

**A NOVEL APPROACH FOR SYNTHESIZING METAL-
ORGANIC FRAMEWORKS THIN FILMS**

BY

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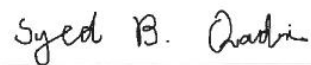
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List of Abbreviations

Abbreviations

Description

Materials & Frameworks

MOFs	:	Metal-Organic Frameworks
PCPs	:	Porous Coordination Polymers
ZIFs	:	Zeolitic Imidazolate Frameworks
MAFs	:	Metal-Azolate Frameworks
IRMOF	:	Isorecticular Metal-Organic Frameworks
SOD	:	Sodalite (Topological Framework Type)
HKUST	:	Hong Kong University of Science and Technology
CAU	:	Christian Albrecht University

Ligands & Organic Molecules

BTC	:	1,3,5-Benzenetricarboxylic Acid
TMA	:	Trimesic Acid (another name for BTC)
Im	:	Imidazole
Hmim	:	2-Methylimidazolate
bIm	:	Benzimidazole
emI	:	2-Ethylimidazole
MeIH	:	Methanol
DMF	:	N,N-Dimethylformamide
CTAB	:	Cetyltrimethylammonium Bromide
MTBS	:	Methyltributylammonium Methyl Sulfate

Deposition & Fabrication Techniques

ALD	:	Atomic Layer Deposition
CVD	:	Chemical Vapor Deposition
PLD	:	Pulsed Laser Deposition
ECD	:	Electrochemical Deposition
DC	:	Direct Current
RF	:	Radio Frequency
CFUMS	:	Closed Field Unbalanced Magnetron Sputtering

Characterization Techniques

XRD	:	X-Ray Diffraction
SEM	:	Scanning Electron Microscope
FESEM	:	Field Emission Scanning Electron Microscope
XPS	:	X-Ray Photoelectron Spectroscopy
FT-IR	:	Fourier Transform Infrared Spectroscopy
HAADF	:	High-Angle Annular Dark Field

Chemical Concepts & Principles

SBU	:	Secondary Building Unit
HSAB	:	Hard And Soft Acids and Bases Principle

Thesis Structure

Chapter 1: Gives a brief introduction about Metal-Organic Frameworks (MOFs), a short overview about the transition from powder to MOF thin film technology, and factors that need to be considered while working towards the commercialization of MOF thin films, and the importance of DC magnetron sputtering in MOFs synthesis along with its basic mechanism.

Chapter 2: Divided into two main sections: (a) ZIF-8 thin films and (b) CAU-17 thin films. Section (a) belongs to the basic introduction to ZIF-8 and its chemistry, detailed information about conventional and vacuum-based thin film technology, and its main parameters of synthesis. Section (b) gives a brief introduction to CAU-17, its chemistry, challenges in its synthesis, and basic synthesis parameters.

Chapter 3: Belongs to the experimental section of MOF thin films synthesis, highlighting the process of conversion of metal-oxide into MOF thin films. The chapter also gives details about the various characterization techniques that have been employed during this research work.

Chapter 4: Divided into two parts: (a) ZIF-8 thin film and (b) CAU-17 thin film. In the first part ZIF-8 structure was confirmed by using characterization techniques such as XRD, XPS, and FE-SEM. Afterwards, the influence of temperature on ZIF-8 synthesis was investigated. The second part of the crystal structure of CAU-17 was verified by using advanced spectroscopy techniques such as EDX, Raman spectroscopy, FT-IR, and XPS. After the material verification, the influence of temperature on CAU-17 formation was investigated. Both parts also discuss the synthesis mechanism of ZnO and Bi₂O₃ thin films and their conversion into ZIF-8 and CAU-17 thin films.

Chapter 5: The chapter provides the main highlights and summary of this research work.

Abstract

A Novel Approach for Synthesizing Metal-Organic Frameworks Thin Films

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Metal-organic frameworks (MOFs), a new emerging class of porous crystalline materials, are considered an ideal material for many applications because of their versatility and ease of synthesis. MOFs are so-called hybrid organic and inorganic materials made of metal nodes and organic linkers. These materials are known for their large surface area, highly porous nature, and structure tunability. Usually, MOFs are produced in powder form, which limits their engineering applications because of poor processability, limited mechanical strength, and weak interaction between substrate and powder. Additionally, MOF powder synthesis techniques use toxic metal salts, are limited to a few types of MOFs, and require harsh conditions for synthesis. A great attention has been given to MOF thin films to overcome the disadvantages of powder MOFs. In this regard, developing a technique that could synthesize a wide range of MOFs is the center of attention of many researchers. In this thesis work, a novel synthesis technique of MOF thin film based on physical vapor deposition is proposed for MOF thin film synthesis that has the potential to grow diverse kinds of MOF on different support materials regardless of their surface nature with improved properties.

