

**ROOM TEMPERATURE SYNTHESIS OF NANOMATERIALS USING
DROPLET CHEMISTRY AND THEIR APPLICATIONS**

BY

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Dedication

I humbly dedicate this work to Allah, my beloved family -especially my wife, Mother and Father whose support, patience and prayer during this period of my work mean the world to me.

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LIST OF ABBREVIATIONS

MD	: Microdroplets
PANI	: Polyaniline
MOF	: Metal-Organic Framework
HKUST-1	: Hong Kong University of Science and Technology 1
AAS	: Aerosol-assisted Synthesis
MS	: Mass Spectrometry
H₃BTC	: Benzene- 1,3,5-tricarboxylic Acid
XRD	: X-ray Diffraction
FT-IR	: Fourier Transform Infrared Spectroscopy
TGA	: Thermogravimetric Analysis
SEM	: Scanning Electron Microscope
BET	: Brunauer–Emmett–Teller Analysis
H-NMR	: Proton Nuclear Magnetic Resonance
TEM	: Transmission Electron Microscope
EDX	: Energy-dispersive X-ray spectroscopy
XRF	: X-ray Fluorescence Spectroscopy

E coli	: Escherichia coli
DESI	: Desorption electrospray ionization
ESI	: Electrospray Ionization
PTC	: Phase Transfer Catalyst
BDC	: Dicarboxylic Acid
TPA	: Terephthalic Acid

ABSTRACT

Full Name: JULDEH JALLOW

Thesis Title: ROOM TEMPERATURE SYNTHESIS OF NANOMATERIALS USING DROPLET CHEMISTRY AND THEIR APPLICATIONS.

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Metal-Organic Frameworks with good crystallinity are important for various applications. These porous materials have been predominantly synthesized using conventional methods such as solvothermal methods which are characterized by long reaction durations and inhomogeneous mixing of reactants. Microdroplet spray methods have been used as alternatives for the synthesis of MOFs like the HKUST-1 within a short period of time. However, these have led to the formation of non-crystalline MOFs with hollow spherical shaped crystals which are different from the known octahedral shaped reported in conventional methods. The hollow spherical shape crystals is a result of very fast solvent evaporation leading to poor crystallization. Synthesizing the HKUST-1 using microdroplet spray route using our flow system in 1 hour produced well defined crystals of octahedral shape which was confirmed by SEM, XRD, FT-IR and BET. Furthermore, the incorporation of solvent adjustment system shows the damaging effects of water in water sensitive MOFs like the HKUST-1. The synthesized HKUST-1 also showed good catalytic properties on nitrogen conversion to nitrates at room temperature which if improved and scaled, can serve as an alternative to high energy demanding methods of nitrates production. The

significance of this study ranges from shorter reaction time compared to conventional methods, the possibility of conducting in-situ coating of the MOF for possible catalytic reactions and the scalability of the method due to minimal waste generation and effective reagent utilization.

Polyaniline (PANI) have been widely used in applications such as sensors, removal of water pollutants, storage devices and capacitors due to its intrinsic electrical properties, low cost and environmental stability. Synthesis methods like electrochemical methods have been used to synthesize PANI. However, problems such as high cost and scalability issues have been encountered. Microdroplet synthesis on the other hand is an effective method of material synthesis that lead to the generation of products within a short period of time through the interaction of reactants in microdroplets at the liquid -air interface. The presence of oil contaminants in the environment from industries and homes has affected aquatic life and the availability of clean water for domestic use. Methods such as coagulation have been employed to purify water from oil contamination. However, membrane filtration have been found to be more effective. Here in, we present the microdroplet synthesis of PANI at room temperature using the Fenton-like reaction in water microdroplets through the aerosol-assisted spray (AAS) method for the first time . The spraying of water produces hydrogen peroxide which eventually reacts with Fe^{3+} to produce hydroxyl radicals. These hydroxyl radicals polymerizes aniline to polyaniline of good electrical conductivity and oil rejection capacity. In-situ coating of the PANI on an alumina ceramic membrane used in oil-water separation by the Cross Flow Filtration System led to a 95% oil rejection rate. The significance of this method is that the reaction is fast, cost-effective and is high scalable unlike many reported synthesis methods.

Silver nanoparticles have been widely synthesized and applied in important fields due to unique antibacterial, antioxidant, catalytic, large surface area and optical properties which are not common

in bulk materials. Due to long reaction times, use of capping agents and high temperatures in some cases, microdroplet synthesis of silver nanoparticles have become viable alternatives for their instant synthesis. Furthermore, storing synthesized nanoparticles such as silver has led to particle aggregation thereby reducing their surface area, hence antibacterial activity. In this study, we report the instant synthesis of silver nanoparticles from water microdroplets using ascorbic acid as a reducing agent. The outcome of this work shows that silver nanoparticles can be produced in seconds using the aerosol-assisted synthesis (AAS) known as the spray method. The results also show the good antibacterial activity of the synthesized silver nanoparticles and as such, a prototype device can be developed to carry out the in-situ production of silver nanoparticles for direct medical use in treating or preventing bacterial infection on skins of living organisms.

ABSTRACT (ARABIC)

ملخص

الاسم الكامل: جولد جالو

.عنوان الأطروحة: التحضير عند درجة حرارة الغرفة للمواد النانوية باستخدام كيمياء القطيرات وتطبيقاتها

التخصص الرئيسي: الكيمياء

تاريخ الحصول على الدرجة: مايو 2025

تعتبر الهياكل المعدنية العضوية ذات البلورية الجيدة مهمة للعديد من التطبيقات. تم تحضير هذه المواد المسامية باستخدام الطرق التقليدية مثل الطرق الهيدروحرارية التي تتميز بفترات تفاعل طويلة واختلاط غير متجانس للمتفاعلات. تم استخدام في فترة زمنية قصيرة. ومع ذلك، HKUST-1 طرق الرش بالقطيرات الدقيقة كبديل لتحضير الهياكل المعدنية العضوية مثل أسفرت هذه الطرق عن تشكيل هياكل عضوية غير بلورية تحتوي على بلورات كروية الشكل المجوفة تختلف عن الشكل الثماني الوجوه المعروف في الطرق التقليدية. يعتبر الشكل الكروي المجوف نتيجة لتبخر المذيب السريع الذي يؤدي إلى بلورة باستخدام طريقة رش القطيرات الدقيقة من خلال نظامنا الجري في ساعة واحدة، مما أنتج HKUST-1 ضعيفة. تم تحضير علاوة على ذلك، BET، FT-IR و XRD و SEM بلورات ذات شكل ثماني الوجوه محددة جيداً تم تأكيدها باستخدام أظهر HKUST-1 يظهر تضمين نظام تعديل المذيب الآثار الضارة للماء على الهياكل المعدنية العضوية الحساسة للماء مثل المحضر أيضاً خصائص تحفيزية جيدة في تحويل النيتروجين إلى النترات في درجة حرارة الغرفة، مما HKUST-1 الـ يمكن أن يكون بديلاً للطرق عالية الطاقة لإنتاج النترات إذا تم تحسينه وتوسيعه. تشمل أهمية هذه الدراسة تقليل وقت التفاعل مقارنة بالطرق التقليدية، وإمكانية إجراء الطلاء الداخلي للهيكل المعدني العضوي من أجل التفاعلات التحفيزية المحتملة، وقابلية توسيع الطريقة بفضل الحد الأدنى من النفايات واستخدام المواد الفعّال

على نطاق واسع في تطبيقات مثل أجهزة الاستشعار، إزالة الملوثات المائية، أجهزة التخزين (PANI) تستخدم مادة البوليانيلين والمكثفات نظراً لخصائصها الكهربائية الذاتية وتكلفتها المنخفضة واستقرارها البيئي. تم استخدام طرق مثل الطرق الكهروكيميائية لتحضير البوليانيلين. ومع ذلك، تم مواجهة مشكلات مثل التكلفة العالية وقضايا القابلية للتوسع. من ناحية أخرى، يُعتبر تحضير المواد باستخدام القطيرات الدقيقة طريقة فعّالة في تحضير المواد التي تؤدي إلى توليد المنتجات في فترة زمنية قصيرة من خلال

تفاعل المتفاعلات في القطبيلات الدقيقة عند واجهة السائل-الهواء. أثرت الملوثات الزيتية في البيئة من الصناعات والمنازل على الحياة المائية وتوافر المياه النظيفة للاستخدام المنزلي. تم استخدام طرق مثل التليبد لتتقية المياه من التلوث بالزيت. ومع ذلك، تم العثور على أن الترشيح الغشائي أكثر فعالية. في هذه الدراسة، نقدم التحضير باستخدام القطبيلات الدقيقة للبولانيليمين في درجة حرارة الغرفة باستخدام تفاعل مشابه لتفاعل فينتون في القطبيلات الدقيقة المائية من خلال طريقة الرش بمساعدة الهباء الجوي لإنتاج الجذور Fe^{3+} لأول مرة. يؤدي رش المياه إلى إنتاج بيروكسيد الهيدروجين الذي يتفاعل في النهاية مع (AAS) الهيدروكسيلية. تقوم هذه الجذور البوليمرية بتحويل الأنيلين إلى بولانيليمين ذو توصيل كهربائي جيد وقدرة عالية على رفض الزيت. أدى الطلاء الداخلي للبولانيليمين على غشاء سيراميكي من الألومينا المستخدم في فصل الزيت عن الماء باستخدام نظام الترشيح المتقاطع إلى معدل رفض زيت يصل إلى 95%. تتمثل أهمية هذه الطريقة في أن التفاعل سريع وفعال من حيث التكلفة وقابل للتوسع بشكل عالٍ مقارنة مع العديد من طرق التحضير المبلغ عنها.

تم تحضير الجسيمات الفضية النانوية على نطاق واسع واستخدامها في العديد من المجالات المهمة بفضل خصائصها الفريدة مثل الخصائص المضادة للبكتيريا، والمضادة للأكسدة، والتحفيزية، والمساحة السطحية الكبيرة، والخصائص البصرية التي لا توجد في المواد السائبة. وبسبب فترات التفاعل الطويلة، واستخدام المواد الحافظة ودرجات الحرارة العالية في بعض الحالات، أصبحت طرق تحضير الجسيمات الفضية النانوية باستخدام القطبيلات الدقيقة بدائل قابلة للتطبيق لتحضيرها بشكل فوري. علاوة على ذلك، أدى تخزين الجسيمات النانوية المحضرة مثل الجسيمات الفضية إلى تكتل الجسيمات مما يقلل من المساحة السطحية وبالتالي النشاط المضاد للبكتيريا. في هذه الدراسة، نُقدم التحضير الفوري للجسيمات الفضية النانوية من القطبيلات المائية باستخدام حمض الأسكوربيك كعامل اختزال. تُظهر نتائج هذه الدراسة أن الجسيمات الفضية النانوية يمكن تحضيرها في ثوانٍ باستخدام طريقة التحضير بالرش المساعد للهوا. تُظهر النتائج أيضًا النشاط المضاد للبكتيريا الجيد للجسيمات الفضية النانوية المحضرة، وبالتالي يمكن تطوير جهاز نموذجي لإجراء التحضير الداخلي للجسيمات الفضية النانوية للاستخدام الطبي المباشر في معالجة أو منع العدوى البكتيرية على جلود الكائنات الحية.

CHAPTER ONE

INTROUCTION

1.1 Background

Microdroplet chemistry is a new method of synthesis of materials by producing charged droplets with enhance properties that facilitate fast reaction rates and formation of valuable products[1]. Compared to their bulk or classical counterparts, microdroplet chemical reactions can take place with reaction rates that can be enhanced by a magnitude of nearly 10^5 - 10^6 [2]. Although most reactions in microdroplets can also take place in bulk phase reactions, they are significantly accelerated in microdroplets to generate products using small volume of reactants within a short reaction time [3]. Research indicates that microdroplets can show reaction acceleration with several orders of magnitude[2]. This is due to the reaction at the air-liquid interface with partial solvation of reactants, one factor that contributes in decreasing the critical energy of the reaction [4]. Several fields of study have been affected by microdroplets. These fields include chemical derivatization, reaction mechanistic studies, high-throughput reaction screening and rapid small-scale, green, and sustainable synthesis[5]. The “catalytic” properties of microdroplet reactions were observed during the establishment of technologies that are droplet related in research[6]. Various processes such as spray methods (e.g. electrospray), drop-casting, flow focusing, acoustic generation, Worthington jetting, droplet suspension and Leidenfrost levitation has been used to produce microdroplets [7].

Classical methods such as solvothermal synthesis, hydrothermal synthesis, Microwave-assisted synthesis, electrochemical synthesis and many other synthesis processes have been employed in producing materials such as nanoparticles, MOFs, polymers and other valuable organic materials. However, these classical methods of synthesis have been found to involve large volumes of solvents, longer reaction times, high temperature, inhomogeneous mixing and generation of large amount of waste. In addition to these shortcomings, the classical methods of synthesis involved rigorous sample preparation and difficulty in producing materials of high quality at the nano level[1, [2, 3,7].

Microdroplet synthesis methods on the other hand involve the use of very small sample volumes, fast reactions and allows the detail study or analysis of materials at the micro and nano level. One synthetic approach of microdroplet research recently is the synthesis of nanoparticles such as silver. These syntheses can be done using devices ranging from microreactors, microsyringe using voltage, sprayers and other microfluidic devices that are designed specifically to generate microdroplets of sizes ranging from micrometers to nanometers. Prior to the use of microdroplets to synthesize nanoparticles, a wide range of techniques were available such as chemical reduction, electrochemical, solvothermal, sol-gel, photochemical reduction and Sono chemical synthesis have been demonstrated and well utilized for the synthesis of silver nanoparticles in the bulk phase. However, most of these synthesis methods in the bulk context require high temperatures, capping agents, or longer reaction times. [3].

Metal-Organic Frameworks with good morphological properties have been used for a wide range of applications ranging from gas adsorption, sensing, catalysis and more. This is due to their large surface area, porosity, and tunable structures. Templating methods, acid-base adjustments, sonochemical methods have been used to synthesize MOF of different morphologies. MOFs are

usually produced using various conventional methods such as solvothermal methods which usually involve heating in closed systems. However, problems such as inhomogeneous mixing and long reaction times have been associated with conventional methods[7]. To solve these limitations, various droplet-based MOF synthesis have been reported. However, most of the reported droplet-based methods involved the use of high temperature and lead to the generation of hollow shaped morphologies different from reported cases especially for MOFs like HKUST-1[8]. So, it is important to facilitate crystal growth in MOF synthesis in ambient temperature in order to ensure the production of well-defined crystals.

Polyaniline (PANI) is an excellent conductive polymer that has been prepared mainly by chemical oxidation using oxidants such as ammonium peroxydisulfate in acidic medium. Polymerization conditions such as temperature and reactant concentration has been adjusted to modify its properties [9]. PANI has been widely considered by researchers in nanotechnology in the area of optoelectrical devices, and sensors [10]. In addition to chemical oxidation, electrochemical polymerization, template-assisted synthesis, and inkjet printing have been reported as methods of PANI synthesis techniques. However, methods such as electrochemical synthesis are not cost effective in addition to the longer reaction times associated to these bulk phased synthesis methods compared to basic droplet-based synthesis that can be used to produce PANI within a short period of time. Although PANI is commonly produced using ammonium peroxydisulfate as an oxidant and is suitable for mass production, it requires a larger amount of chemicals which will result in difficulty of separating the PANI with by-products which is environmentally unfriendly [11]. Therefore, producing PANI from microdroplets with effective reagent utilization and enhanced reaction rates will open up a new pathway for its synthesis and possible application on a wide range of research fields.

To overcome the challenges highlighted above, it is important to use alternative synthesis methods with shorter reaction time and good material yield. By using the room temperature microdroplet synthesis method, this work aims to effectively produce Cu MOF, polyaniline and silver nanoparticles using better and more affordable reaction conditions. It also aims use these materials on nitrogen conversion to nitrates, oil-water separation and antibacterial study respectively.

1.2 Problem Statement

Due to the long reaction times, high amount of chemicals requirement leading to excessive waste generation, catalyst involvement and the use of high temperatures in some instances, classical synthesis of MOFs, nanoparticles and polymers poses limitations to effective material synthesis especially at small scale levels like nano levels. Although much improvement have been observed, the use of microdroplet synthesis at high temperatures to overcome problems encountered with classical methods have led to other set-back especially in the area of MOF synthesis. High temperature synthesis can lead to decomposition of organic linkers in MOFs , polymer chains during synthesis and also particle aggregation in silver nanoparticles thereby reducing their surface area which is ideal for various applications like anti-bacterial study.

Overcoming these shortcomings can be achieved using microdroplet synthesis methods at room temperature. The room temperature microdroplet synthesis will bring about a combination of favorable factors in the synthesis process. In the MOF synthesis, it will allow enough time for crystallization to occur due to a decrease in residence time in the reaction and slow solvent evaporation leading to the synthesis of MOF with defined and regular crystals. In addition to the prevention of polymer chain disruption due to high temperatures, the room temperature synthesis will allow the formation of polyaniline of high conductivity, stability and good surface roughness

ideal for water retention and oil rejection. Finally, our synthesis route will facilitate the in-situ production of silver nanoparticles for direct medical use without any capping agents and particle aggregation.

1.3 Objective of the Study

This work involve the production of Cu-MOF, Polyaniline and Silver nanoparticles at room temperature using microdroplet synthesis method as an alternative to both classical methods used in synthesizing these materials. It also aims to use these materials on various applications such as nitrate production, oil-water separation and antibacterial study. The following are the objectives of this work:

- Carry out the room temperature microdroplet synthesis of Cu-MOF (HKUST), Polyaniline and Silver Nanoparticles.
- Characterize the synthesized materials using X-ray Diffraction(XRD), Fourier Transform Infrared Spectroscopy (FT-IR), Proton Nuclear Magnetic Resonance (H-NMR), Thermogravimetric Analysis (TGA), Scanning Electron Microscopy (SEM), and Transmission Electron Microscopy (TEM),
- Optimize the conditions of synthesis to improve yield and material characteristics.
- Investigate the efficiency of the MOF on nitrogen conversion to nitrates, Polyaniline for oil-water separation and the silver nanoparticles for antibacterial study.

1.4 Significance of the study

Various classical methods have been used to produce and apply these materials. But they have been found with shortcomings that can be avoided in microdroplet synthesis. To ensure reactions with accelerated rates and better material structures, synthesis must be done in conditions that prevent structural deformation like in room temperature. The importance of this microdroplet synthesis at room temperature is to make sure that the synthesized materials do not undergo structural decomposition due to high temperature, are produced in less than one hour and their characteristics can be modified by changing reaction conditions like pressure.

1.5 Scheme of Research Findings Reporting

To facilitate reading and understanding, the thesis is arranged in the following five chapters

- Chapter 1: Describes the problems associated with classical methods of MOF, PANI and silver nanoparticle synthesis. Advantages of using room temperature microdroplet synthesis. Discussion on the problem statement, significance of the study and the research plan completes this chapter.
- Chapter 2: Provides an overview of the current literature in microdroplet synthesis and applications.
- Chapter 3: Room temperature microdroplet synthesis of copper Benzene-1,3,5-tricarboxylic acid MOF (HKUST-1) and its application on nitrogen conversion to nitrates.
- Chapter 4: Room temperature microdroplet synthesis of Polyaniline using Fenton-like reaction and its application on oil-water separation.
- Chapter 5: Room temperature In-situ microdroplet synthesis of silver nanoparticles and its application on antibacterial study.

- Chapter 6 (Conclusion): A summary of the research findings is presented.

CHAPTER TWO

LITERATURE REVIEW

2.1 Overview of Microdroplet Reactions and Synthesis

Microdroplet chemistry has recently gained important focus as a result of the catalytic role it plays at the air-liquid interface in speeding up chemical reactions[7], [12]. Several studies have shown that the reactions in microdroplets can occur in one or more orders of magnitude faster than their bulk-phase counterparts [2,15]. This acceleration is linked to reactions taking place at the air-liquid interface, where partial solvation of reactants lowers the energy barrier needed for the reaction to take place[5,13]. The unique properties of microdroplet reactions are anticipated to influence various fields, including chemical derivatization, mechanistic studies, high-throughput reaction screening and sustainable small-scale synthesis[12,16]. The discovery of the catalytic nature of microdroplets coincided with advancements in droplet-based technologies[6]. Microdroplets ranging from in size from micrometers to nanometers, can be easily generated using techniques such as electrospray, drop-casting, flow focusing, acoustic generation, droplet suspension and leidenfrost levitation[1]. Among these, sprayed microdroplets have been effectively combined with mass spectrometry (MS) for molecular analysis and quantification. Desorption electrospray ionization (DESI), the first ambient ionization method, involves spraying microdroplets onto a surface to extract molecules for analysis[16].

Before their application in reaction acceleration, microdroplets produced via electrospray ionization (ESI) and inductive ESI were utilized to monitor bulk phase reactions in real time, including those sensitive to air and moisture, as well as heterogeneous reactions[12,18]. The choice

between using microdroplets for reaction acceleration or monitoring depends on their lifetimes and the extent of desolvation, which marks the final stage of droplet evolution. Electrospayed microdroplets serve as a straight example, showcasing both functions within a single system. By increasing the distance between the electrospray emitter and the MS inlet, the lifetime of the microdroplets are prolonged, enabling the transition from capturing snapshots of bulk-phase reaction mixtures to observing accelerated reactions on the microdroplet surface[3].

2.2 Factors That Enhance Rate Acceleration in Microdroplet Reactions

2.2.1 Enthalpy Effects: Partial Solvation of Reactants

At the air-liquid interface, partial solvation of reactants lowers the critical energy barrier of the reactions, leading to an increase in intrinsic rate constants within the surface of the microdroplets[19, 20]. In the condensed phase, rate constants are often influenced by ion-pairing and solvent interactions, which obscure the inherent reactivity of the reacting species. Typically, rate constants in gas-phase reactions are about six orders of magnitude higher than those in solution-phase reactions. In the condensed phase, the process of desolvation presents a significant energy barrier for reactants to reach the transition state, illustrating the solvent barrier effect. This effect alone can result in a difference of 2-20 kcal mol⁻¹ in activation energy between gas-phase and solution-phase reactions, which aligns with the observed six orders of magnitude difference in rate constants [19].

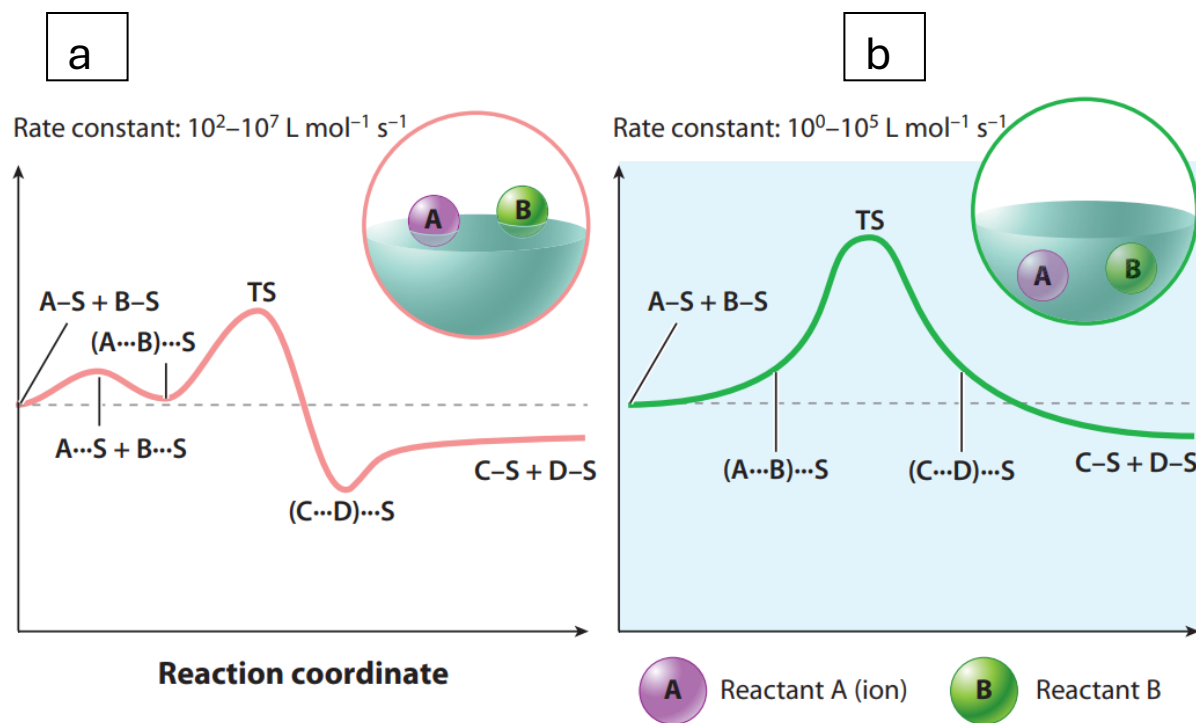


Figure 2.1: A figure showing rate constant dependence on (a) Microdroplets (b) Bulk phase reactions.

2.2.2 Entropy Effects

Solute molecules exhibit a more ordered orientation at and near the droplet surface compared to the interior, reducing the entropy and increasing the free energy of the initial state[20]. The ordering is likely due to the electrostatic repulsion caused by the higher concentration density near the interface. Such alignment of reactant molecules lowers entropy and raises the free energy of the initial state. For instance, the phosphorylation of ribose in bulk solution is thermodynamically unfavorable, with a ΔG of $+5.4 \text{ kcal mol}^{-1}$. However, in microdroplets, the same reaction becomes favorable, with a ΔG of $-1.1 \text{ kcal mol}^{-1}$ as the entropy barrier is overcome by the alignment of reactant molecules in the microdroplet environment. This ordered orientation can also extend to solvent molecules. Numerous theoretical and experimental studies have shown that interfacial water forms layered structure due to restricted rotational freedom of water dipoles near the surface. Water near the interface tends to adopt ice-like structures at both gas-liquid and solid-liquid interfaces making it less polar than bulk water[22,23].

2.2.3 Fast Solvent Evaporation

Rapid solvent evaporation can lead to increased reagent concentrations thereby accelerating reaction rates[5,24]. However, uncontrolled evaporation can significantly raise reagent concentrations, creating a concentration effect that influences the reaction rate. This effect is beneficial for achieving both high reaction rates and yields, as it enhances the reaction both kinetically and thermodynamically. In thin-film reactions, solvent evaporation can result in supersaturated reagents, further favoring reactions with high rates and yields particularly for reversible organic reactions[24].

Evaporation also facilitates direct mass transfer in microdroplets through the coffee ring effect[25]. In microdroplets, flow is directed from regions of low surface tension to high surface tension. Solvent evaporation can induce surface tension gradients, driving Marangoni flow within the droplets[27, 28].

2.2.4 Fast Diffusion and Mixing

Efficient diffusion in small volumes can lead to reaction behaviors that differ from those in bulk solutions[29,30,31]. The partial-solvation hypothesis explains when reactions in the surface region are accelerated, achieving very high-rate constants, while reactions in the droplet interior resembles bulk conditions. Although the surface region constitute a small fraction of the microdroplet, the overall reaction acceleration can far exceed the contribution from the other regions alone. This is because efficient diffusion in microdroplets allows a large fraction of reactants to undergo fast surface reactions. If the reaction rate at the surface is much faster than the interior, reactants diffuse to the surface, react and then diffuse back to the bulk. This process continues until the equilibrium is reached[1,32]. Microdroplets generated under ambient conditions experience turbulence from gas motion, liquid jets and solvent evaporation, which enhance diffusion and mixing[33,34]. So, larger diffusion coefficients and smaller droplet sizes lead to greater reaction acceleration and reduced anisotropy in microdroplets.

Additional factors that contribute to accelerated reaction rates in microdroplet reactions include extreme PH values, unusual dielectric constants and surface potentials[31,35]. These factors collectively enhance the unique reactivity observed in microdroplet environments.

2.3 Relationship Between Microdroplet Reactions and Bulk Phase Reactions.

2.3.1 Reactions can occur both in bulk and microdroplets with significant acceleration in microdroplets

Numerous reactions have been observed to occur in both bulk and microdroplet environments, but they proceed significantly faster in microdroplets due to factors such as partial solvation, rapid solvent evaporation, high dielectric constants and other mechanisms discussed earlier[3] . An example is the Katritzky reaction, which involves the pyrylium ion reaction with functional amines to produce N-substituted pyridinium cations. This reaction is particularly suited for microdroplet studies due to high ionization efficiencies of pyrylium and pyridium ions in mass spectrometry (MS). In microdroplets, this reaction have been estimated to accelerate by over 100 times compared to its bulk phase counterpart. For example, the triphenylpyrylium cation (mass a mass -to -charge ration, m/z of 309) reacts with p-methoxyaniline to form the corresponding pyridinium product ($m/z=414$). This reaction proceeds rapidly and reach completion within a 10th-minute dwell time with high yield and complete consumption of the reagents, as illustrated in figure 2a. In contrast, the bulk solution-phase reaction show no measurable progress within the same time frame, as demonstrated in figure 2b. This stark difference highlights the dramatic acceleration and efficiency of reactions in microdroplets[36,37].

