxidation to FDCA. Our past work described the effective use of interfacial coupling between the g-C₃N₄ nanosheet and amorphous CoB nanoparticles as a highly active composite for oxygen evolution reaction (OER) catalyst [75]. To the best of our knowledge, this is the first study of its kind to explore the use of CoB/g-C₃N₄@NiF as an electrocatalyst for the electrochemical oxidation of HMF. From this standpoint, we report the electrochemical HMF oxidation into FDCA, which is considered a value-added product catalyzed by nanosheet CoB/g-C₃N₄ on the nickel foam (NiF) under basic conditions.

3.2. Experimental section

3.2.1. Materials

Cobalt chloride (CoCl₂), Sodium borohydride (NaBH₄), Potassium hydroxide (KOH), 5-Hydroxymethylfurfural (HMF), 5-Hydroxymethyl-2-furan-carboxylic acid (HMFA), 2,5-Diformylfuran (DFF), 2,5-Furandicarboxylic acid (FDCA), and 2-formyl-5-furan carboxylic acid (FFCA), were purchased from Sigma-Aldrich, Dorset, UK. The nickel foam with purity greater than 99.99% was obtained from Sigma-Aldrich. All chemicals were utilized as obtained without any additional purification.

3.2.2 Synthesis of CoB/g-C₃N₄ composite

The synthesis of CoB/g-C₃N₄ was carried out as follows. As-prepared g-C₃N₄ (50 mg) was dispersed in 6.0 ml ethanol-water (1:1) solution, and the resulting mixture was sonicated for 5 min. After homogenization, 73.4 mg of CoCl₂ was added, and the solution was kept under

stirring. After 15 min of stirring, the solution was transferred to an ice bath, and an aqueous solution of sodium borohydride (67.6 mg dissolved in 3.0 mL H₂O) was injected into the solution under stirring. The solution was kept under stirring on an ice bath for 30 min. The formation of cobalt boride can take place onto the surface of g-C₃N₄. The method of synthesis is shown in Fig. 4.

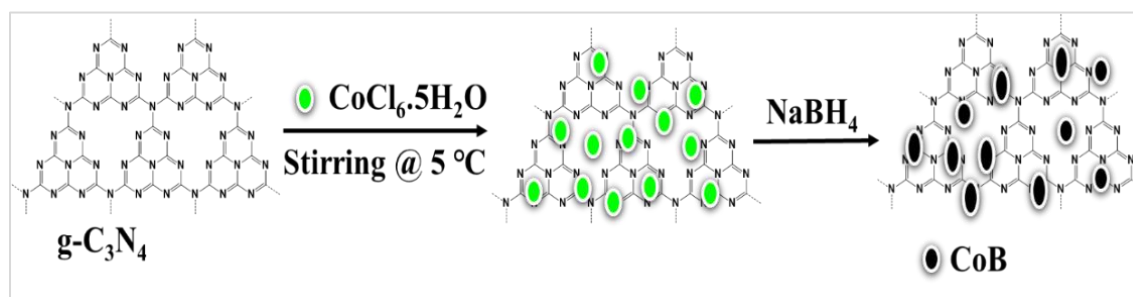


Figure 4: Synthesis of CoB/g-C₃N₄ nanosheet.

3.2.3. Electrode Preparation and Electrochemical Oxidation of HMF

The ink solution was prepared as follows: 5.0 mg of the catalyst, dispersed in 460 μL of water and 500 μL of ethanol, and 40 μL of a 1.66 weight% Nafion solution were added. The resulting mixture was sonicated for at least 1 h to form a homogenous suspension. An appropriate amount of the suspension was deposited on a pre-cleaned nickel foam electrode (1.0 cm^2) and allowed to dry under airflow at ambient temperature. The catalyst loading on the NiF electrode was 1.0 mg cm^{-2} . NiF was selected as a substrate and is stable in basic environments. A three-electrode cell system was used to investigate the activity of the electrocatalyst. The electrochemical oxidation of HMF was measured using a BioLogic VSP-3 potentiostat with a three-electrode configuration. Electrolysis of HMF oxidation experiments was conducted in 30 mL of a 1.0 M KOH solution with 10 mM HMF as substrates. The nickel foam covered with electrocatalysts ($1 \times 1\text{ cm}^2$) was directly used as the working electrode, while a graphite electrode and an SCE electrode served as the counter electrode and reference electrode, respectively.

3.2.4. Evaluation of Electrocatalytic Activity

The working electrode CoB/g- C_3N_4 @NiF, a graphite electrode as a counter electrode, and SCE were employed. The potentials described in this manuscript were converted to the RHE as a reference scale, according to the following equation:

$$E (\text{vs. RHE}) = E (\text{vs. SCE}) + 0.242\text{V} + 0.059 \times \text{pH} \quad (3.1)$$

The electrolyte volume in each electrochemical cell was 25.0 mL. After chronoamperometry measurements, the collection of produced products was taken with a syringe for LC analysis. Before electrochemical tests, high-purity nitrogen was used to bubble the electrolyte solution

to eliminate the dissolved oxygen. The electrochemical measurements were conducted utilizing a BioLogic VSP-3 potentiostat electrochemical station at room temperature.

3.2.5. Product Quantification Using LC

HMF oxidation products were monitored using LC with the following conditions: An electrolyte solution of 10.0 μL was used during chronoamperometry at 1.37 V vs. RHE. A mixture of mobile phase solvents (A and B) was used in LC separation. Solvent A was methanol and solvent B was 5 mM ammonium formate. The quantification and separation were performed by applying an isocratic elution of 30% A and 70% B for a run time of 10 min, at a 0.2 mL min^{-1} flow rate. The quantification and identification of the product were verified from the calibration curves of commercially purchased pure reactants, intermediates, and final products. The yield (%) of oxidation products and the conversion (%) of organic substrates were evaluated based on the following two equations:

$$\text{Yield (\%)} = \frac{(\text{no. of mole of product formed})}{\text{number of mole of initial substrate}} \times 100\% \quad (3.2)$$

$$\text{Conversion (\%)} = \frac{\text{no. of mole of substrate consumed}}{\text{no. of mole of the initial substrate}} \times 100\% \quad (3.3)$$

The product formation faradaic efficiency (FE) was calculated using the following equation:

$$\text{FE \%} = \frac{n \times F \times \text{mole of the product}}{\text{Total charge passed}} \times 100\% \quad (3.4)$$

F is the Faraday constant (96 485 C/mol) and n is the electron transfer for each product formation.

3.2.6. Structural Characterizations

The catalyst was characterized by scanning electron microscopy (SEM) with a Thermo-Fisher Energy-dispersive X-ray spectroscopy (EDS) system. The detector at 15 kV and X-ray photoelectron spectroscopy (XPS) was operated on a K-alpha XPS spectrometer (Thermo Scientific ESCALAB 250Xi, Waltham, Massachusetts, USA). Spectra were held in C 1s, N 1s, Co 2p, and B 1s. The binding energy (BE) values were described as the C 1s peak's binding energy of 284.6 eV.

3.3. Results and Discussion

The CoB/g-C₃N₄ nanosheet synthesis is illustrated in Fig. 4, where g-C₃N₄ was used as supporting material. The sodium borohydride was used as a reducing agent to form the CoB on the surface of the g-C₃N₄ nanosheet. TEM confirmed the development of the nanosheet. The morphology (nanoparticles) and size of CoB (~80 nm) are clearly shown in Fig. 5c. The scanning electron micrographs (SEM) confirmed the two-dimensional sheets of g-C₃N₄ SEM of the Cobalt boride catalyst as a particle-like morphology with a uniform dispersion of CoB/g-C₃N₄ on the surface of nickel foam. The structure of CoB/g-C₃N₄ was shown in Fig.5a at high magnification. Fig. 5b-d shows the bare nickel foam before and after modification by the CoB/g-C₃N₄ catalyst deposited onto the nickel foam. The preparation of CoB/g-C₃N₄ on the nickel foam was conducted via the drop-casting method.

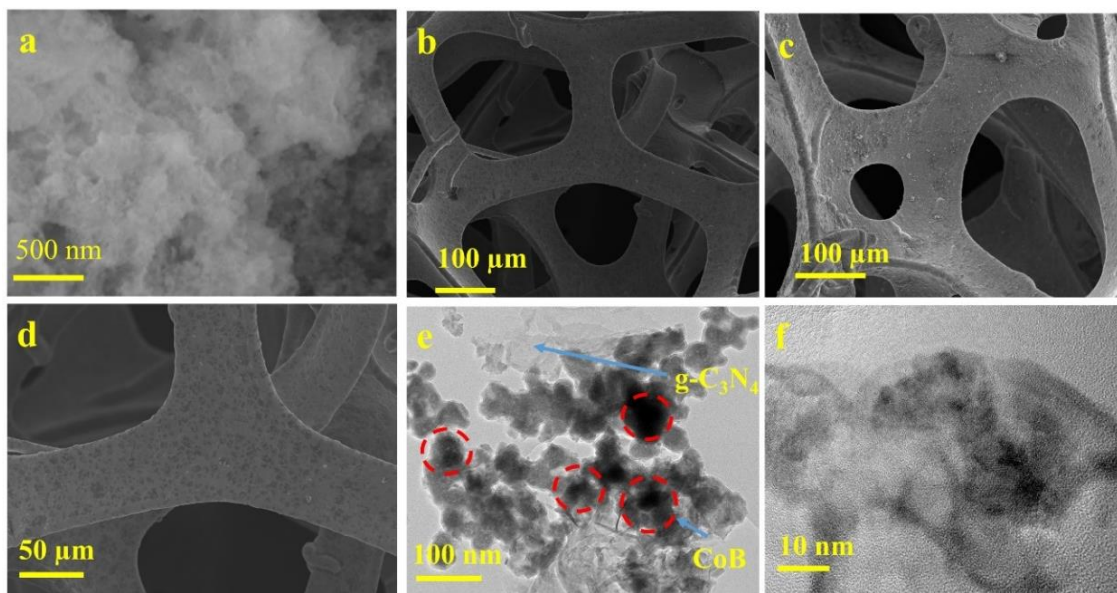


Figure 5: (a) SEM of CoB/g-C₃N₄ high magnification, (b) SEM of bare nickel foam, and (c–d) SEM of CoB/g-C₃N₄@NiF, (e–f) TEM of CoB/g-C₃N₄ at low and high magnification, respectively.

Fig. 6a displays SEM elemental mapping images of the as-prepared CoB/g-C₃N₄@NiF, showing the complete distribution of the nickel foam by CoB/g-C₃N₄ catalysts. The mapping proved the existence of nickel, cobalt, carbon, nitrogen, and boron, and their homogenous distribution on the nickel foam's surface (Fig. 6b–f).

SEM and elemental mapping spectroscopy were used to analyze the structure and composition of the CoB/g-C₃N₄@NiF electrocatalyst after the stability test (named post-HMF CoB/g-C₃N₄@NiF). The low magnification of Fig. 6a–b indicates that the overall structure of the composite has been preserved. However, a thorough examination of the high magnification SEM images (Fig. 6c) reveals the presence of featureless monoliths, which are not present in the fresh sample (Fig. 6a). The elemental mapping images (Fig. 7e) show that the post-HMF CoB/g-C₃N₄@NiF consisted of Ni, Co, C, N, B, and an amount of oxygen [76].

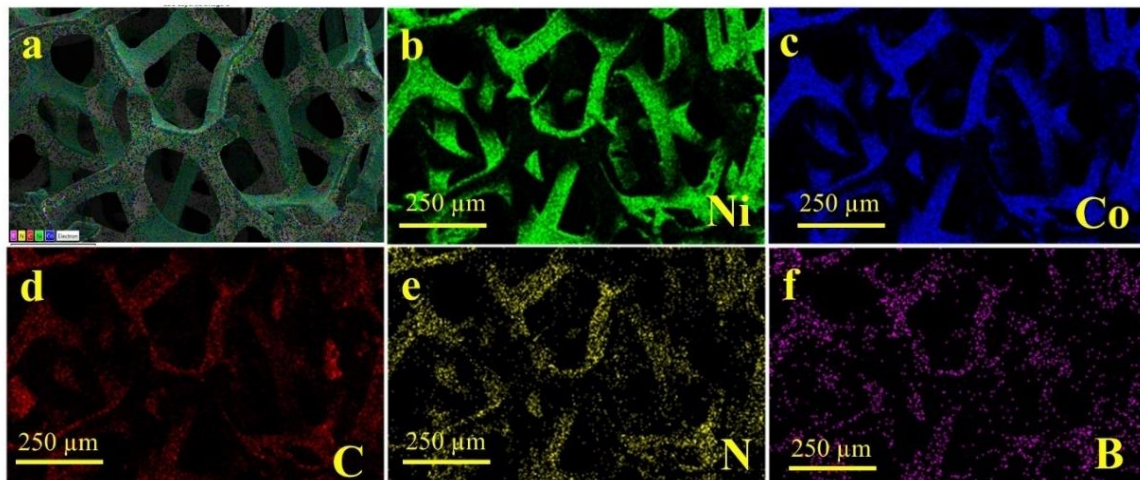


Figure 6: Elemental mapping images of the as-prepared CoB/g-C₃N₄@NiF; (a) all of the elements are shown together, and the individual ones (b-f) for Ni, Co, C, N, and B marked in the various visible colors.

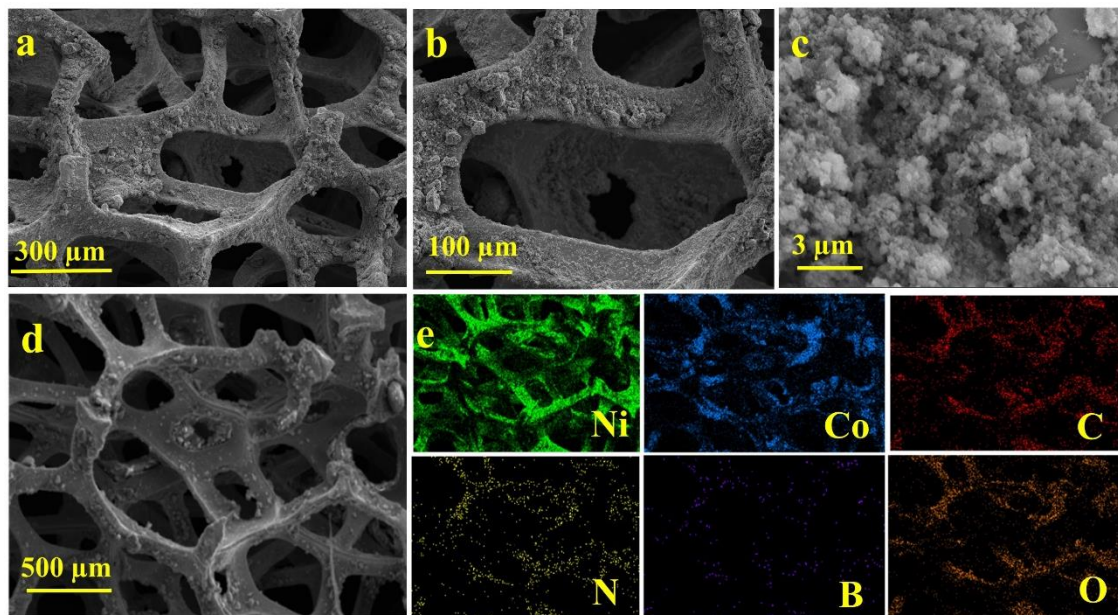


Figure 7: (a-c) SEM picture of post-HMF CoB/g-C₃N₄@NiF at various magnifications. (d-e) SEM and the elemental mapping pictures of post-HMF CoB/g-C₃N₄/NiF show a uniform distribution of Ni, Co, C, N, and B, as well as substantial amount of oxygen.