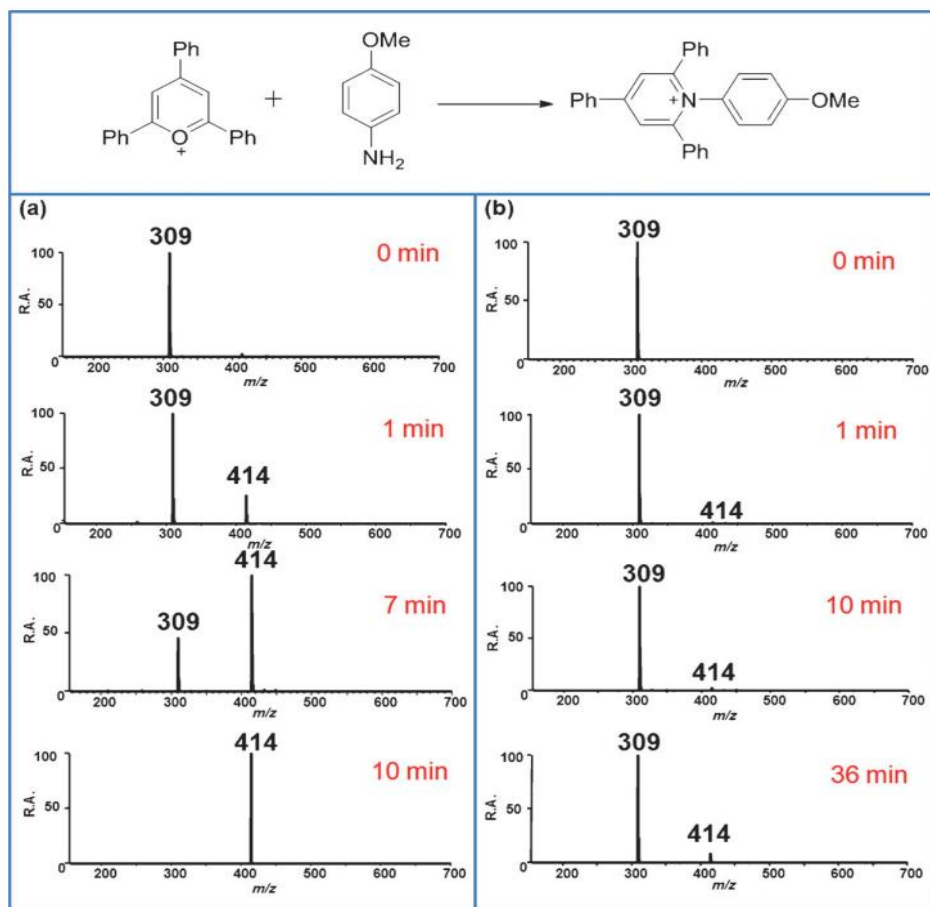


Figure 2.2: A figure showing the mass spectra of Katritzky reaction of pyrylium cation ($m/z=309$) and p-methoxyaniline to produce pyridium cation ($m/z=414$) carried out in (a) paper spray MS (b) bulk-phase environment.

2.3.2 Reactions cannot occur in bulk but can be driven in microdroplets

Reactions in microdroplets that do not occur in bulk can be viewed as an extreme example of reaction acceleration[37]. Organic reactions involving two immiscible phases have significant applications in chemical, pharmaceutical, and polymer synthesis. Typically, such two-phase reactions either do not proceed or are extremely slow without the addition of phase-transfer catalyst (PTC). PTCs facilitate the transfer of a soluble reactant from one phase to the other immiscible solvent or bring reactants to the interface of the two phases[26]. For example, Zare et al demonstrated the two-phase oxidation of benzylalcohols to their corresponding aldehydes or ketones using sodium hypochlorite in microdroplets, entirely without the need for PTCs. In this process, microdroplets of reactants from two immiscible phases collided, driving the reactions on their surfaces. This approach eliminates the drawbacks such as thermal stability, high costs, and the need for catalyst separation and recycling. The study showed that various alcohols could be oxidized to aldehydes and ketones within milliseconds, achieving moderate to good yields whereas no products formation was observed in the bulk phase reaction without a catalyst, as illustrated in figure 3. The method was successfully scaled up achieving an isolated rate of 1.2 mg min^{-1} for synthesizing 4-nitrobenzylaldehyde from 4-nitrobenzylalcohol in the presence of sodium hypochlorite. The biphasic nature of this process, which eliminates the need for a phase transfer catalyst, significantly enhances synthetic efficiency[27,39].

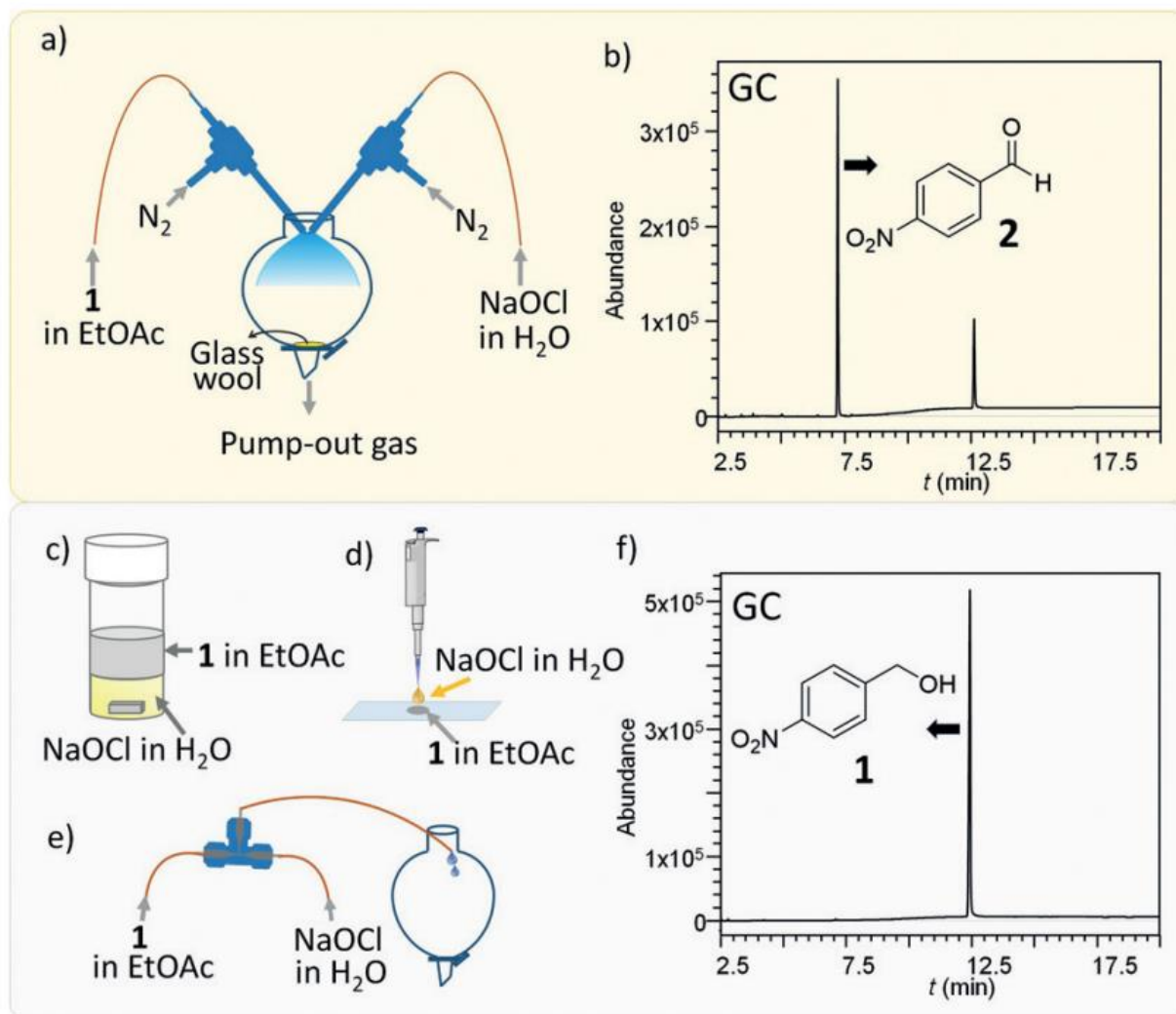


Figure 2.3: A figure showing conversion of benzyl alcohols into aldehydes and ketones in microdroplets and bulk phase reactions.

2.3.3 Reactions can occur both in bulk and microdroplets but with different reaction products

While most reactions studied in microdroplets follow pathways similar to those in classical synthesis methods, few exceptions demonstrated different outcomes[3]. One such example is the accelerated reaction between phenylhydrazine and phthalic anhydride or phthalic acid in electrospray in microdroplets. In this case, the reaction yielded 2-phenyl-2,3-dihydrophthalazine-1,4-dione on a submillisecond timescale with over 90% yield achieved without an external catalyst at room temperature. In contrast, the bulk-phase reaction under the same conditions (no catalyst and at room temperature) produced 2-(2-phenylhydrazinecarbonyl)benzoic acid instead[39]. This highlights a unique divergence in reaction pathways between microdroplet and bulk-phase environments.

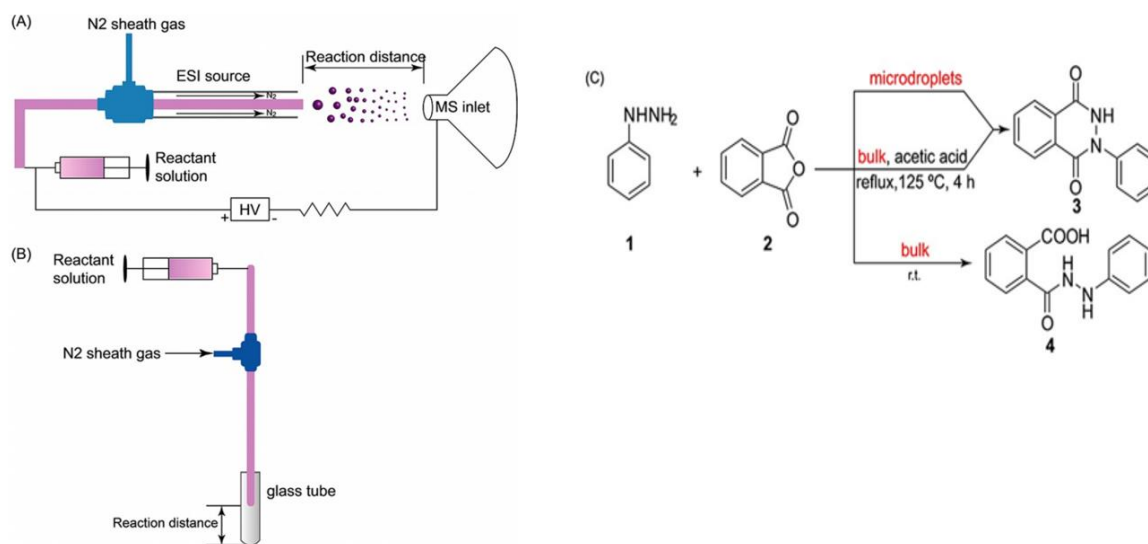


Figure 2.4: A figure showing a reaction yielding different products in microdroplet synthesis method and bulk-phase method.

2.4 Some Microdroplet Generation and Synthesis Methods

2.4.1 Microdroplet Spray Method

This approach involves generating individual microdroplets containing reactants and/or catalysts within an aerosol. Various spray techniques such as electrospray[40] , sonic spray, nanoelectrospray, and thermospray have been employed in this synthetic route[41]. The reaction rate in this method is influenced by droplet size and lifetime and these variations in reaction behavior are analyzed and confirmed by mass spectrometry[17].

2.4.2 Individual Levitated Microdroplets

This technique focuses on studying the behavior and reactions within a single microdroplet isolating droplets with volumes ranging from nanoliters to microliters. A well-known phenomenon in this method is the levitation of evaporating droplets near solid surfaces heated above the liquid's boiling point. Under these conditions, a vapor layer forms beneath the droplet, allowing it to levitate-a process known as the leidenfrost effect[43,44].

2.4.3 Microdroplet–Microdroplet Collisions

In this method, two streams of droplets containing different reactants collide to produce a product. It has been widely used for the rapid synthesis of nanoparticles such as gold and silver nanoparticles within seconds. This approach is also effective for multiphase reactions such as liquid-liquid heterogeneous reactions which typically require phase transfer catalyst. An example is the oxidation of alcohols to aldehydes and ketones without PTC unlike in bulk-phase reactions[27,45].

2.4.4 Thin Films

This method involves depositing microdroplets onto a substrate. In a typical thin-film experiment, the reaction mixture is drop-cast onto a substrate and the product formation is monitored over time as the solvent partially or fully evaporates[46]. As the solvent evaporates, new phases form making thin films complex reaction systems[6]. Thin films can also form when microdroplets are collected on a substrate. Key advantage of thin films is their potential for extended lifetimes[24].

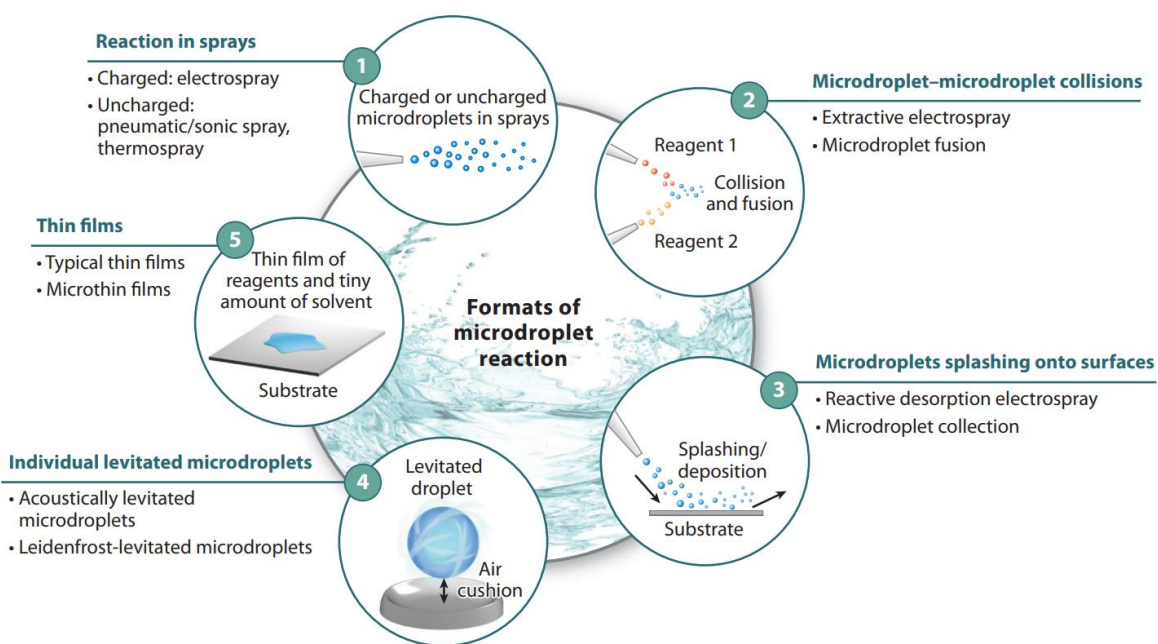


Figure 2.5: A figure showing Microdroplet Synthesis Methods

2.5 Reported Microdroplet Synthesis of MOFs

Due to the limitations of traditional MOF synthesis methods, such as hydrothermal and solvothermal methods, many material chemists have turned to microdroplet-based approaches to leverage their unique properties. Below is a summary of some reported microdroplet synthesis of MOFs and their diverse applications.

He et al[14] pioneered the synthesis of a copper-based metal-organic framework $[\text{Cu}_3(\text{TMA})_2(\text{H}_2\text{O})_3]_n$ commonly referred to as HKUST-1, where TMA means the linker trimesic acid and its TiO_2 nanocomposites, within micrometer-sized droplets using rapid aerosol spray method. They systematically studied the effects of synthesis temperature and precursor components ratios on the material physicochemical properties. Theoretical calculations on mass and heat transfer within the microdroplets revealed that rapid solvent evaporation and high heat transfer rates are primary driving forces. The quick shrinkage of droplets due to evaporation leads to sharp increase in precursor supersaturation, accelerating nucleation and crystal growth. The HKUST-1 nanomaterials produced through this aerosol method exhibited excellent crystallinity and high surface area and strong photostability comparable to those synthesized by traditional wet chemistry methods. By embedding TiO_2 within the HKUST-1 matrix, the composite maintained a large surface area significantly enhancing CO_2 photoreduction efficiency compared to pure TiO_2 . In-situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) analysis suggested that the improved performance was due to HKUST-1's stable and high adsorption capacity. While He and his team demonstrated promising advancements in addressing the mass and heat transfer challenges of bulk-phase synthesis methods, their method had some drawbacks. The high synthesis temperature caused the linker to decomposed as evidenced by the XRD and FT-IR results in figures A and B. Additionally, this approach produced

hollow spherical shaped crystals differing from the typical octahedral shapes obtained through the classical methods. Despite these limitations, the work highlights the potential of microdroplet synthesis for rapid and scalable productions of MOF-based nanomaterials with significant applications.

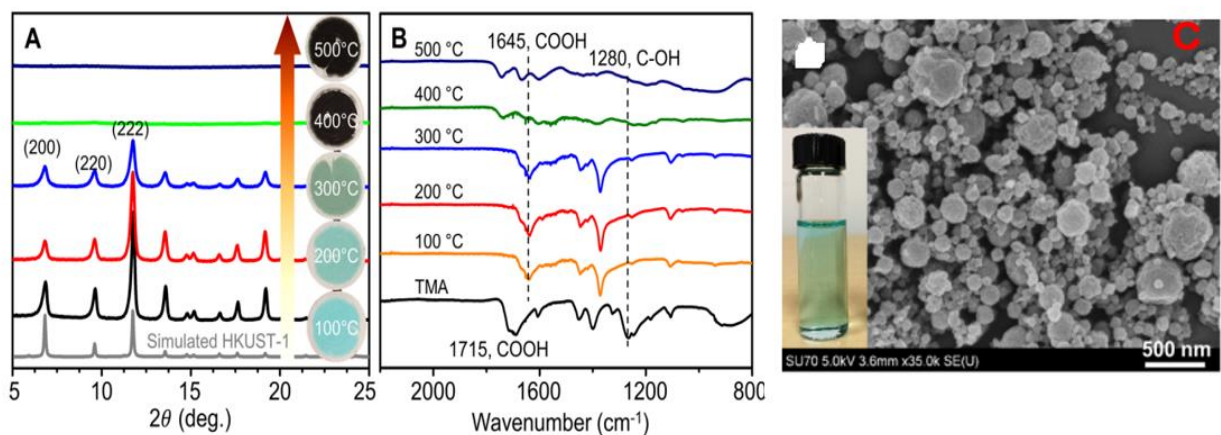


Figure 2.6: A figure showing (a) XRD (b) FT-IR and (c) SEM from Rapid Formation of HKUST-1 in Microdroplets used for the production of nanocomposite for CO₂ photoreduction reported by He et al.

Following the work on the synthesis of HKUST-1 and its nanocomposite at various temperatures, He and his team [46] also explored the synthesis and characterization of mixed linker MOFs (Cu-TMA/Cu-BDC where TMA stands for trimesic acid while BDC 1,4-benzenedioic acid) using the microdroplet-based spray process. Their goal was to investigate the relationship between the properties of mixed-linker MOFs and their component compositions. The resulting mixed linker MOF displayed unique characteristics in terms of morphology, crystalline phases and surface chemistry and pore structures. To gain deeper insights, they employed two-dimensional correlation spectroscopy to analyze the relations among surface functional groups which are not accessible through conventional infrared or Raman spectra. The 2D-COS results indicated that surface chemistry of mixed-linker MOFs can be finely tuned by adjusting precursor conditions. Additionally, CO₂ adsorption measurements on these MOFs revealed the ability to control preferential adsorption sites and adsorption kinetics. While this study demonstrated how synthetic parameters can be optimized for better results, it also highlighted recurring issue; the formation of hollow spherical shaped MOF crystals similar to those highlighted above. This irregular crystalline morphology is attributed to rapid crystallization caused by extremely fast solvent evaporation in microdroplets. The accelerated evaporation reduces the residence time of solvents and reactants leading to incomplete nucleation and crystallization process.

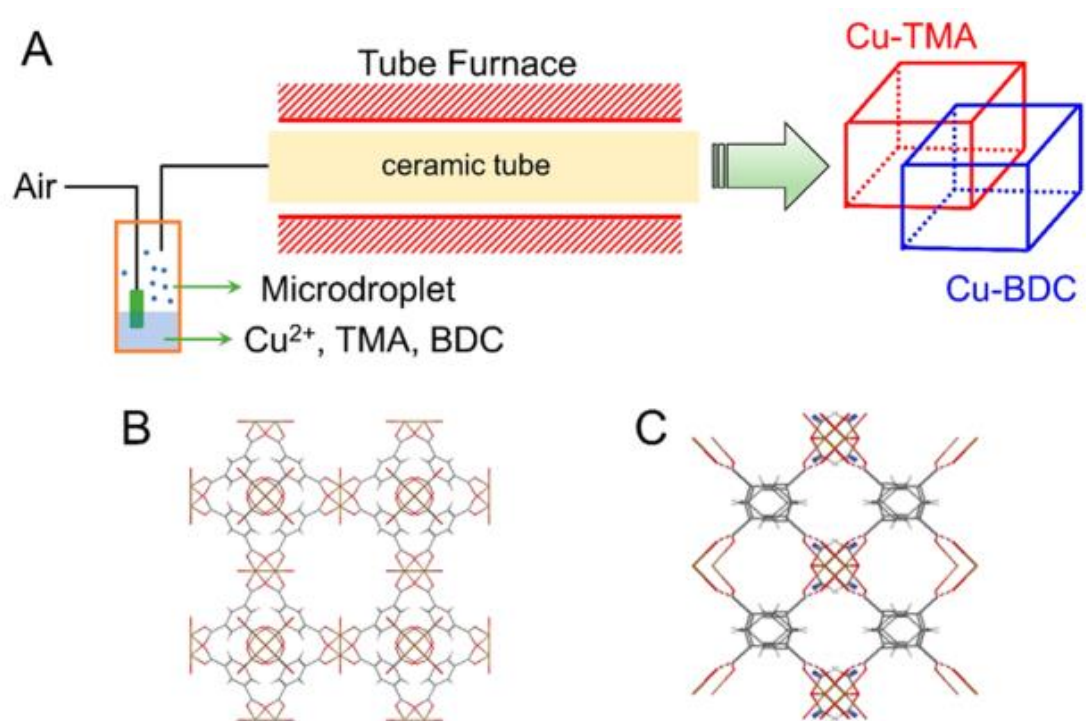


Figure 2.7: A figure showing (a) microdroplets synthesis set-up of mixed linker (b) Structure of Cu-TMA MOF (c) Structure of Cu-BDC MOF.

To address the issue of poor crystalline nanoparticles formation in MOF synthesis as observed in previous studies, Sun et al [8] developed a continuous synthesis method of high quality HKUST-1 MOF crystals and composites using aerosol -assisted synthesis (AAS). The employed solvents with high donor number and low vapor pressure such as DMSO and DMF, to slow down solvent evaporation and promote proper crystal growth. These solvents were found to be more suitable for producing HKUST-1 with well-defined octahedral shapes compared to ethanol and water which evaporates too quickly.

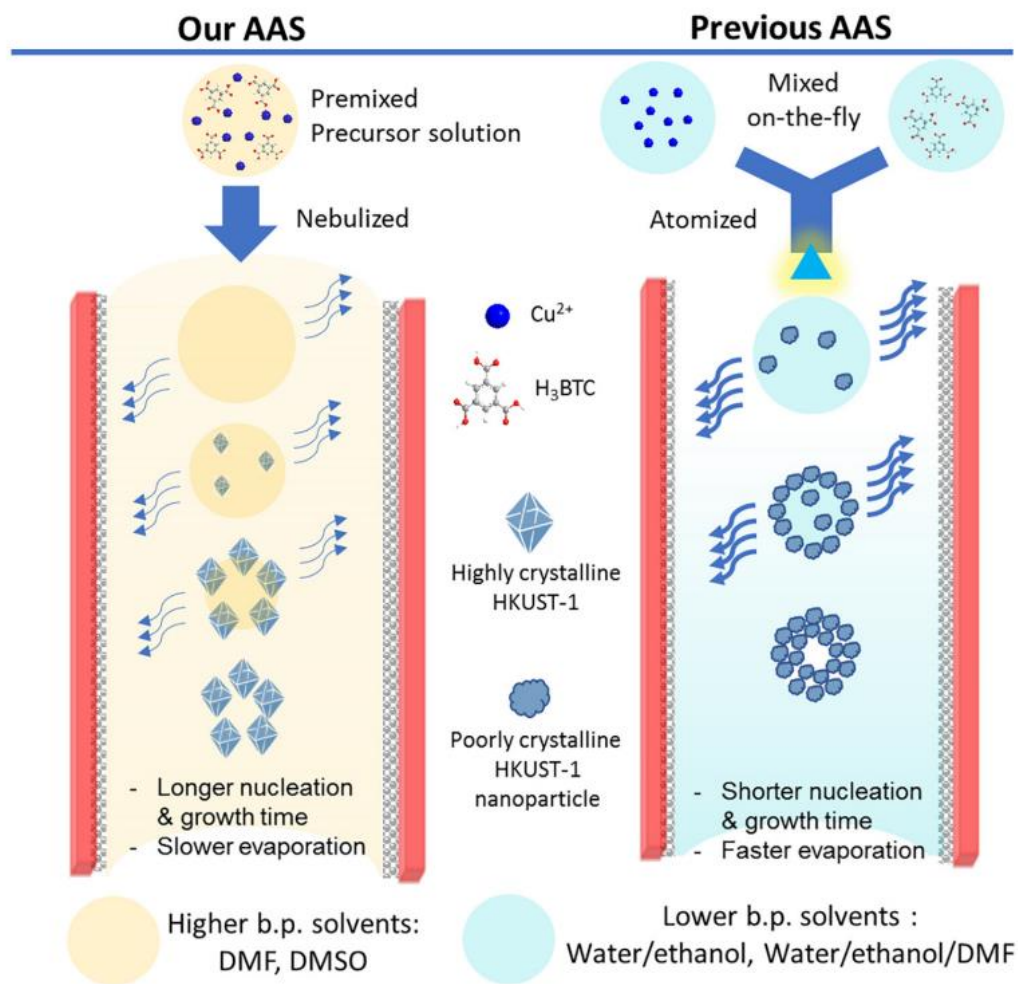


Figure 2.8: A figure showing the microdroplet synthesis of HKUST-1 using AAS.

In addition to adjusting factors such as temperature and solvents, pressure has also been explored as a key parameter in MOF synthesis using the microdroplet spray method. In 2022, Chen et al[47] investigated the role of operating pressure in the rapid formation of copper 1,4-benzenedicarboxylate (Cu-BDC) MOF through microdroplet approach. They studied the formation of Cu-BDC MOF under various flow regimes by modulating the operating pressures. Their findings revealed changes in crystal size, morphology and surface oxidation as pressure changes. Heat and mass transfer calculations considering the transition of flow regimes indicated that these variations were linked to differences in microdroplet evaporation rates. The study also suggested that under sub-ambient pressure, the dissociation of solvents molecules from Cu-BDC increased the number of open metal sites, enhancing CO₂ binding affinity. This work demonstrates the synthesis of MOFs at significantly low operating pressures and open new possibilities for the controlled synthesis of MOFs tailored for selective gas adsorption.

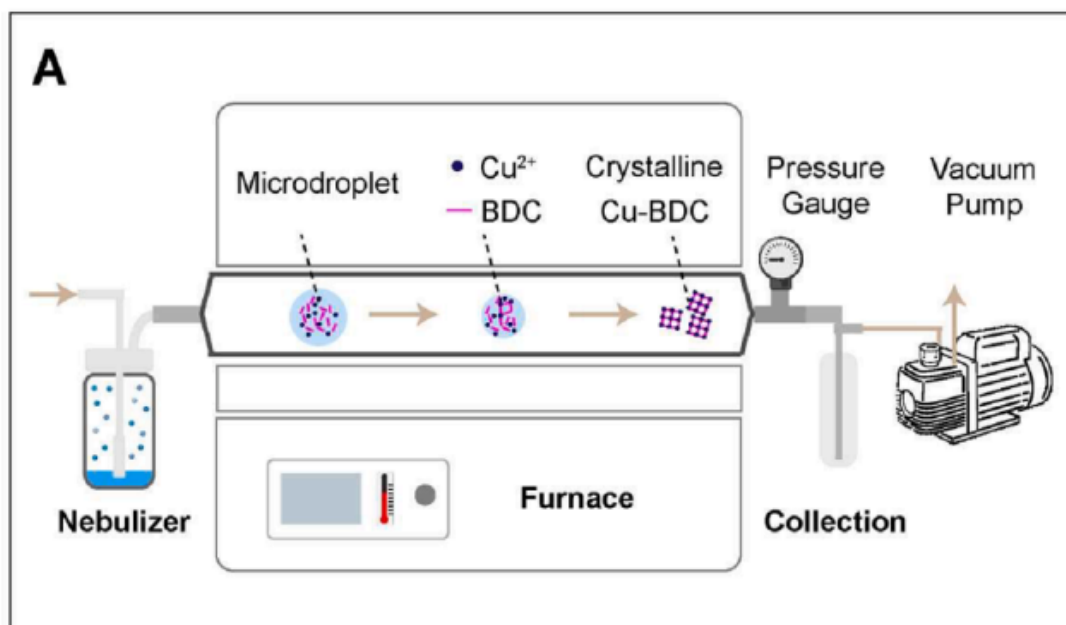


Figure 2.9: A figure showing microdroplet synthesis of MOF under varied pressure

Similar to Chen and his group, He et al[39] also carried out a pressure-regulated synthesis of Cu-(TPA).DMF) in microdroplets for selective CO₂ adsorption. Detailed characterization showed that pressure variations significantly affected both morphologies and crystalline structures of the MOF. Numerical simulations also revealed that the morphology changes are mainly attributed to variations in supersaturation ratios which are caused by different microdroplet evaporation rates due to the regulation of operating pressure, while the crystalline structure variations are closely related to the dissociation of DMF molecules at lower operating pressures. Besides, the dissociation of DMF molecules decreased the surface area of the MOF crystals but gave rise to massive coordinatively unsaturated metal sites which greatly enhanced the interaction of CO₂ with the MOF crystal and thus led to improved CO₂ adsorption capacity and selectivity.

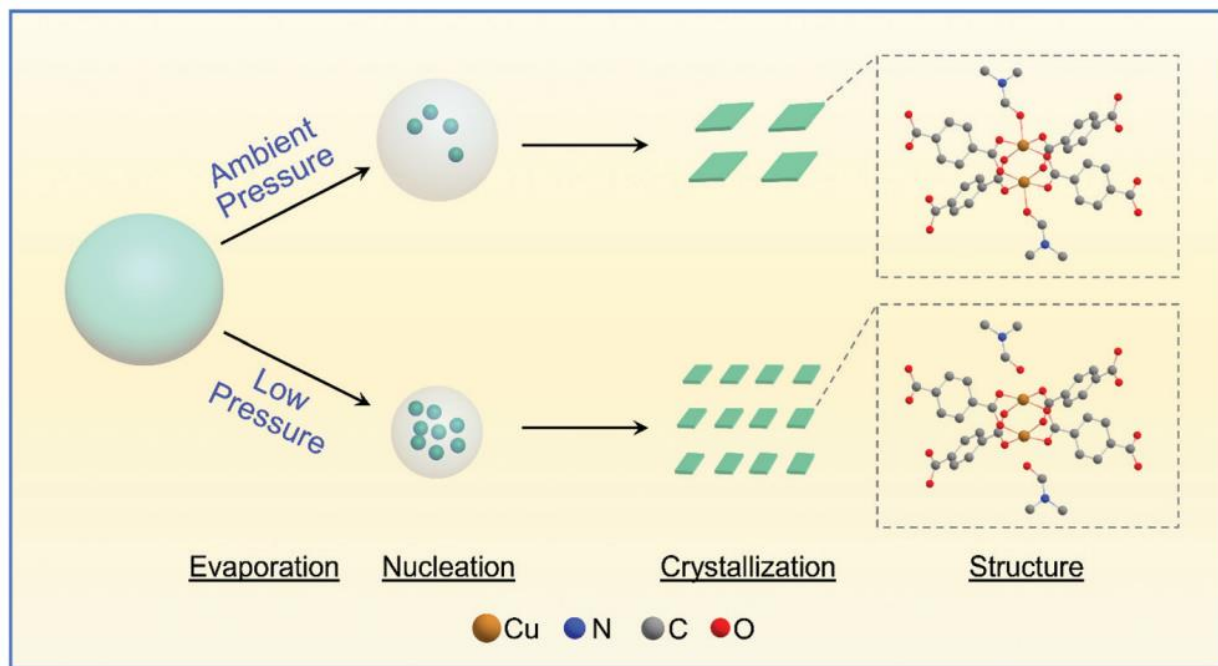


Figure 2.10 A figure showing spray method synthesis of MOF using pressure control system.

2.6 Report Synthesis of Polyaniline (PANI)

While PANI has been widely produced and applied across various fields, the aerosol spray method for synthesizing PANI has, to the best of our knowledge, not been reported. Related methods including ink printing, microfluidic devices, and other similar techniques have been documented. Some of these reports involve PANI composite materials.

Wang et al[48] conducted droplet-based microfluidic synthesis of (Au nanorod Ag)-polyaniline Janus nanoparticles, which were used as a surface-enhanced Raman scattering (SERS) nanosensor for detecting mercury. In their work, they introduced a quick and simple method for synthesizing (Au nanorod Ag)-polyaniline Janus nanoparticles using a droplet-based microfluidic platform. This platform allowed precise control over droplet volumes and the manipulation of individual droplet during the synthesis process leading to excellent dispersion and uniform size of the nanoparticles. The microfluidic approach also significantly reduced the reaction time for creating these nanoparticles. The nanoparticles were demonstrated as highly sensitive and selective sensors for detecting Hg^{2+} via SERS, with strong Raman intensity increases due to the binding affinity between PANI and Hg^{2+} . A linear relationship was found between the Raman intensity of PANI and Hg^{2+} ion concentration in the range of 1-150nM with a detection limit of 0.97 nM for Hg^{2+} . Additionally, the nanoparticles SERS nanosensor was successfully used for detecting Hg^{2+} in real water samples. This droplet-based microfluidic synthesis method offers new potential for designing and fabricating novel nanoparticles that could be applied in various fields, including catalysis, photovoltaics, biosensors and environmental studies.

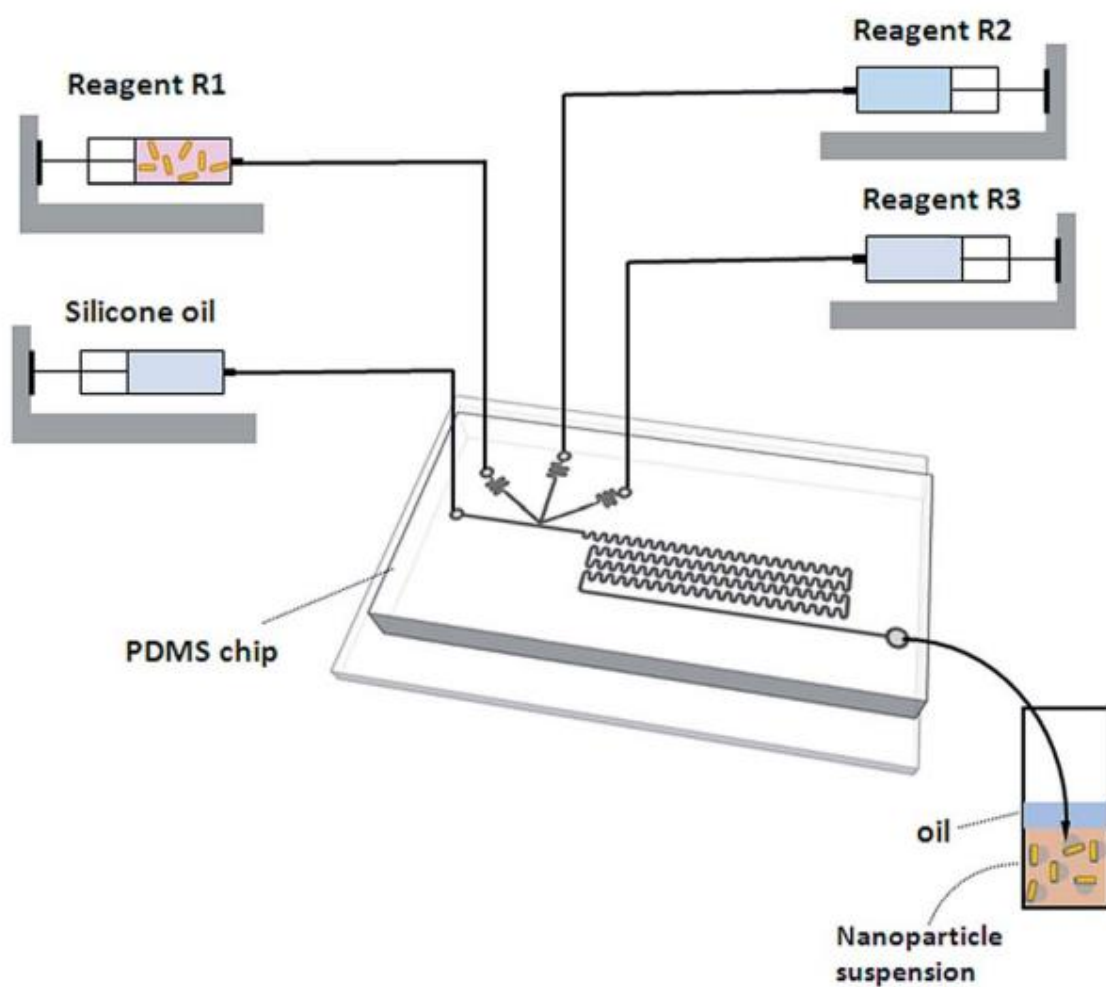


Figure 2.11: A figure showing droplet-based microfluidic synthesis of (Au nanorod@Ag)– polyaniline Janus nanoparticles.

In 2016, Rattanarat et al[49] developed a graphene-polyaniline modified electrochemical droplet-based microfluidic sensor for high-throughput detection of 4-aminophenol. They introduced the use of graphene-PANI modified carbon paste electrode integrated with droplet-based microfluidic sensor for the first time to detect 4-aminophenol in pharmaceutical formulations. The researchers employed a simple T-junction microfluidic platform with an oil flow rate of 1.8 mL/min and an aqueous flow rate of 0.8 mL/min, to continuously generate aqueous testing microdroplets. The microchannel was designed to ensure the aqueous droplet covered all three electrodes, enabling electrochemical measurements within a single droplet. They investigated various parameters such as flow rates, water fraction and applied detection potential to optimize the conditions. The use of graphene modified PANI significantly enhanced the current response in cyclic voltametric detection of ferrocyanide, when compared to an unmodified electrode.

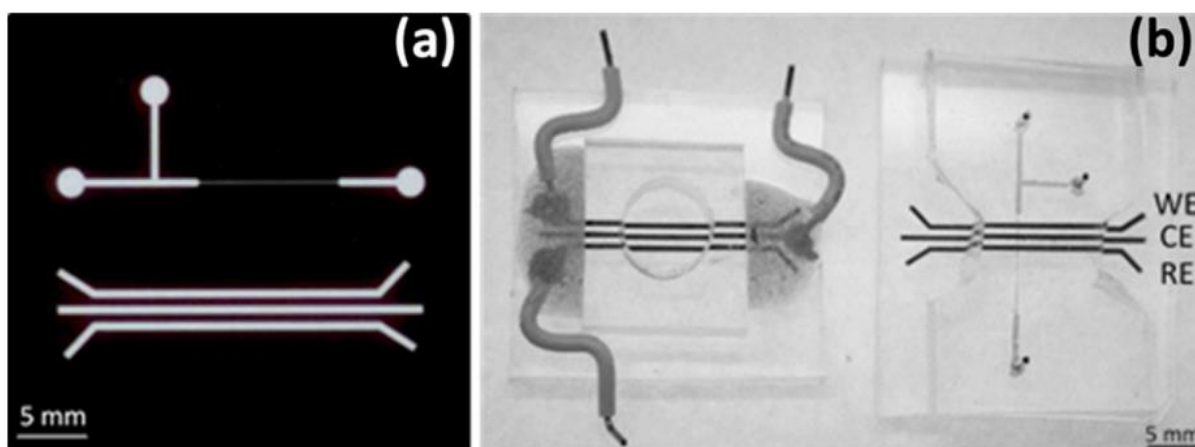


Figure 2.12: A figure showing (a) Electrochemical microfluidic set up (b) Electrochemical batch cell and microfluidic Device made up channels coupled with electrodes.

Ying Teo et al[50] developed an in-situ method for synthesizing conductive polyaniline patterns using micro-reactive inkjet printing. They created a platform technology called micro-inkjet printing to address the challenges of reactive inkjet printing of PANI on nonporous substrates. This technique involves four key elements: single printing, no evaporation of first ink, equilibrium of the fluid properties of the droplet before impact and precise positioning of reactive inks. These components allow for the deposition of pattern PANI on a glass substrate. The proposed printing method for PANI aims to have potential applications in chemical sensors, electrochromic displays and biosensors, as it enables cost-effective production of conducting polymers on non-porous substrates.

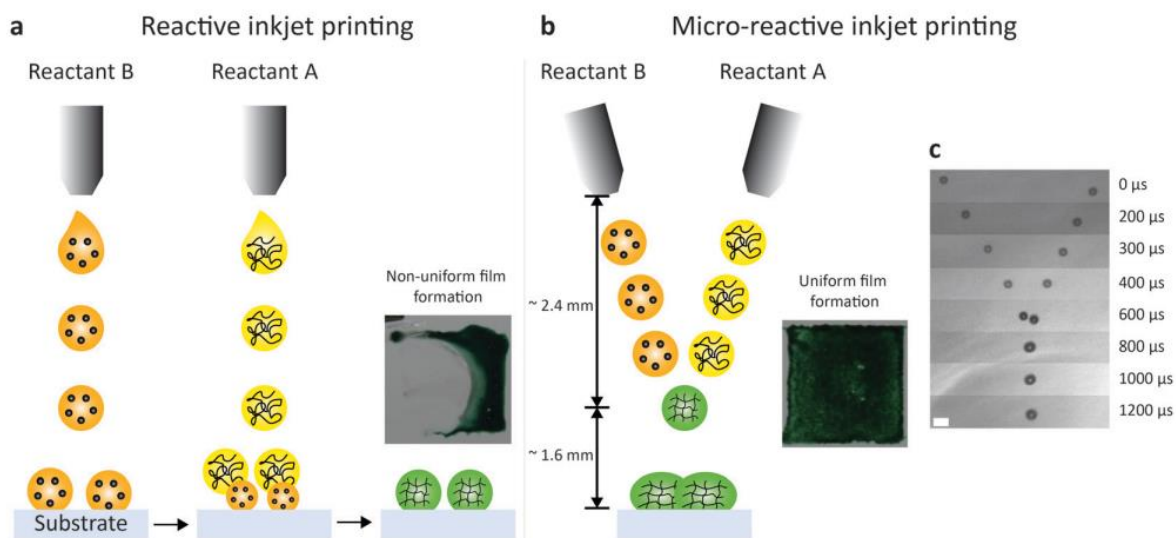


Figure 2.13: A figure showing (a) Conventional inkjet printing (b) Micro-reactive inkjet printing

2.7 Reported Microdroplet Synthesis of Nanoparticles

Long et al[51] synthesized water- and oxygen-resistant polycarbonate-encapsulated perovskite nanoparticles (PC-PNPs) in milliseconds using a single-step microdroplet reaction. Using a microliter syringe with a flow rate that was regulated with a peristaltic pump at $0.5 \mu\text{L min}^{-1}$ an N,N-dimethylformamide (DMF) solution consisting of PC, $\text{CH}_3\text{NH}_3\text{Br}$, and PbBr_2 was electro sprayed on a copper grid at +20kV. Particle imaging velocimetry systems, and high-speed optical camera were constructed to study the kinetics of the accelerated crystallization of the PNPs and their encapsulation by the PC within the microdroplets. Travel distance between syringe tip and the receptor was changed to adjust reaction time due to the high velocity of the droplets from the initial set up. These changes scattered the droplets and pushed them towards the counter electrode

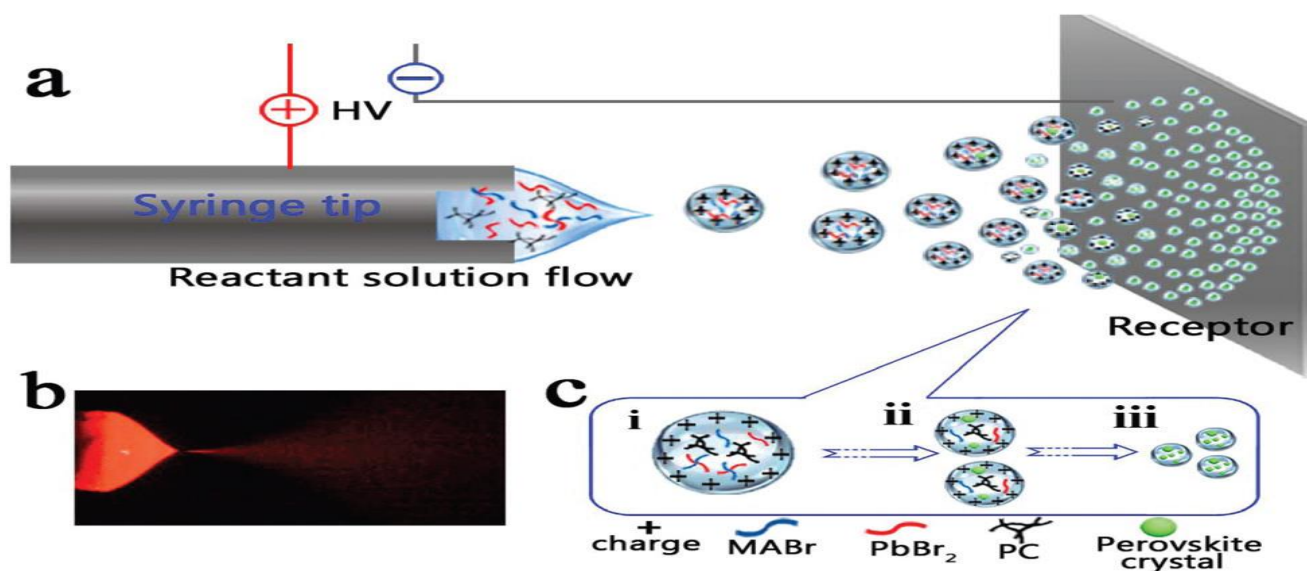


Figure 2.14: A figure showing (a) Demonstration of the Synthesis of PC-PNPs. (b) Electro spray diagram for the Synthesis (c) Stages of droplet formation and synthesis of PC-PNPs.

TEM was used to study the changes in the size of particles during their ejection at different times. Particles ranging from 200 -300nm were generated as early as 2.8ms with a clear distinction between the reactants and precursor. At approximately 12ms, the PC and reactants combined which led to the subsequent formation of the PC-PNPs. Several small particles can be seen in the droplets at around 45ms and droplet size also decreases significantly due to solvent evaporation. Spherical PC-encapsulated nanoparticles were obtained when the droplets landed on the copper receptor at 100ms with sizes less than 160nm.[51] A study of the optical properties of the PC-PNPs shows a characteristic absorption at 505nm as well as green emission at 528nm which agrees with reported values.

Jae Kyoo et al[4] fused two microdroplets with different reactants to study the kinetics of the spontaneous formation of gold nanoparticles and changing the distance between the tip of the sprayer to the grid plate where the fused particles are collected. Aqueous microdroplets of 100 μ M HAuCl₄ solution interacted with 400 μ M NaBH₄ solution with no voltage applied. The reaction took place as microdroplets interacted and moved towards the grid. Fused aqueous microdroplets remained nearly the same size within the observed reaction time or time taken to strike the glass slide. This shows that minimal evaporation of the microdroplets took place during travelling. [4]

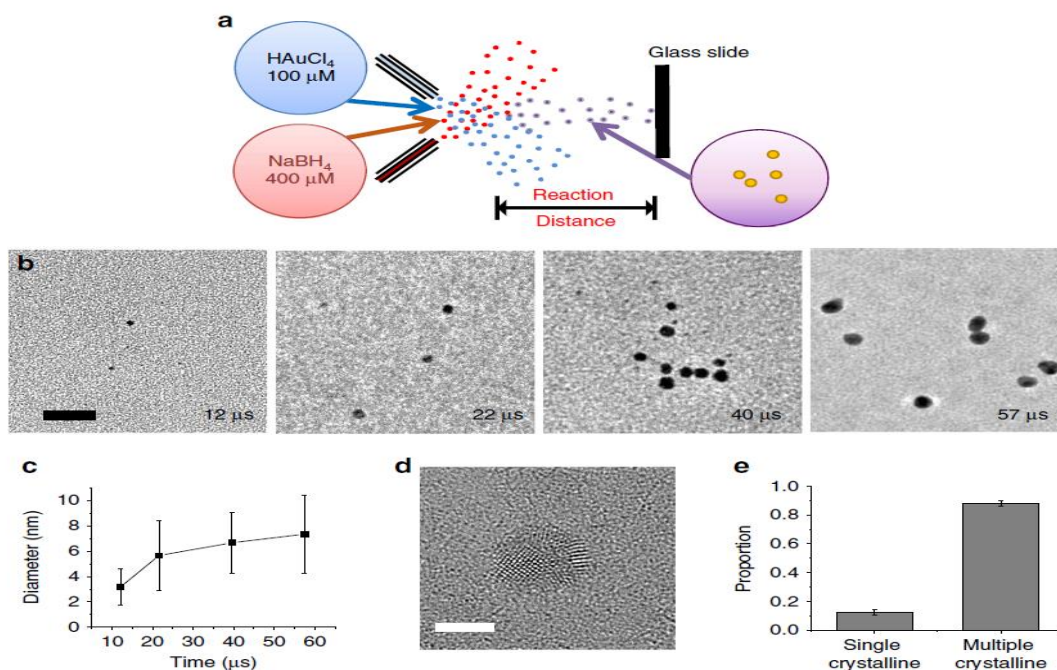


Figure 2.15: A figure showing (a) Experiment setup. (b) TEM images at different times (c) Particle diameter changes with time (d). TEM image of various crystalline structures of a particle (e). Proportions of single and multiple crystals in the microdroplets.

TEM images show the change in gold nanoparticles with time of reaction and nanoparticles of 3nm were formed as early as 12 μs . A mean diameter of 7nm was formed at maximum reaction time of 57 μs while rate of particle growth rate was 0.24 nm μs^{-1} . When compared to bulk methods, the initial nucleation of gold nanoparticles occurred minimally at 2.8×10^4 -fold faster with a growth enhancement factor of 1.2×10^5 even when higher quantities of reactants are involved in bulk reactions and the AuNP size in the microdroplet was ~ 2.1 times bigger than those formed in the bulk reactions. In the control experiment, aqueous microdroplets of 100 μM HAuCl_4 with water microdroplets without any reducing agent were fused. Surprisingly, larger particles of about 30

nm were observed in addition to the usual 7nm particles detected earlier. However, non-specific aggregation of the gold nanoparticles occurred due to the absence of a capping agent. The reducing agent free formation of gold nanoparticles is attributed to two factors; large electric fields exist across the water-air interface. This leads to the non-uniform distribution of ions throughout the microdroplets. These electric fields led to the reduction of the gold precursor without the reducing agent. Additionally, water surface is rich in hydroxide ions and since HAuCl_4 has high reduction potential, it can be easily reduced while the hydroxyl ions are oxidized. [4]

Basuri et al[52] used a home-built electro sprayer source to spray colloidal aqueous silver and gold nanoparticles that were first prepared by Turkevich method on a 0.145mm thick precleaned glass slide. After electro spraying, the imprinted droplets were transferred to the stage of a dark field microscope (DFM) for imaging. Silver nanoparticles in the electro sprayed microdroplets on the DFM image were arranged in two forms; particles are evenly distributed in the microdroplets and localization on the periphery was detected and a droplet distribution ratio of 3:7 was calculated respectively. The concentration gradient of reactants that led to the even distribution of silver nanoparticles is attributed to the time of flight of the droplets. This phenomenon was also observed for gold nanoparticles. To understand the effects of electrospray on particle size and shape in droplets, TEM studies were conducted. Results show that some particles showed aggregation around the core while others are separated at the periphery. Particle sizes decrease from the center towards the periphery of the droplets. Pictures from TEM measurements indicate that the droplets on the TEM grid are much smaller than the droplets on the DFM. These results show that charged aqueous microdroplets from the electrospray can consist of various sizes and shapes and are distributed differently. This distribution may be due to anisotropic distribution of electric fields

and forces that act on the nanoparticles within a droplet. The location of the particle is especially influenced by the centripetal force due to the rotation of the droplet, electrostatic force coming from the charge, and liquid buoyancy in the charge droplet. Another possible reason for the existing particle distribution is also attributed to droplet impact on the surface of the glass slide. Drying can result in the coffee ring effect, also an anisotropic distribution scenario of the solute. Applied potential, tip to collector distance as well as nebulization gas pressure were optimized or varied to illustrate the effects of electrospray variables on the properties of droplets. It was found that droplet size reduces with a rise in gas pressure, applied voltage, distance from the release of the droplets to the glass slide, surface tension, amount of excess charge and vapor pressure of the solvent. Changes in travel distance in particular changes distribution of nanoparticles within the droplets. This similar effect was observed in a change in gas pressure because when gas pressure is decreased, the droplet velocity reduces, there will be a drop-in rate of desolvation which will also give the particle enough time to reorganize and localized at the water-air interface of the droplet. This change in nanoparticles distribution within a droplet change changes the chemistry of the droplet. [52].

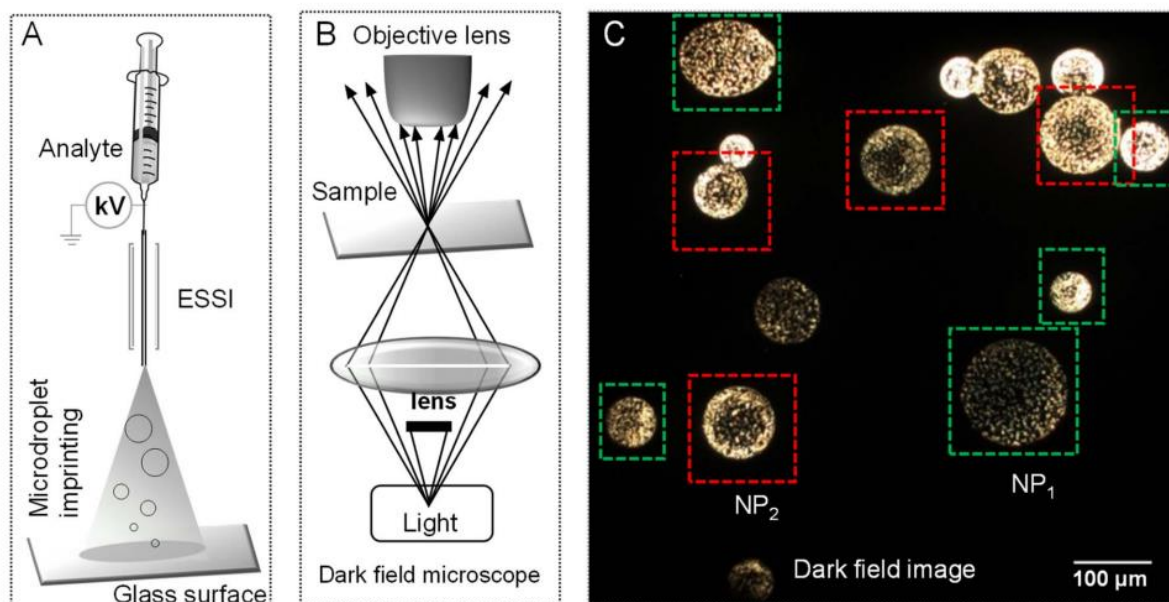


Figure 2.16: A figure showing (a) Droplet Deposition set-up (b) Dark Field Microscopy of Microdroplets (c) Dark Field Image of Microdroplets.

2.8 Mass Spectrometry and Microdroplet Synthesis

Mass spectrometry (MS) is gaining increasing attention in reaction monitoring due to its ability to provide structural characterization, along with its high specificity, sensitivity and speed[7,53]. MS allow for tracking reaction progress and kinetics, screening catalysis and investigating reaction mechanism by identifying reaction intermediates. Electrospray ionization (ESI) and its variants have been particularly useful in these applications. With real-time structural data, MS has uncovered previously unknown reaction pathways and detailed mechanisms in complex systems such as organometallic and multicomponent reactions. Given the unique characteristics of microdroplet reactions, MS has been employed to examine differences between them and bulk-phase reactions by monitoring reactions and studying their mechanisms[1,53]. Below are a few examples of microdroplet synthesis processes studied using MS.

2.8.1 Influence of Inlet Capillary Temperature on the Microdroplet Chemistry Studied by Mass Spectrometry

In many studies of microdroplet chemistry using electrospray ionization mass spectrometry, the effect of the heated inlet capillary on the reaction rate is often considered negligible or not considered at all. Banerjee et al[54] investigated this in the context of two reactions in microdroplets: the Pomeranz -Fritsch synthesis of quinoline and the Combes quinoline synthesis. The reagents were Electrosprayed with methanol and aqueous solutions, forming small and large microdroplets at flow rates of 1 and 20 $\mu\text{L}/\text{min}$, respectively. They varied the inlet capillary temperature from 100 to 350 $^{\circ}\text{C}$. Contrary to the assumptions that inlet temperature has minimal impact on the reaction rate, they discovered that the Pomeranz-Fritsch reaction was significantly accelerated at high temperatures for both solvents and droplet sizes. In contrast, the Combes

synthesis exhibited the opposite trend. They attributed these contrasting behaviors to balance between two competing effects: evaporative cooling and the heating of bare ions ejected from the droplet within the heated inlet. This finding highlights the importance of considering these factors when interpreting microdroplet reactions studied by electrospray or similar ambient ionization MS technique.

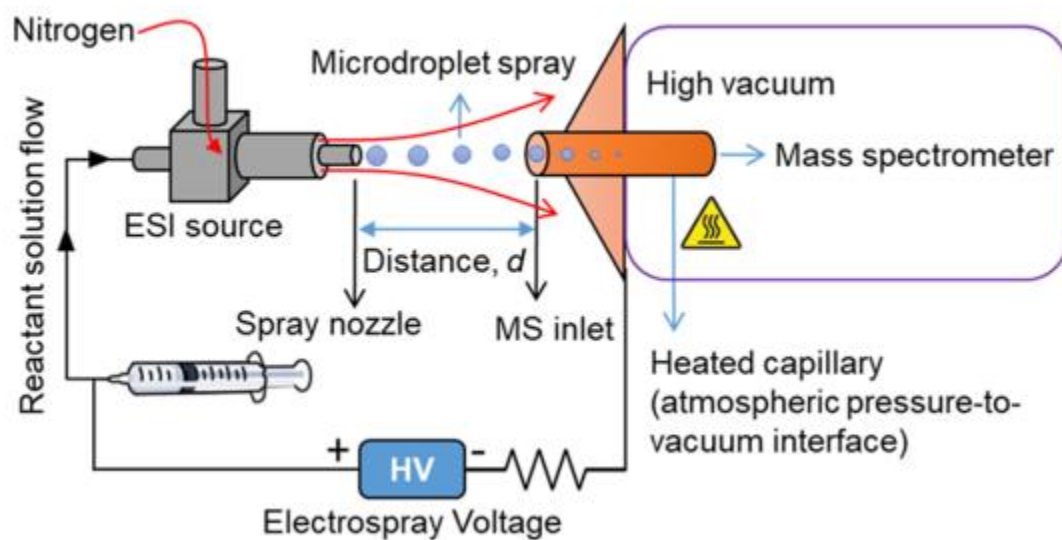


Figure 2.17: Experimental setup for Microdroplet Analysis using ESI-MS.