XPS studied the catalyst surface composition and oxidation states of CoB/g-C₃N₄, and the findings are displayed in Fig. 8. The peak of C 1s at 284.6 eV was retained as a reference to find the elements' binding energy. The core level of the N 1s spectrum can be divided into three distinct peaks at 399.9, 397.6, and 397.3 eV: The weak peak was caused by the N-(C)₃ groups, and the other peak was caused by the C-N=C bond in which the nitrogen has a sp² hybridization. Deconvolution of the C 1s spectrum generated two peaks, centered at 286.73 and 283.66 eV, ascribed to C=N/C=O and C-C, respectively [77]. The high-resolution Co 2p spectrum of CoB/g-C₃N₄ assigned four peaks at 795.9, 780.7, 802.8, and 785.8 eV, respectively (Fig. 8b). Two peaks at 795.9 and 802.8 eV were described as two satellite peaks of cobalt (II) ions. The spectra of B 1s of the CoB/g-C₃N₄ showed a peak at 192.0 eV, related to the boron Oxo-species, and a weak peak at 191.4 eV due to the boron cobalt bond, which confirms the formation of CoB [78]. The spectra of XPS are presented in Fig. 8d.

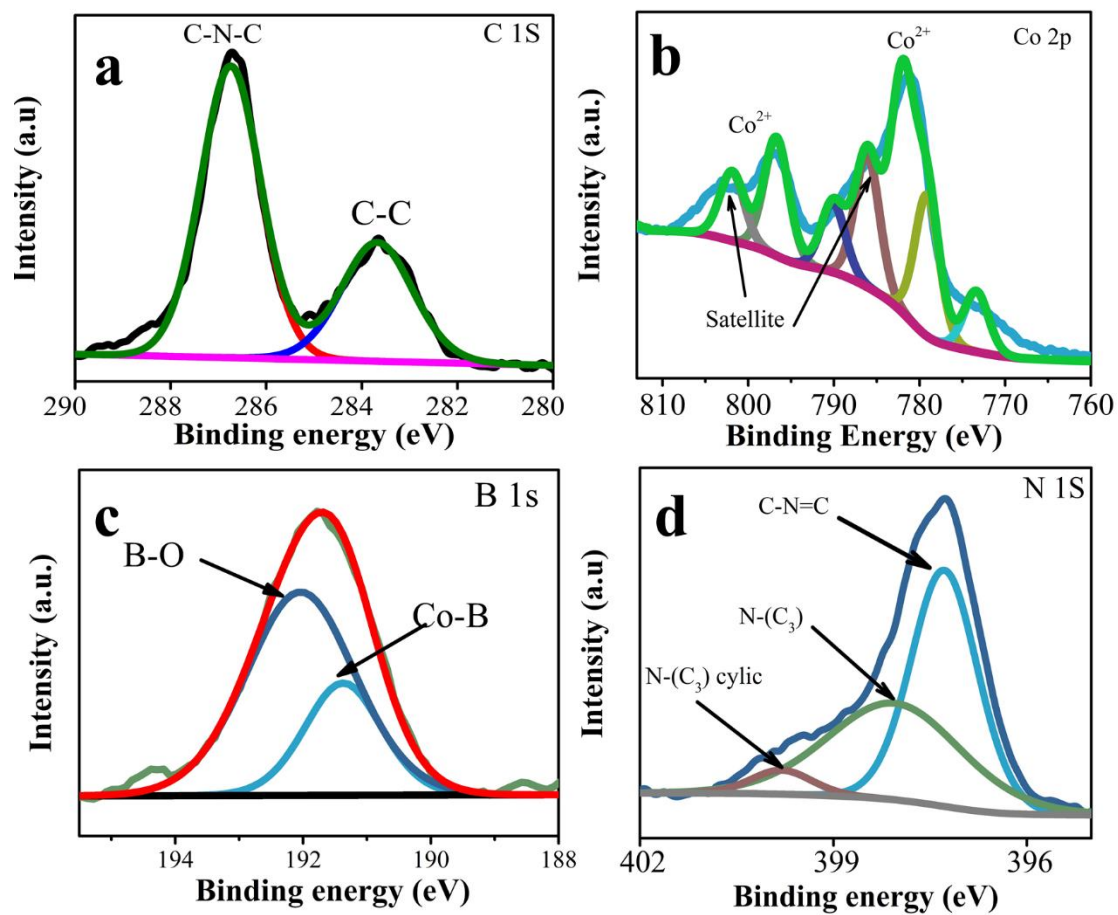


Figure 8: XPS spectra of C 1s, Co 2p, B 1s, and N 1s.

CoB/g-C₃N₄ showed specific surface areas of 86.8 m² g⁻¹. The surface area was studied using Brunauer–Emmett–Teller (BET) analysis and explored by nitrogen adsorption-desorption isotherms (Fig. 9). The porous structure of NiF facilitates mass transport, abundant electrolyte contacts interfaces, and increasing active site availability for fast electrochemical kinetic, which improves the electrochemical performance. The d-spacing was computed to be 0.35 nm, which is in good agreement with the (002) lattice plane of CoB [79]. Energy-dispersive X-ray spectroscopy (Fig. 10) also indicated the presence of CoB in CoB/g-C₃N₄.

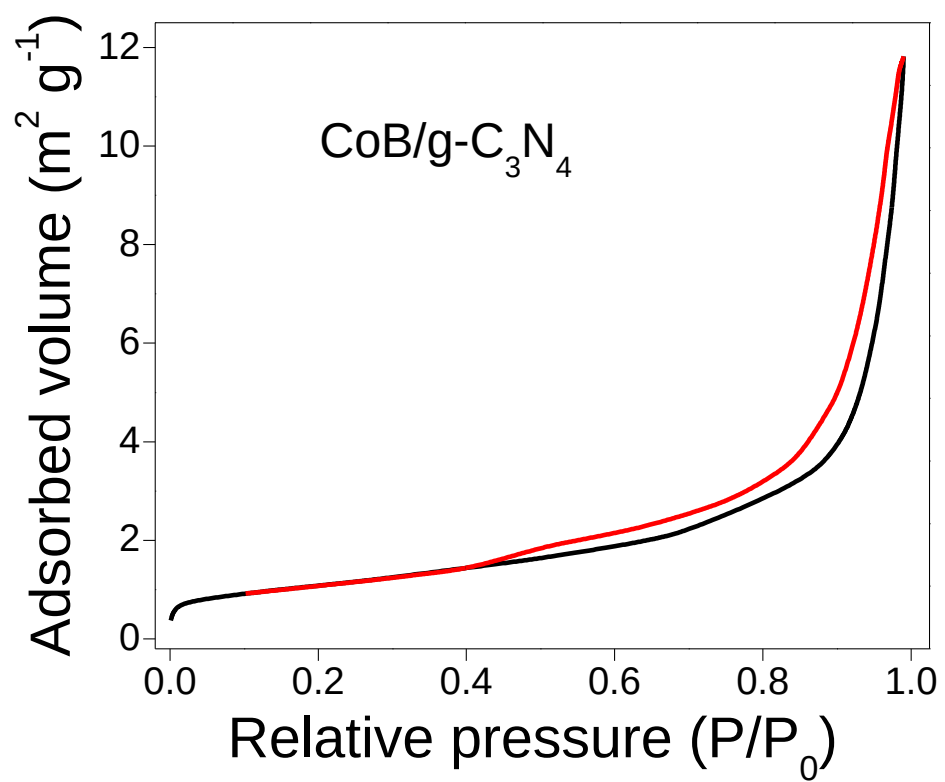


Figure 9: Nitrogen adsorption-desorption isotherms of CoB/g-C₃N₄

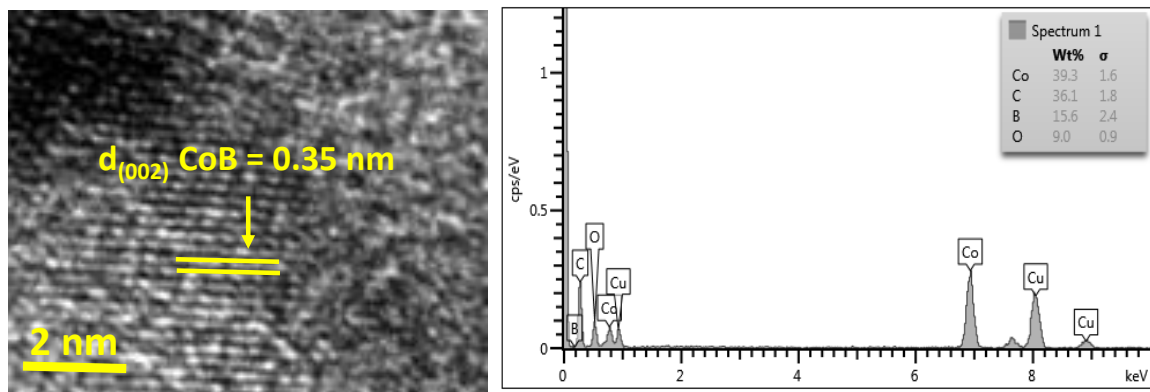


Figure 10 :High-resolution transmission electron microscope (HR-TEM) and energy-dispersive X-ray spectroscopy (EDS) of CoB/g-C₃N₄

3.4. Electrochemical Oxidation of HMF

Since it was known that CoB was a very active catalyst for water splitting under strongly basic conditions, in this work, we first attempted to study its catalytic performance for HMF oxidation in an alkaline medium. The oxidation of HMF was conducted with a CoB/g-C₃N₄@NiF catalyst electrode in a supporting electrolyte composed of 1.0 M KOH. Based on the polarization curve shown in Fig. 11, it is clear that linear sweep voltammetry (LSV) of CoB/g-C₃N₄@NiF in the absence of HMF shows an anodic current beyond 1.50 V vs. RHE. This catalytic current confirmed the occurrence of the oxygen evolution reaction. The addition of 10 mM of HMF shifts the current catalytic onset to low potential to 1.37 V vs. RHE., which indicates that CoB/g-C₃N₄@NiF could preferably catalyze the oxidation of HMF at a lower potential compared to the one required for OER in the basic medium. The catalytic current density improved dramatically after 1.31 V. It reached a 20 mA/cm² current density at 1.37 V vs. RHE, 150 mV less than water oxidation (1.52 V vs. reversible hydrogen electrode (RHE) to arrive at 20 mA cm⁻²). It ought to be noticed that the blank nickel foam (NiF) was less active compared to the HMF oxidation using CoB/g-C₃N₄@NiF. Moreover, the previously reported onset potential of 1.25 to 1.3 V vs. RHE is comparable with the Co⁴⁺ formation area observed herein, indicating a similar type of active species [70].

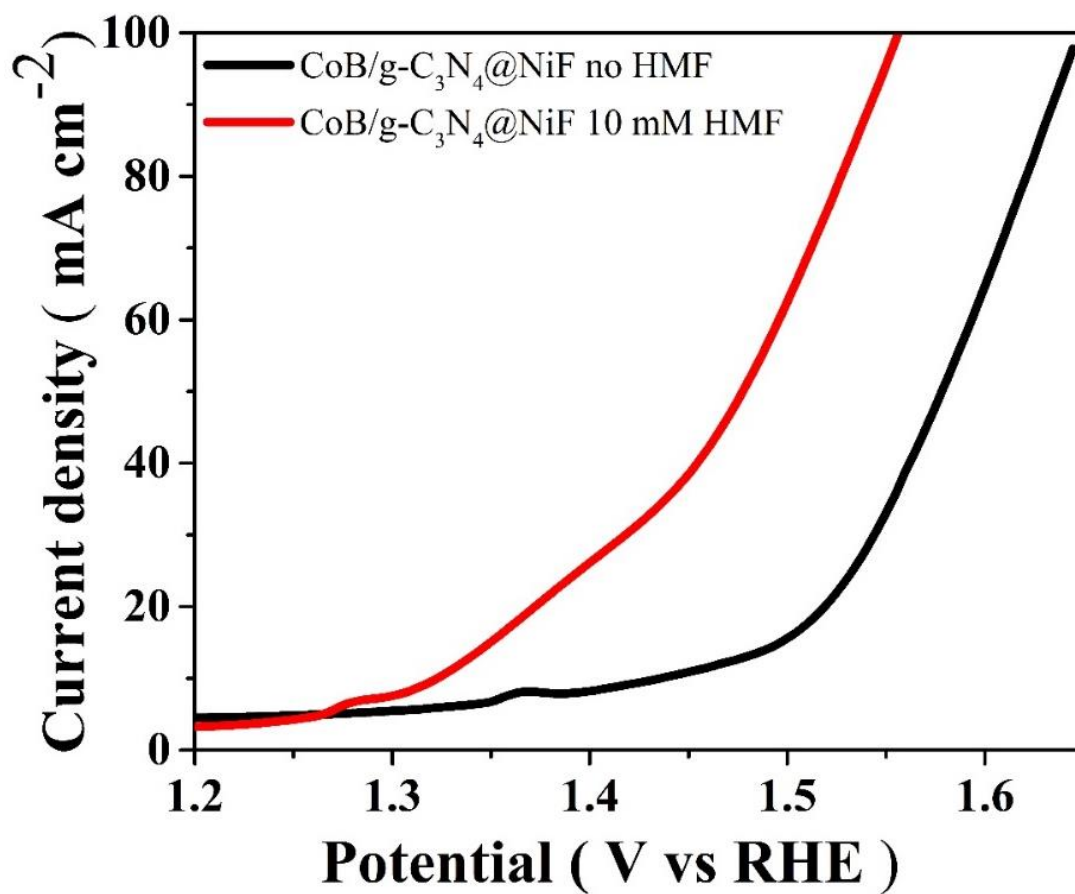


Figure 11: LSV of CoB/g-C₃N₄@NiF in the absence and existence of HMF in 10 mM concentration in a supporting electrolyte solution of 1.0 M KOH with a scan rate of 10 mVs⁻¹.

Fig. 12a introduces the two-potential pathway for HMF electrochemical oxidation to FDCA. The first path is via the initial oxidation of the aldehyde to yield HMFCa as an intermediate product, while the second path proceeds by the initial oxidation of alcohol to obtain DFF. The latter is unfavorable. The two pathways converge at the formation of FFCA before the final FDCA product. To recognize and evaluate the final product and oxidation intermediates of HMF oxidation and decide the Faradaic efficiencies, CoB/g-C₃N₄@NiF-catalyzed HMF oxidation was performed at an applied potential of 1.37 V vs. RHE in 10.0 mL of 1.0 M KOH as the supporting electrolyte and with 10 mM of HMF substrate. The transformation of all the HMF to FDCA needs around 58 Coulomb charges if 100% Faradaic efficiency is to be accomplished.

Liquid chromatography (LC) with a UV detector was used to monitor the reaction after electrocatalysis. Fig.11b shows the oxidation intermediate of HMF (FFCA, 2,5-formylfurancarboxylic acid, and HMFCa, 2,5-hydroxymethylfurancarboxylic acid) and the final oxidation product FDCA during electrolysis. FDCA was the main oxidation product, and the formation of the reaction intermediates was insignificant. It showed the increase in the final formation product and the decline of the HMF over time. The formation of FDCA from HMF is indicated by the decline of HMF and the gradient of FDCA. After passing the charge of approximately 58 Coulomb, the LC trace of HMF vanished even though FDCA increased to the highest value, which indicated the total transformation of HMF.

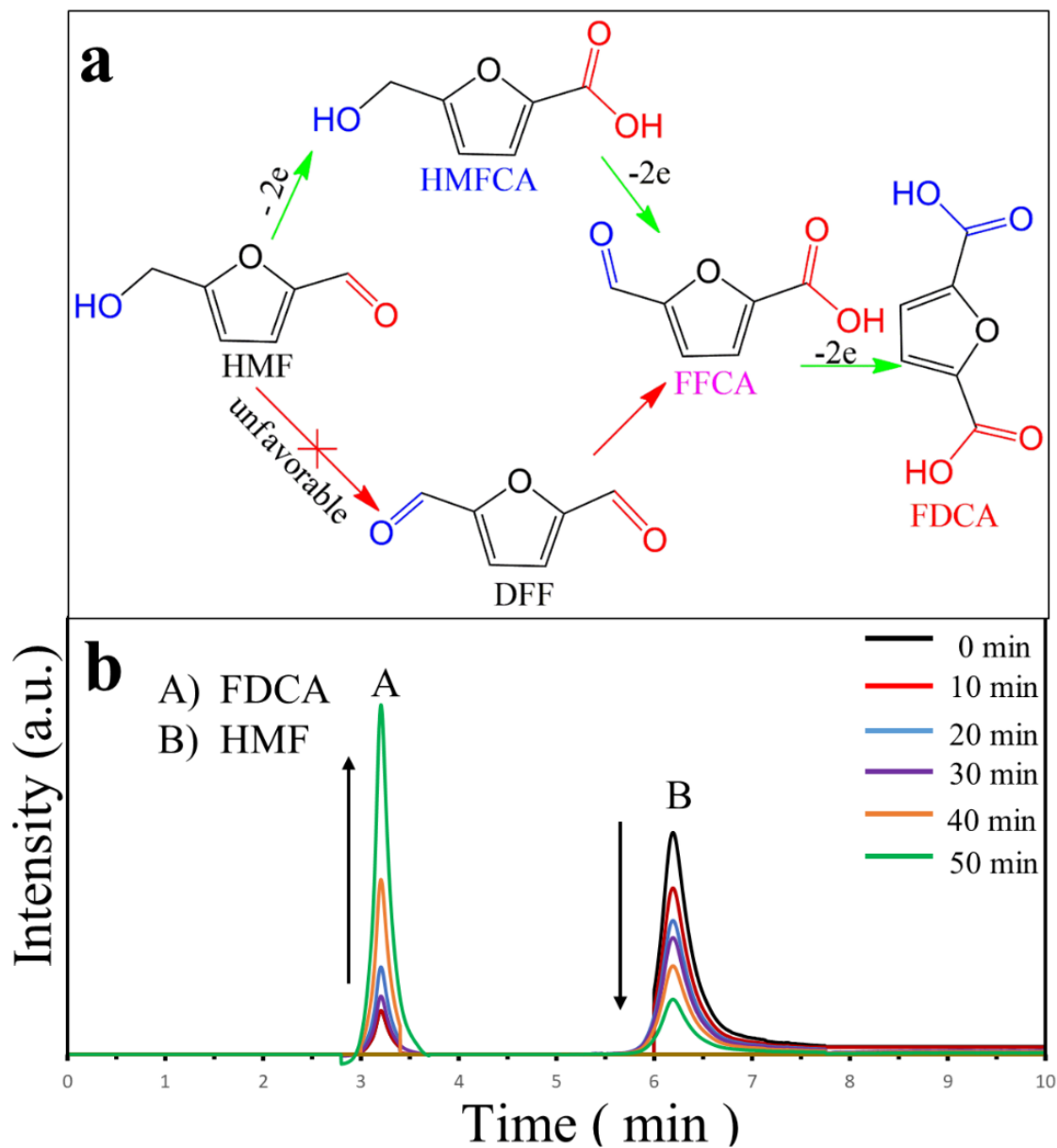


Figure 12: (a) HMF electrochemical oxidation reaction pathways. The first pathway starts with the oxidation of the aldehyde group to form HMFCFA. The second pathway starts with the oxidation of the alcohol group of HMF to give DFF over CoB/g-C₃N₄@NiF. (b) HMF concentration change and the oxidation product over electrolysis time.

Fig. 11a displayed the HMF change and the yields of possible oxidation intermediate products and the eventual outcome during electrolysis. The results show that faradaic efficiencies of 95% for FDCA formation and 93% for HMF conversion are achieved. Electrooxidation of HMF catalyzed by CoB/g-C₃N₄@NiF obeyed the steps of aldehyde oxidation through the HMFCa route (Fig. 11a), as shown by the comparatively higher concentration of HMFCa relative to that of DFF during electrolysis. This route follows that described for aerobic HMF oxidation reactions. However, the DFF route could be omitted, and we noted that the development and utilization of DFF during electrolysis are unfavorable.

A 64.0% HMF as the starting substrate was transformed into FDCA after 10 min of electrolysis, and residue amounts of FFCA and HMFCa as intermediates were detected. As the intermediaries do not build up throughout the process, a quick conversion of FFCA and HMFCa into FDCA is proposed. A complete HMF transformation was accomplished in 50 min along with a high FDCA yield of 96.5%, and 95.0% faradaic efficiency was attained. The remarkably high yield of 98.5% emphasizes the increased activity of CoB/g-C₃N₄ for electrocatalytic HMF oxidation at the applied potential, particularly considering an HMF decomposition rate of 12%/ hour (for a 10 mM of HMF in 1.0 M KOH solution). Transformation of HMF to FDCA is clearly shown in Fig. 12a with the decrease in HMF concentration and increase in FDCA concentration over the electrolysis process. The change concentration of HMF and its oxidation intermediates FFCA and FDCA during electrolysis caused unity faradic efficiency for HMF conversion and the formation of FDCA. Three consecutive cycles were performed to study the robustness toward HMF oxidation, reflecting the robust stability of CoB/g-C₃N₄@NiF for HMF oxidation, as shown in Fig. 13b.

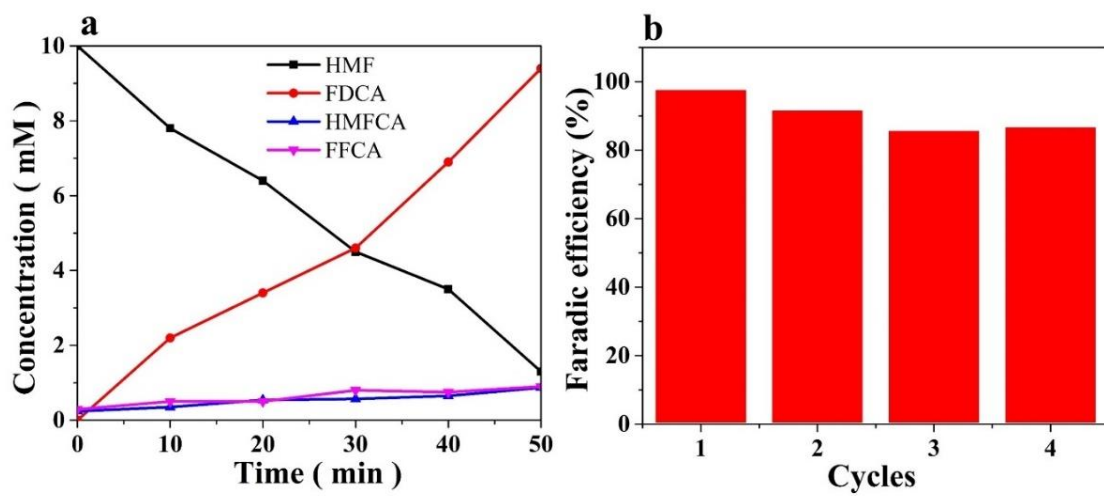


Figure 13: (a) LC chromatogram traces of the various products at different reaction times following an HMF electrochemical oxidation reaction with the flow rate of 0.2 mL/min. (b) Faradic efficiency CoB/g-C₃N₄@NiF with 10 mM HMF in 1.0 M KOH solution for four consecutive electrolysis.

3.5. The Role of CoB/g-C₃N₄@NiF for HMF Oxidation

Luo et al. [70] reported an example of selectivity-tuned oxidation of HMF by varying the oxidation states of an electrocatalyst using CoOxHy as the model electrocatalyst. A plausible mechanism is described in which radical species are first produced by the oxidation and deprotonation of the formyl group in HMF. The carbon atom is then further oxidized, and the O atom in H₂O attacks it to form carboxylate. The CoB/g-C₃N₄ plays a vital role in the reaction mechanism through a surface phase change and surface structure with a high surface-area-to-volume ratio, making CoB/g-C₃N₄ an efficient catalyst in basic conditions. It is worth mentioning that the active site in the catalyst was cobalt boride, and the g-C₃N₄ offered a surface area for both the substrate and the product. Fig. 13 illustrates the proposed mechanistic pathway to produce FDCA from HMF. The hydroxide ions attach the carbonyl group to the HMF side by a nucleophilic addition reaction. The formation of germinal diol took place via hydration after a proton departed from the aldehydic group of HMF molecules. Because of the large hydroxyl groups adsorbed on top of the CoB/g-C₃N₄@NiF surface, the dehydrogenation of diol occurs to form the carboxylic group. From that point, the other alcohol part was dehydrogenated due to the deprotonated reaction by the base. The C-H bond activation occurred due to the hydroxide ion and the aldehyde group formation. Electrogenenerated Co³⁺ and Co⁴⁺ species function as chemical oxidants but play distinct roles in selective HMF oxidation. Luo et al. observed that Co³⁺ could only oxidize formyl groups to form carboxylate, but Co⁴⁺ is required for the initial hydroxyl group oxidation with much faster kinetics. Table 1 presents a comparison table for our work vs. previously reported

literature. Our work revealed that the catalytic activity of CoB/g-C₃N₄ was significantly higher than previously reported work in the literature.

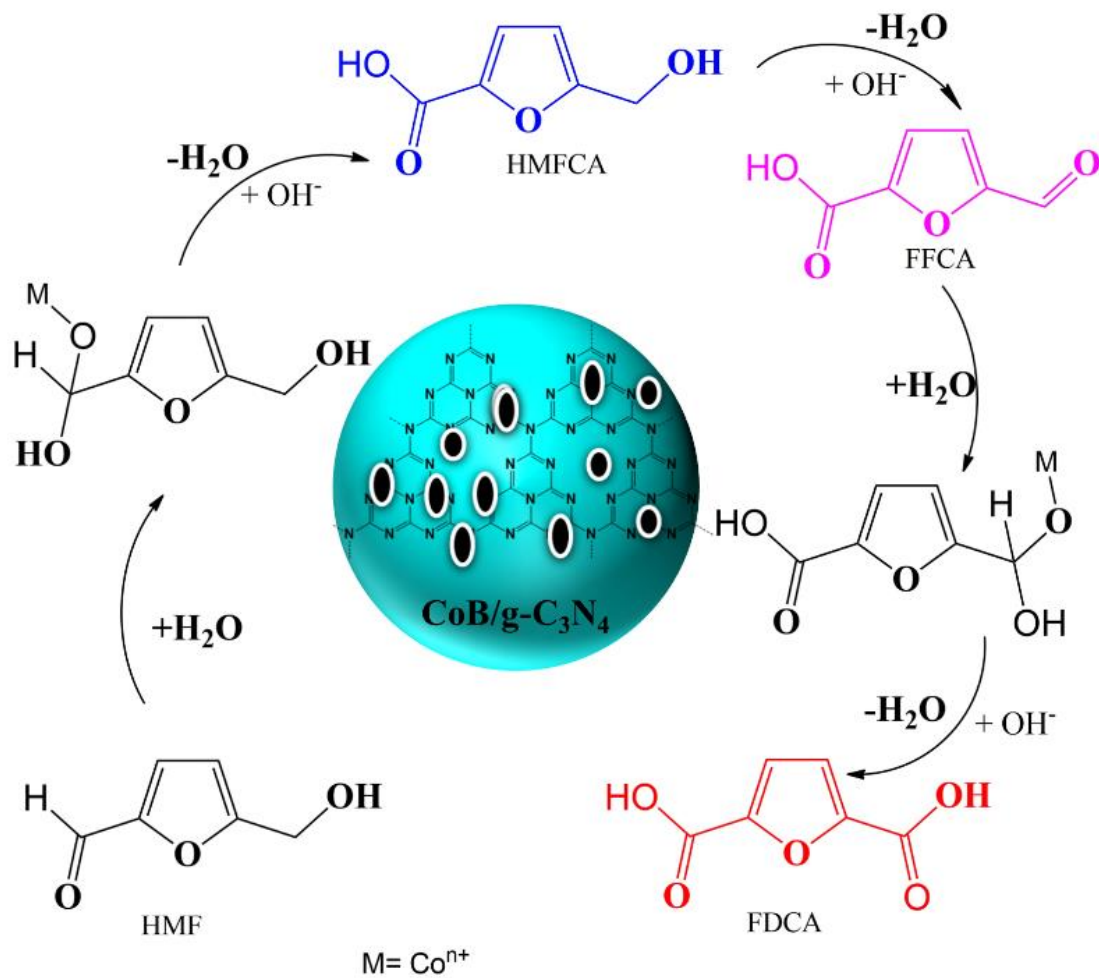


Figure 14: Proposed mechanism of the electrochemical HMF oxidation to FDCA over a CoB/g-C₃N₄ nanosheet.

Table 1: Comparison of the total electrolysis performance of dual-function catalysts

Electrode Materials	Time (hrs)	HMF Conc. (mM)	Electrolyte	HMF Electrooxidation and HER		Faraday Efficiency (%)	FDCA (Yield%)	Ref.
				Current Density (mA cm ⁻²)	Potential Window			
CoB/g-C ₃ N ₄	~0.8	10	1.0 M KOH	50	1.47	95.0	97.0	This work
				10	1.32	94.3	96.0	
NiCoBDC	1	10	1.0 M KOH	20	1.55	83.1	99.0	[80]
Ni ₃ N@C	1	10	1.0 M KOH	50	1.55	99.0	98.0	[81]
				10	1.46			
Ni ₂ P	1	10	1.0 M KOH	50	1.58	98.0	98.0	[82]
				10	1.44			
Ni ₃ S ₂	1	10	1.0 M KOH	50	1.58	96–99	98.0	[39]
				10	1.46			
Co-P	1	50	1.0 M KOH	20	1.44	100	90.0	[83]
NiCoFe-LDHs	1	5	1.0 M KOH	20	1.51	96.0	~85	[84]
NiOOH	1	5	0.1 M KOH	-	1.47	96.0	96.0	[85]
ACT\TEMPO	4	20	pH 10	-	1.40	93.5	93.5	[86]
CuCo ₂ O ₄	1	10	1.0 M KOH	150	1.37	94.0	93.7	[68]
MoO ₂ -FeP@C	~2.7	10	1.0 M KOH	-	1.32	97.8	98.6	[87]
N-Ni ₃ S ₂ -MoO ₂	-	50	1.0 M KOH	20	1.57	90	90	[88]

3.6 Conclusions

We have shown the selective and efficient electrocatalytic HMF oxidation into FDCA using cobalt boride dispersed on a graphitic carbon nitride modified NiF composite in an alkaline medium. A high percentage of FDCA was accomplished at about 95% faradaic efficiency. The intermediates and products formed were examined by LC, showing that oxidation of HMF proceeds through the HMFCA intermediate rather than the DFF pathway. CoB/g-C₃N₄@NiF is a promising catalyst for selective electrochemical oxidation of HMF, paving the way toward a green chemistry approach.

CHAPTER 4

Droplet flow assisted electrocatalytic oxidation of selected alcohols under ambient condition

Abstract

This study reports using a droplet flow assisted mechanism to enhance the electrocatalytic oxidation of benzyl alcohol, 2-phenoxyethanol, and hydroxymethylfurfural at room temperature. Cobalt phosphide (CoP) was employed as an active electrocatalyst to promote the oxidation of each of the individual substrates. Surface analysis of the CoP electrocatalyst using scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDS), X-ray photoelectron spectroscopy (XPS), as well as electrochemical characterization, revealed that it had excellent catalytic activity for each of the substrates studied. The combined droplet flow with the continuous flow electrochemical oxidation approach significantly enhanced the conversion and selectivity of the transformation reactions. The results of this investigation show that at an electrolysis potential of 1.3 V and ambient conditions, both the selectivity and yield of aldehyde from substrate conversion can reach 97.0%

4.1 Introduction

Electrochemical organic synthesis is one of the most promising organic synthetic tools available, potentially providing a more sustainable and environmentally friendly pathway to produce a wide range of chemical compounds. This is because it eliminates chemical waste by avoiding chemical oxidants and reductants, which is typical of the conventional chemical synthesis approach, and it can operate under mild reaction conditions [89]. More importantly, this synthesis protocol allows for a simple selective transformation of a substrate into useful intermediates or products with high functional group tolerance using only electricity [90]. In this synthesis approach, the applied potential and current to the reaction system can be easily controlled to regulate the redox reactions at the electrode interface [91]. To achieve selective transformation, a "controlled potential" higher than the substrate's redox potential must be supplied to the electrode to initiate the required chemical reaction.