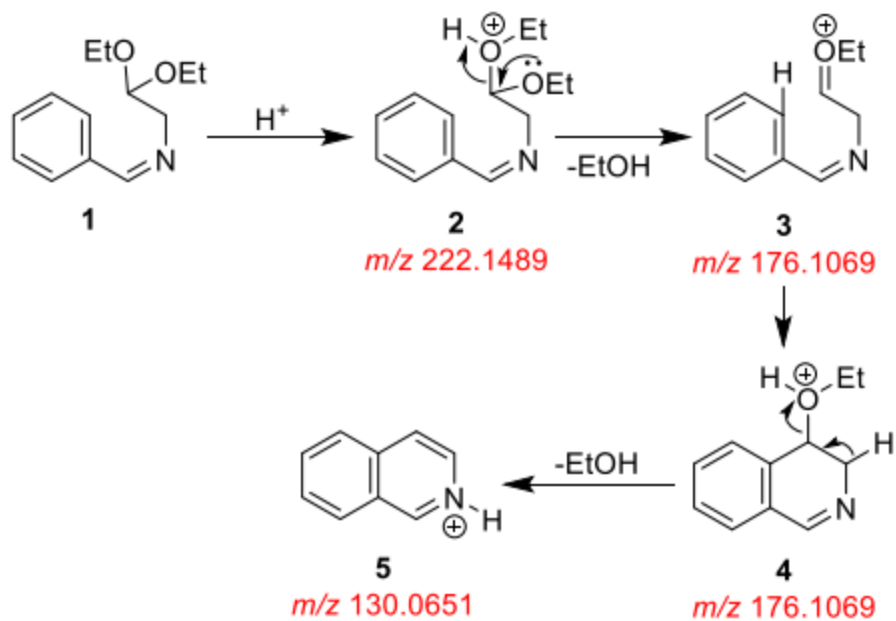
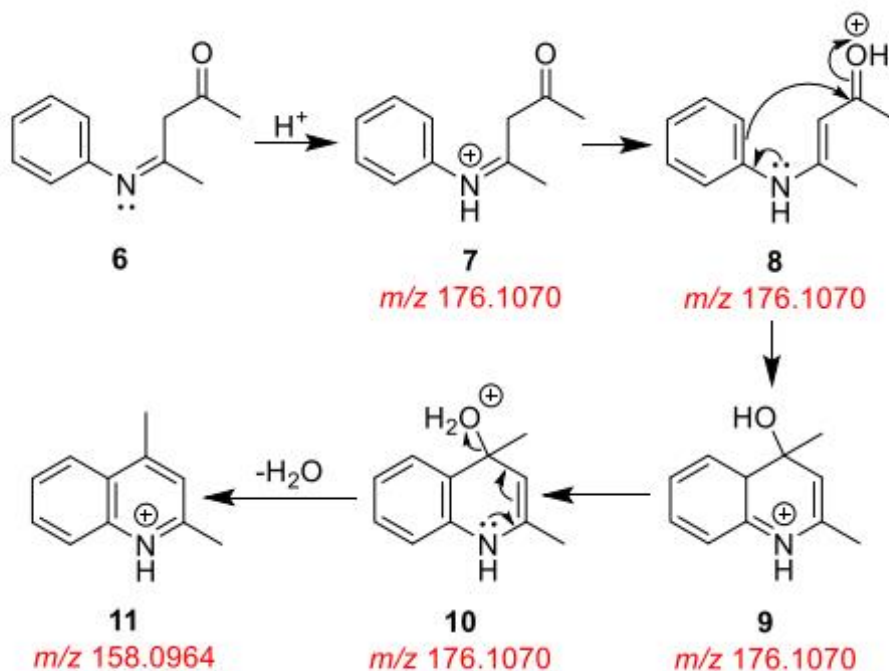


Figure2.18: Plausible Mechanism of the Acid-Catalyzed Pomeranz–Fritsch Synthesis of Isoquinoline 5 Starting from the Benzalaminoacetal 1 in Microdroplet.



^aThe theoretical m/z values of all ionic species are given in red color below their structures.

Figure 2.19: Plausible Mechanism of the Acid-Catalyzed Combes Synthesis of Quinoline 11

Starting from 4- (Phenylimino)-2-pentanone 6 in Microdroplets.

2.8.2 Reaction Acceleration Revealed by Mass Spectrometry in the Hantzsch reaction.

Santos et al[7] conducted the Hantzsch reaction in bulk and followed it with electrospray ionization mass spectrometry (ESI-MS) to identify the reaction intermediates. They discovered that the synthesis of symmetric 1,4-dihydropyridines primarily follows the diketones reaction pathway out of four possible pathways. This information was obtained by spraying a plume of charged droplets from the aliquot of the bulk reaction mixture at atmospheric pressure. The droplets were quickly drawn into heated inlet of a mass spectrometer, where they are rapidly desolvated, releasing ionized components that reflected the reaction occurring in the bulk medium. Interestingly, by altering the reaction conditions, an accelerated version of the Hantzsch reaction was observed in droplets formed during electrospray ionization. By mixing the reagents and gradually increasing the distance between ESI emitter and the MS inlet, the desolvation time of the charged microdroplets in the air was lengthened. As a result, ionized reagents initially observed in the mass spectrometer at shorter distances were gradually replaced by reaction intermediates, and eventually, the final product. All these processes took place on a millisecond timescale, making the reaction rate in droplets approximately 10⁵ times faster than in bulk. Notably, this acceleration occurred without any heating in the droplets. The use of a 1-meter tube allowed for convenient observation of the transition from no acceleration to significant acceleration, though smaller initial droplets, which form easily and also provide substantial acceleration at shorter distances. This example highlights how ESI can be used both to monitor bulk reactions and as a platform for accelerated reactions.

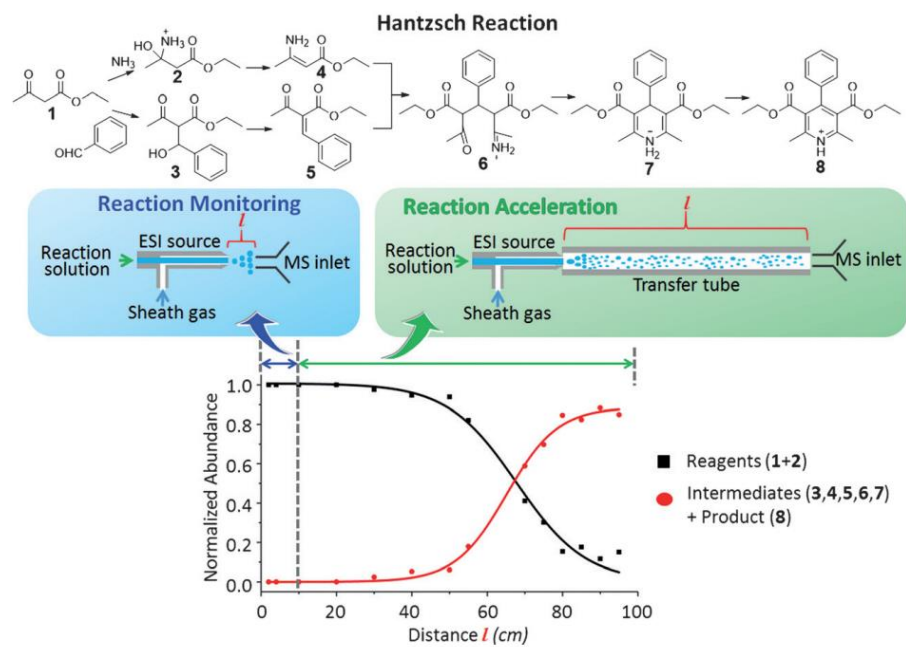


Figure 2.20: Hantzsch Reaction in Electrospray MS in using microdroplets.

CHAPTER THREE

ROOM TEMPERATURE SYNTHESIS OF COPPER METAL-ORGANIC FRAMEWORK (MOF) USING DROPLET CHEMISTRY AND ITS APPLICATION IN NITROGEN CONVERSION TO NITRATES.

3.1 Introduction

Metal-organic frameworks (MOFs) represent a rapidly expanding class of crystalline materials characterized by their highly ordered structures[55], tunable porosity, and diverse functionalities[56]. MOFs are produced from metal ions or clusters coordinated to organic ligands, forming porous networks[3,4] that have been widely studied for applications in energy storage[59], catalysis[8], sensors[60] and drug delivery [61] due to their high porosity[62], large surface area[63], well-defined channels and cavities[64], and the possibility to modify their chemical and structural properties to suit intended applications [65]. Bulk-phase methods (conventional methods) like solvothermal, hydrothermal and micro-wave assisted synthesis have been widely used to produce MOFs with most involving heating precursor solutions in closed systems[5,6,7]. However, these bulk-phase synthesis methods are characterized by longer reaction times, slow heat transfer, inhomogeneous mixing [65], the use of high temperature, limited batch processes [47], low efficiencies, substantial chemical wastes, high costs, difficult scaling up and the employment of multistep procedures [14]. Furthermore, using conventional methods like hydrothermal method to synthesize water sensitive MOFs such as copper Benzene-1,3,5-tricarboxylic acid (Cu-BTC) MOF can lead to phase changes, structural

decomposition[9,10,11,12] and loss of crystalline shape[71]. So, employing synthetic methods that will preserve the structural characteristics of the MOF is very important.

Recently, microdroplet synthesis have been applied in MOFs synthesis to facilitate rapid solvent phase transitions by generating micrometer-sized aerosols droplets to produce materials of important characteristics[72]. In the MOF microdroplet synthesis, reactants undergo rapid and uniform mixing in very confined spaces leading to more uniform reactions which is important for generating MOFs with good structural properties[46]. Small solvent volumes with fast reaction rates in microdroplet synthesis leads to controlled nucleation and uniform growth of MOF crystals[1,8, 15]. In addition to the turnability of the MOF structure in the microdroplet synthesis, the synthesis process is highly reproducible which can ensure consistent quality across various production batches[47]. Furthermore, the rate of heat and mass transfer can be increased significantly in microdroplets due to their small dimensions[73] which facilitates quick nucleation and crystal formation[65].

A common approach used in microdroplet synthesis of MOFs is the spray method also known as aerosol-assisted synthesis where precursor solutions are atomized or nebulized into aerosols which serve as microreactors in a flow system with rapid solvent evaporation, nucleation and crystallization (the three stages of microdroplet synthesis of MOFs) taking place to rapidly produce the MOF[65]. These microreactors lead to fast solvent evaporation, an increase in heat transfer rates which affect nucleation and crystallization [17, 18]. Fast solvent evaporation and high heat transfer rates lead to decrease droplet sizes, increase supersaturation ratios of precursor solutions and ensure orderly nucleation and crystallization[1,4,6]. As the first step in MOF formation in microdroplets, various factors affect and control how solvent evaporation takes place in microdroplet aerosols[56]. The vapor pressure of solvents, precursor concentration [8], reaction

time, pressure and temperature[66] have been found to play important roles in modulating MOFs in aerosol spray route.

Temperature in particular is one of the most common parameters employed in synthesizing MOFs in microdroplet synthesis. High temperature ensures fast solvent evaporation[76] and solute diffusion leading to shorter reaction times in the droplet synthesis route[77]. However, MOFs produced from these cases tend to be underdeveloped due to fast solvent evaporation leading to shorter residence time of the droplets[1,21]. Since there is not enough time for proper crystallization to take place, these cases have led to the production of hollow spherical shaped MOFs for example instead of the usual octahedral crystals of the Cu-BTC MOF. Furthermore, high temperatures can also lead to the collapse of MOFs structures due to decomposition of organic linkers. He et al[14] carried out the microdroplet synthesis of Cu-BTC MOF and its composite at various temperatures using a furnace tube but amorphous samples were produced at temperatures of 400 °C and higher. To produce Cu-BTC MOF with well-defined octahedral shaped crystals, it is important to ensure slow solvent evaporation in order to increase residence time of the precursor solutions. This can be done by using low vapor pressure solvents like DMSO and DMF or regulating synthesis temperature[1,22,23].

Here in, we carry out the microdroplet synthesis of Cu-BTC MOF (HKUST-1) using a spray flow system at room temperature. This will slow down solvent evaporation and increase residence time of the droplets, ensuring that there is enough time for orderly crystallization to occur. In this case, solvent evaporation is entirely facilitated by the repeated nebulization of the precursor solutions and the continuous circulation of the microdroplets in the flow system. Our set-up consist of an air compressor used for nebulization, pressure controlling system, a sprayer that produces microdroplets and a peristalsis pump that facilitate the repeated movement of the atomized droplets

in the flow system. To optimize our synthesis conditions, we incorporated a solvent adjustment system with various ethanol to water ratios and DMF to water ratios at a fix pressure. The solvent adjustment system was incorporated to study the effects of water in the surface chemistry and crystallinity of the MOF. The results show the successful synthesis of the MOF in the microdroplets at room temperature. We also observed that water has a damaging effect [61] on water sensitive MOFs like Cu-BTC. Systematic material characterization was done to identify the role of droplet formation and solvent adjustment on the characteristics of the MOF and the results correspond to the conventionally reported Cu-BTC MOF. The synthesized material was used as a catalyst in the room temperature conversion of nitrogen gas to nitrates and results obtained from the ion chromatography show that the synthesized material is suitable as a catalyst for the production of nitrates. The significance of this work is that we do not require high temperature to facilitate solvent evaporation, nucleation and crystallization in the droplet synthesis unlike other reported cases. Reaction time is significantly less compared to reported conventional methods that have been used to synthesized Cu-BTC MOF. Another advantage of this method is that it is possible to do in-situ coating of the synthesized MOF for use as a catalyst in various applications. Because it is a continuous flow system with minimal waste production and effective reagent consumption, this method can be easily scalable.

XRD patterns of the synthesized materials were obtained using an XRD instrument (Rigaku Ultima IV, Kuraray Co. Ltd. Japan). The IR study of the samples was done using Thermo Nicolet 6700 FT-IR spectrophotometer, USA. Scanning Electron Microscope (SEM, Thermo Scientific Quattro S, USA) was used to study the morphology of the synthesized MOF. The porosity and surface area of the MOF were determined using nitrogen adsorption–desorption isotherms using the

Quantachrome equipment and the thermal stability of the synthesized MOF was determined using Thermogravimetric Analysis (SDT Q600 developed by TA Instruments).

3.2 Materials and Methods

3.2.1 Materials

Copper (II) acetate monohydrate ($\text{Cu}(\text{OAc})\cdot 2\text{H}_2\text{O}$ from Alfa Aesar), 1,3,5 Benzene tricarboxylic acid (H_3BTC , 98% purity from Sigma-Aldrich), Ethanol (99.8 % purity from Sigma Aldrich), Dimethylformamide (DMF, 99.8% purity from Sigma Aldrich), Deionized Water. All materials were used without further purification.

3.2.2 Material Synthesis

Our set up used in this microdroplet synthesis consists of a sprayer, pressure control system and nebulization device, and pump that facilitates the repeated flow of the precursor solution. Precursor solutions were prepared by dissolving 0.247g of H_3BTC and 0.70g of ($\text{Cu}(\text{OAc})\cdot 2\text{H}_2\text{O}$) in 60ml of 100% ethanol. The solution was sonicated for 10 minutes to allow uniform dissolution of reactants in the solvent. As shown in figure 3.1, the solution flows through a pump and enters the sprayer where nebulization takes place with the help of the air pressure from the pressure control system. The cycle is repeated for 1 hour for complete solvent evaporation, nucleation and eventually MOF formation at 15 rpm. The precipitate produced after complete solvent evaporation and MOF formation is then washed with ethanol and water through centrifugation for 10 minutes at 5000 rpm and dried in an oven at 60°C . To explore the effects of water on the microdroplet synthesis of the MOF, the reaction was optimized by synthesizing the MOF in 75% and 50% ethanol. To prove the formation of the MOF in the microdroplet synthesis flow system, a sample prepared in 75%

ethanol was dried in a desiccator at room temperature. In another microdroplet synthesis, the same masses of H_3BTC and $(\text{Cu}(\text{OAc})_2 \cdot 2\text{H}_2\text{O})$ were dissolved in various DMF to water ratios (100%, 75% and 50%) and the same synthesis route followed as shown in figure 3.1.

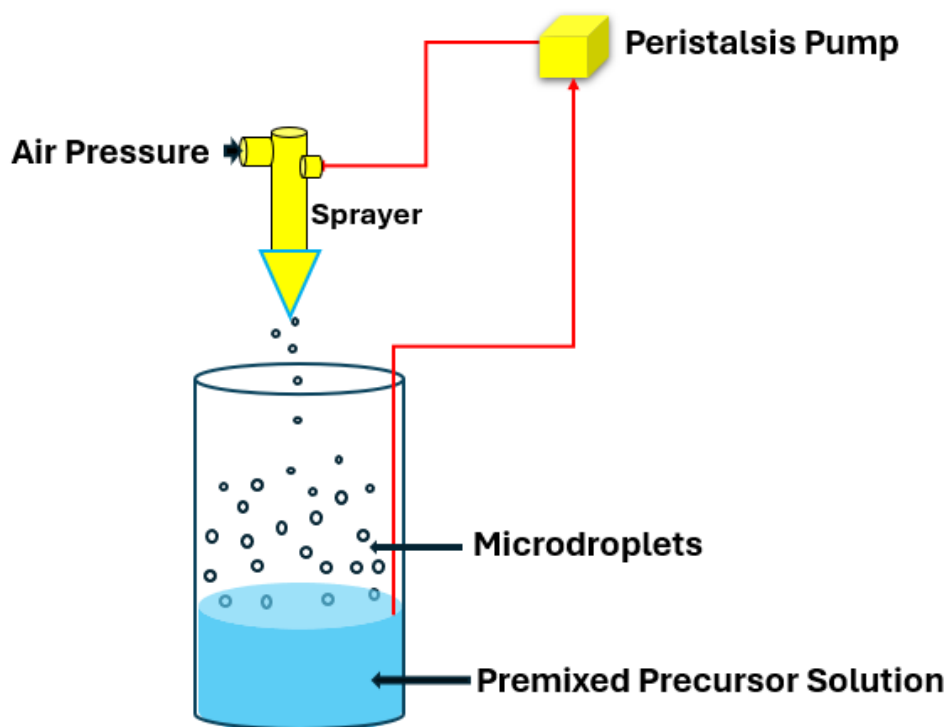


Figure 3.1: A figure showing the Room Temperature Microdroplet Synthesis of Cu-BTC MOF(HKUST-1).

3.3 Results and Discussion

3.3.1 XRD

We carried out XRD to study the crystallinity of our synthesized material and compared it with the sample produced from the solvothermal synthesis method. The diffraction patterns produced through microdroplets match with the solvothermal sample with major crystalline phases 200, 220, 222, 400, 500, 440, 731, 751 observed showing the successful synthesis of the MOF in microdroplet synthesis despite a drastic reduction in reaction time at room temperature as highlighted in figure 3.2 . It is also important to indicate that the XRD pattern of samples produced in microdroplet synthesis and dried in desiccator (75% ethanol-d) matches both the sample from solvothermal synthesis and other microdroplet synthesized samples dried in dessicator. This is confirmation of the formation of the Cu-BTC MOF from microdroplets. There is a decrease in peak intensity observed as the amount of water used in the synthesis increases for samples from both ethanol and DMF. This can be related to the collapse of MOF networks consisting of functional groups from the linker that are not coordinated to the Cu^{2+} ions [2,13] because of

hydrogen bonding formed between the carboxylic groups of the linker and water.

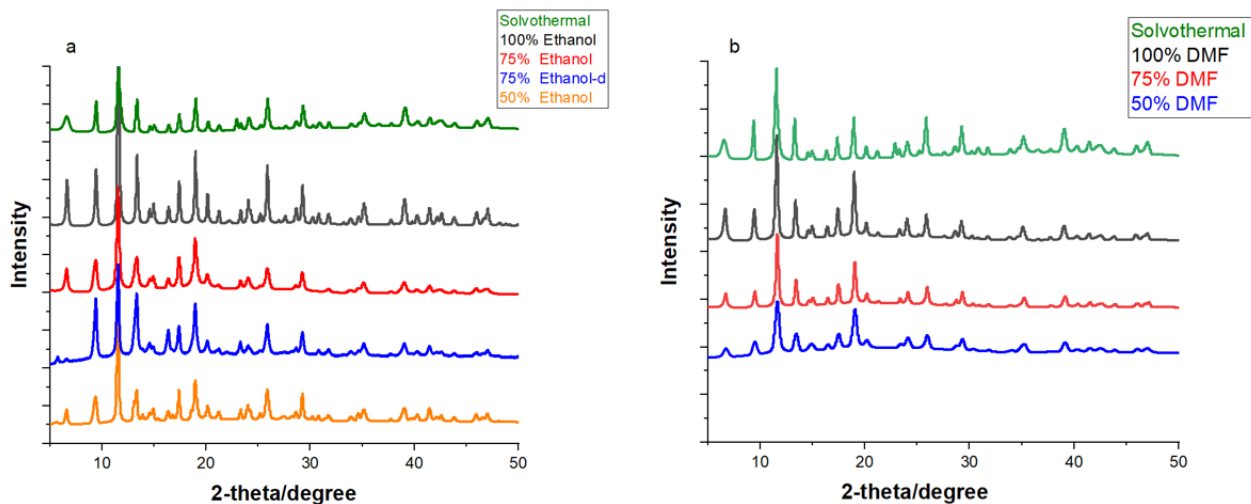


Figure 3.2: A figure showing XRD patterns of the Cu-BTC MOF produced from (a) different ethanol to water ratios (b) different DMF to water ratios in the microdroplet synthesis compared to the sample produced from the solvothermal method. (75% Ethanol-d correspond.

3.3.2 FTIR

The surface functional groups of the synthesized samples were studied using FTIR. As shown in Figure 3.3, the FT-IR peaks of the samples produced from the microdroplet synthesis using ethanol and also DMF match the sample synthesized in the solvothermal method. A major characteristic peak at 1700 cm^{-1} observed in the free H_3BTC shows the stretching vibrations of the C=O bond before coordination with the Cu^{2+} ions for both ethanol and DMF samples. After coordination, the peak shifted to 1645 cm^{-1} and 1643 cm^{-1} for ethanol and DMF samples respectively indicating the successful deprotonation of the linker and its coordination with the Cu^{2+} ion [8,16,17]. An adsorption band observed around 1260 cm^{-1} in the free H_3BTC which is associated with its C-O bond disappears after coordination with the Cu^{2+} ions. This is an indication of sufficient deprotonation during synthesis[14]. A characteristic peak at 725 cm^{-1} and 720 cm^{-1} for ethanol and DMF samples respectively correspond to Cu-O bond. A large broad band due to stretching vibrations of OH groups caused by the presence of trapped solvents (ethanol and water) is observed at around 3400 cm^{-1} [1,11,12]. This is particularly visible in the samples produced from high percentage of water. The FT-IR results agree with the XRD results.

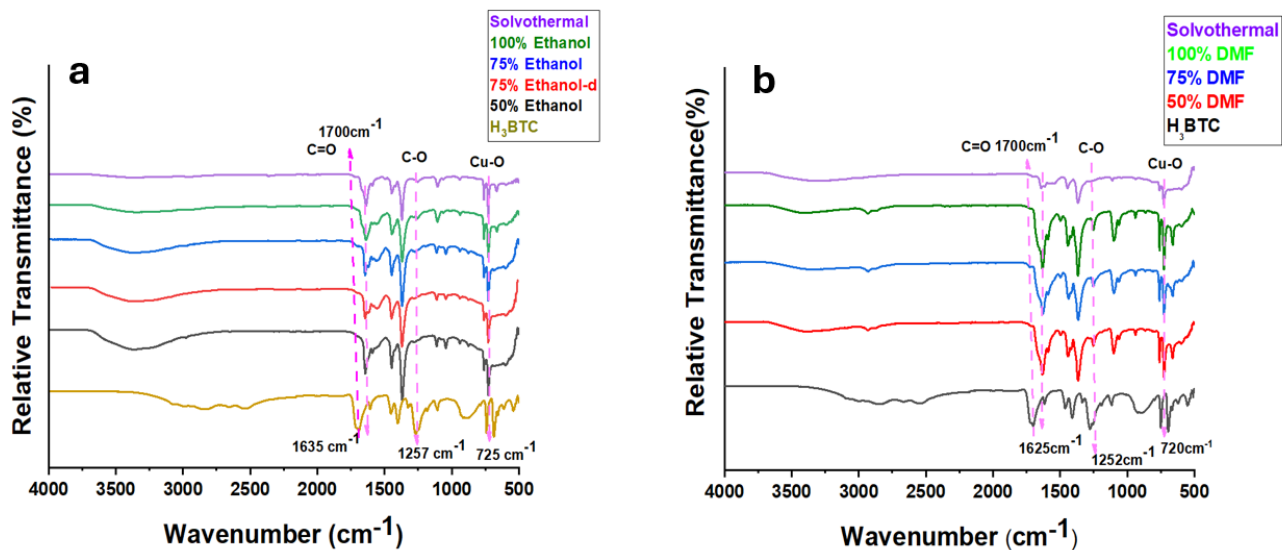


Figure 3.3: A figure showing FT-IR spectra of the Cu-BTC MOF produced from (a) different ethanol to water ratios (b) different DMF to water ratios in the microdroplet synthesis compared to the sample produced from the solvothermal method. (75% Ethanol-d correspond to the sample dried in desiccator).

3.3.3 TGA

The TGA of the Cu-BTC MOF synthesized with varying solvent ratios of ethanol and DMF reveals significant differences in thermal behavior and stability. For ethanol-based samples, the TGA curve demonstrates an initial weight loss of physically adsorbed water and residual solvents below 100°C, decomposition of coordinated solvents and partial breakdown of the organic linker between 100°C and 300°C, and complete framework collapse above 300°C. The 100% ethanol sample shows the highest thermal stability compared to the 75% and 50% ethanol samples. The final weight is consistent across all ethanol-based samples indicating that the solvent ratio primarily affects the initial stages of thermal decomposition rather than the final degradation of the framework[8, 32, 33, 34].

The DMF-based samples display similar thermal decomposition behavior, with some distinctions. The desorption of adsorbed water and residual solvent below 100°C is minimal and slightly decreases as the DMF concentration decreases. Between 100°C and 350°C, a pronounced weight loss is observed, with the 100% DMF sample showing the highest thermal stability[76]. However, the framework collapse temperatures for DMF-based samples are generally lower than those of ethanol-based samples. The final weight (~40–50%) is slightly lower for DMF samples, possibly due to differences in decomposition mechanisms.

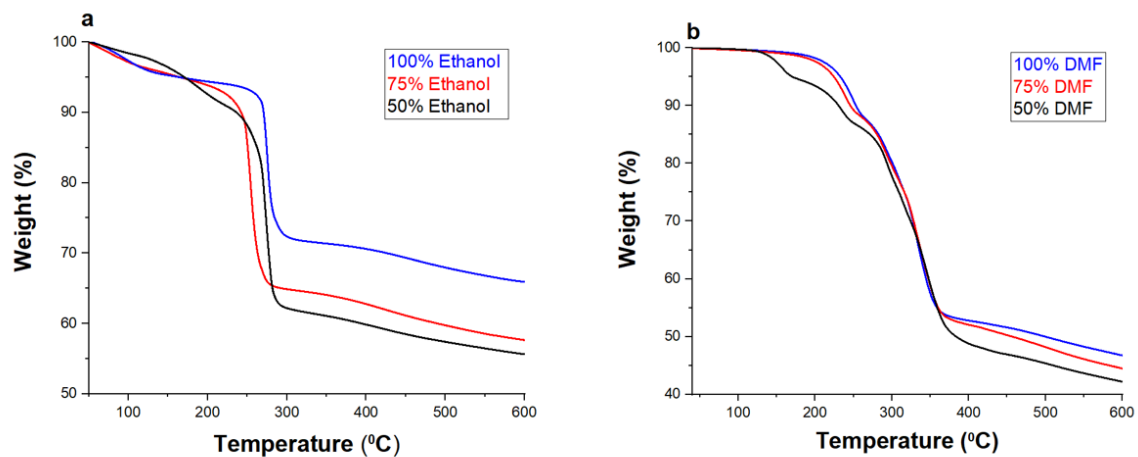


Figure 3.4: A figure showing TGA of the Cu-BTC MOF produced from (a) different ethanol to water ratios (b) different DMF to water ratios in the microdroplet synthesis.

3.3.4 SEM

To determine the morphology of the synthesized materials, two representative samples (100% ethanol and 100% DMF) were selected for SEM analysis. As shown in figure 3.5, the SEM micrographs show a mixture of crystals with different sizes of predominantly regular octahedral shape consisting of smooth and well-defined edges. This observed morphology is consistent with reported cases of conventional methods used in synthesizing Cu-BTC MOF [11,13]. Compared to ethanol samples, a slight particle aggregation was observed in the samples produced using DMF. This may be due to slow nucleation and crystallization caused by the slow evaporation of DMF during microdroplets synthesis.

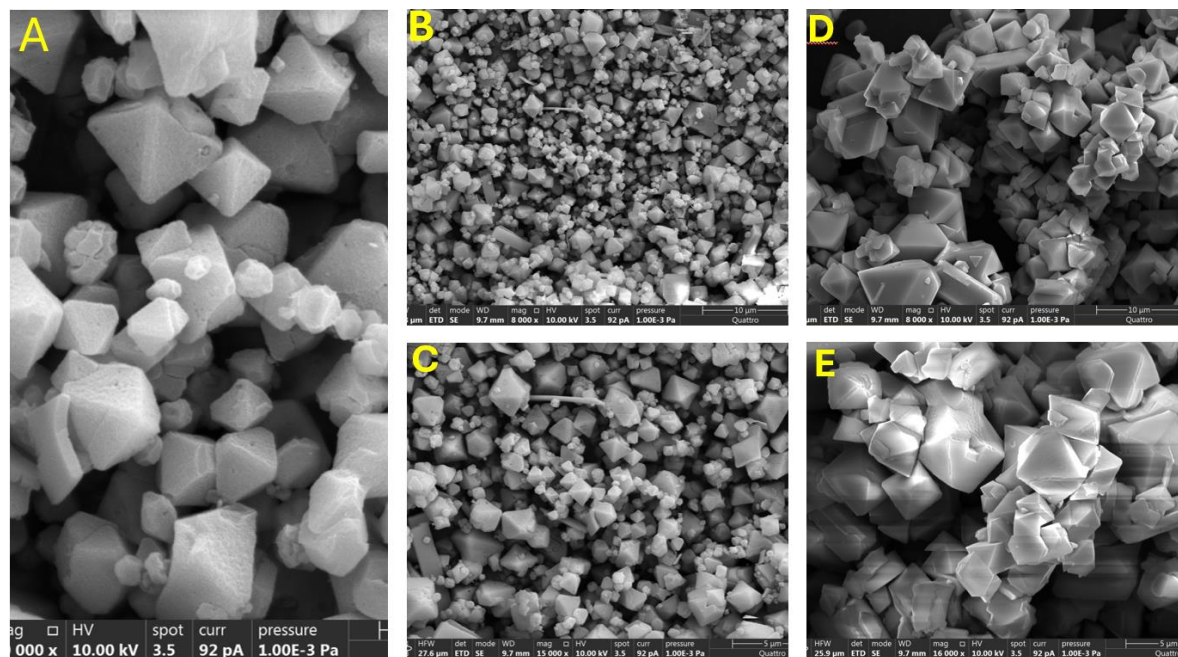


Figure 3.5: A figure showing SEM images of representative samples (A=3 μ m, B=10 μ m, C=5 μ m) produced using 100% ethanol and (D= 10 μ m, E=5 μ m) produced using 100% DMF.

3.3.5 Brunauer–Emmett–Teller Analysis (BET)

Two representative samples (100% ethanol and 100% DMF) were analyzed by N₂-adsorption-desorption method to study the porosity and surface area of the material synthesized in the microdroplets method. As shown in figure 3.6a, the sample produced from 100% ethanol shows a rapid uptake of N₂-adsorption at relatively low pressure ($P/P_0 < 0.01$) indicating the presence of micropores. However, an increase uptake of N₂ at higher pressures indicates the presence of mesopores confirming the hierarchical pore structures (Micromesopores) of the material[8, 22, 26]. It has a BET surface area of 870 m²g⁻¹ and average pore diameter of 1.778 nm.

The N₂-adsorption and desorption isotherm for the sample produced from 100% DMF shown in figure 3.6b illustrates a type IV isotherm. The BET surface area and average particle diameter are 6967 m²g⁻¹ and 1.850 nm[86].

Table 3.1: A table Showing total surface area (m² g⁻¹), Total pore volume (cm³ g⁻¹), Micropore and mesopore Volumes (cm³ g⁻¹) and Average Pore Diameter (nm) of two representative samples produced from microdroplet synthesis.

Sample	S _{BET} (m ² g ⁻¹)	Total Pore Volume (cm ³ g ⁻¹)	Micropore Volume (cm ³ g ⁻¹)	Mesopore Volume (cm ³ g ⁻¹)	Average Pore Diameter (nm)
100% Ethanol	870	0.519	0.296	0.223	1.778
100% DMF	697	0.736	0.116	0.619	1.850

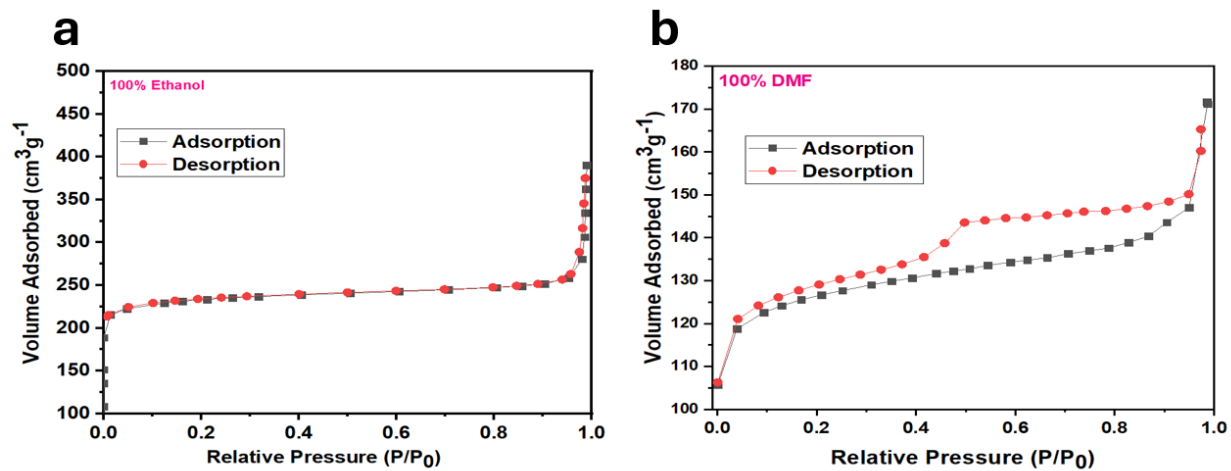


Figure 3.6: A figure showing (a) N₂- adsorption–desorption isotherm of sample produced using 100% Ethanol. (b) N₂- adsorption–desorption isotherm of sample produced using 100% DMF.

3.4 Room Temperature Conversion of Nitrogen to Nitrates (NO_3^-) using Cu-BTC MOF as a Catalyst

To test the synthesized MOF as a catalyst for the production of nitrates from nitrogen, the sample produced from 100% ethanol was selected as a representative sample. A microbubbler was used for the direct conversion of nitrogen to nitrate at room temperature. The full set up consists of a gas source, pressure controlling system (PCS) and the reaction vessel. The pressure from the gas source was used to generate microbubbles. The H_2O_2 generated from the microbubbles interacts with the catalyst to produce hydroxyl radicals ($\text{HO}\cdot$) which eventually activates N_2 to nitrate (NO_3^-) as a product. The Air/ N_2 serves as a source of nitrogen while the water in the reaction tube provides oxygen for the formation of nitrates[87]. Bubbling was done for 2 hours without sonication or applied potential. The product was filtered to remove any residue from the used catalyst and analysis was done using ion chromatography. Contrary to other methods of nitrate production like the high temperature catalytic oxidation of ammonia, this method is simple, does not require applied potential and was carried out at room temperature. Extensive research and advancement in this work could open a new pathway for nitrates generation on a large scale, particularly for fertilizer production.

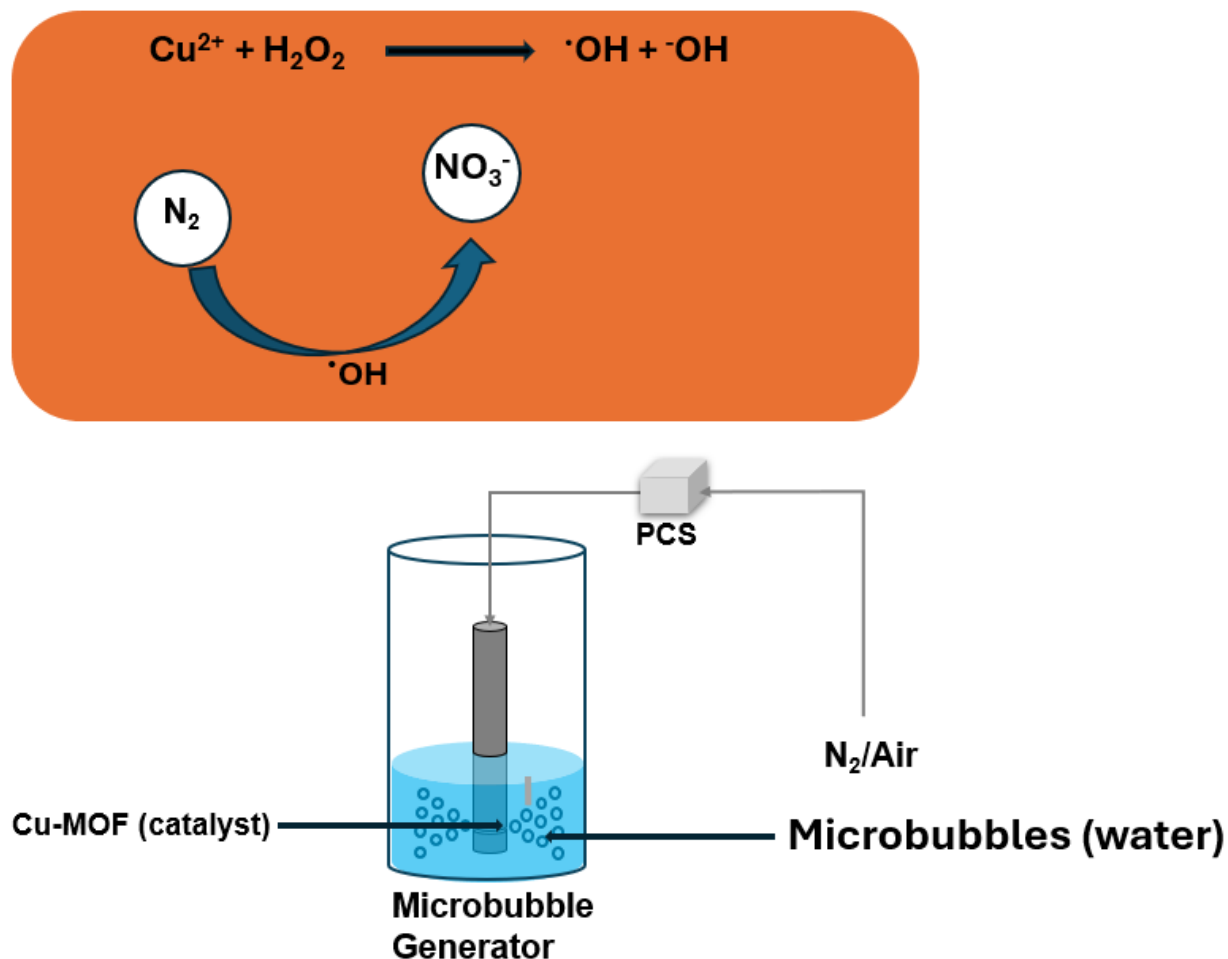


Figure 3.7: A figure showing the Room Temperature Conversion of Nitrogen to Nitrate Using Cu-BTC MOF As a Catalyst Using a Microbubbler.

The formation of nitrates was determined by injecting 5mL of the sample in an ion chromatography instrument consisting of an anion suppressor detector at 0.25mL/min flow rate at 30⁰C column temperature. 4ppm (4mg/L) KNO₃ was used as a standard to validate the retention time and quantify the produced nitrates from our method. As shown in figure 3.8a, linearity was established using a linear regression of peak area ratio versus the concentration of nitrate in mg/L. Figure 3.8b shows the ion chromatography peaks of the samples used in the conversion process along with the

standard. Note that the 25mg highlighted on the chromatogram corresponds to the amount of catalyst added in the reaction for the respective gas sources (Air/N₂). The retention time of the produced NO₃⁻ was observed in the range of 7.0-7.3 minutes. Since the area under the peak is proportional to the concentration of the ion in a sample, we quantified the concentration of NO₃⁻ produced from the reaction, by converting peak area using the standard from the calibration curve. As highlighted in table 3.2, when we bubbled N₂ in the solution containing 25 mg of the catalyst for 2 hours, we produced a higher amount of NO₃⁻ (41.3 μmol/L) compared to when we used air (24.2 μmol/L) for the same period with the same amount of catalyst was used.

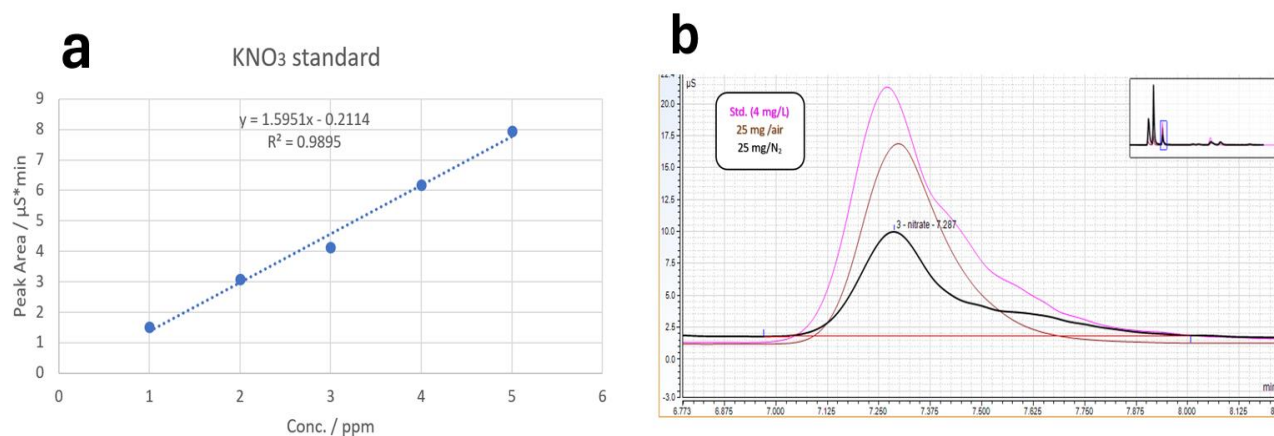


Figure 3.8: A figure showing (a) Calibration Curve (b) Ion Chromatogram showing the nitrate peaks produced from different gas sources and standard.

Table 3.2 A table showing results from nitrogen conversion to nitrates in 2 hours Using Sample Produced From 100% Ethanol as a Representative Sample.

Sample	Amount of Catalyst Used	Gas Source	NO ₃ ⁻ conc. (μmol/L)
Standard (KNO ₃)	-	-	64.5
100% Ethanol	25 mg	N ₂	41.3
100% Ethanol	25 mg	Air	24.2

CHAPTER FOUR

ROOM TEMPERATURE SYNTHESIS OF POLYANILINE (PANI) USING FENTON-LIKE REACTION IN WATER MICRODROPLETS AND ITS APPLICATION IN OIL-WATER SEPARATION.

4.1 Introduction

Conducting polymers are an important family of organic compounds made up of monomer units with conjugated chemical bonds that under doping, can become conductive and have become popular due to their unique properties[1, 2]. They have the ability to replace metals due to their conductivity, low density, and easy processability[89]. One important member of this family of conducting polymers is polyaniline (PANI). PANI is unique and popularly used in research and various applications due to its simplicity, low cost [90], intrinsic electrical conductivity[91], high environmental stability[92], cheap and easy availability of monomers[93] high polymerization efficiency[94] and the ability to be doped by acids[95]. It has been used in important applications such as solar cells[91] and batteries[83], sensors[96], removal of water pollutants, catalysts, storage devices and supercapacitors[97]. Electrochemical oxidative polymerization and various chemical polymerization methods have been conventionally used in bulk-phased reactions and reported for PANI synthesis[1,12]. However, they are usually characterized by longer reaction times, and some are difficult to scale up particularly for electrochemical methods. Ammonium peroxydisulfate has been commonly used to produce PANI as an oxidant on a large scale. However, the oxidant is stoichiometrically consumed in the reaction and as a result, the reaction will require large amount of chemicals for PANI production in large scale leading to difficulty in purification post synthesis.

Recently, microdroplet synthesis have been applied as a new synthesis route to produce valuable materials in a variety of fields in chemistry and its related fields. They involved the production of charged droplets[51] that exhibit unusual reaction properties especially at the air-liquid interphase which are not usually observed in bulk phase reactions[7]. Reported cases have shown that microdroplet synthesis can exhibit reaction accelerations by one or more orders of magnitude compared to their bulk counterparts[13]. Various factors are responsible for the unique characteristics associated with microdroplet synthesis. Partial solvation of reactants at the air-liquid interface[1], decrease in entropy of the solute molecules due to their ordered orientation on and near the droplet surface[99], fast solvent evaporation can also lead to increase in concentration which enhances reaction rates[35], unusual dielectric constants and effective diffusion [3] have been reported to have enhanced reaction rates in the confined volumes of microdroplets in material synthesis. Although PANI has been synthesized and used extensively in various scientific disciplines, to the best of our knowledge, the microdroplet synthesis of PANI have not been reported yet.

On a daily basis, large volumes of oil enter the environment from industries, homes and many other sources[100]. Although natural processes eliminate some of these oils, a significant part of it contaminates water bodies making it difficult for aquatic organisms' survival and water use domestically[101]. Oil-water mixtures exist in categories. However, the emulsified oil-water mixtures tend to be more difficult to separate due to the smaller droplet diameters created by the presence of surfactants[102]. Separation methods like coagulation and flocculation have been applied to separate oil emulsions to some extent[86]. However, membrane filtration have been found more suitable due to low cost and better efficiency [25]. Due to the presence of an electric

double layer and the hydrophilic amine functional groups present on the surface of PANI, it has good adsorption capabilities and excellent oil rejection rate[104].

Here in, we present the chemical oxidative polymerization of PANI in water microdroplets using the spray method which is also referred to as the aerosol-assisted synthesis method. Our set-up consist of a sprayer, an air compressor used for nebulization of the precursor solution, a peristalsis pump that facilitates the continuous flow of the solution and a pressure controlling system for determining the rate of droplet generation. In this synthesis method, we used the Fenton-like reaction to carry out the polymerization of aniline in water microdroplets at room temperature. The aerosol spray method is used to produce hydrogen peroxide from sprayed water microdroplets [105] which reacts with Fe^{3+} in reaction stages to produce hydroxyl radicals[106]. As a strong oxidant, the produced hydroxyl radicals initiates the polymerization of aniline to polyaniline.

In the bulk phase, water is considered relatively inert and fairly stable. However, in its microdroplets form, water generates redox reactions and a series of radical-initiated reactions at the air-liquid interface[87]. Without the use of catalyst or applied potential, sprayed water droplets spontaneously produced hydrogen peroxide as a result of strong electric fields at the air-water interface which is enhanced by the separation and heterogeneous distribution of hydronium ions and hydroxide ions[13, [30,31]. This high electric field at the interface is sufficient to ionize hydroxide ions to hydroxyl radicals which eventually recombine to produce hydrogen peroxide[32, 33, 34, 35, 36]. Zare et al [87] carried out the N_2/air conversion to nitric acid by producing hydrogen peroxide in water microdroplets which further reacted with Fe^{2+} in the Fenton reaction to produce reactive hydroxyl radicals. These hydroxyl radicals facilitate the production of nitric acid. They confirmed the production of hydrogen peroxide using strip essays and a quantitative determination using potassium titanium oxalate (PTO) based spectrophotometric method by

measuring its absorbance at 400nm. J Colussi [105] also demonstrated the mechanism of hydrogen peroxide production from sprayed water droplets. These reported cases show that hydrogen peroxide can be successfully produced from water microdroplets. We relied on this principle to produce the hydrogen peroxide which initiates the Fenton-like reaction leading to PANI synthesis. The synthesized PANI solution was coated on an alumina ceramic support by spray coating to form a PANI membrane for separation of oil-water emulsion. The results obtained from the oil-water separation confirms the effective use of PANI as a viable material for oil contaminated water purification. It is important to note that hydroxyl radicals are produced in two instances in this reaction. Sprayed water droplets produce hydroxyl radicals due to high electric fields on their surface which eventually recombine to produce hydrogen peroxide. The interaction of hydrogen peroxide with Fe^{3+} leads to excess hydroxyl radical generation in the reaction. This allows the presence of excess hydroxyl radicals available for polymerization as an oxidant.

In this work, we have shown that polyaniline can be successfully produced by the reaction of Fe^{3+} with the droplet-generated hydrogen peroxide in a Fenton-like reaction in a short period of time at room temperature for the first time. The significance of this method is that, in addition to being carried out at room temperature, large volumes of PANI can be produced within a short period of time. Since the synthesis is done in a flow system that consist of repeated flow of the precursor solution, in-situ coating of the PANI on a substrate can be done at the time of synthesis. Because it is a continuous flow system with minimal waste production and effective reagent consumption, this method can be easily scalable. If this process can be scaled economically, it would significantly enhance the production of PANI on a large scale for various applications. Also, we have successfully used the synthesized PANI for oil-water separation and our results highlight the efficiency of our synthesis and the unique properties of PANI mentioned in this work.

600 MHz (JEOL, Japan) spectrometer was used to do the Nuclear Magnetic Resonance (NMR) study. The IR spectra of the samples were measured using Thermo Nicolet 6700 FT-IR spectrophotometer. Transmission Electron Microscopy (TEM) Analyses was performed to examine the size, shape, and morphology of the synthesized material. Scanning Electron Microscope (SEM, Thermo Scientific Quattro S, USA) was used to study the morphology and elemental composition of the PANI coated on the alumina for oil-water separation. XRD instrument (Rigaku Ultima IV, Kuraray Co. Ltd. Japan) was used to observed the decrease on the crystallinity of the alumina as a result of the coated PANI

4.2 Materials and Method

4.2.1 Materials

Aniline (Sigma -Aldrich Co.), Iron III Chloride (FeCl_3 , Sigma Aldrich), Hydrochloric Acid (HCl), Deionized Water. All materials were used without further purification.

4.2.2 Material Preparation

The set up used in this microdroplet synthesis of PANI consist of a sprayer, pressure controlling system, air compressor and a peristalsis pump that facilitates the repeated flow of precursor solution. 0.4M aniline was added in 50 mL of water followed by 200 μL of 1M HCl and 0.3M of FeCl_3 . As shown in figure 4.1, the reaction started by reaction solution flowing from the reaction vessel through the peristalsis pump into the sprayer. Nebulization by the air compressor leads to the production of microdroplets from the sprayer. Produced droplets return to the reaction vessel and flow through the peristalsis pump and the cycle is repeated for 30 minutes. After the synthesis is complete, 20 mL methanol and 10 mL water is added to the resulting solution to dissolve

unreacted monomers and remove impurities. Vacuum filtration is carried out to obtain the polyaniline. To ensure that all unreacted monomers are removed, the purification was repeated until a clear filtrate was obtained followed by drying the PANI residue at 60°C for 1 hour. To optimize our reaction conditions, we changed the concentrations of the aniline (monomer), HCl(dopant) and Fe^{3+} to study their effect on the formation and conductivity of polyaniline.

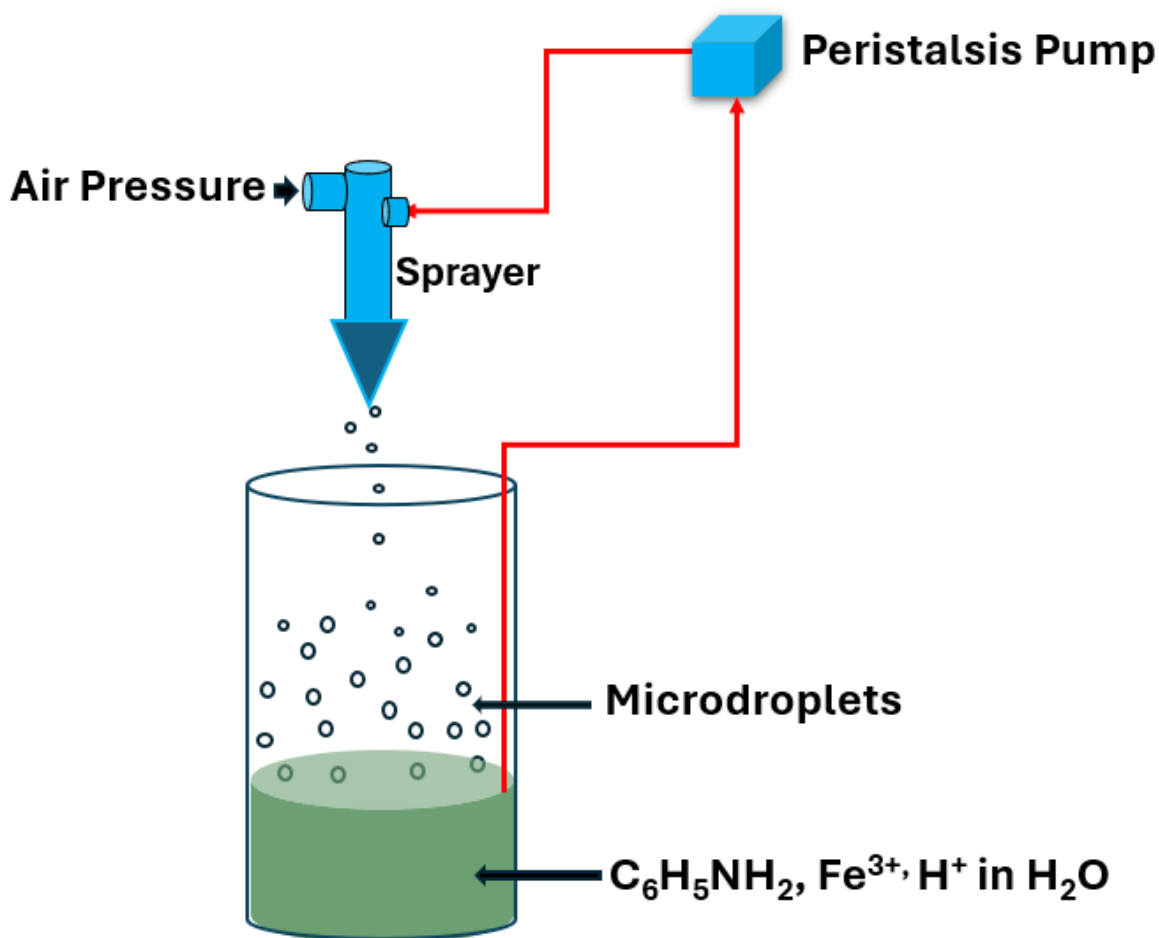


Figure 4.1: A figure showing the room temperature synthesis of PANI using Fenton-like reaction in water microdroplets.

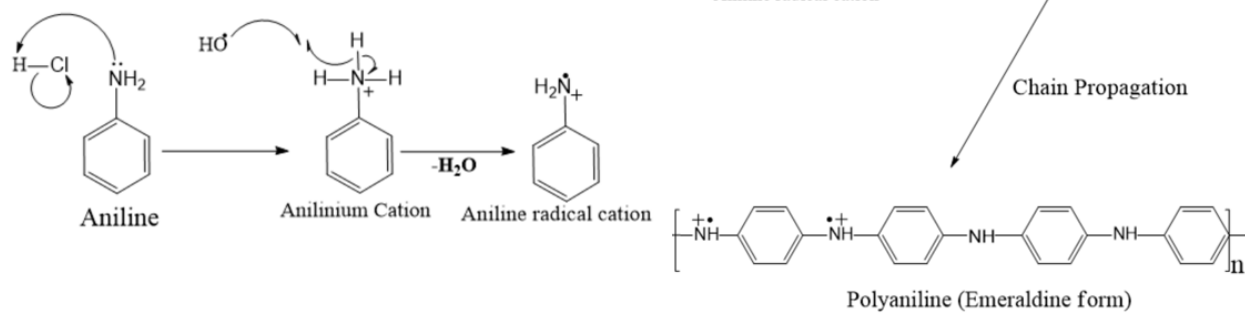
4.2.3 Proposed Reaction Mechanism of PANI Synthesis using Fenton-like Reaction in Water Microdroplets.

The microdroplet synthesis of PANI in this work takes place in two stages; the spontaneous synthesis of hydrogen peroxide from sprayed water microdroplets which reacts with Fe^{3+} in the Fenton-like reaction to produce hydroxyl radicals. This is followed by the initiation of polymerization of aniline to polyaniline by the hydroxyl radicals. When water is sprayed, charged microdroplets consisting of H^+ or OH^- are produced in excess[113]. These ions of opposite charges repel each other towards the outermost layers of the water microdroplets by electrostatic means leading to the production of high electric fields. On the surface of the charged droplets, electric fields ionizes OH^- to hydroxyl radicals[29, 31]. According to the study conducted by Colussi, the generation of the hydroxyl radicals and subsequently hydrogen peroxide is as a result of exothermic electron transfer experienced by the partially hydrated and surface-bound HO^- and H^+ ions in water microdroplets which is not typically observed in bulk water because the production of hydroxyl radicals in bulk phase is quite endothermic.



The hydroxyl radicals recombine to produce the hydrogen peroxide [114]. The produced hydrogen peroxide initiates the Fenton-like reactions with Fe^{3+} in the following reaction steps.

The generated hydroxyl radicals ($\bullet\text{OH}$) then oxidizes aniline to polyaniline in acidic medium.



4.3 Results and Discussion

4.3.1 Mass Spectrometry (MS)

To determine the intermediates produced from our reaction, we carried out the mass spectrometry analysis of our optimized sample (a sample produced from 0.6M aniline) using electrospray ionization mass spectrometry. The electrospray ionization mass spectrometry spectrum of the polyaniline synthesized from the Fenton-like reaction in water microdroplets is shown in figure 4.2 with oligomers up to the 6-mer clearly detected. Samples were prepared by dissolving 5mL of polyaniline in N-methylpyrrolidone (NMP). Subsequent oligomers differ by about 90Da or a mass approximately equal to that of an aniline molecule showing that the major product of this synthesis is indeed polyaniline. This is proof by the addition of an aniline unit to subsequent intermediates up to the 6-mer. The observed oligomers are a result of the protonation of the aniline radical generated from the reaction of aniline monomer units with the hydroxyl radicals (highlighted in the reaction mechanism) produced from the Fenton-like reaction. The proposed structures of the main oligomers detected from the mass spectrometry is highlighted in figure 4.3. Although the final product of the synthesis was the emeraldine form of polyaniline, none of the detected oligomers has equal number of benzoid and quinoid groups with more benzoid groups observed as seen in figure 4.3. This may be due to the extensive protonation of the quinoid groups by the presence of HCl in the intermediate which was eventually stabilized for the formation of the emeraldine PANI as a final product[4,40].

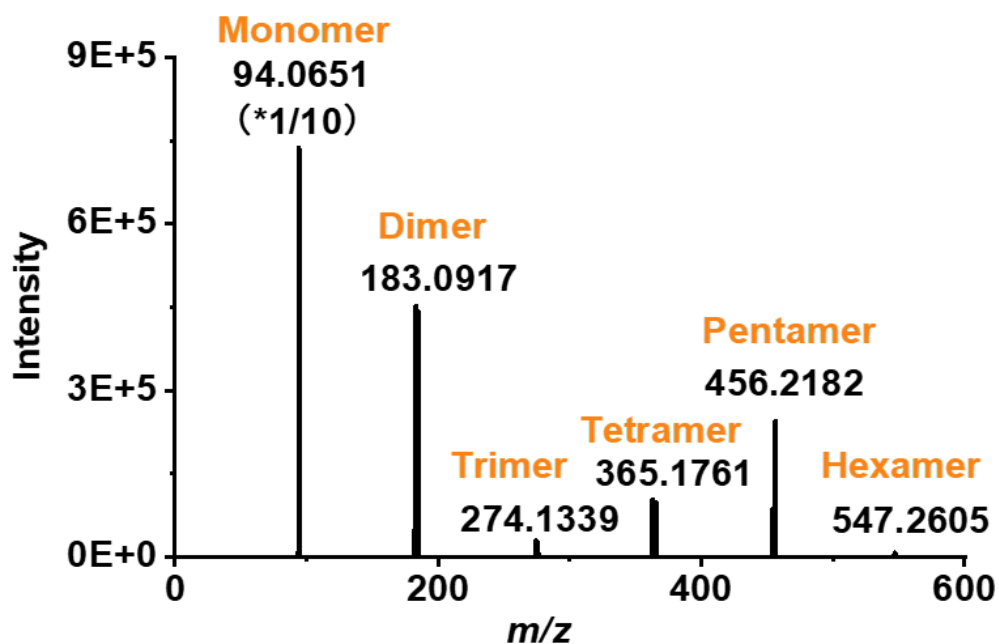


Figure 4.2: A figure showing ESI mass spectrum of polyaniline synthesized by Fenton-like reaction in water microdroplets at room temperature.