Carbonyl molecules, such as ketones and aldehydes play key roles in synthetic organic chemistry due to their widespread use as precursors in the pharmaceutical and chemical industries [92]. In the classical chemical oxidation approach, alcohols are often oxidized to aldehydes or ketones in the presence of oxidants such as bromate, chromate, or manganates. However, the hazardous nature of these oxidants, and their likelihood of contaminating the target intermediates, has served as a significant drawback affecting this transformation approach. It has also been challenging to use these oxidants for the oxidation of a wide range of alcohols [93]. The electrochemical oxidation approach was recently advanced as a simple and highly efficient pathway for the selective oxidation of alcohols to primary intermediates. This method offers an appealing alternative to the classical approach. It does not require a

chemical oxidant and only generates hydrogen as a by-product of the reaction without product contamination [94].

The published literature has widely explored the direct electrochemical selective oxidation of alcohols to aldehydes or ketones. Most of the documented studies have explored the use of noble metals as catalytic electrodes, such as Ru [94], and Pt [95], in various electrochemical cell configurations, including batch mode [95][96] and continuous flow setup [94]. Furthermore, most of these investigations reported moderate yield and selectivity with extended reaction time for the target aldehydes and ketones. Based on our findings, we believe that combining a microdroplet flow reaction with a continuous flow electrochemical cell should provide a highly efficient and rapid pathway for the selective oxidation of alcohols in the aqueous medium. Over the years, microdroplet flow chemistry has proven to be an important tool in speeding up reaction kinetics and for high throughput applications. These unique characteristics of microdroplet reaction stem from its interfacial features related to its enormous surface-area-to-volume ratio, allowing it to offer a faster reaction rate than the bulk flow counterpart [96][97]. Droplets provide a confined, high-surface area for chemical reactions, enhancing conversion and selectivity. Droplet-assisted reaction mechanisms are well-known, and several pieces of literature have already been discussed in detail [98]. Several reports have attributed this fast reaction rate to be due to the inherent interfacial properties that includes [97][99]: reagent (s) confinement [100][101], partial solvation [97][102][103][104], pH extremes [105][106], and ordered molecule orientation. Although most previous research on reaction acceleration with microdroplets is often carried out in organic solvents, aqueous microdroplet reactions are rarely reported.

Over the years, metallic phosphide has evolved as a highly efficient electrocatalyst for oxidation reactions due to its high reactivity in an aqueous medium. These transition metal species facilitate the deployment of oxyhydroxide species in an aqueous medium that has demonstrated excellent catalytic activity and effectiveness in the electrochemical oxidation reaction. Cobalt phosphide (CoP) is highly sought as an active electrocatalyst among these transition metal species due to its ease of preparation. Phosphorus (P) has a lower electronegativity than sulfur, nitrogen, and oxygen. It can, however, aid in the formation of oxides, hydroxides, and phosphate active centers on the catalyst surface, resulting in improved electrochemical performance. Even though the electrochemical oxidation active sites are only found on the catalyst's surface atoms, such reported thick or bulk cobalt phosphide nanostructures suffer from low utilization and exposure of the active sites, limiting their electrochemical activities. As a result, further improvement of the electrochemical oxidation performance of cobalt phosphide is still needed.

Hence, this study investigated the selective oxidation of selected alcohols (benzyl alcohol, 2-phenoxyethanol, and Hydroxymethylfurfural (HMF) for the first time using a modified continuous electrochemical reactor that incorporates a microdroplet flow component. Moreover, CoP on the nickel foam (CoP@NiF) synthesized by the electrodeposition method was employed as the catalytic electrode. Furthermore, several potentials were tuned and optimized to achieve the highest yield and selectivity for the target aldehyde in the shortest period. Applying the microdroplet flow-continuous flow electrochemical technique.

4.2 Experimental section

4.2.1 Chemicals

Cobalt (II) chloride hexahydrate ($\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$), sodium dihydrogen phosphate (NaH_2PO_4), potassium chloride, nickel foam, benzyl alcohol (BA), 2-phenoxyethanol (2-PE), hydroxymethylfurfural (HMF), potassium hydroxide (KOH), ammonium formate, tetrabutylammonium tetrafluoroborate (Bu_4NBF_4) and acetonitrile. All reagents were purchased from Sigma Aldrich and used without any further purification.

4.2.2 Synthesis of CoP@Ni Foam

The CoP was deposited on the nickel foam by using the electrodeposition method. In brief, cobalt chloride hexahydrate ($\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$) and sodium dihydrogen phosphate (NaH_2PO_4) were used as cobalt and phosphorus sources, respectively. A supporting electrolyte of KCl was dissolved in a specific volume of deionized water under nitrogen gas purging. The electrodeposition of CoP film was performed by using a standard three-electrode system: the working electrode was cleaned bare NiF, the counter electrode was platinum, and the reference electrode was silver/silver. Then, the applied potential of -1.0 V was polarized into the Ni foam surface. Finally, the working electrode was rinsed with deionized water and dried at room temperature after the electrodeposition. The method of synthesis is shown in Fig. 15.

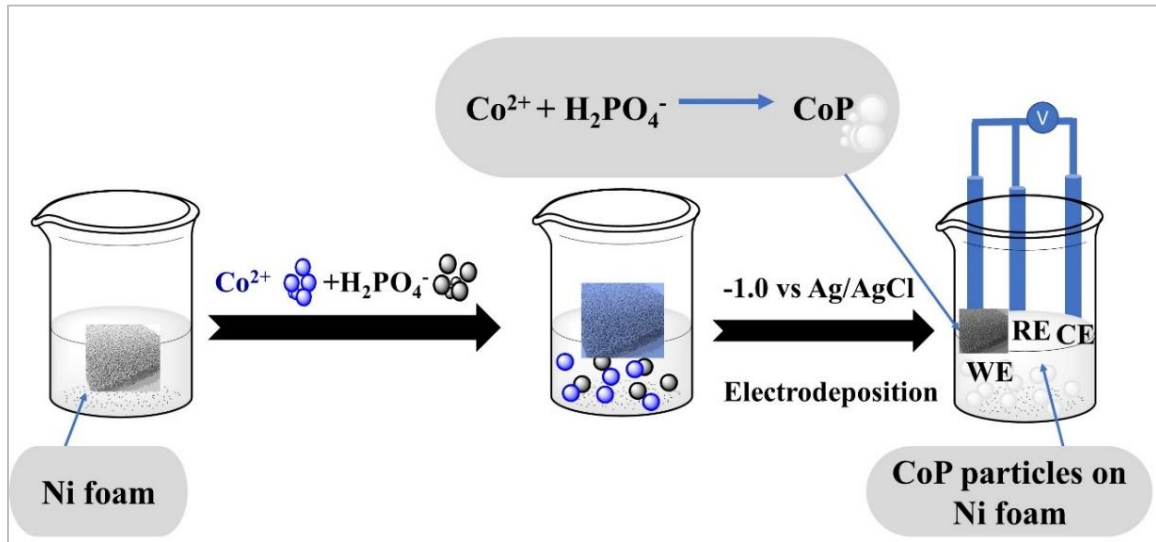


Figure 15: Schematic diagram of CoP@NiF synthesis.

4.2.3 Structural characterization

The surface characterization of the prepared CoP@NiF electrode was performed using field emission scan electron microscopy (FE-SEM) coupled with energy-dispersive X-ray spectroscopy (EDS). An X-ray photoelectron spectrometer was used to collect the surface elemental composition (Thermo Scientific ESCALAB 250Xi, Waltham, Massachusetts, USA). The C1s hydrocarbon peak at 284.60 eV was used to calibrate all binding energies.

4.2.4 Droplet-assisted electrochemical oxidation of alcohols

All electrochemical experiments were conducted using CH Instruments 1140A potentiostats (CH Instruments, Inc., Austin, USA). An undivided electrochemical cell (EuroCell) with a 50 mL volume (working solution, 0.21 L and GSG-ME) was modified to suit a droplet-flow assisted configuration. Fig.16 shows the schematic diagram of the droplet-assisted electrochemical flow reactor used in this work. A nickel foam was used as the anode while the cathode was a platinum electrode and was connected to a direct current power source (Ealing High voltage power supply, 0-50 V).

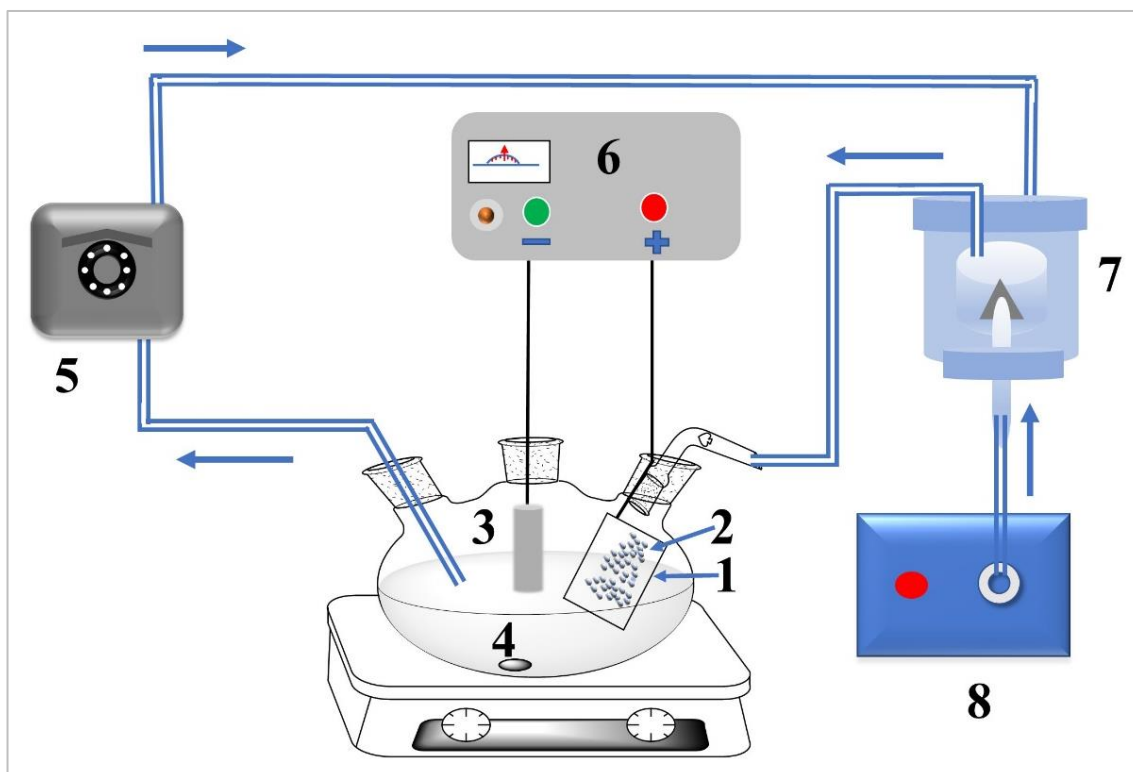


Figure 16: The experimental setup of the droplet assisted electrosynthesis reactor includes: (1) CoP@NiF (the anode), (2) droplet formation, (3) platinum electrode acting as the cathode, (4) magnetic stirrer, (5) peristaltic pump, (6) DC power supply, (7) nebulizer junction for mixing natural air with the untreated sample to form a droplet spray at the anode surface, and (8) air pump.

The electrodes were placed 1.5 cm from the reactor's bottom and 2.0 cm apart as an inter-electrode gap. An air pump connected to the sample flow recirculatory system was used to create a nebulized mist of the sample solution directed at the anode surface. For all the experiments, the bulk sample solutions were stirred magnetically. The electrochemical droplet assisted condition setup was set CoP@NiF as the anode, and the Pt electrode was used as the cathode. A mixture of 30 ml of acetonitrile and H₂O (1:1) as supporting electrode and 0.2 mmol of Bu₄NBF₄. The concentration of the different alcohol substrates was 2.0 mmol. All the experimental electrolysis was repeated three times.

4.2.5 Liquid Chromatography Analysis

High performance liquid chromatography (HPLC, Shimadzu) was used in monitoring the electrochemical oxidation process. Data acquisition and quantification are conducted with Lab Solutions, LC Ver.5.91, Shimadzu. An autosampler (CTC-Pal (Analytics AG)) ultra IBD column (100 x 2.1mm x 3µm particle size; Restek, USA) was used for the separation of target analytes. Isocratic elution using solvent A (5.0 mM ammonium formate) and solvent B (acetonitrile) was applied at a flow rate of 0.04 ml/min. The injection volume was 2.0 µL with the isobaric condition.

Standard solutions of reactants and products, such as benzyl alcohol, 2-phenoxyethanol, and HMF, were used to obtain the calibration curves. The alcohol concentrations and their oxidation products were determined from the peak areas. Percent (%) conversion and selectivity were calculated using the following formulas:

$$\text{Conversion \%} = \frac{(C_{r_0} - C_r)}{C_{r_0}} * 100 \quad (4.1)$$

$$\text{Selectivity} = \frac{C_p}{(C_{r_0} - C_r)} * 100 \quad (4.2)$$

denotes the reactant's initial concentration, C_r and C_p denote the reactant's and product's concentration during the reaction respectively [107].

4.3 Results and Discussion

The particles of cobalt phosphide were synthesized by an electrodeposition technique using a potentiostat. A three-electrode system was employed, in which the nickel foam serves as a working electrode. The highly conductive Ni foam allows the continuous transfer of electrons across its entire structure, initializing the useful reduction of cobalt (II) ions and dihydrogen phosphate ions to give a net reaction to produce cobalt phosphide [108].

The structural details of bare nickel foam (NiF) and modified CoP@NiF were investigated using scanning electron microscopy (SEM). As illustrated (Fig. 17 a-c), the structure of bare nickel foam was retained while the surface became rougher in the modified CoP (Figure 17 d). High magnification of CoP@NiF showed the surface become dense and entirely covered by the CoP particles (Fig.17e). The energy-dispersive X-ray spectroscopy (EDS) elemental mapping confirmed the homogenous distribution of Co and P on NiF (Fig. 18a-d).

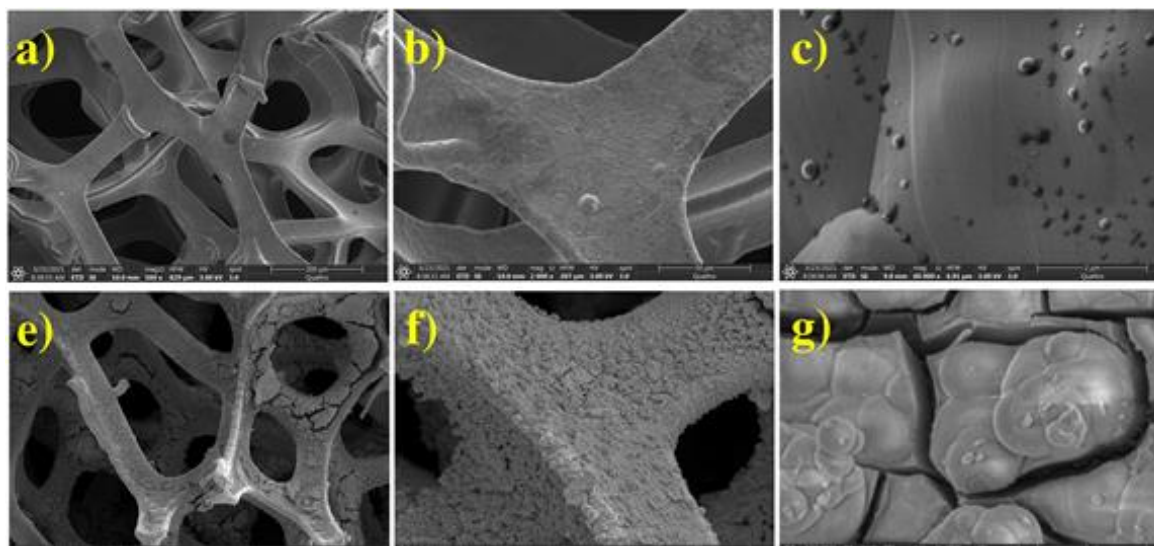


Figure 17: (a-c) low magnification SEM of bare NiF, (e-f) Low and high magnification SEM of CoP@NiF,

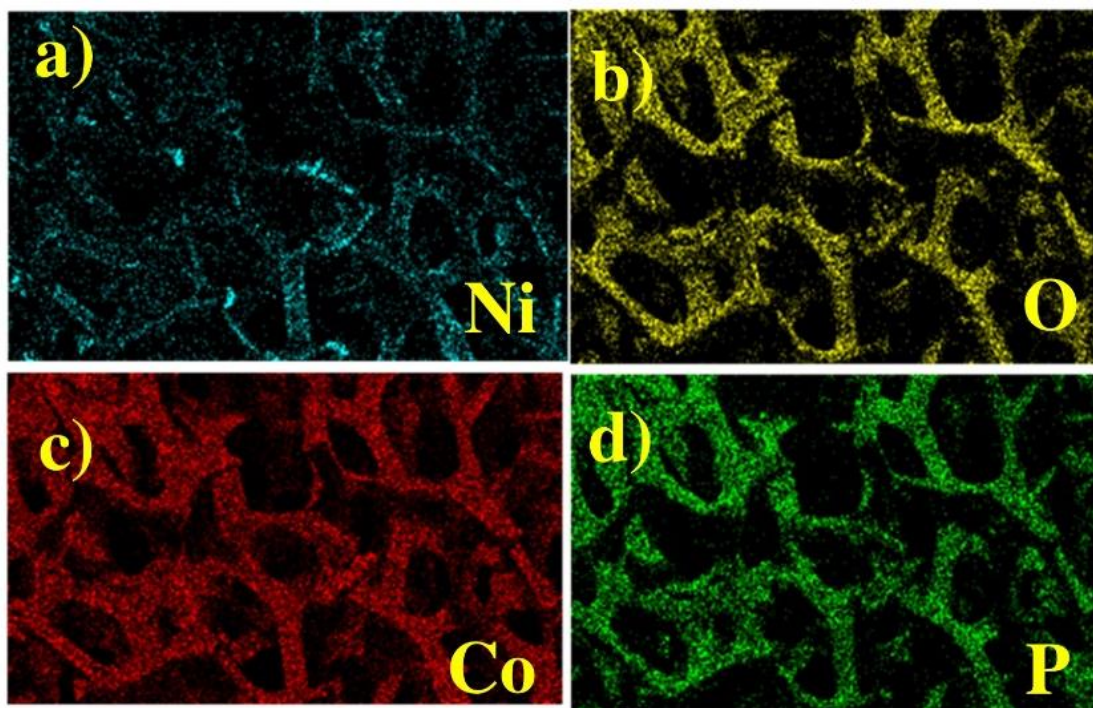


Figure 18: (a-d) the element mapping of Nickel, oxygen, cobalt, and phosphorous, respectively.

The surface chemical state of CoP@NiF is investigated using XPS. The survey spectra of CoP@NiF (Fig. 19a) show that Co, P, Ni, and O elements coexist in the electrocatalyst. This was completely consistent with the EDX results. The binding energies (BEs) 781.10 (2p_{3/2}) and 795.59 (2p_{5/2}) eV are ascribed to the binding energies Co 2p_{3/2} and Co 2p_{1/2} in CoP, respectively whereas the BEs 779.6 and 795.1 eV are attributed to (2p_{3/2}) and (2p_{5/2}) [109]. Satellite peaks are the two remaining deconvoluted peaks, found at 786.54 eV and 803.74 eV. Furthermore, the high-resolution XPS spectra of P 2p core levels can be deconvoluted into three peaks, respectively positioned at 129.5 eV for P 2p_{3/2}, 130.7 eV for P 2p_{1/2}, and 133.58 eV for oxidized P species. The phosphate is represented by a wide peak at 135.4 eV, indicating surface oxidation [110][111]. The peaks at 781.2 and 134.4 eV are attributed to oxidized Co and P species formed by the surface oxidation of CoP. The high-resolution C spectra of O 1s support the findings, which can be deconvoluted into three peaks of P-O (533.2 eV), C-O (531.9 eV), and Co-O (531.3 eV).

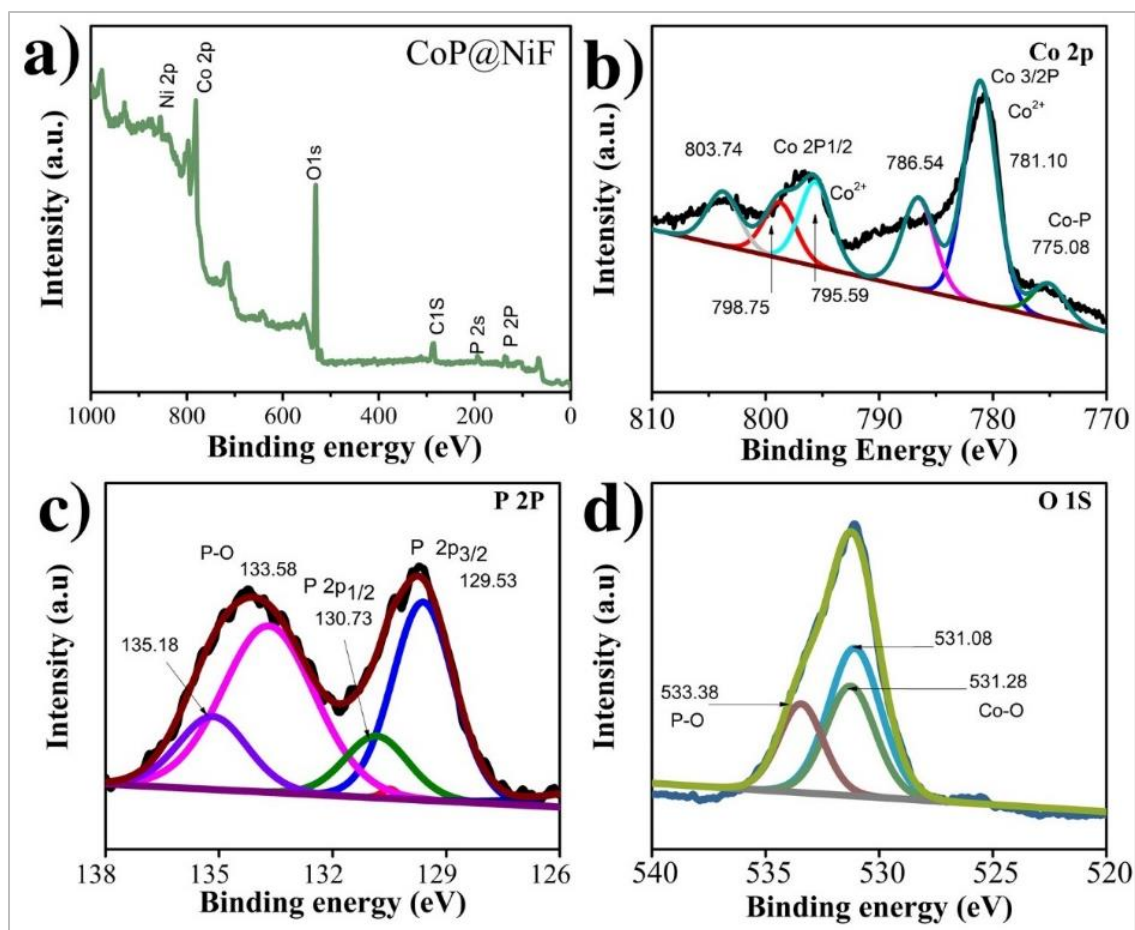


Figure 19: XPS spectra of CoP@NiF. (a) survey, (b) Co 2P, (c) P 2P and (d) O 1s.

Furthermore, compared to the binding energies of metallic Co 2p_{3/2} (778.1–778.2 eV) and elemental P 2p_{3/2} (130.2 eV), the peaks of Co 2p_{3/2} and P 2p_{3/2} have shifted positively and negatively. Revealing electron transfer from Co atoms to P atoms in CoP sheets, suggesting a partial positive charge for Co centers and a partial negative charge for P centers [112]. This type of charge transfer facilitates the adsorption and desorption of intermediates and products during electrochemical oxidation of various substrates [113] [114].

Cyclic Voltammetry (CV) studies were performed to examine the prepared electrode's catalytic activity for alcohol oxidation. For this approach, a three-electrode system cell was used in which bare nickel foam, platinum electrode, and Ag/AgCl serve as the working, counter, and reference electrodes, respectively. The CV results indicate that after adding benzyl alcohol to the acetonitrile-water mixture solvent, the current density was increased significantly, which was attributed to the alcohol-oxidation reaction (Fig. 19a). The same was observed with the addition of 2-phenoxyethanol in Fig. 19b. However, 2-phenoxyethanol shows a lower current density increment compared to benzyl alcohol.

Furthermore, the addition of HMF also enhanced the current density. These findings show that the prepared CoP electrocatalyst exhibits significant catalytic activity toward the oxidation of alcohols. It is worth mentioning that the bare nickel foam showed lower current density and low capacitive current for all the substrates, as illustrated in Fig. 19. Fig. 19d depicts a five-hour duration chronoamperometry curve for the CoP@NiF electrode in the presence of the electrolytes. No significant changes in current density were observed for the entire period investigated, demonstrating the chemical stability of the electrocatalyst under the applied experimental conditions.

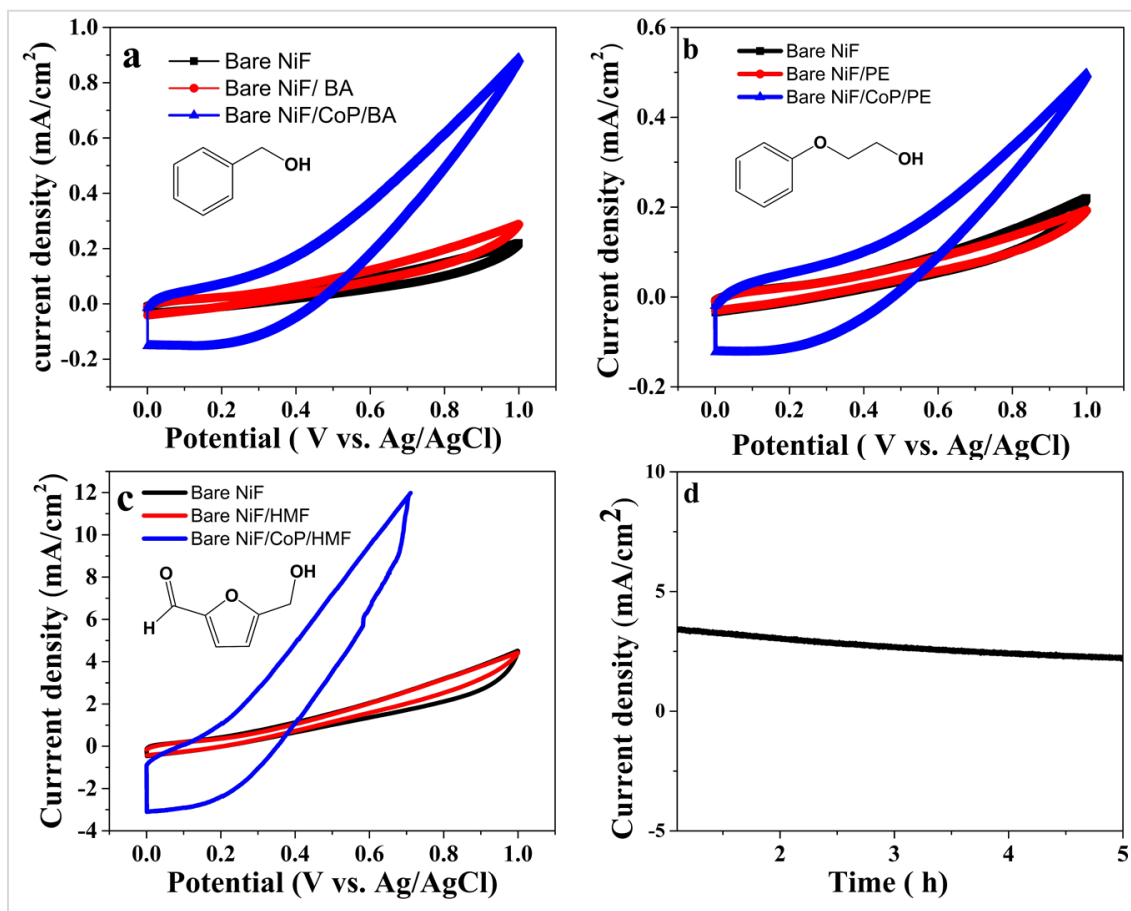
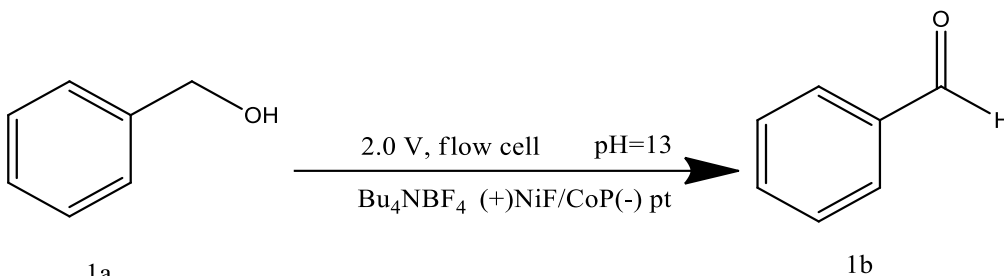


Figure 20: The CV of a different substrate of CoP@NiF electrocatalysts in 1.0 M KOH: (a) benzyl alcohol, (b) 2-phenoxyethanol, (c) HMF, (d) current-time curve of the CoP@NiF.

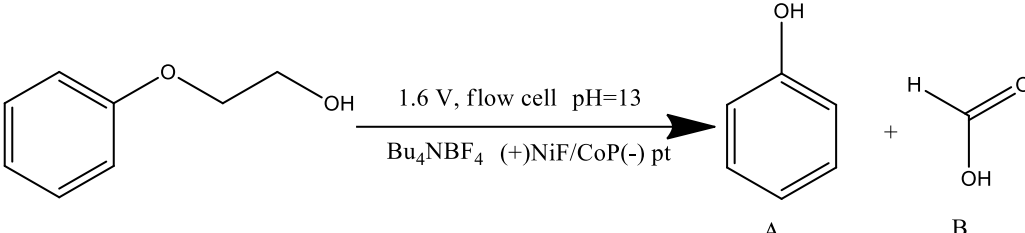
Our investigation of the reaction condition starts with benzyl alcohol (1a), which was initially exposed to a batch condition (no droplet flow) in an undivided cell (Table 2, entry 1). This approach yielded a 47% selectivity for benzaldehyde (1b) after 1 hour of electrolysis at 2.0 V. A mixture of acetonitrile and water (1:1) was employed as a solvent to increase the starting material's solubility. The selectivity of generating benzaldehyde was achieved by employing a low concentration of potassium hydroxide, which reduced the possibility of the Cannizzaro reaction.

Table 2: Optimization of droplet-assisted electrochemical oxidation of benzyl alcohol.

 <chem>c1ccccc1CO</chem> 1a $\xrightarrow[\text{Bu}_4\text{NBF}_4 \text{ (+)NiF/CoP(-) pt}]{2.0 \text{ V, flow cell } \text{pH}=13}$ <chem>c1ccccc1C=O</chem> 1b			
Entry	Potential (V)	%Conversion	% Selectivity
1	2.0	32.0	47.0
2	0.5	45.2	54.0
3	1.0	45.2	78.4
4	1.5	46.1	82.5
5	2.0	83.5	94.0
* Reaction conditions: Benzyl alcohol (2.0 mmol) and KOH (0.01 M), the temperature at 25 °C, electrolysis time is 60 min. The stirring rate is 250 rpm, and the flow rate is 12.5 $\mu\text{L}/\text{min}$.			

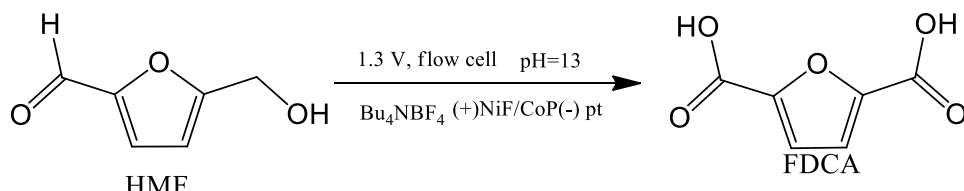
The continuous electrochemical flow cell with a droplet flow mechanism was then used in the next phase. The selectivity of generating benzaldehyde with this method reached 93 % for the same experimental conditions, whereas the (1a) conversion was only 63.5%. The increased conversion and product selectivity facilitated by the flow droplet mechanism were attributed to the enhanced surface reaction at the electrode interface. The effect of electrical potential variation on the conversion and selectivity was also studied, as shown in Table 3. Although there was no change in the conversion of benzyl alcohol at lower potentials (0.5 – 1.5 V), the potential was discovered to impact the product selectivity significantly.