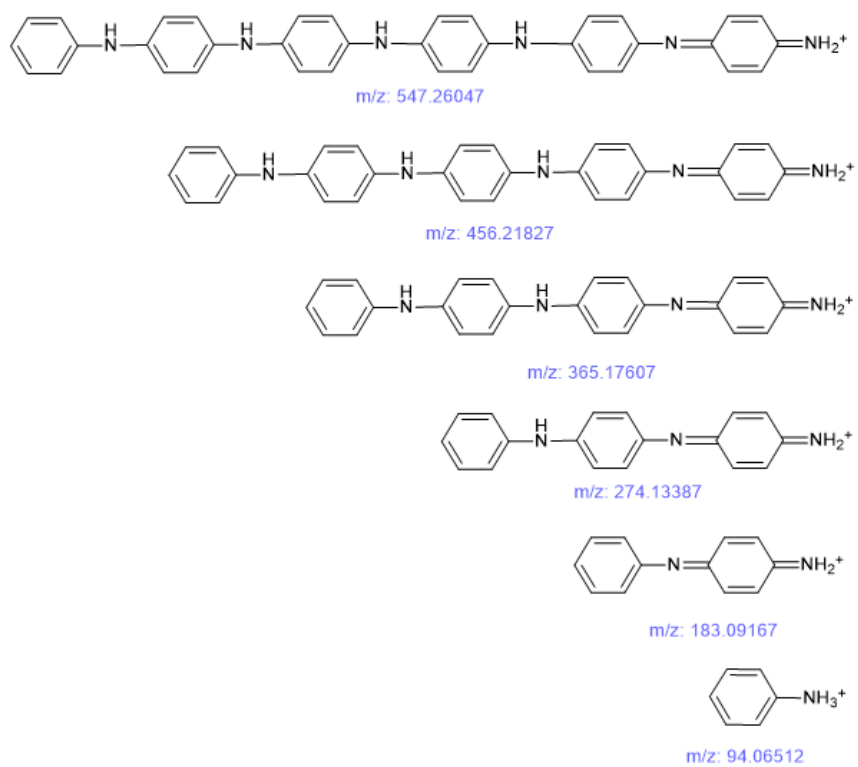


Figure 4.3: Proposed structures of the main series of oligomers present in figure 4.2.

4.3.2 ^1H -NMR

To explore the structural details and chemical shifts in the synthesized PANI, we conducted ^1H -NMR. DMSO- d_6 was used as a solvent to dissolve the PANI. 200 μl of the PANI solution was added into an NMR tube followed by 400 μl of DMSO- d_6 . The mixture was sonicated for 30 minutes to ensure uniform dissolution of the PANI before running the analysis. The ^1H -NMR spectra of the PANI synthesized from different aniline concentrations. To prove our synthesis, we also run the NMR of PANI produced from the classical method of synthesis. As shown in figure 4.4, the spectra of the samples produced from the microdroplets (figure 4.5 and 4.6) matches with the sample generated from classical method. The formation of PANI is indicated by the appearance of three distinct peaks of aromatic protons at $\delta=7.0\text{--}7.3\text{ ppm}$ [117]. The characteristic DMSO- d_6 peak is observed at $\delta=2.5\text{ ppm}$ [101]. The highly intense peak at $\delta=4.5\text{ ppm}$ corresponds to water coming from the synthesis process. The N-H protons resonance peak overlapped with water molecules at around $\delta=4.0\text{ ppm}$ making it impossible for it to appear.

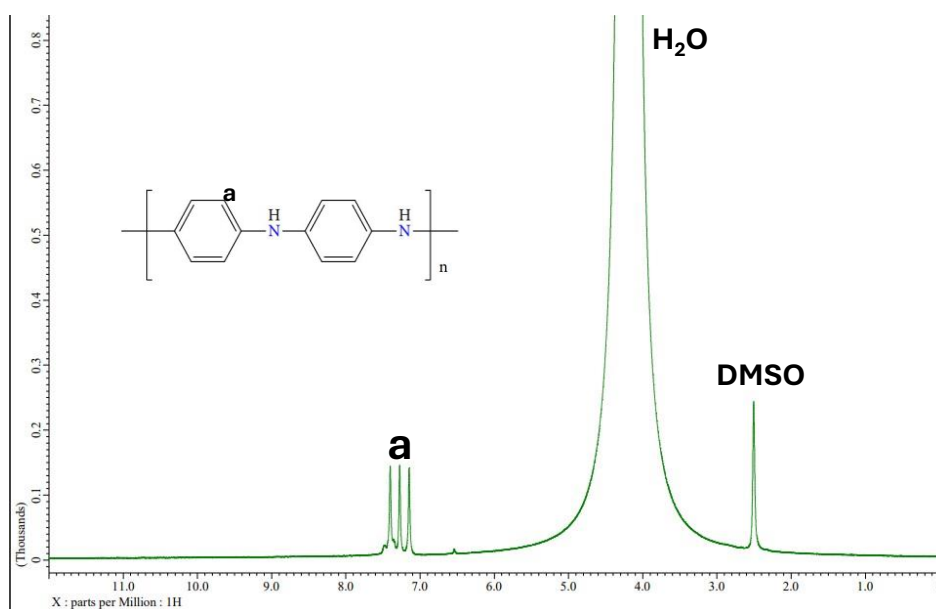


Figure 4.1: A figure showing ^1H -NMR results of PANI through classical method at room temperature.

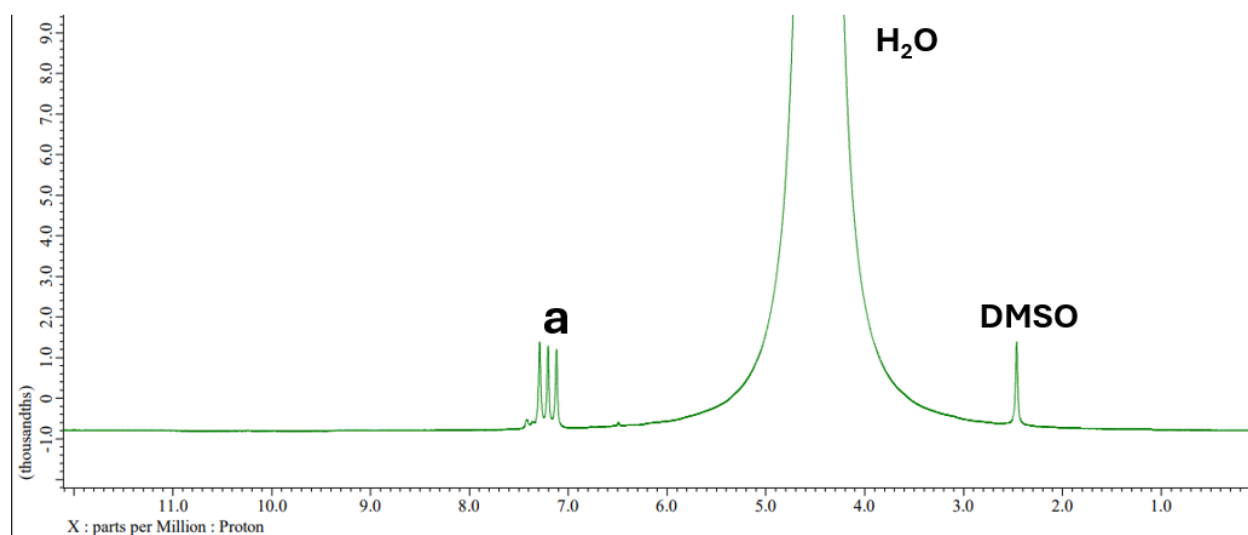


Figure 4.2: A figure showing ^1H -NMR results of PANI produced from 0.4M aniline using Fenton-like reaction in water microdroplets at room temperature.

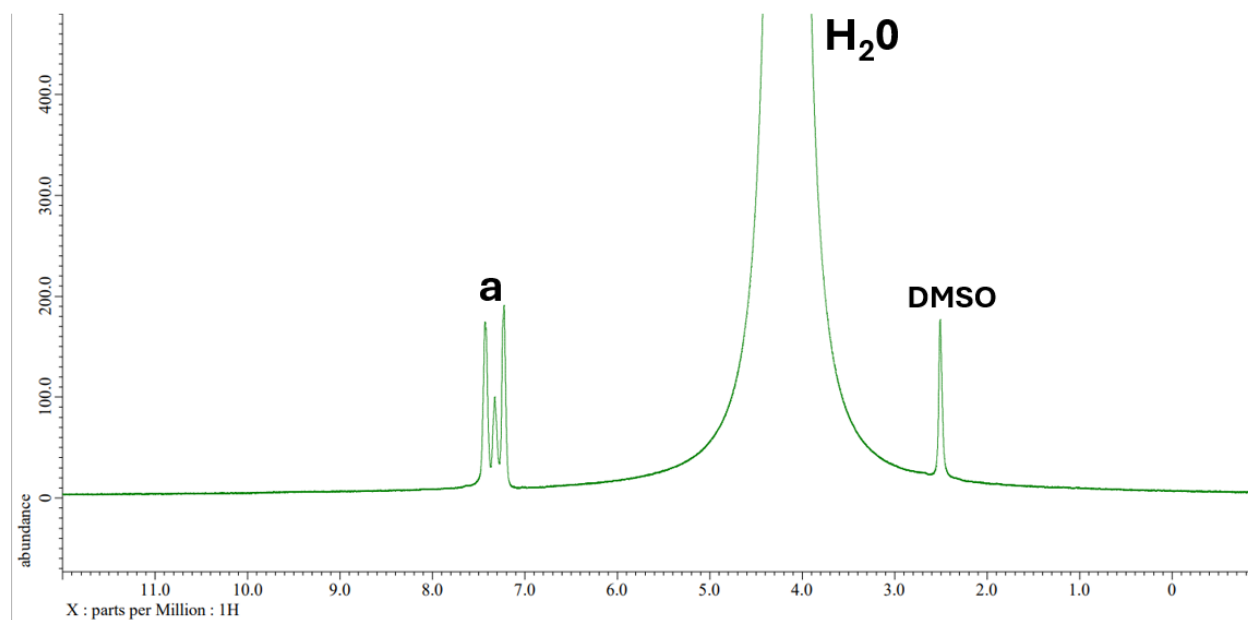


Figure 4.3: A figure showing ¹H-NMR results of PANI produced from 0.6M aniline using Fenton-like reaction in water microdroplets at room temperature.

4.3.3 FTIR

The surface chemistry of the samples of polyaniline produced from different aniline concentrations through the microdroplet synthesis route was studied using FTIR. As shown in figure 4.7, the stretching vibrations of C-H sp^2 and C=C modes of the benzoid groups are observed at 3054 cm^{-1} and 1442 cm^{-1} respectively. A 1106 cm^{-1} is attributed to the bending vibrations of C-H bonds while the C-N stretching vibrations are observed at 1304 cm^{-1} for aromatic conjugation. Two N-H bands are observed; band at 3259 cm^{-1} is related to its stretching modes while the band at 1582 cm^{-1} is related to the bending vibrations[13,42].

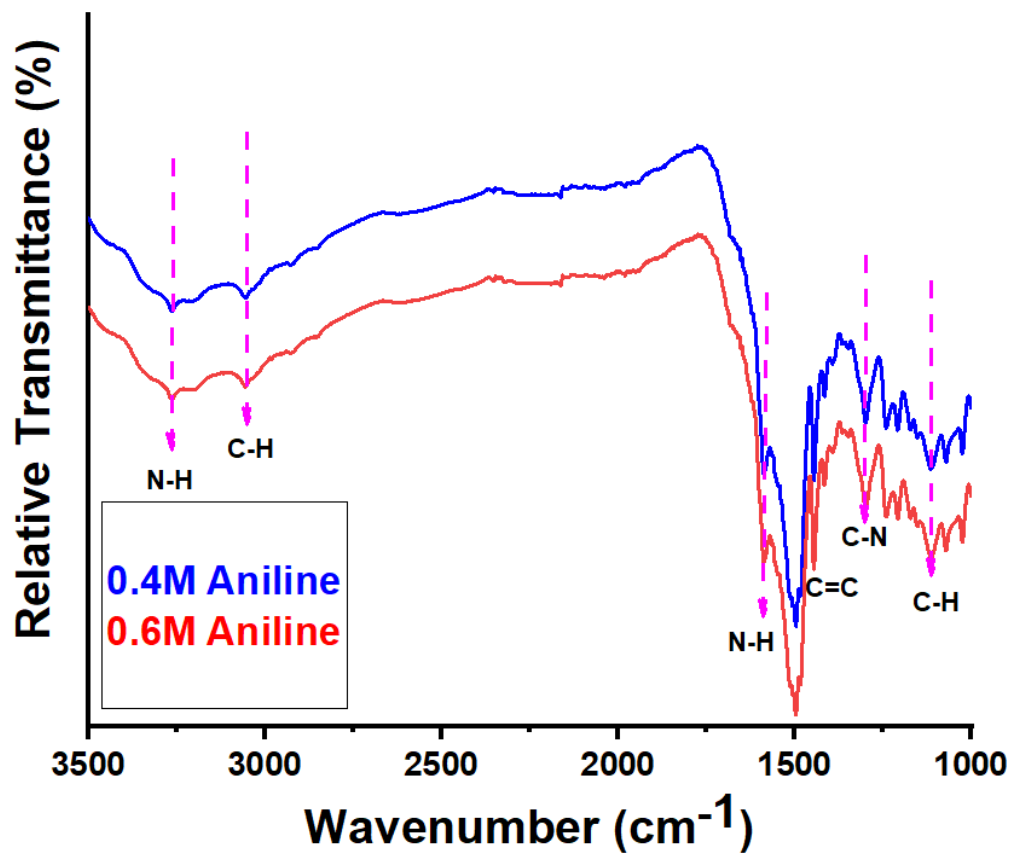


Figure 4.4 A figure showing FT-IR of the polyaniline produced from different aniline concentrations using Fenton-like reaction in water microdroplets at room temperature.

4.3.4 TEM

Transmission electron microscope(TEM) was used to study the morphology and structure of the synthesized PANI. The morphology of the PANI changes as the concentration of aniline used in the reaction increases . At lower concentration of 0.4M, irregular dense crowded bead-like clusters with better structural visibility observed at higher magnifications around 200 nm was highlighted in figure 4.8 [41,43,44]. When the concentration of aniline increased to 0.6M in figure 4.9, PANI nanofibers that are agglomerated and twisted into wrinkled interconnected networks were observed. Dark spots seen on the structures indicate the multilayer PANI while low dense areas are associated with PANI nanostructures exfoliation[116].

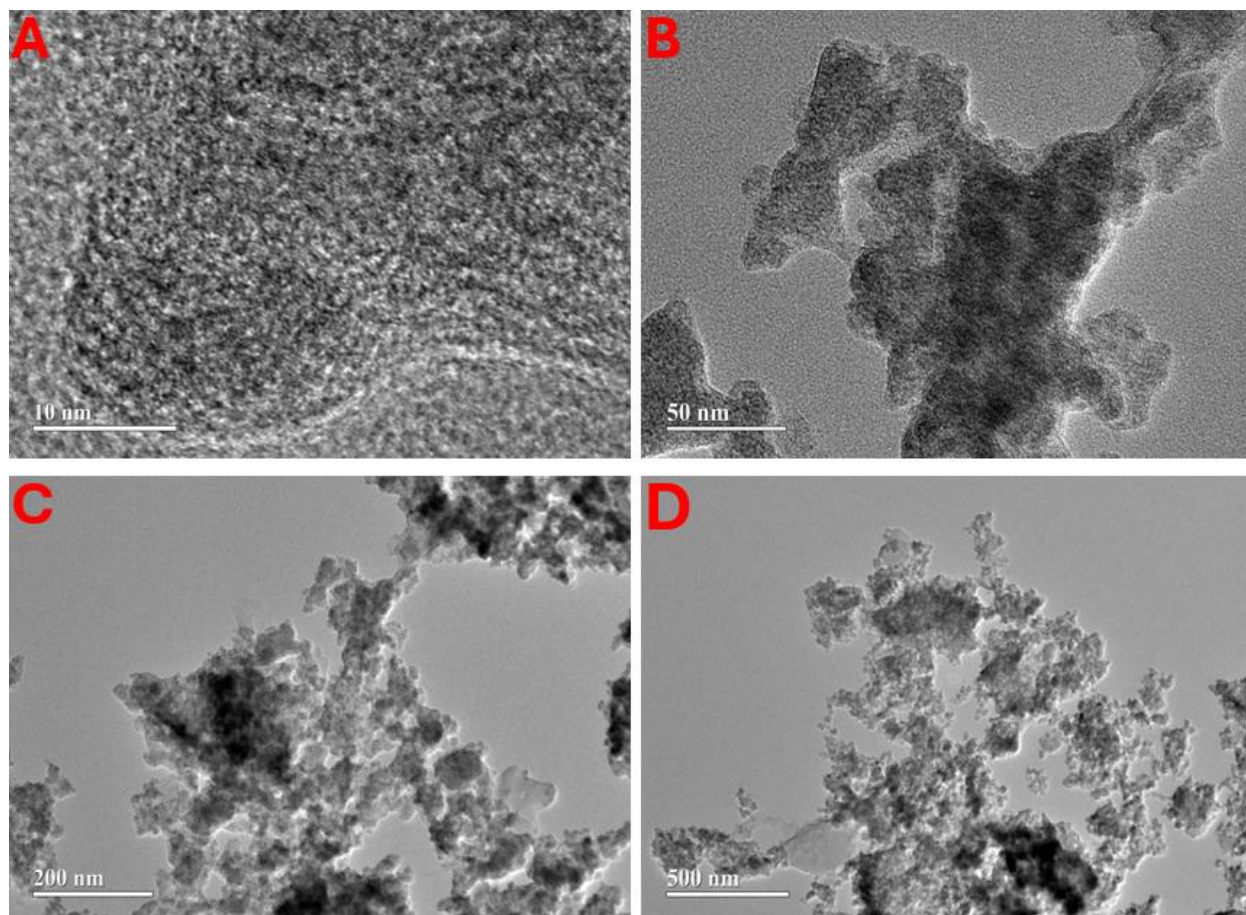


Figure 4.5 A figure showing TEM results of PANI produced from 0.4M aniline using Fenton-like reaction in water microdroplets at room temperature.

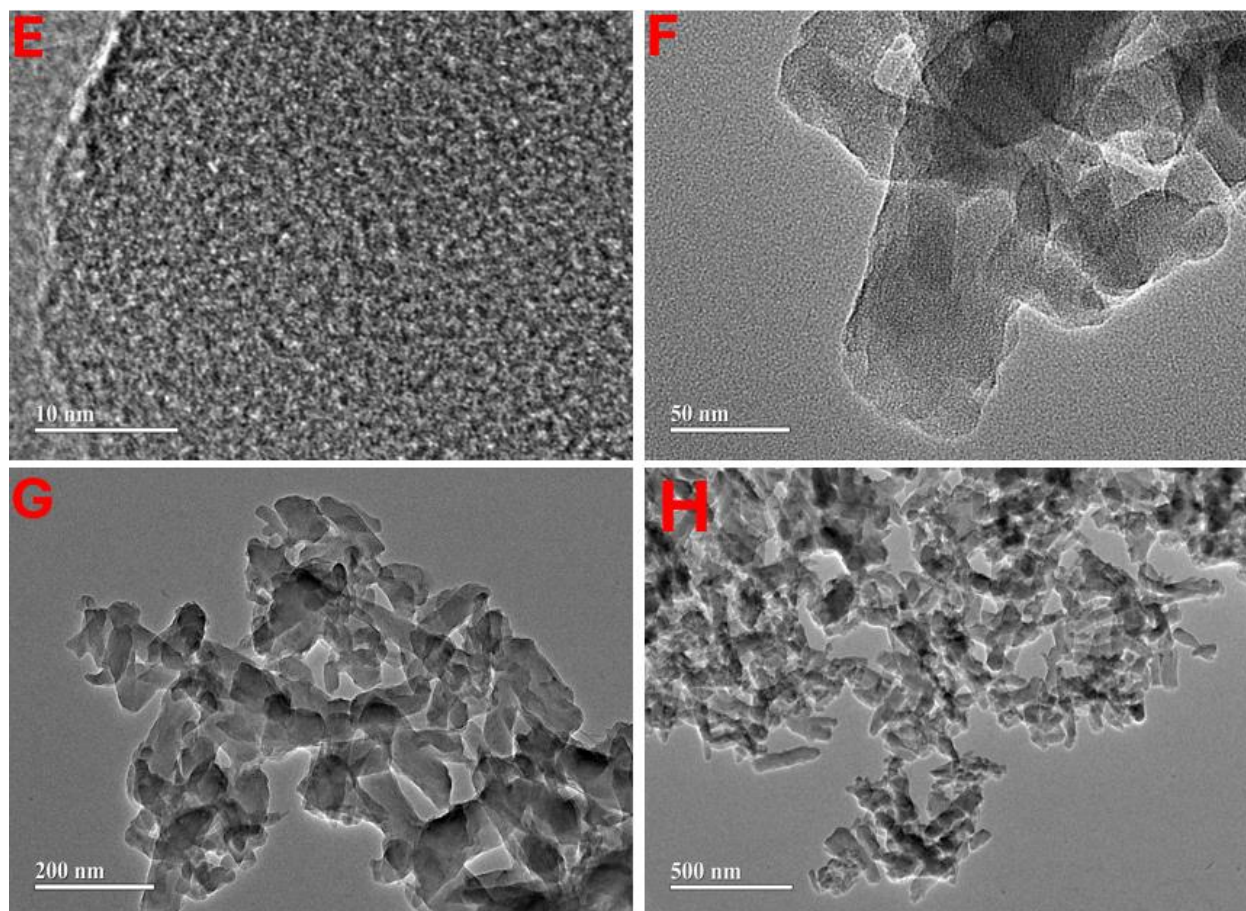


Figure 4.6 A figure showing TEM results of PANI produced from 0.6M aniline using Fenton-like reaction in water microdroplets at room temperature.

4.3.5 CONDUCTIVITY STUDY

Figure 4.10 shows the conductivity of polyaniline produced in various reaction conditions in the microdroplet synthesis method. Conductivity increases as the concentration of aniline used in the polymerization process increases. When 0.4M aniline was used with 0.3M Fe^{3+} and 1M HCl in 30 minutes, the conductivity was found to be $5.70 \times 10^{-3} \text{ S cm}^{-1}$. The conductivity changed to $6.04 \times 10^{-3} \text{ S cm}^{-1}$ when we increased the aniline concentration to 0.6M with the same Fe^{3+} and HCl concentrations in 30 minutes synthesis duration. This increase in conductivity may be due to a higher degree of polymerization leading to the formation of longer polyaniline chains with better delocalization of electrons and increased doping sites[122]. To further analyze and optimize reaction conditions, we synthesized the PANI in different Fe^{3+} concentrations using 0.4M aniline, 1M HCl and in 30 minutes (Table 2). The conductivity of PANI decreased as the Fe^{3+} concentration used decreased. This is due to the fact that a decrease in Fe^{3+} concentration will lead to reduce hydroxyl radical production which is essential for the aniline polymerization to PANI. To study the effects of doping on the produced PANI, we introduced different HCl concentrations in the synthesis process. Although a slight change in conductivity was observed, the highest value $5.70 \times 10^{-3} \text{ S cm}^{-1}$ was obtained when we used 1M HCl in the synthesis process compared to 0.1M and 0.2M HCl concentrations. This increase in conductivity is caused by an increase in doping level which is the main factor contributing to PANI conductivity. The higher the concentration of HCl, the higher the dopants (charge carriers) enhancing their conductivity. Finally, we studied how the formation of PANI in microdroplet synthesis is affected by reaction time. In 30 minutes, the conductivity was found to be $5.70 \times 10^{-3} \text{ S cm}^{-1}$. As the reaction time was increased to 45 minutes, the conductivity increased to $8.79 \times 10^{-3} \text{ S cm}^{-1}$. However, we observed a decrease in conductivity

to $3.87 \times 10^{-3} \text{ S cm}^{-1}$ after 1 hour. This is maybe due to over oxidation of the aniline monomers in acidic medium.

Table 1: Different Aniline Concentrations with 0.3M Fe^{3+} and 1M HCl in 30 Minutes

Aniline Concentration (M)	Conductivity ($\times 10^{-3} \text{ S cm}^{-1}$)
0.4	5.70
0.6	6.04

Table 2: Different Fe^{3+} Concentrations with 0.4M Aniline and 1M HCl in 30 Minutes

Fe^{3+} Concentration (M)	Conductivity ($\times 10^{-3} \text{ S cm}^{-1}$)
0.3	5.70
0.24	3.92
0.18	3.49

Table 3: Different HCl Concentrations With 0.4M Aniline and 0.3M Fe^{3+} in 30 Minutes

HCl Concentration (M)	Conductivity ($\times 10^{-3} \text{ S cm}^{-1}$)
0.1	5.17
0.2	5.29
1	5.70

Table 4: Different Reaction Times In 1M HCl, 0.4M Aniline and 0.3M Fe^{3+}

Reaction Time	Conductivity ($\times 10^{-3} \text{ S cm}^{-1}$)
30 mins	5.70
45 mins	8.79
1 hr.	3.87

Figure 4.7 Conductivity measurements of polyaniline produced in different reaction conditions using Fenton-like reaction in water microdroplets at room temperature.

4.4 Oil-Water Separation

4.4.1 Preparation of Alumina Ceramic Support/PANI Membrane

Due to the rigid structures of polyaniline, it has the ability to form stable and rough nano coatings. The large number of amino groups and the presence of electric double layers ensures PANI's hydrophilicity and underwater superoleophobicity which allows PANI nanofibers to effectively dispersed in water and allows water to filter through while rejecting oil[42,47,48]. The membrane was prepared by in-situ coating. The bare alumina ceramic membrane was washed with HCl to remove surface oxides and then rinsed with deionized water. The cleaned bare membrane was then immersed into the reaction mixture for the in-situ coating during polymerization process. After the synthesis, the coated membrane was dried at 60°C in an oven for 1 hour. The drying temperature was maintained below the thermal stability of the PANI to avoid the breakdown of the polymer chains. To confirm the successful coating of the PANI on the alumina support, we carried out detail FT-IR, SEM, EDX, XRD and contact angle characterization of the membrane and the bare alumina before using it for oil-water separation.

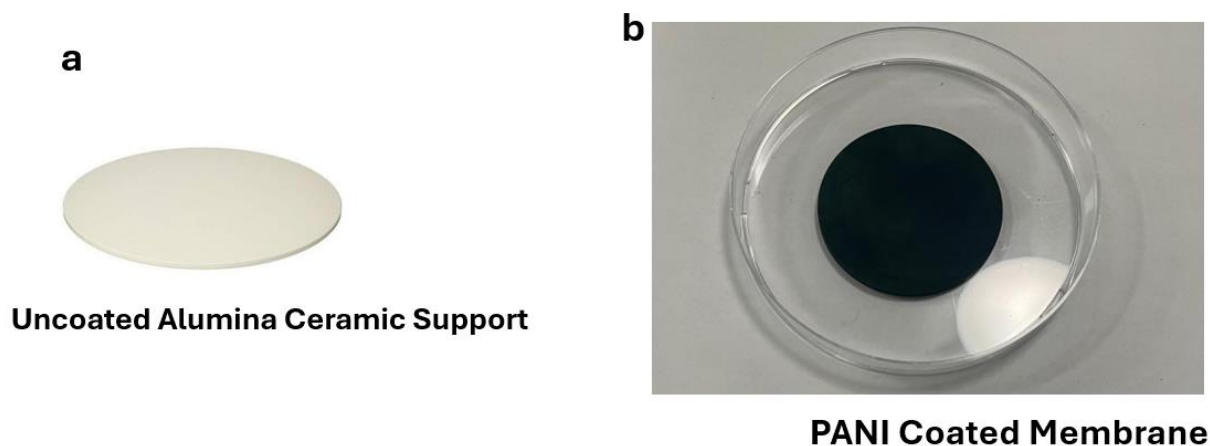


Figure 4.8: A figure showing the (a) alumina ceramic support (b) PANI/alumina ceramic support Membrane.

4.4.2 FT-IR

The FT-IR of the PANI coated on the alumina ceramic support is shown in Figure 8. The spectrum of the alumina ceramic support shows an Al-O bond at 550cm^{-1} . When PANI was coated on its surface, major characteristic peaks of PANI were observed indicating that the PANI is successfully coated on the surface of the support. The stretching vibrations of C-H and C=C modes of the benzoid groups are observed at 2900 cm^{-1} and 1420 cm^{-1} respectively[40]. A peak at 1099 cm^{-1} is attributed to the bending vibrations of C-H bonds in the aromatic ring while the C-N stretching vibrations are observed at 1305 cm^{-1} for the aromatic conjugation[118]. Two N-H bands are observed; band at 3332 cm^{-1} is related to its stretching modes while the band at 1636 cm^{-1} is related to the bending vibrations[120]. In addition to the N-H bond observed at 3332 cm^{-1} , an additional peak is seen near it leading to the formation of a doublet. This may be due to the presence

of OH groups originating from water during coating. Also, the presence of other oligomers in the solution may be the cause of the presence of an extra peak since the polymerization process was not under control.