Table 3: Optimization of droplet-assisted electrochemical oxidation of 2-phenoxyethanol.

 <chem>CCOCc1ccccc1</chem> $\xrightarrow[\text{Bu}_4\text{NBF}_4 \text{ (+)NiF/CoP(-) pt}]{1.6 \text{ V, flow cell pH=13}}$ <chem>Oc1ccccc1</chem> (A) + <chem>OCC=O</chem> (B)			
Entry	Potential (V)	% Conversion	% Selectivity
1	0.5	6.0	10.0
2	1.0	8.0	12.0
3	1.2	56.5	71.0
4	1.6	92.0	96.0
* Reaction conditions: Phenoxyethanol (2.0 mmol), NaOH (1.0 M) [b] determined by HPLC, temperature at 25 °C, electrolysis time is 60 min. The stirring rate is 250 rpm, and the flow rate is 12.5 $\mu\text{L/min}$.			

In the next stage, we investigated the transformation of 2-phenoxyethanol using the droplet flow-assisted electrochemical oxidation approach. According to reports, at a potential of 1.6 V, the oxygen atom of a phenoxy molecule of 2-phenoxyethanol may be oxidized to generate a positively charged radical that can then be utilized to construct polymer chains. Its oxidation potential is approximately 1.0 V higher than that of most phenols. Based on these findings, we limit our voltage variation in this study to 1.6 V for 2-phenoxyethanol conversion. The experimental results are displayed in Table 4. In entry 1, a mixture of CH₃CN/H₂O (1:1) was used; only a 6.0 % conversion was achieved. This lower conversion may be due to the insolubility of the substrate, so no electrochemical oxidation is expected to occur under this condition. Entry 2 involves a control experiment with the bare nickel foam without the electrocatalyst, which also shows a lower conversion of 8% for 2-phenoxyethanol and a selectivity of 12%. In the case of entry 3, when NaOH 1.0 M was used as a supporting electrolyte, 56.5% conversion of 2-phenoxyethanol was achieved (entry 3). In the former entry 4, the major products of this entry were phenol and formic acid with 92%. According to the HPLC results, the major products of this reaction were phenol and formic acid. It is essential to keep in mind that the formation of formic acid increased over time, reaching its peak at 40 minutes of electrolysis and then immediately disappearing after 1.0 hours.

Table 4: Optimization of droplet-assisted electrochemical oxidation of HMF.

 HMF FDCA			
Entry	Potential (V)	% Conversion	% Selectivity
1	0.5	66.0	68.5
2	0.7	88.0	91.6
3	1.0	75.0	83.5
4	1.3	95.0	96.0
5	1.6	86.0	88.0
* Reaction conditions: HMF (20 mM) and KOH (1.0 M), the volume of electrolyte (30 mL), 5 mL of HMF in the nebulizer box, and temperature at 25 °C for 60 min. The stirring rate is 250 rpm, and the flow rate is 12.5 μL/min			

With the insight that CoP@NiF supported catalysts can drive the oxidation of various alcohols, the oxidation of BA, 2-PE, and HMF was investigated at room temperature and atmospheric pressure. Fig. 21 depicts the decrease in alcohol concentration and the formation of aldehyde as a function of reaction time. It is clear that the formation of benzaldehyde occurred even within the first 10 minutes. The concentration of benzaldehyde increased dramatically as the reaction progressed. It is worth noting that no significant benzoic acid was detected in the reaction medium, indicating that the electrode has a high selectivity to produce only benzaldehyde. However, as shown in Figure 4b, the change in 2-PE concentration over time revealed two main products: phenol and acetic acid.

On the other hand, HMF oxidation produced intermediate and interstitially high yields of FDCA in a short time. In fact, the reaction had reached 60% FDCA formation after 30 minutes. The fast conversion indicates that the main difference between microdroplets and bulk solutions is the large surface area and confined space of the droplet on all different substrates [115].

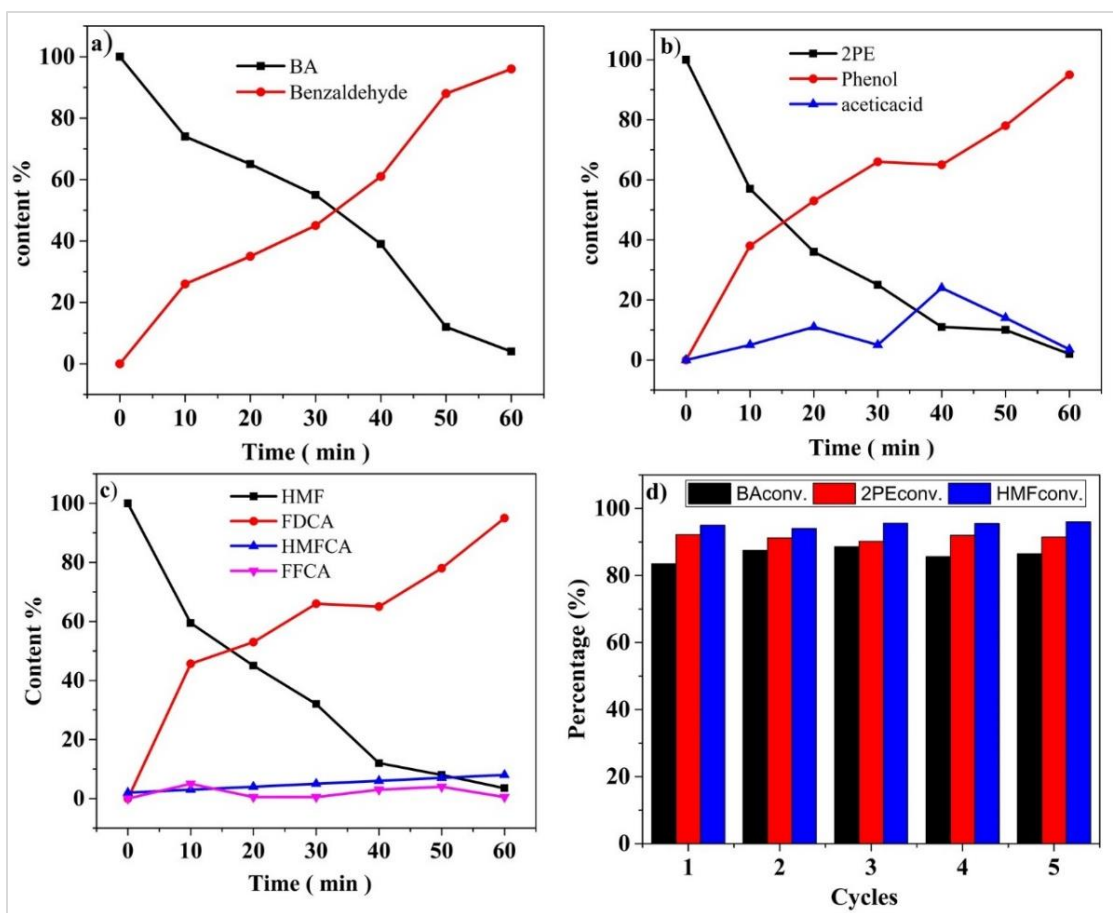


Figure 21: Evolution of reactant substrate and product concentrations for (a) BA, (b) 2-PE, and (c) HMF. (d) Effect of recycling on the electrocatalytic oxidation of CoP@NiF for the conversion of different substrates.

The ability to recycle an electrode is a critical factor in determining electrode stability. The recyclability of the CoP@NiF electrode was investigated by electrolyzing it several times. As shown, the CoP@NiF is an efficient, recyclable electrocatalyst for the selective electrochemical oxidation of BA, 2-PE, and HMF substrates. The electrochemical oxidation of the substrates as a function of different runs is illustrated in Fig. 20d. Table 5 compares our present work to previous work in the literature, and it demonstrates fast and high conversion that is superior to the published literature.

Table 5: Comparison of electrochemical oxidation of alcohol using various electrocatalysts.

Catalyst	Substrate	Product	Conv. %	Yield %	Condition	Time (min)	Ref.
Nickel oxy-hydroxide electrode	BA (*)	Benzaldehyde, Benzoic acid	-	86%	0.01 M NaOH	300	[116]
Au NP-modified carbon-fiber-thread electrode	BA	Benzaldehyde	-	50- 55	KOH, LiClO ₄	-	[95]
	1-PE	Acetophenone	-	38- 65	KOH, LiClO ₄		
TEMPO (0.1 mmol)	BA	Benzaldehyde	92.0	-	Carbonate buffer	120	[117]
NHPI (0.1 mmol)	BA	Benzaldehyde	57.0	-	Acetate buffer		
Co-P on Cu foam	HMF	FDCA	99.0	85.3	Deep eutectic solvents, 0.5 M NaHCO ₃	-	[118]
Carbon anode	BA	Benzaldehyde	-	95.0	Undivided, 30–34°C HCl as supporting electrolyte nitrate as mediator	-	[119]
CoP@NiF	BA	Benzoic acid	95.0	96.0	Droplet assisted method	60	This work
	2-PE	Phenol& CH ₃ CO ₂ H	96.0	96.0			
	HMF	FDCA	95.0	96.0			

(*) BA, benzyl alcohol; TEMPO: (2,2,6,6-tetramethylpiperidin-1-yl)oxyl, (NHPI) N-hydroxyphthalimide, 2-PE (2-phenoxyethanol).

4.4 Conclusion

To conclude, a fast and straightforward transformation of alcohols and HMF into the corresponding intermediates using droplet assisted flow with a continuous flow electrochemical reactor was demonstrated for the first time. The selectivity and yield of benzaldehyde can be tuned by electrolysis potential. The results show that at 1.5 V and 318.15 K, both the selectivity and the yield of benzaldehyde can reach above 98.8% with the system under ambient conditions. An accelerated droplet synthesis approach of alcohol and its derivatives has been achieved.

CHAPTER 5

Droplet Assisted Approach for Electrocatalytic Reduction of Nitrogen using mixed Amorphous Iron oxide to Ammonia under ambient condition

Abstract

In ambient circumstances, electrocatalytic N_2 reduction to NH_3 is an appealing approach for artificial N_2 fixation. Electrochemical nitrogen reduction reactions can offer a valuable source of ammonia, but the process is limited by the low production rate and poor conversion efficiency at the cathodic electrode. Here, we have designed a unique iron oxide for electroreduction of nitrogen to ammonia in a neutral electrolyte and mild conditions, achieving excellent faradic efficiency and a high ammonia yield rate of $35.6 \text{ g h}^{-1} \text{ mg}^{-1} \text{ cat.}$ at -1.0 V . The $\text{C-Fe}_2\text{O}_3$ on graphite felt ($\text{C-Fe}_2\text{O}_3@\text{GF}$) was synthesized by hydrothermal under a nitrogen environment for electrochemical reduction of nitrogen. The graphite is used as a substrate due to its supermicropores, which function as a more active site for Fe_2O_3 to be exposed. Due to the supermicropore nature of the graphite felt substrate, more active sites of $\text{C-Fe}_2\text{O}_3$ could be exposed, increasing electron transport, and creating open pathways for rapid H_2 release. These findings can support the development of Fe-based electrocatalysts for NRR at atmospheric pressure.

5.1. Introduction

Ammonia is the world's second-most manufactured chemical (170 Mt per year), with more than 80% used for fertilizers and the remainder for refrigerants or chemical feedstocks [120][121]. Transformation of nitrogen into ammonia utilizing an electrochemical strategy, particularly whenever coupled with an environmentally friendly power source, is a promising elective route in the energy and chemical industry [122]. Due to the very strong nitrogen triple bond energy, it is incredibly hard to create ammonia from nitrogen directly [123]. The Haber-Bosch process, which requires high temperatures and pressure to produce ammonia from N_2 and H_2 over iron-based catalysts, has been used in industry [124]. However, this cycle process consumes 5% of the world's natural gas annually and approximately 2% of total power, resulting in a significant contribution of global carbon dioxide [125]–[127]. Urgent need to develop an environmentally and sustainably benign method to produce ammonia under ambient conditions.

The electrochemical synthesis of ammonia with renewable energy-driven electricity is seen as a game-changing, ecologically benign, and long-term strategy for ammonia production [128]–[130]. The energy consumption and CO_2 emissions associated with NH_3 synthesis can be greatly lowered by hydrogenating N_2 at lower temperatures and pressures using controlled electrochemical potentials with an estimated energy cost of less than $10 \text{ kWh kgNH}_3^{-1}$ at % Coulombic efficiency [131]. Moreover, due to the slow kinetics of the nitrogen reduction reaction (NRR) and the need for an active catalyst effective at dissociating the strong N_2 triple bond, efficient electrochemical synthesis of NH_3 under moderate conditions has yet to be established [132], [133].

Recently, metal-based electrocatalysts have been developed, demonstrating the feasibility of electrochemical ammonia production [134]–[139]. However, their low Faradic efficiency and excessive cost limit usage in industrial applications. Furthermore, the competition of side reactions of hydrogen evolution reactions, poor selectivity, and low yield of NRR due to the high stability of the N_2 molecule are important challenges in the electrochemical generation of NH_3 by NRR [140]. So, it is crucial to design an effective electrocatalyst that can quickly suppress HER yet trigger NRR.

Currently, electrochemical ammonia synthesis on valuable metals such as Ru [129], [141], [142] Pt, Pd [137], and Au [132], [143], nonprecious metals such as carbon-based materials, Ni and Fe, has been demonstrated. Fe-based catalysts have attracted a lot of attention due to their inexpensive cost and high activity for NH_3 production. For example, Licht et al. showed a high NH_3 generation rate and faradaic efficiency (up to 35 %) utilizing Fe_2O_3 catalysts in a molten hydroxide electrolyte cell at 200 °C [144]. However, high-temperature electrolysis has a significant power supply and facility needs, making it incompatible with intermittent renewable sources such as wind and sun [131]. On the contrary, a recent room-temperature investigation of NRR on carbon nanotube-supported Fe_2O_3 nanoparticles revealed an NH_3 production rate of $0.22 \text{ g cm}^2 \text{ h}^{-1}$ but with a poor Faradaic efficiency of 0.15 % [145]. Understanding the influence of various chemical states of Fe on NRR activity and selectivity will facilitate the development of efficient, cost-effective catalyzes for electrochemical NH_3 production. All research on Fe-based catalysts for N_2 RR has focused chiefly on [133], [145], [146], while other chemical states of Fe-based compounds (such as Fe and Fe_3O_4) are still being studied.

In this paper, we present a new facial one-pot approach for producing phase-controlled iron-based catalysts contained in carbon and oxygen by pyrolyzing a simple iron acetate as an iron-containing catalyst and a carbon source. The synthesis was conducted using sequential thermal treatments with solid iron oxalate salt underflows of nitrogen gas and elevated temperatures. The catalyst has good ammonia production, activity, selectivity, and stability.

5.2 Experimental Section

5.2.1 Chemicals

Ammonium chloride, ferric acetate, sodium nitroferricyanide. Sodium salicylate, Sodium hydroxide, Sodium hypochlorite, and Sodium nitroferricyanide dihydrate. All chemicals were analytical reagent grades, and they were utilized exactly as supplied, with no additional purification. Amide dihydrate. The anode and cathode chambers were separated using a Nafion 117 proton exchange membrane obtained from ElectroCell.

5.2.2 Synthesis of C-Fe₂O₃

About 50 mg of ferric acetate was added to the furnace boat, then the material was calcined under nitrogen for 6 hr, under the flow of nitrogen gas. After that, the C-Fe₂O₃ was formed, and the catalyst was collected. The above procedure was repeated at different calcination temperatures from 400 -700 °C.

5.2.3 Preparation of Catalyst Electrodes

A 5.0 mg of iron oxide catalyst and 40.0 μL of Nafion solution (1.66 wt%) were dispersed in 600 μL of ethanol and 360 μL of water by ultrasonication for 1.0 hrs. To form a homogeneous ink. Then, the dispersion was loaded onto a graphite felt electrode substrate with an area of 4.0 * 3.0 cm² and then dried under ambient conditions. Subsequently, the

homogeneously dispersed ink was drop-casted to the graphite felt electrode to achieve a catalyst loading of 0.22 mg cm^{-2} .

5.2.4 Characterizations

XRD data were collected using a Labx XRD-6100 X-ray diffractometer, with a Cu K α radiation (40 kV, 30 mA) of wavelength 0.154 nm (Shimadzu, Japan). SEM images were obtained using a Quanta FEG 250 field-emission SEM with an accelerating voltage of 20 kV. TEM characterizations were performed using a HITACHI H-8100 electron microscopy (Hitachi, Tokyo, Japan) operated at 200 kV. Using Mg as the exciting source, XPS data were acquired on an ESCALABMK II XPS. FTIR spectrum was taken on an IR spectrophotometer. The absorbance data of the spectrophotometer was evaluated using a UV–Vis spectrophotometer.

5.2.5 Electrochemical measurements

Initial LSV characterization of the catalyst was conducted using graphite felt electrode as an ideal, flat substrate electrode (loading amount: 0.22 mg cm^{-2}) at a scan rate of 25 mV s^{-1} in both N_2 and Ar saturated 10 mM HCl electrolytes (gas purging rate = 70 mL min^{-1}). A three-electrode set-up was used in all measurements. A platinum wire was used as a counter electrode (CE), and Ag/AgCl (sat. KCl) was used as the reference electrode (RE). Further experiments oriented towards optimization were conducted using GF as a substrate to produce a higher surface area.

The electrolyte used in this study is 0.1 M Na_2SO_4 . The typical amount of electrolyte used in this study is 25.0 mL. The larger amount of 20 mL was used to allow electrolyte sampling for the long-term electrolysis experiment. The N_2 and Ar gases used in the experiments were

high-purity, Alphagaz-grade (purity: 99.999%). Before each measurement, the electrolyte was purged with the high-purity gas for 30 min at a constant flow rate of 70 ml min⁻¹. Subsequently, electrochemical measurements or electrolysis were conducted with continuous gas purging with the gas inlet positioned close to the working cathode. And all the potentials were adjusted to RHE according to the following equation

5.2.6 Method of ammonia determination

The amount of ammonia produced was calculated using the indophenol blue method and ultraviolet spectroscopy. In detail, a 4.0 mL of sample was taken. Then 50 µL of the oxidizing solution (which contains 0.4 M sodium salicylate and 0.32 M sodium hydroxide), 500 µL of coloring solution (sodium hypochlorite and 0.75 M sodium hydroxide), and 50 µL of catalyst solution (0.1g sodium nitroferricyanide (III) dehydrate diluted to 10 ml with deionized water) were added respectively to the same solution. Absorbance measurements were performed after 2.0 hr at $\lambda = 690$ nm (675 nm). The calibration curve below was used to calculate the ammonia concentration. The NH₃ concentration was calculated to form the calibration curve (Fig. 22). The rate of NH₃ yield and FE% were calculated using the following equation:

$$R_{\text{NH}_3} (\mu\text{g h}^{-1} \text{mg}^{-1}\text{cat.}) = \frac{x(\mu\text{g mL}^{-1}) \times V(\text{mL})}{t(\text{h}) \times m(\text{mg}^{-1})} \quad (5.1)$$

$$FE(\%) = \frac{3 \times x(\mu\text{g mL}^{-1}) \times V(\text{mL}) \times 10^{-6} \times F}{17 \times Q} \times 100\% \quad (5.2)$$

where ($\mu\text{g mL}^{-1}$) is the ammonia concentration generated, V (mL) is the electrolyte solution volume, m is the mass of the catalyst, and t (s) is the reaction time. The faradaic constant (96485.34) is denoted by F, while the total charge transmitted through the electrode during NRR is denoted by Q.

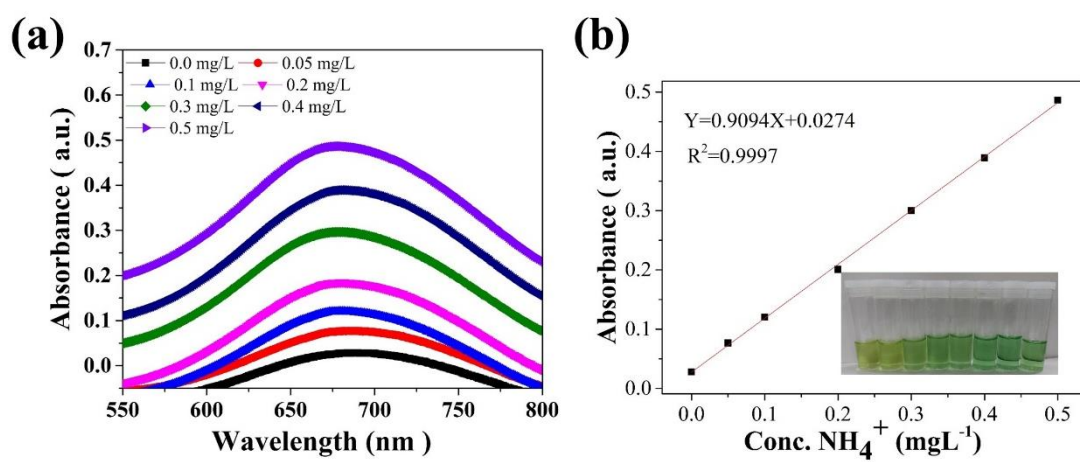


Figure 22: UV-Vis curves of indophenol assays with NH_4^+ ions after incubated for 2 h at room temperature. (b) Calibration curve used for calculation of NH_4^+ concentrations

5.3 Result and Discussion

The chemical composition and the structure of the resultant nanoparticles were investigated by XRD and SEM. As shown in Fig. 23, phase-pure α -Fe₂O₃, a-Fe₂O₃, C-Fe₃O₄, and Fe₃O₄ are formed after calcining the iron oxalate precursor under nitrogen gas. In Fig. 23c it is clearly shown that the XRD patterns at 500 °C have low crystallinity structures. However, when the temperature increases the composite becomes more crystalline. Because of its instability below 570 °C, most authors identify FeO as the major conversion phase that decomposes to Fe₃O₄ and α -Fe [147]. Moreover, the presence of the carbon matrix is useful for enhancing electronic conductivity.

The XRD patterns of samples Fe400, Fe500, Fe600, and Fe700 are shown in Fig. 23c. For Fe400, the sample became amorphous, which can be attributed to water loss from ferric acetate. At Fe500, the thermal breakdown of FeC₂O₄ and the creation occurred, resulting in the formation of hematite (α -Fe₂O₃). Parts of hematite are converted into maghemite (c-Fe₂O₃) and C-Fe₂O₃ at 600 °C. At 700 °C, magnetite (Fe₃O₄) dominated the result, with a trace of hematite

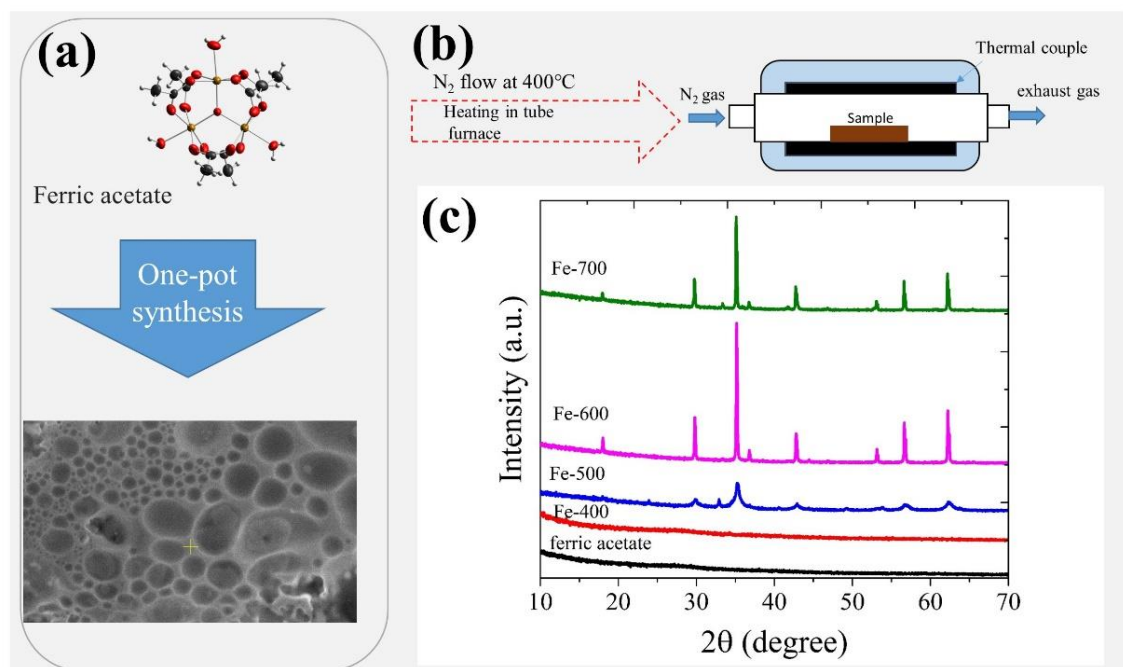


Fig. 23: C-Fe₂O₃ XRD patterns at various temperatures b) schematic of Fe₂O₃ tube furnace synthesis, c) XRD of iron oxide at different temperatures.

$\text{Fe}_2\text{O}_3\text{-C}$ was successfully produced in this study using a one-step hydrothermal process and deposited on graphite felt support as a catalytic electrode. The surface morphology and structural features of the produced $\text{C-Fe}_2\text{O}_3$ were investigated using FESEM/EDS, as shown in Fig. 24. The XRD (Fig. 24a) shows an amorphous peak catalyst feature. A smooth surface having a porous structure that is interconnected. This honeycomb-like structure was caused by the decomposition of acetate ions during the heating process, as shown by the high-resolution FESEM image (Fig. 24c). The results of the $\text{Fe}_2\text{O}_3\text{-C}$ surface elemental mapping obtained from the EDS investigation are also demonstrated in Fig. 24d. The elemental mapping of F, O, and C was apparent throughout the whole surface of the catalyst.

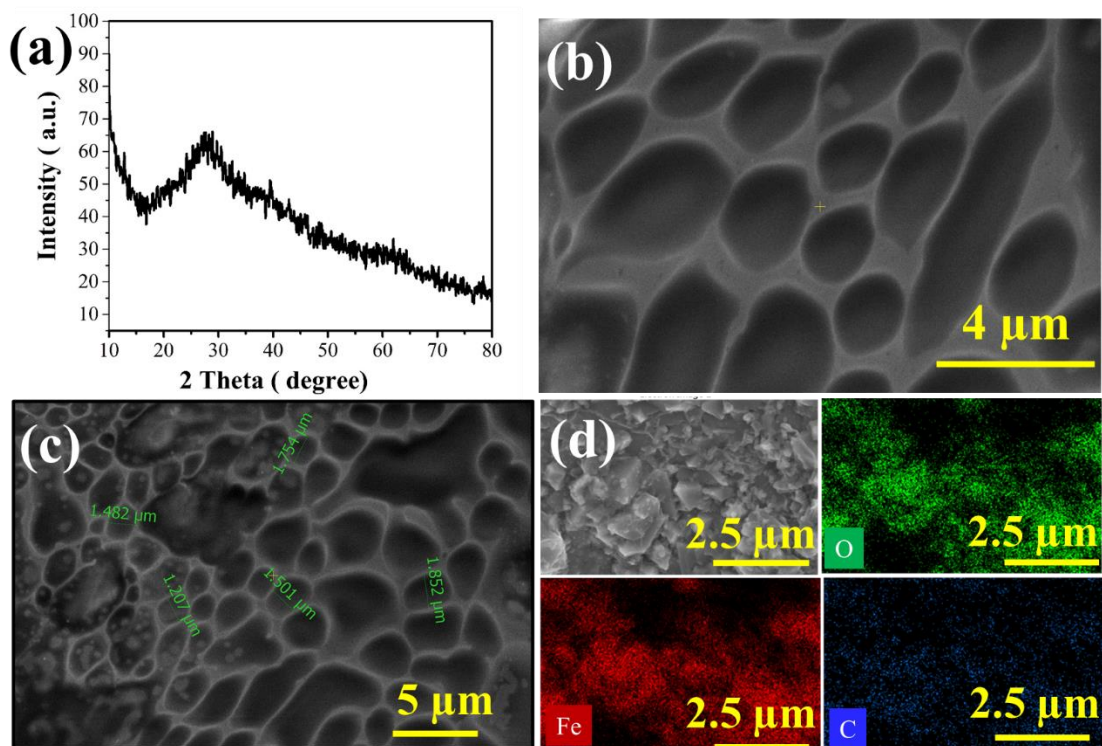


Figure 24: a) XRD of Fe-400 catalyst, (b,c) the SEM of the Fe-400 d) the SEM elemental distributions of O, Fe, and C.

The XPS of the three products was conducted to further confirm the chemical bonding structure and chemical composition. The XPS survey spectra in Fig. 25a show the presence of carbon, oxygen, and iron elements in as-prepared products. Fig. 25b–d shows the high-resolution C1s, O 2p, and Fe2p, XPS spectra of different samples, respectively. For the C1s spectrum (Fig. 25b), the dominant peak located at 284.7 eV can be ascribed to sp² hybridized graphitic carbon. Fe 2p spectra of C-Fe₂O₃ could also be divided into six peaks located at 709.35 eV (Fe²⁺ 2p 3/2), 713.11 (Fe³⁺ 2p_{3/2}), 717.11 (satellite peak), 722.06 (Fe²⁺ 2p 1/2), 725.96 (Fe³⁺ 2p_{1/2}) and 730.36 eV (satellite peak), respectively [148]. The Fe 2p_{3/2} and Fe 2p_{1/2} peaks of Fe-500 (Fe) were located at 710.28 eV and 724.08 eV respectively, and their separation ($\Delta = 2p_{3/2} - 2p_{1/2}$) was 14 eV. These properties were comparable to those of the reference Fe₂O₃ [149]. Therefore, the obtained peaks were attributed to Fe (III) in the Fe-500 sample.

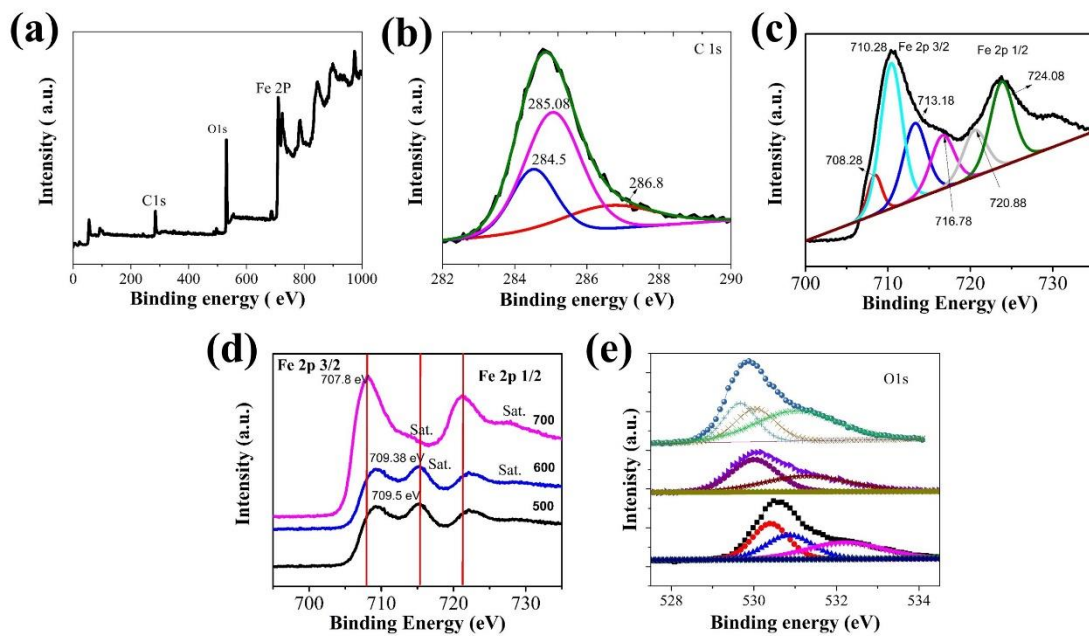
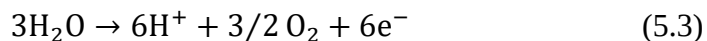


Figure 25: (a) XPS survey spectrum for C-Fe₂O₃, (b) C 1s, (c) Fe 2p, and (d) Fe 2p regions, (e) O 1s.