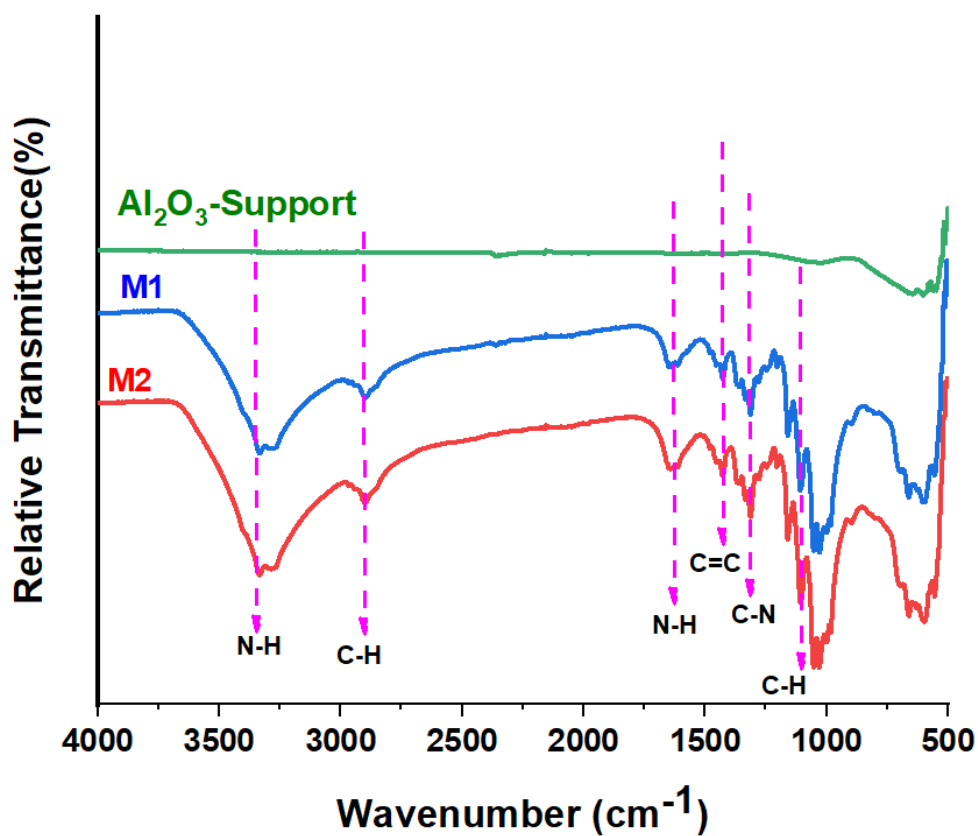


Figure 4.9: A figure showing FT-IR of alumina ceramic support, (M1) PANI produced from 0.4M Aniline, (M2) PANI produced from 0.6M Aniline, coated on the alumina ceramic support

4.4.3 XRD

To further ascertain the successful coating of the PANI on the alumina support, we carried out XRD analysis. Since PANI is amorphous, the XRD patterns highlighted on figure 4.13 show almost entirely alumina peaks. Characteristic peaks with 2θ values 37.0° , 40.0° , 45.0° , 54.4° , 59.4° , 68.4° , 70.0° , and 79.0° corresponding to crystalline alumina phases 104, 110, 113, 024, 116, 214 and 300 were detected. However, the presence of PANI on the surface of the alumina led to decrease in peak intensity or crystallinity of the alumina support showing the presence of PANI on the prepared membrane as shown in M1 and M2 which correspond to the two PANI/alumina ceramic support membranes[125].

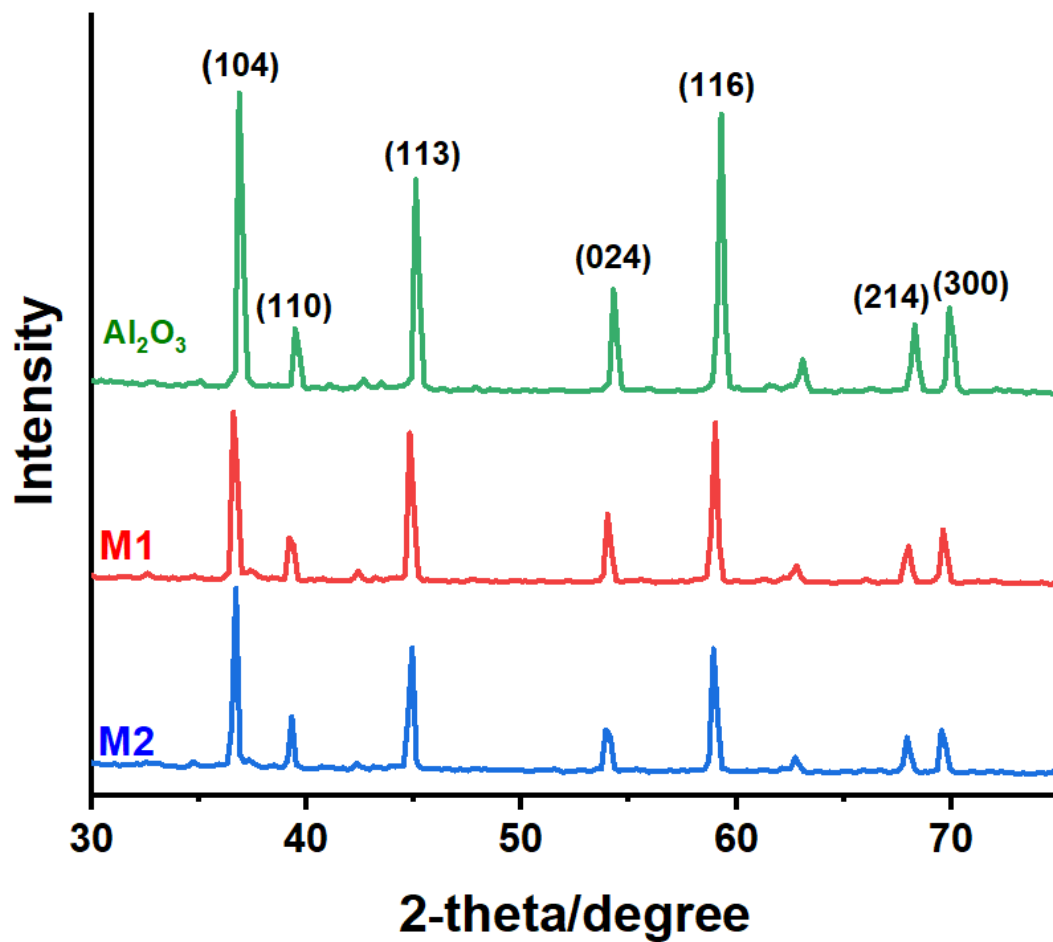


Figure 4.10 A figure showing XRD of alumina ceramic support, (M1) PANI produced from 0.4M aniline, (M2) PANI produced from 0.6M Aniline, coated on the ceramic support.

4.4.4 SEM

To dig into the morphological features of the synthesized material coated on the alumina support, SEM micrographs of the alumina support and coated PANI were recorded at different magnifications. As shown in figure 4.14, micrographs of the alumina ceramic support in figure 4.14a, b and c show smooth surfaces of irregular shapes and sizes with extensive pores sizes of $0.5\mu\text{m}$ [124]. These pores are too large to effectively filter water or reject oil at a reasonable percentage. When PANI was grown on the surface of the alumina, the surface morphology was completely altered due to the formation of the PANI nanoparticles on the surface of the support. It can be seen from figure 10d to i, that the PANI nanoparticles are uniformly distributed on the surface of the alumina to make a porous layer ideal for oil-water separation. In addition, the surface of the ceramic alumina was quite rough when the PANI was coated on it compared to the micrograph of its bare form. These rough surfaces enhances the surface area, wettability and reduce fouling which is ideal for effective oil-water separation[101], [126].

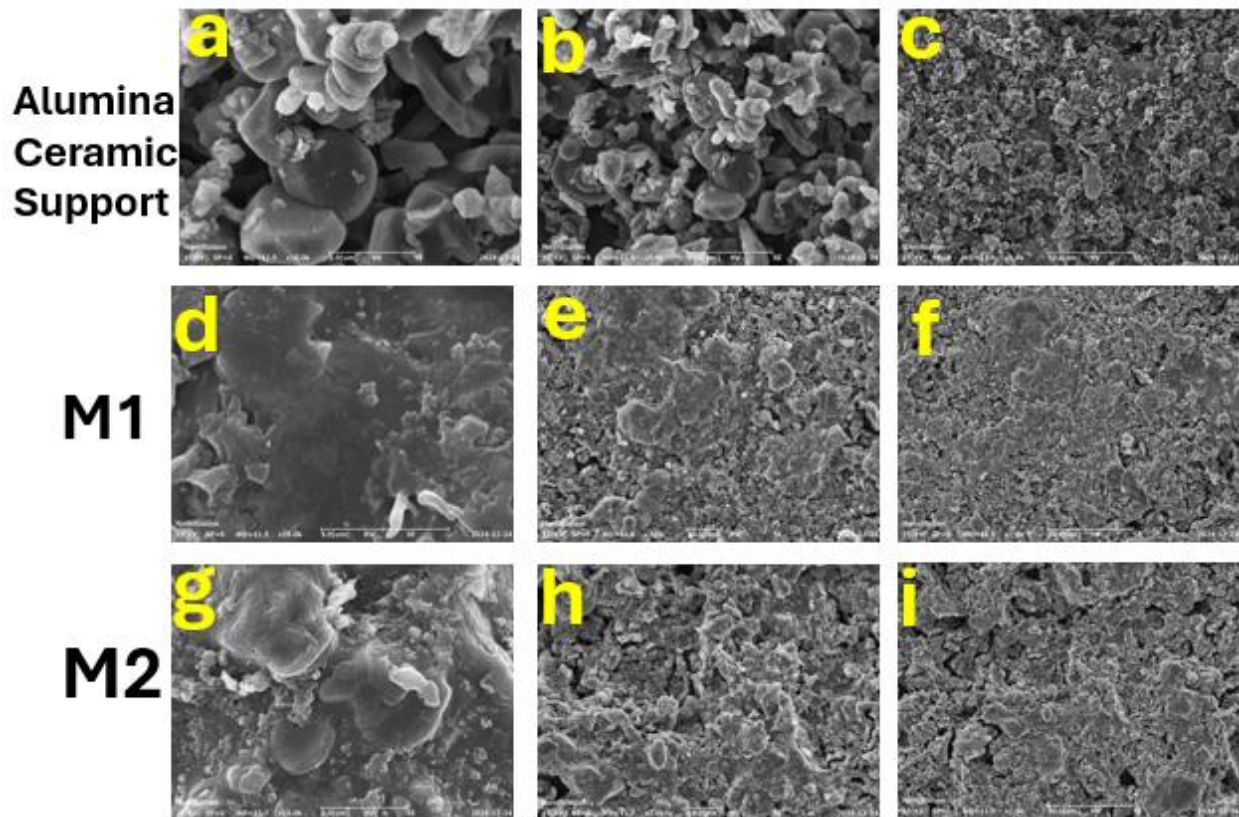


Figure 4.11: A figure showing SEM of alumina ceramic support, (M1) PANI produced from 0.4M aniline, (M2) PANI produced from 0.6M aniline, coated on the ceramic support.

4.4.5 EDX

The elemental composition (EDX) of the alumina support and PANI coated membrane was studied and shown in figure 4.15. Results from the alumina ceramic support shows the presence of Al, O and Si only[95]. Further analysis of the PANI coated membrane revealed the presence of C and N in addition to the Al, O and Si already detected on the bare alumina. The presence of C and N is attributed to the growth of PANI on the surface of the alumina ceramic support[42,49]. So, all the elements we expected on the surface of the prepared membrane were found and this confirms the successful coating of the PANI on the surface of the alumina ceramic support.

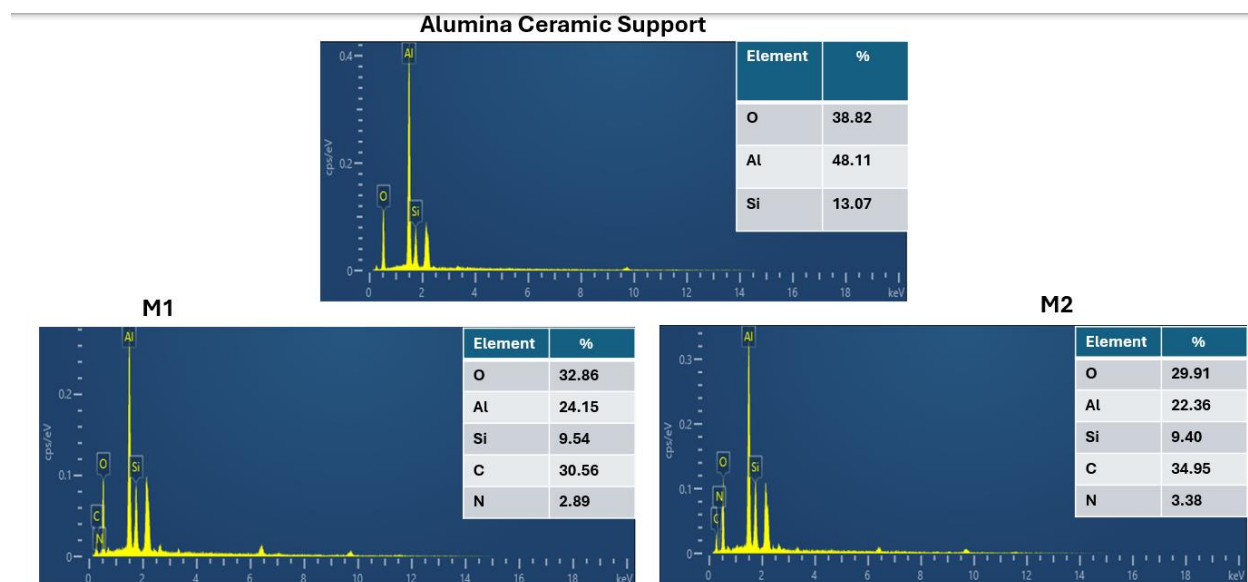


Figure 4.12: A figure showing EDX of alumina ceramic support, (M1) PANI produced from 0.4M aniline, (M2) PANI produced from 0.6M aniline, coated on the ceramic support.

4.4.6 Mapping

The elemental composition of the prepared membrane was also confirmed by the mapping analysis shown in figure 4.16. Dot concentrations are a representation of each element on the surface of the membrane. The highly dense presence of Al, O and Si shows that they are the main elements of the alumina support prior to the coating of the PANI. When the PANI was coated, the dot concentrations of C and N were clearly visible and showed a significant presence on the surface of the membrane[9,49]. This is a further confirmation of the successful coating of the PANI on the surface of the alumina ceramic membrane.

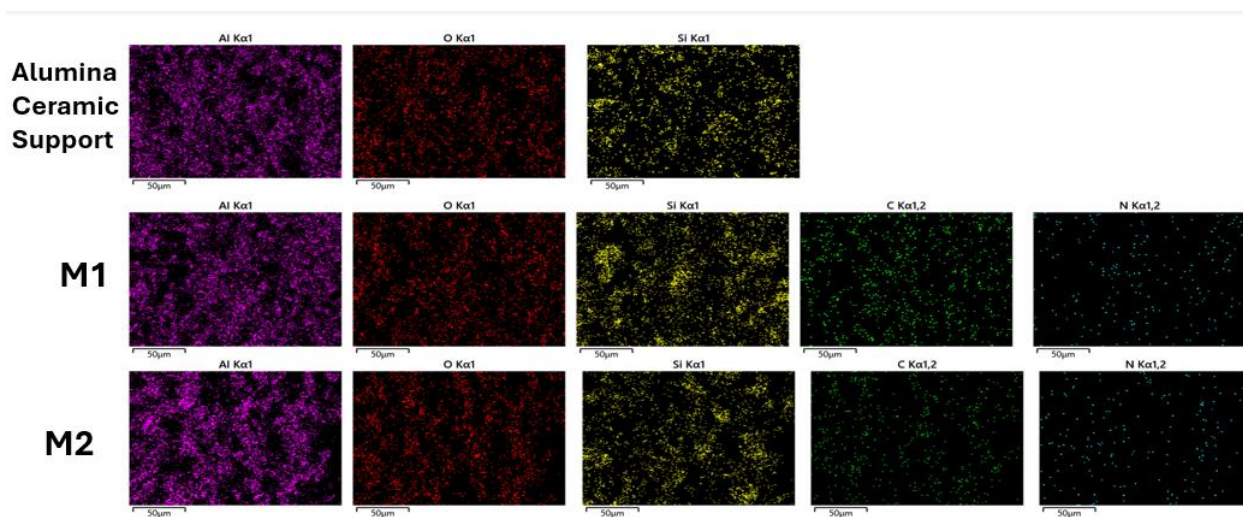


Figure 4.13: A figure showing elemental mapping of alumina ceramic support, (M1) PANI produced from 0.4M aniline, (M2) PANI produced from 0.6M aniline, coated on the ceramic support.

4.4.7 Water Contact Angle

To analyze the surface wettability of our membrane which is very important for the behavior of the membranes during fouling, we measured the water contact angle (WCA) of the three PANI/alumina ceramic membrane in air. The membranes for both M1 and M2 appeared superhydrophilic as the WCA was recorded as 0° [9,49]. The superhydrophilicity of the PANI/alumina ceramic support membrane can be explained by the presence of amine functional groups on its surface which helps in absorbing and filtering water and rejecting oil.

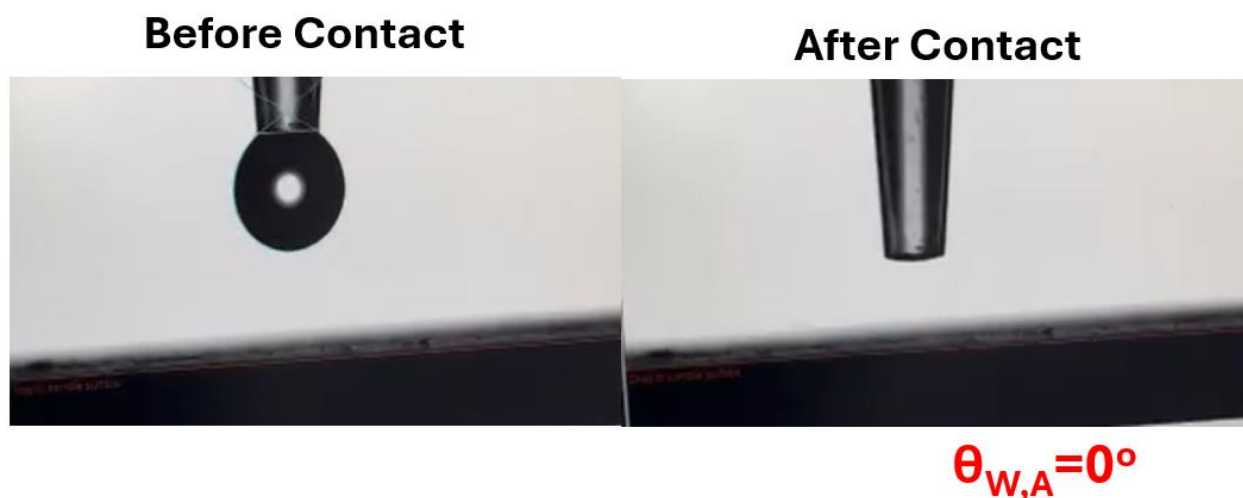


Figure 4.14 Water contact angle of alumina ceramic membranes (M1 and M2) modified with PANI produced by Fenton-like reaction in water microdroplets.

4.4.8 Preparation of the Oil-water Emulsion and Separation Procedure

The oil-water separation was carried out using the Cross Flow Filtration System using the dead-end filtration setup (HP 4750 stirred cell, Sterlitech, U.S.A.) with argon gas used as the source of pressure. The oil-water emulsion was prepared by mixing 0.2 g of diesel oil and 1.0 g of sodium dodecyl sulfate (SDS) in 1 Liter of water for 24 hours as reported by Salhi et al[95]. After the separation using the two membranes, we calculated the permeate flux and oil rejection using the following equations: $\text{Flux} = \frac{V}{At}$ and $R = \frac{C_f - C_p}{C_f} \times 100\%$ where V is volume of permeate in liters, A is the area of the membrane in m² and t is the time taken for measurement of permeate in hours, C_f and C_p are the oil concentrations in the feed and permeate solutions respectively. In this study, M1 and M2 refer to the alumina ceramic membrane modified with PANI prepared from 0.4M and 0.6M aniline concentrations respectively.

4.4.9 Oil-Water Separation Performance

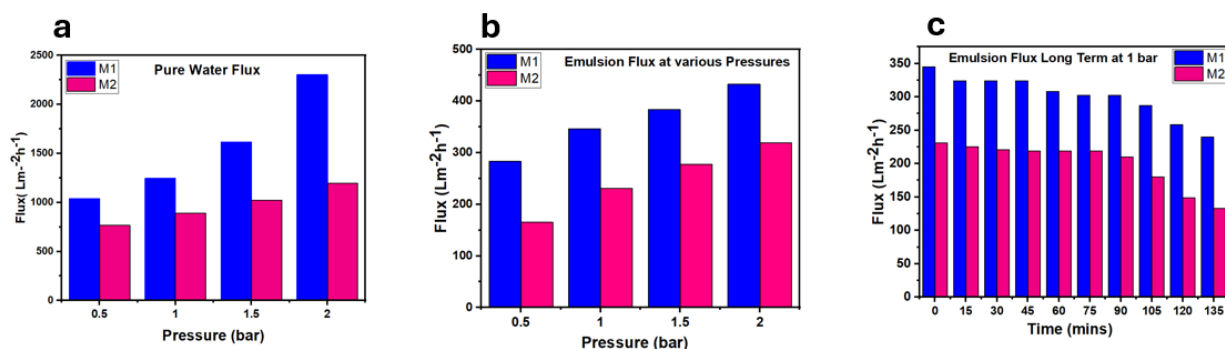


Figure 4.15: Permeate flux of (a) pure water at various pressures (b) emulsion at various pressures and (c) emulsion for long term at 1 bar and 1 minute permeate volume measurement time.

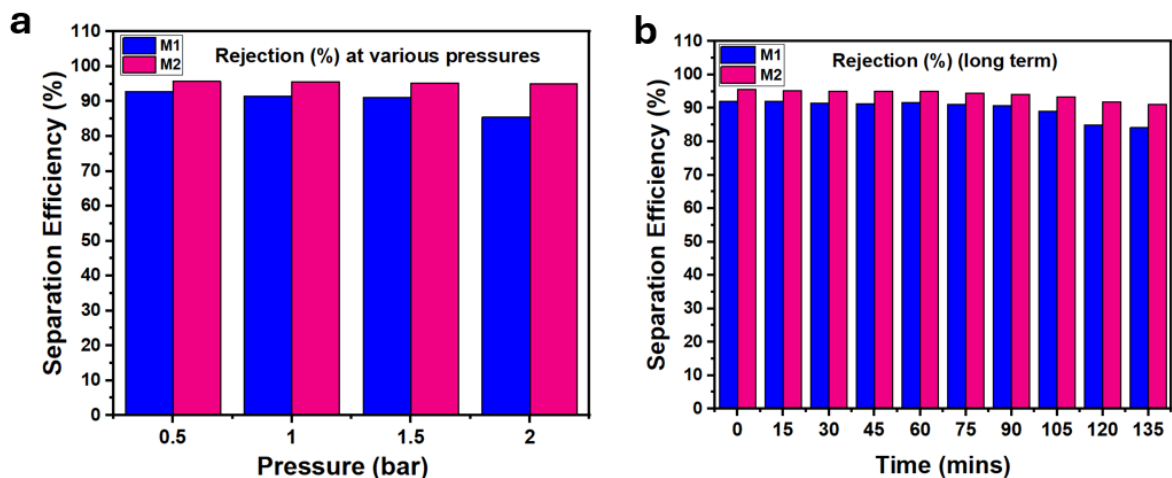


Figure 4.16: Separation efficiency of oil-water emulsion at (a) various pressures (b) long term at 1 bar and 1 minute permeate volume measurement time.

After the successful characterization of the modified alumina ceramic membrane with PANI, the membranes were first tested by measuring the effects of transmembrane pressure on DI water (pure water) flux. As expected, pure water flux increased as transmembrane pressure increases. Also, the highest flux was observed with the alumina ceramic membrane modified with PANI prepared using 0.4M aniline (M1). The highest pure water flux measured is $2303 \text{ Lm}^{-2}\text{h}^{-1}$ for M1 and $1197 \text{ Lm}^{-2}\text{h}^{-1}$ for M2 at 2 bars.

To study the ability of the prepared membranes to separate oil-water emulsions, we measured the permeate flux of the emulsion at various pressures and also at a constant pressure of 1 bar for a long period of time. Although permeate flux increase with increase transmembrane pressure, there is a huge decrease in flux observed from the emulsion compared to the pure water flux. This may be due to the fouling of the membrane caused by the presence of oil droplets navigating into its pores since the oil is emulsified into tiny droplets that may eventually fit into certain pores of the

membrane[9]. Like the case of the pure water flux, higher permeate flux was observed in M1 than M2 with highest flux values recorded as $450 \text{ Lm}^{-2}\text{h}^{-1}$ and $345 \text{ Lm}^{-2}\text{h}^{-1}$ respectively for the oil-water emulsion as shown in figure 4.18. We also recorded the permeate flux of the emulsion at 1 bar in 1 minute at various time intervals with measurements done up to 135 minutes. Permeate flux decrease with time for both M1 and M2. Also, high flux measurements were seen in M1. This is also attributed to the continuous fouling of the membrane with time, reducing its ability to allow water to filter through its pores. The general increase in permeate flux with increased pressure is expected. This is because mass transfer is directly proportional to applied pressure in the filtration system.

Finally, we measured the oil-water separation of the membranes with various pressures and also with time using TOC analysis. The separation efficiency of M2 is constant at 95% for all pressures while the highest for M1 was observed around 92%, which decreased to around 86% at 2 bars. At 1 bar with a permeate volume measurement of 1 minute at various time intervals up to 135 minutes, the percentage rejection of 95% and 92% for M2 and M1 respectively remained up to nearly 105 minutes with a slight decrease observed from 120 to 135 minutes. This shows that the membranes are stable under a pressure of 1 bar for a period of time. The 95% rejection rate of M2 is comparable to reported membranes on oil-water separation as shown in table 4.1.

In comparing the two membranes, we observed a decrease in flux measurements and increase separation efficiency as the aniline concentration used in the PANI synthesis increases. This is because as aniline concentration increases, a denser polymer network of PANI forms with smaller pore sizes which decreases permeate flow and hence increase rejection rate. The presence of amine groups from the PANI on the surface of the membrane also increases hydrophilicity and oleophobicity of the surface.

Table 4.1 A table of merits showing reported membranes used for oil-water separation from literature

Base Material	Modification	Pressure (bar)	Separation Efficiency (%)	Reference
Alumina Ceramic Membrane	PANI(0.6M)	1.0	95	This work
ZIF-8	PVDF-ZnO	0.35	92.93	[127]
Bentonite hollow fiber (B·H·F.)	magnesium bentonite (MB)	3.5	97	[128]
Ceramic Membrane alumina	PANI(1M)	1.5	97	[49]
Polysulfone	polyaniline and cellulose nanocrystals	-	63.4	[103]
PSF membranes	Poly (AA-co- ACMO)	-	84–95	[129]

CHAPTER FIVE

IN-SITU SYNTHESIS OF SILVER NANOPARTICLES USING ASCORBIC ACID AS A REDUCING AGENT IN WATER MICRODROPLETS FOR DIRECT MEDICAL APPLICATION IN BACTERIAL INFECTION TREATMENT.

5.1 Introduction

The synthesis and applications of nanomaterials like silver nanoparticles in various scientific disciplines have gained significant popularity in recent years[1,2]. This is due to their unique antibacterial [132], antioxidant, catalytic, large surface area and optical properties[133] that bulk phase materials significantly lacked. As a result, they have been applied to various domains like photovoltaics, optics, catalysis, medical imaging and therapy[131]. Because the shape and size of these nanoparticles play important roles in their chemical and physical properties, various synthetic methods have been applied to achieve desired material features for a number of applications [3,4]. Bulk phased methods such as Sol-Gel Method, Electrochemical Synthesis, Vapor Deposition methods and many more have been employed to synthesize silver nanoparticles [135]. However, these methods are characterized by long reaction times, inhomogeneous mixing, application of voltage and the employment of high temperatures[1]. Furthermore, these bulk or conventional methods of nanomaterial synthesis involved the use of capping agents to stabilize the nanoparticles and become structural directing agents [4] and also pH adjustments to prevent aggregation[136].

The antimicrobial effects of silver nanoparticles are well documented with both qualitative and quantitative studies used in determining how it can be used to deal with microorganisms such as bacteria[137]. Silver nanoparticles have shown the ability to alter and suppress bacterial growth in

various environments and as a result, they have been incorporated into various health products that are commercially available. M,A Haque et al [132] produced silver nanoparticles using the Polyol Method to do a quantitative study of their antimicrobial activities using kinetic growth essays and colony-forming units (CFU) essays in combination with quantitative modelling[132]. Greulich et al [137] also synthesized silver nanoparticles by reducing silver nitrate with glucose for antimicrobial studies and comparing the effects of the synthesized silver nanoparticles on bacteria with silver ions.

Despite the progress on the use of so many conventional methods to synthesize silver nanoparticles and their applications in antimicrobial activity, shortcomings have been highlighted due to particle aggregation[136] caused by longer storage of the silver nanoparticles and potential defects during synthesis. To remedy these shortcomings and enhance the antimicrobial activities, it is important to employ in-situ synthesis methods that can be applied for direct medical use.

Recently, microdroplet synthesis have been applied as a new synthesis route to produce valuable materials like silver nanoparticles. They involved the production of charged droplets that exhibit unusual reaction properties especially at the air-liquid interphase which are not usually observed in bulk phase reactions[51]. Reported cases have shown that microdroplet synthesis can exhibit reaction accelerations by one or more orders of magnitude compared to their bulk counterparts[3]. Various factors are responsible for the unique characteristics associated with microdroplet synthesis. Partial solvation of reactants at the air-liquid interface, decrease in entropy of the solute molecules due to their ordered orientation on and near the droplet surface[11,12], fast solvent evaporation, unusual dielectric constants and effective diffusion have been reported to have enhanced reaction rates in the confined volumes of microdroplets in material synthesis[7,11]. The microdroplet synthesis of silver nanoparticles have indeed been reported. For example, Hong et al

[138] carried out the microdroplet synthesis of silver nanoparticles using sodium borohydride (NaBH_4) as a reducing agent. However, the use of a reducing agent like NaBH_4 is not green and its involvement in bacterial studies may interfere with biological systems especially for used on the antibacterial treatment on human body.