To study the catalytic performance of C-Fe₂O₃@GF for NRR, electrochemical experiments were performed in 1.0 M KOH by using a divided microflow reactor separated by a Nafion membrane. The NRR response measure in the cell can be shown as follows



The generated proton ion is moved through the Nafion membrane to produce ammonia at the cathode [120].



UV-vis absorption spectra of the electrolytes stained with indophenol indicator after charging at -1.0 V for 2 h under various conditions. For NRR testing in 0.1 M Na₂SO₄ at room temperature and 1.0 atmosphere, C-Fe₂O₃@GF was coated on a graphite felt electrode (C-Fe₂O₃@GF, loading: 5.0 mg) using a flow cell reactor, as illustrated in Fig.27b.

The linear sweep voltammetry (LSV) curves show a slight current density decrease by the N₂ test, showing that the NRR process occurs in 0.1 M Na₂SO₄ electrolyte, as shown in Fig. 27a. Aside from high-efficiency electrocatalysts, the design and development of high-performance electrochemical NRR reactors are vital for NH₃ generation. Several published studies have confirmed that flow-type electrochemical reactors are highly beneficial for boosting NRR performance due to efficient mass transfer and high N₂ coverage on the catalyst [145], [146], [150]. The C-Fe₂O₃ was assembled in a homemade two-compartment flow cell for electrochemical NH₃ synthesis.

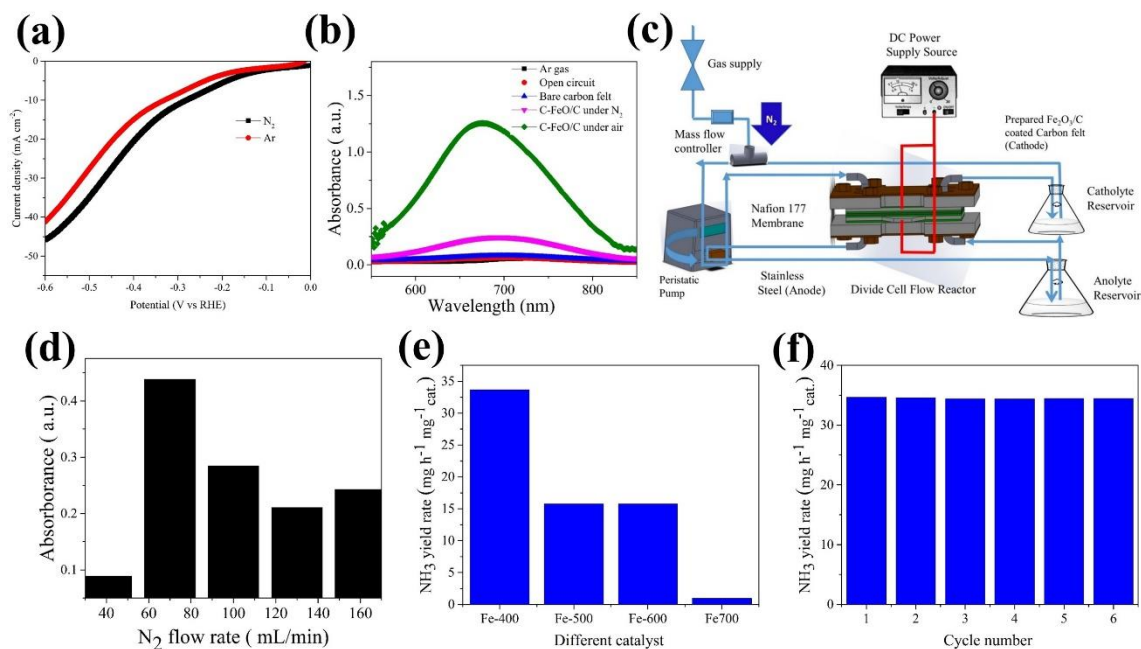


Figure 26: a) LSV curve of Fe_2O_3 (catalyst loading: 5 mg cm^{-2}) recorded at a scan rate of 5 mV s^{-1} in Ar and N_2 atmospheres. b) After charging at -1.0 V for 2 hours under varied settings, the UV-vis absorption spectra of the electrolytes stained with indophenol indicator were obtained. c) illustration of flow-cell used in the NRR testing, d) the effect of N_2 flow, e) NH_3 yield rates of C- Fe_2O_3 .

Fig. 26c describes a flow cell with two compartments for anode, cathode, and gas supply. Electrolyte streams separated the C-Fe₂O₃ as the cathode and stainless steel as the anode in this case. To avoid the crossover transfer of product NH₃ to the anode, an ion exchange membrane was inserted between the anolyte and catholyte. The two-compartment flows were mixed within a gas-tight system in the flow to a cathodic compartment in which the droplet assisted was formed. During the electrolysis, the gaseous reactant was supplied in a flow-through mode utilizing a mass flow controller at a constant flow rate of 70 mL min⁻¹. A peristaltic pump with a constant flow rate of 5.0 mL min⁻¹ was used to circulate 25.0 mL of the catholyte and anolyte. In the catalyst layer, droplets and a solid two-phase interface were formed, allowing an electrocatalytic N₂ reduction process at the catalyst sites through electron and proton transfer. As shown in Fig. 26f, Fe₂O₃@C shows a minor change in NH₃ yields after six cycle tests.

The NH₃ generated was measured spectrophotometrically using the indophenol blue method [145]. We also electrolyzed N₂-saturated solutions at open circuit potential and Ar-saturated solutions at -1.0 V. The corresponding UV-vis absorption spectra are presented in Fig. 27a, enabling a more accurate assessment that excludes background contributions. Clearly, the bare graphite felt electrode exhibits little NRR activity, indicating that C-Fe₂O₃ is the active species catalyzing N₂ electro-reduction.

Furthermore, the N₂ flow rate does not affect C-Fe₂O₃@GF performance (Fig. 27b), implying that N₂ diffusion is a rate-determining step for NRR. At a low flow rate, the nitrogen is not enough for the formation of ammonia. However, when the rate of nitrogen increases to 40 ml min⁻¹ it leads to high ammonia formation which is attributed to a sufficient supply of nitrogen and hydrogen from electrolytes for nitrogen reduction. At a higher flow rate than

the 40 ml min^{-1} decrease of ammonia formation observed without change, it yields an even more increased flow. With a higher nitrogen flow rate, the retention time of nitrogen molecules in the cathode is significantly reduced, making critical adsorption and activation of nitrogen molecules on the catalyst less achievable [151]. Given the possibility of trace levels of NH_3 in the supplying gas and atmosphere, high-purity gas (Ar/N_2 , purify: 99.999%) flowing through the electrolyte in a sealed electrolyzer with no applied voltage was conducted. The UV-vis absorption spectra (Fig. 27d) demonstrate that no NH_3 was found, indicating that no interference from the environment or providing gas was present.

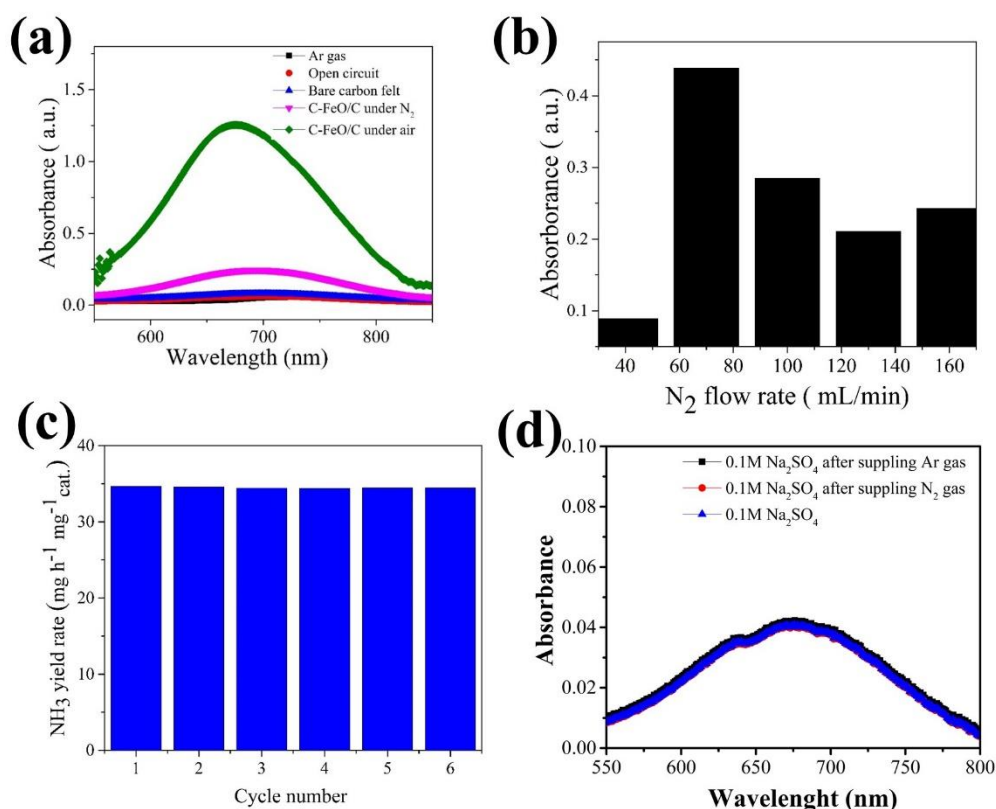


Figure 27: a) UV-vis absorption spectra of the electrolytes stained with indophenol indicator after charging at -1.0 V for 2 h under various conditions, b) the effect of N_2 flow, c) recyclability of the catalyst, d) Absorption spectra of the 0.1 M Na_2SO_4 electrolyte stained with indophenol after supplying Ar or N_2 with no applied voltage

Table 6: The comparisons of NRR performance for the Iron oxide with the recently reported electrocatalysts under ambient conditions.

Catalyst	Electrolyte	NH ₃ yield	FE	Ref.
C-Fe ₂ O ₃ @GF	0.1 M Na ₂ SO ₄	35.0 µg h ⁻¹ mg ⁻¹ cat	15.2	This work
Fe ₂ O ₃ -CNT	Diluted KHCO ₃ solution	0.218 µg h ⁻¹ cm ⁻²	0.15%	[145]
Fe ₃ O ₄ /Ti	0.1 M Na ₂ SO ₄	3.42 µg h ⁻¹ cm ⁻²	2.6%	[152]
FeOOH nanorods	0.5 M LiClO ₄	23.32 µg h ⁻¹ mg ⁻¹ cat.	6.7%	[153]
γ-Fe ₂ O ₃	0.1 M KOH	0.212 µg h ⁻¹ mg ⁻¹ cat	1.9%	[133]
P-Fe ₂ O ₃ /CC	0.1 M Na ₂ SO ₄	6.78 µg h ⁻¹ cm ⁻² (13.56 µg h ⁻¹ mg ⁻¹ cat.)	7.66%	[154]
Au-Fe ₃ O ₄ NPs	0.1 M KOH	21.42 µg h ⁻¹ cm ⁻²	10.54	[140]
Fe/Fe ₃ O ₄	0.1M PBS	0.19 µg h ⁻¹ cm ⁻²	8.29	[155]
Fe ₂ O ₃ /TiO ₂ /C	1.0 M KOH	2.70× 10 ⁻¹⁰ mol mg ⁻¹ s ⁻¹	0.31	[156]
Fe-N/C-CNTs	0.1 M KOH	34.83 µg·h ⁻¹ ·mg ⁻¹	9.28	[157]
Fe ₂ O ₃ /Cu	0.1 M KOH	15.66 µg h ⁻¹ mg ⁻¹	24.4	[158]
FePc/C	0.1 M Na ₂ SO ₄	137.95 µg h ⁻¹ mg ⁻¹	12.28	[159]
γ-Fe ₂ O ₃ -NC/CF	0.1 M HCl	11.7× 10 ⁻¹⁰ mol cm ⁻² s ⁻¹	12.28	[160]
rGO/Fe@Fe ₃ O ₄ /CP freestanding electrode	0.2 M NaHCO ₃	1.3× 10 ⁻¹⁰ mol cm ⁻² s ⁻¹	6.25	[161]
Fe ₃ C/Fe ₂ O ₃ /Fe/C	6 M KOH	0.60 µg h ⁻¹ cm ⁻²	0.348%	[162]

5.4 Conclusions

In conclusion, C-Fe₂O₃@GF is reported as a highly active and long-lasting electrocatalyst for N₂ conversion to NH₃, with a high FE of 15.2 and a high NH₃ yield of 35.5 g h⁻¹ mg⁻¹_{cat.} at -1.0 V in 0.1M Na₂SO₄. The C-Fe₂O₃@GF also had great selectivity and was quite stable under long-term or repeated electrolysis.

CHAPTER 6

GENERAL CONCLUSIONS AND FUTURE WORKS

In the first part of this work, CoB/g-C₃N₄ nanosheet was dispersed on the surface of nickel foam and applied electrochemical oxidation of 5-hydroxymethylfurfural into 2,5-furandicarboxylic acid. Electrolysis at a constant voltage in combination with liquid chromatography resulted in the synthesis of FDCA with a yield of 97 % and a faradaic efficiency of about 95 %. The reaction product and intermediate were studied by liquid chromatography. The CoB/g-C₃N₄@NiF is a promising catalyst for the selective electrochemical oxidation of HMF, opening the way for a more environmentally friendly approach to electrosynthesis.

In the second part of this work, a new droplet-assisted approach catalyzed by the CoP@NiF was successfully used in the electrochemical oxidation of electrocatalytic oxidation of benzyl alcohol, 2-phenoxyethanol, and hydroxymethylfurfural at ambient conditions. Different voltage and recyclability were optimized in this conversion. The approach demonstrated a high conversion rate for the chosen alcohol. The effectiveness of the droplet-assisted technique in accelerating conversion was established.

In the last part of the thesis, a designed a unique iron oxide for electro reduction of nitrogen to ammonia in a neutral electrolyte, and mild conditions was reported. At -1.0 V, the faradic efficiency was outstanding, and the ammonia output rate was substantial, at 35.6 g h⁻¹ mg⁻¹ cat. For electrochemical nitrogen reduction, C-Fe₂O₃@GF was produced in a nitrogen atmosphere. These discoveries could help researchers create Fe-based electrocatalysts for NRR at atmospheric pressure.

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❖ **Publications**

1. **M. A. Suliman**, Basheer C., Droplet Assisted Approach for Electrocatalytic Reduction of Nitrogen using mixed Iron oxide to Ammonia under ambient condition, New J. Chem.. submitted. IF 3.591
2. Taofiq Abdulraheem Olarewaju, **Mohammed Altahir Suliman**, Chanbasha Basheer, Hian Kee Lee, Hollow Fiber Membrane-protected Zinc Oxide-coated

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 6. **M.A. Suliman**, M. H. Suliman, A. Adam, C. Basheer, Z.H. Yamani, M. Qamar, Interfacial coupling of amorphous cobalt boride with g-C₃N₄ nanosheets for superior oxygen evolution reaction, *Mater. Lett.* 268 (2020) 127593. doi:10.1016/j.matlet.2020.127593. IF 3.423
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8. M.A. Gondal, **M.A. Suliman**, M.A. Dastageer, G. Chuah, C. Basheer, D. Yang, A. Suwaiyan, Visible Light Photocatalytic Degradation of Herbicide (Atrazine), "Journal Mol. Catal. A, Chem. (2016). doi:10.1016/j.molcata.2016.10.015. IF 5.062

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