Here in, we present a model that is used to carry out the instant microdroplet synthesis of silver nanoparticles using ascorbic acid as a reducing agent at room temperature for the in-situ application in the medical field for antibacterial cure. The model involved the development of a prototype device that can be used for in-situ synthesis of silver nanoparticles at medical centers. This will ensure that the nanoparticles are used instantly at the time of synthesis thereby enhancing their activity due to larger surface area. The significance of this work is that it will prevent the aggregation of the silver nanoparticles caused by longer storage, enhances the surface area of the particles and therefore improve their activity. The set-up used in this synthesis consist of a sprayer, a nebulization device and a glass slide used to collect the produced droplets. The silver nanoparticles obtained from this synthesis method showed excellent antibacterial activity and the results highlights that the development of a medical device for the in-situ and direct use of silver nanoparticles is possible and more effective than the normal synthesis and store methods previously used.

5.2 Materials and Method

5.2.1 Materials

Silver Nitrate (AgNO_3 , 99% purity, Sigma Aldrich), Ascorbic Acid ($\text{C}_6\text{H}_8\text{O}_6$, 99% purity, Sigma Aldrich), Deionized Water. All materials were used without further purification.

5.2.2 Method

The instant microdroplet synthesis of the silver nanoparticles was done in a set up consisting of a sprayer, peristalsis pumps, air compressor and a pressure controlling system. As shown in figure 5.1, aqueous solutions of 0.05M silver nitrate and 0.05M ascorbic acid were passed through peristalsis pumps into the sprayer. With the help of the air pressure coming from the compressor, the precursor solutions interact in the sprayer and are generated as nebulized droplets containing silver nanoparticles and are collected on a glass slide. In this synthesis, ascorbic acid serve as a reducing and stabilizing agent and the reaction takes less than a minute to complete. The droplets containing the silver nanoparticles on the glass slide are dried in a desiccator and subsequent characterizations are done to ascertain the formation of the nanoparticles. To optimize our synthesis conditions, the precursor concentrations were changed.

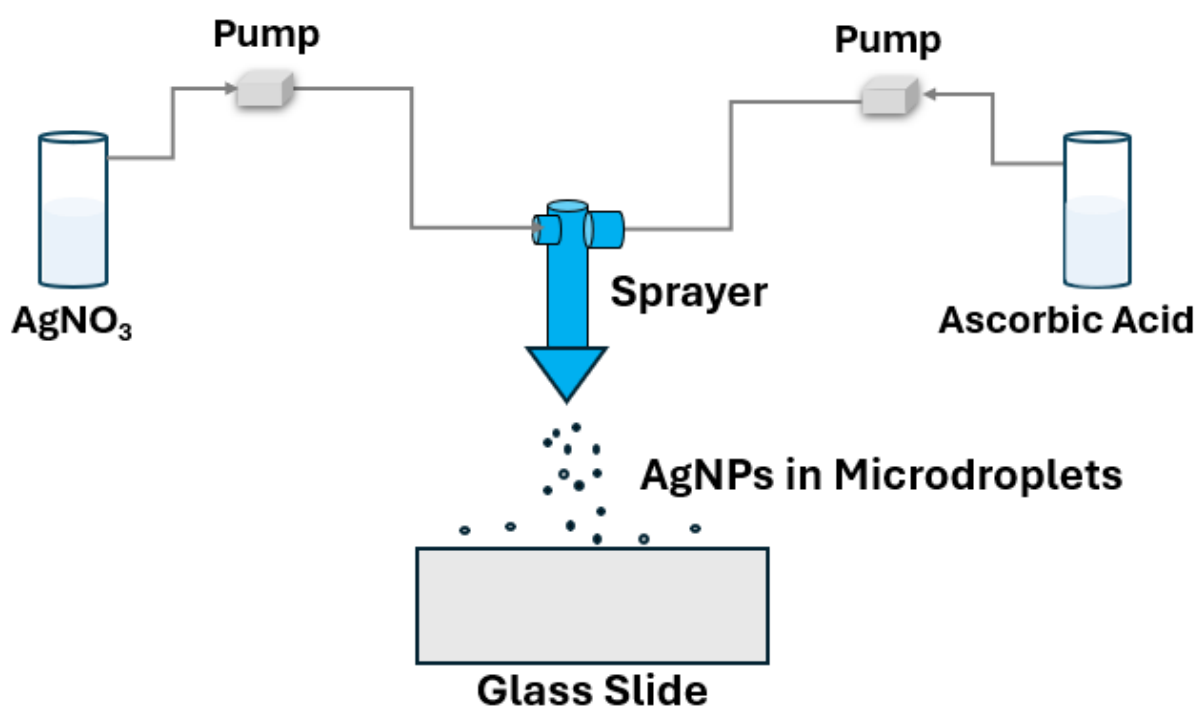


Figure 5.1: A figure showing the Room Temperature of Silver Nanoparticles in Water Microdroplets using Ascorbic Acid as a Reducing Agent.

5.3 Results and Discussion

5.3.1 XRD

After the synthesis and drying of the silver nanoparticles on the glass slide, a sample was collected to do the XRD analysis. As shown in figure 5.2, the XRD pattern of the silver nanoparticles show crystalline peaks that specify silver crystallites[130] and are identical to results reported in other publications. 2θ values of 38.2° , 44.3° , 64.4° , 77.4° and 81.5° corresponding to planes 111, 200, 220, 311 and 222 respectively highlight the successful synthesis of the silver nanoparticles [1,14] in the microdroplets using ascorbic acid as a reducing agent despite an extremely short reaction method.

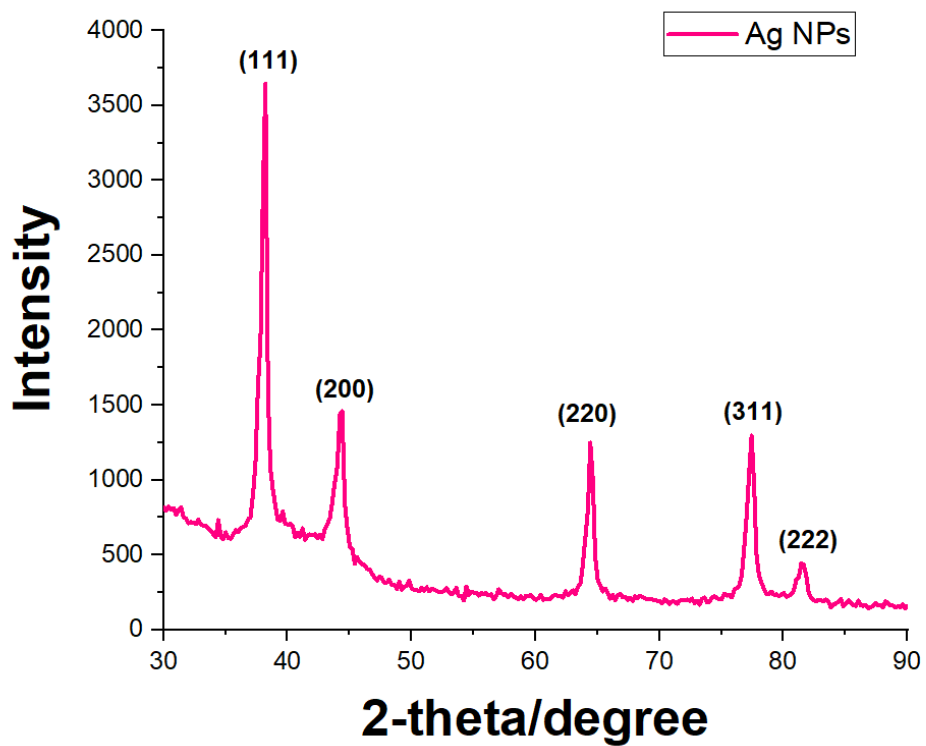


Figure 5.2: A figure showing the XRD patterns of the silver nanoparticles (Ag NPs) synthesized in the microdroplet spray method using ascorbic acid as a reducing agent.

5.3.2 FTIR

To study the surface chemistry of the silver nanoparticles synthesized from the microdroplet synthesis method, we carried out FT-IR to identify the presence of functional groups. The stretching vibrations of the Ag-O and C-H bonds were observed at 644 cm^{-1} and 936 cm^{-1} respectively. A Band at 1667 cm^{-1} correspond to the stretching vibrations of the C=C of the aromatic ring of the ascorbic acid. The band at 1745 cm^{-1} correspond to the C=O of carbonyl carbon on the aromatic ring of the ascorbic acid. The peak at 1084 cm^{-1} is due to the stretching vibration of the C-O while the band around 3400 cm^{-1} is attributed to the presence of OH groups[5,15,16].

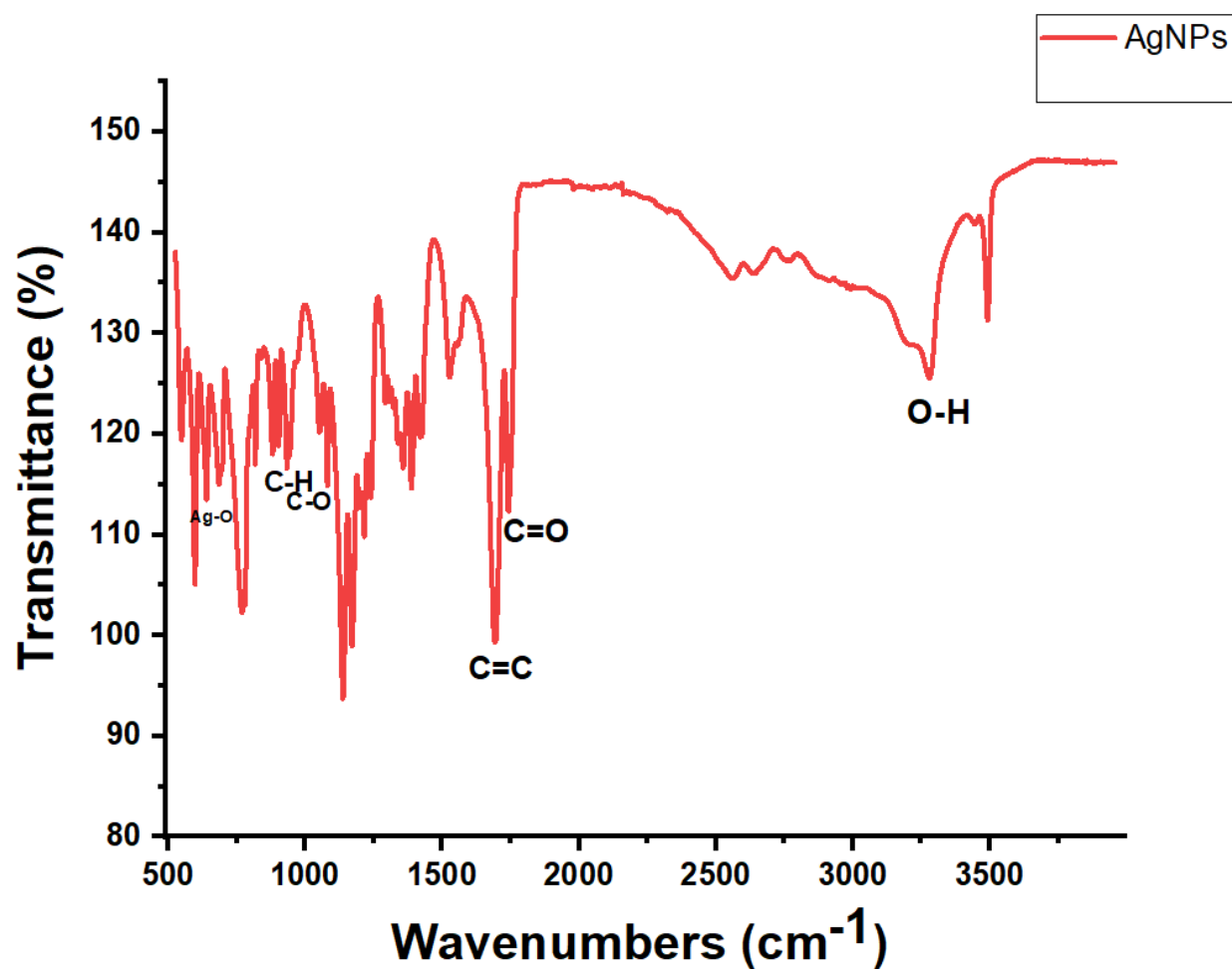


Figure 5.3: A figure showing the FT-IR spectrum of the silver nanoparticles (Ag NPs) synthesized in the microdroplet spray method using ascorbic acid as a reducing agent.

5.3.3 TEM

Figure 5.4 shows the TEM images of the silver nanoparticles produced using ascorbic acid as a reducing agent from the microdroplet synthesis route. The nanoparticles produced in the microdroplets collected on a glass slide 12 cm from the sprayer can be seen distributed over the surface of the glass slide with various resolutions. The distribution of particles over the surface of the glass slide is a confirmation of the formation of the AgNPs inside the released microdroplets from the sprayer[140]. Closer look revealed that, in addition to small nanoparticles, larger particles caused by particle aggregation of the AgNPs were observed. This is due to the absence of shape controlling agent in the synthesis. However, since the aim of this work is in-situ synthesis for medical applications, particle aggregation is not expected to hinder the activity of the silver nanoparticles.

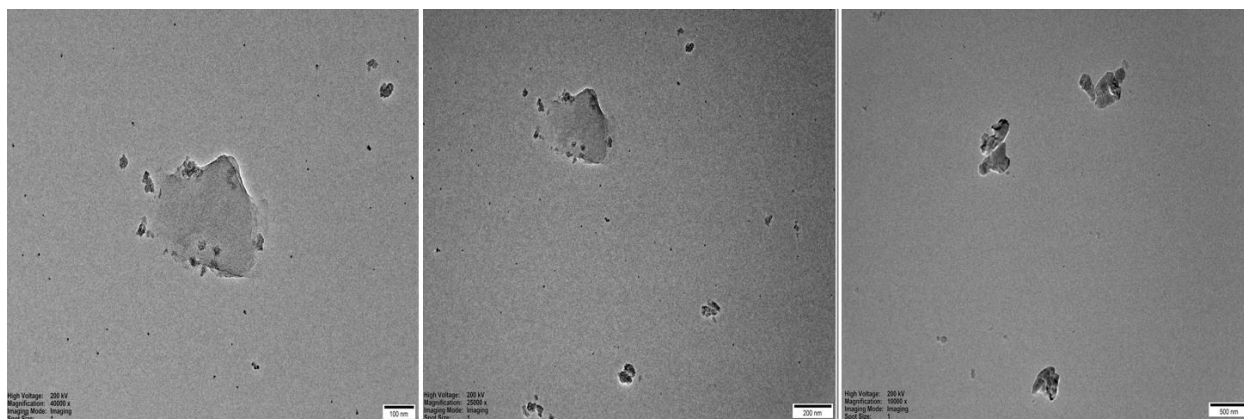


Figure 5.4: A figure showing the TEM micrographs of the silver nanoparticles (Ag NPs) synthesized in the microdroplet spray method using ascorbic acid as a reducing agent.

5.3.4 EDX and Micro-XRF

The EDX analysis was done to examine the elemental composition of the synthesized silver nanoparticles from the microdroplet spray method. As shown in figure 5.5, the main peak signal observed was that of Ag with 95.7% at 3 keV confirming the presence of elemental silver nanoparticles in the sample. 3.8 % and 0.5 % of carbon and oxygen were found to be present in the sample while 0% nitrogen was detected[17,18]. The absence of nitrogen is an indication of the complete reduction of AgNO_3 by the ascorbic acid in the synthesis process. This is further confirmed by the absence of N-H in the FT-IR study of the same sample[142]. In addition to the EDX study we did, we also carried out the micro-X-ray fluorescence (micro-XRF) of the same sample of AgNPs. The percentage of Ag detected in the sample was 99.88% [144]. This is another confirmation of the successful reduction of the silver nitrate to silver nanoparticles by the ascorbic acid.

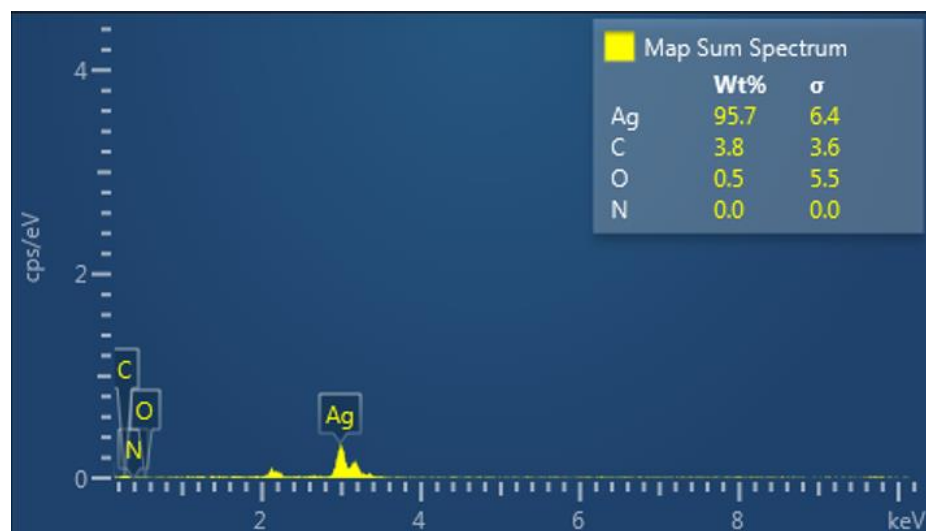


Figure 5.5 A figure showing the EDX of the silver nanoparticles (Ag NPs) synthesized in the microdroplet spray method using ascorbic acid as a reducing agent.

Table 5.1 A table showing the elemental composition of the silver nanoparticles synthesized from water microdroplets using ascorbic acid as a reducing.

Element	Percentage (%)
Ag	99.88
Ni	0.12

5.4 Anti-bacterial Activity of the Silver Nanoparticles

5.4.1 Analysis Procedure

The anti-bacterial activity of the silver nanoparticles produced from the microdroplet synthesis was tested using the Disk Diffusion Method. Before conducting the study, we carried out a detail culturing of the bacterial strain. Cryopreserved bacterial cultures of *Escherichia coli* and *Bacillus cereus* were resuscitated on a three-day incubation in rich Luria Broth medium at 37°C and 120 revolutions per minute (rpm). Then, since the synthesis method used in this work is instant, we sprayed the microdroplets containing the silver nanoparticles on filter papers which will be subsequently used for the anti-bacterial study. The study was carried out on two concentration categories in order to determine the smallest concentration suitable for in-situ synthesis and application of silver nanoparticles in wound treatment in medical fields. One was the variation of different concentrations of AgNO_3 (0.05mM 0.5 mM, and 0.75 mM) numbered as 1,2 and 3 respectively at a constant ascorbic acid concentration of 0.5 mM. The second phase involve the variation of ascorbic acid concentrations (0.75 mM and 1 mM) numbered as 4 and 5 respectively with 0.5 mM AgNO_3 as shown in figure 5.6.

In the Disk Diffusion method, we used a solid agar plate made in rich medium (Luria Broth, LB) which is streaked around 100 μL of fresh bacterial culture approximately 106CFU/mL[130]. As shown in figure 5.6, two solid agar plates were prepared, one for each bacterial strain. The bacterial strains are spread over the entire surface of the plate and small circular pieces of the filter papers on whose surface the silver nanoparticles are spread, are placed on the surface of the plate numbered from 1 to 5 representing the individual concentrations of the silver nanoparticles

prepared for the study. The plates were incubated for 24 hours at 37⁰C. The silver nanoparticles on the filter papers then diffused around the hole and then created a zone of inhibition of bacterial growth. The effect or degree of inhibition by the synthesized silver nanoparticles was determined by measuring the diameter of the zone of inhibition[142].

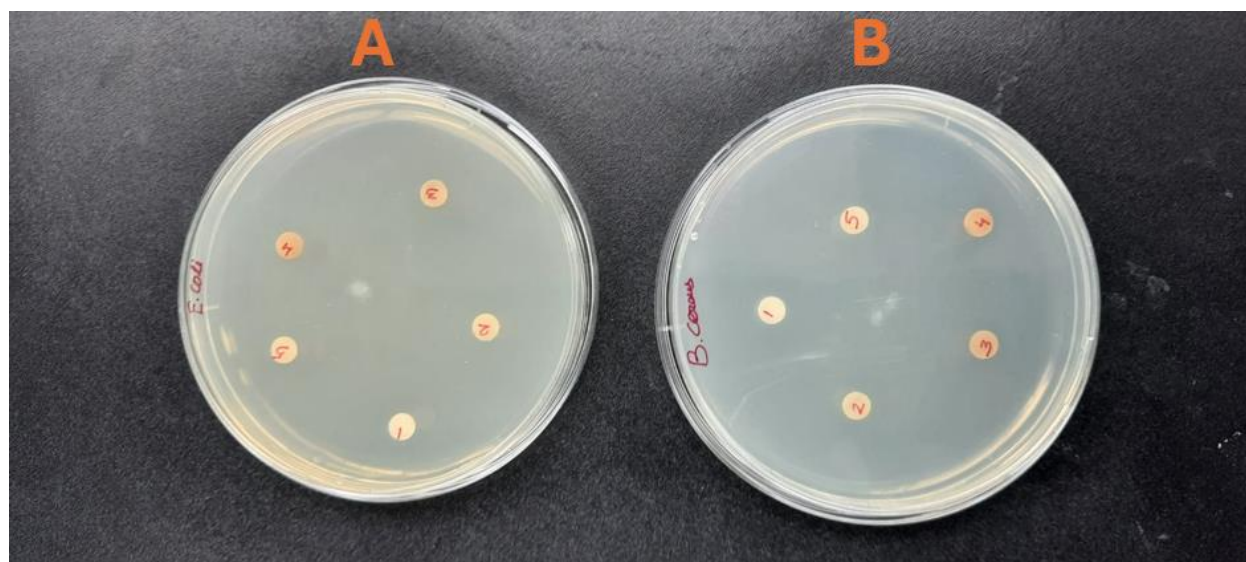


Figure 5.6 A figure showing agar plates spread with (a) E coli (b) Bacillus cereus bacterial strains with five filter papers spread with different concentrations of silver nanoparticles numbered from 1 to 5 before inhibition .

5.4.2 Results from the Anti-bacterial Study of Silver Nanoparticles

After incubating 24 h at 37⁰C, the diameter of the zone of inhibition of silver nanoparticles was determined. As shown in figure 5.7, only sample 3 (0.75 mM AgNO₃ and 0.5 mM ascorbic acid) and 4 (0.5 mM AgNO₃ and 0.75 mM ascorbic acid) showed measurable inhibition with diameters 8 mm and 9mm respectively with sample 2 (0.5 mM AgNO₃ and 0.5 mM ascorbic acid) showing a slight activity. There was no activity detected from sample 1 and 5 indicating their lack of antibacterial resistance as per this synthesis method. The order of antibacterial effect of the synthesized samples is 4 > 3 > 2. It is observed that the highest anti-bacterial activity was measured from the sample with high ascorbic acid concentration. This is because high ascorbic acid concentration can lead to smaller nanoparticles of large surface area and reactivity. In addition to being a reducing agent, ascorbic acid also serves as a stabilizing agent in this synthesis. An increase in concentration may lead to the generation of stabilized nanoparticles inside the microdroplets.

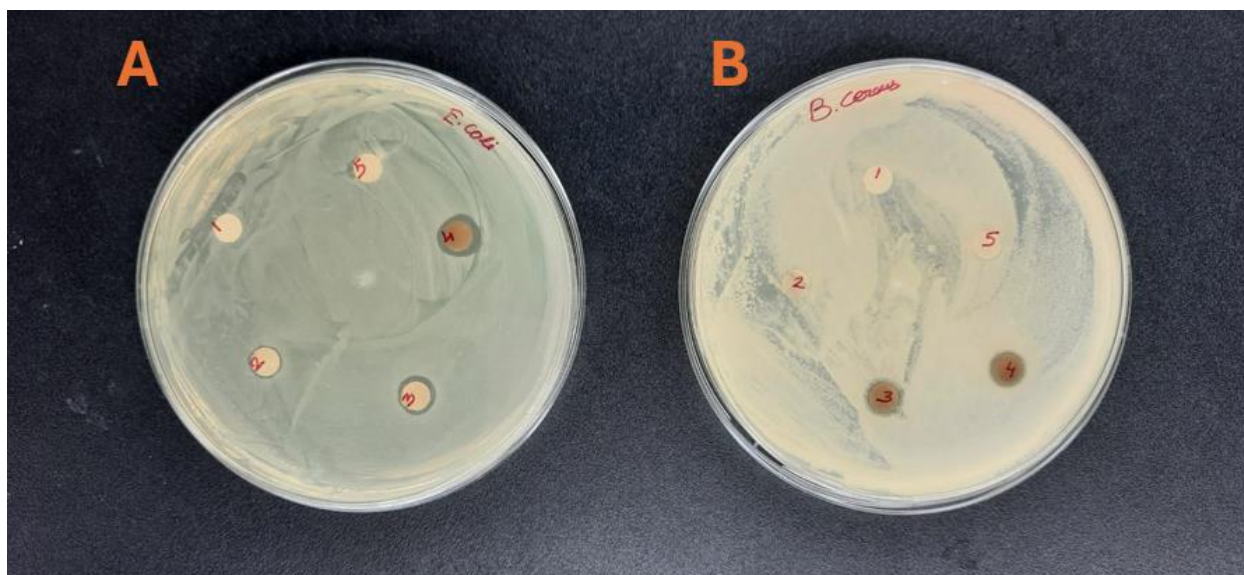


Figure 5.7 A figure showing agar plates spread with (a) *E. coli* (b) *Bacillus cereus* bacterial strains with five filter papers spread with different concentrations of silver nanoparticles numbered from 1 to 5 after inhibition.

6.0 CHAPTER SIX

CONCLUSION

In this work, we successfully carried out the room temperature synthesis of three materials: HKUST-1, PANI and Silver nanoparticles. The HKUST-1 with well-defined octahedral shape was successfully synthesized using the microdroplet spray method at room temperature. The formation of these octahedral crystals is a result of an increase in residence time due to slow solvent evaporation leading to uniform crystallization at room temperature. The applied method serves as a good alternative to conventional methods of MOF synthesis due to shorter reaction time and better precursor mixing. Furthermore, it solves the problem of changed in morphology of the HKUST-1 reported in microdroplet spray methods. The synthesis of the MOF in various ethanol to water ratios and also DMF to water ratios showed that water as a solvent affects the coordination of metal precursors to linkers such as benzene-1,3,5-tricarboxylic acid due to hydrogen bonding. The synthesized material was found to be suitable as a catalyst for the room temperature conversion of nitrogen to nitrates. Further investigation into the possible incorporation of other materials for composite formation and the use of the synthesized MOF on applications such as CO₂ capture will be pursued in subsequent studies.

Polyaniline (PANI) was successfully synthesized using the Fenton-like reaction in water microdroplets at room temperature. Hydrogen peroxide was first produced from the sprayed water microdroplets and then reacted with Fe³⁺ to generate the hydroxyl radicals which polymerized aniline monomers to PANI. The PANI showed good conductivity and high oil rejection capacity when it was coated on the surface of an alumina ceramic membrane. Separation efficiency was tested using various pressures and long term. The prepared membrane, especially M2, showed

good stability at all pressures with a 95% rejection. A decreased in flux and increase rejection percentage was observed as the concentration of aniline used in the in-situ coating during the microdroplet synthesis. This is attributed to the denser polymeric chain formed on the surface of the ceramic membrane as more aniline concentration is used.

Finally, we have successfully produced the silver nanoparticles within a short period of time in microdroplets and subsequent characterization shows the formation of the nanoparticles within droplet environments. Furthermore, antibacterial studies show that it is possible to do an in-situ synthesis of the nanoparticles for direct medical applications. This method can serve as an alternative way of producing nanoparticles without worrying about particle aggregation due to storage since the nanoparticles can be synthesized at the time they are needed.

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cloud point extraction,” *J. Anal. At. Spectrom.*, vol. 33, no. 3, pp. 383–394, 2018, doi: 10.1039/C7JA00335H.

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Academic Background

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M.Sc. Chemistry; CGPA: 3.844/4.0

2017-2020 :University of The Gambia; BSc Chemistry (Summa cum laude)

2013-2016 :The Gambia College, School of Education

(Higher Teachers Certificate (HTC), Distinction)

Subject: Science and English

Work Experience

2023 to date : Graduate Assistant KFUPM, Saudi Arabia

Duties and Responsibilities

- ❖ **Instructor; CHEM 101 and CHEM 102 practical; Introductory chemistry courses**
- ❖ **Prepare of experimental reagents**
- ❖ **Laboratory results analysis and interpretation**
- ❖ **Synthesis of MOF, Polyaniline and Silver Nanoparticles using Droplet-Chemistry**
- ❖ **Using analytical techniques including XRD, FTIR, TGA, NMR, MS among others**

2016 to 2022 : Chemistry and Core Science teacher

Masroor Senior Secondary School, The Gambia

Duties and Responsibilities

- ❖ **Prepare laboratory reagents and instruments for high school chemistry practical.**
- ❖ **Conduct trainings in laboratory safety and protocols**
- ❖ **Prepare, administer, grade tests and assignments to evaluate students' progress**
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Awards and Positions

- ❖ **President; Chemical Society of The Gambia (CSG) -2021-2023**
- ❖ **Best Graduating Student; University of The Gambia Class of 2020**
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Additional Skills

- ❖ **Good research and analytical skills**
- ❖ **Proficiency in Microsoft excel, word, PowerPoint, Chem Draw, Origin**
- ❖ **Advanced verbal and written Skills**
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- ❖ **Good presentation skills**

Personal Interests and Affiliation

- ❖ **Member of the Chemical Society of The Gambia**
- ❖ **Member of the Chemistry Club, UTG**
- ❖ **Member of The Gambia Chemical Committee for Establishment of Standards
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Under Review

- ❖ **ROOM TEMPERATURE SYNTHESIS OF COPPER METAL-ORGANIC FRAMEWORK USING DROPLET CHEMISTRY AND ITS APPLICATIONS IN NITROGEN CONVERSION TO NITRATES**
- ❖ **ROOM TEMPERATURE SYNTHESIS OF POLYANILINE (PANI) USING FENTON-LIKE REACTION IN WATER MICRODROPLETS AND ITS APPLICATION IN OIL-WATER SEPARATION**