ملخص الرسالة

نهج مبتكر لتصنيع أغشية رقيقة من الأطر المعدنية العضوية

محمد زين عظيم

ماجستير في علوم وهندسة المواد

المشرف: د. قاسم أحمد درموش

وهي فئة ناشئة من المواد البلورية المسامية، مادة مثالية للعديد من التطبيقات (MOFs)، تُعتبر الأطر المعدنية العضوية نظراً لتعدد استخداماتها وسهولة تصنيعها. وتُعرف هذه الأطر بأنها مواد هجينة عضوية وغير عضوية، مصنوعة من عقد معدنية وروابط عضوية. وتتميز هذه المواد بمساحة سطحها الكبيرة، ومساميتها العالية، وقدرتها على ضبط بنيتها، عادةً ما تُنتج الأطر المعدنية العضوية على شكل مسحوق، مما يحد من تطبيقاتها الهندسية نظراً لضعف قابليتها للمعالجة ومتانتها الميكانيكية المحدودة، وضعف التفاعل بين المادة المتفاعلة والمسحوق. بالإضافة إلى ذلك، تستخدم تقنيات تصنيع مسحوق الأطر المعدنية العضوية أملاحاً معدنية سامة، وتقتصر على أنواع قليلة منها، وتتطلب ظروفًا قاسية للتصنيع. وقد أولي اهتمام كبير لأغشية الأطر المعدنية العضوية الرقيقة للتغلب على عيوبها. في هذا الصدد، يُركّز العديد من الباحثين على تطوير تقنية قادرة على تخليق مجموعة واسعة من الأطر العضوية المعدنية. في هذه الأطروحة، تُقترح تقنية جديدة لتخليق أغشية الأطر العضوية المعدنية الرقيقة، تعتمد على الترسيب البخاري الفيزيائي، لتخليق هذه الأغشية والتي تتمتع بإمكانية إنتاج أنواع مختلفة من الأطر العضوية المعدنية على مواد داعمة مختلفة، بغض النظر عن طبيعة سطحها، مع تحسين خصائصها.

CHAPTER 1

INTRODUCTION

Chapter 1

Metal-Organic Framework Thin Film

1.1 Introduction to MOFs

Metal-organic frameworks (MOFs) are the newly emerging domain of porous crystalline materials, a so-called organic-inorganic hybrid material that comprises metal-containing nodes and organic ligands. The term “porous coordination polymers (PCPs)” is also used to classify MOFs [1], [2]. The chemistry behind MOFs is based on “reticular chemistry,” which is described as the joining of molecular building blocks via strong bonds to develop a crystalline open framework [3]. In the MOF structure, the linker acts as a ‘strut’ and is defined as an organic secondary building unit (SBU). Metallic nodes are called ‘joints’ and are known as inorganic SBUs. There are three main components of MOF, which consist of its (i) topology, (ii) metal ions, and (iii) linkers [4]. Usually, node elements that have been employed in the construction of MOFs belong to transition metals, alkaline earth metals, basic metals, and rare earth metals. The most utilized classes of linkers are associated with O- and N-donors [5], [6]. MOFs are renowned for their highly porous nature and large surface areas of up to $2000 \text{ m}^2 \text{ g}^{-1}$ [7]. Structural diversities are another property of MOF, and up to 90,000 MOFs have been synthesized as of 2020 [8]. Interesting behaviors such as breathing, gate opening, open metal site, and ready functionalization are some of the beauties of MOFs observed in limited MOF materials [9].

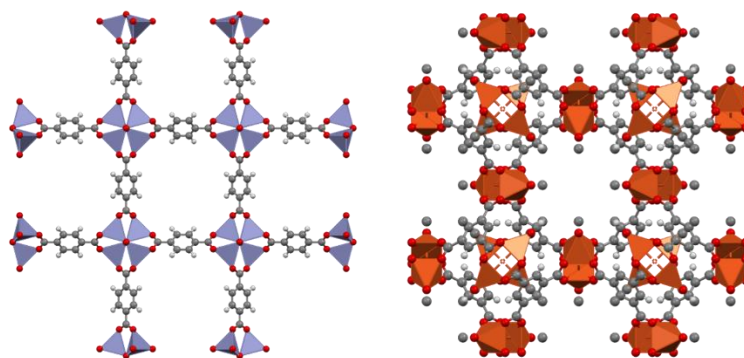


Figure 1.1: Crystal structure of MOF-5 (left) and HKUST-1 (right).

The considerable advancement in MOFs started in 1999 when MOF-5 and HKUST-1 were synthesized and characterized [9], [10]. The structure of both MOFs is shown in Figure 1.1. HKUST-1, also named as MOF-199, belongs to the class of copper-based MOF constructed by Cu^{2+} metal ions with benzene tricarboxylic acid, renowned for its nanoscale porosity, high thermal stability, pores functionalization, and consists of far superior properties in contrast to zeolites. It found its application in the purification of air by removing toxic gases, carbon dioxide, and ammonia [11], [12], [13]. MOF-5 belongs to the family of zinc-based MOFs, and it is one of the most famous and extensively investigated materials discovered by Omar M. Yaghi. It is also known as IRMOF-1 (IRMOF = Isoeticular MOFs), which consists of a cubic topology [14]. It has a similar framework to zeolite, which is made of $[\text{Zn}_4\text{O}]^{6+}$ clusters and 1,4-benzenedicarboxylate as a linker [15], [16]. In addition, it is known for its large surface area of $2900 \text{ m}^2/\text{g}$ and permanent porosity [14], [17]. Over the last two decades, >100,000 MOFs have been synthesized and discovered, which continuously increases their demand in diverse areas of research, for instance, gas sensors, CO_2 reduction, supercapacitors, and membranes [18], [19]. Figure 1.2 shows the survey of MOFs application in different areas over the last five years (2020 to 2024).

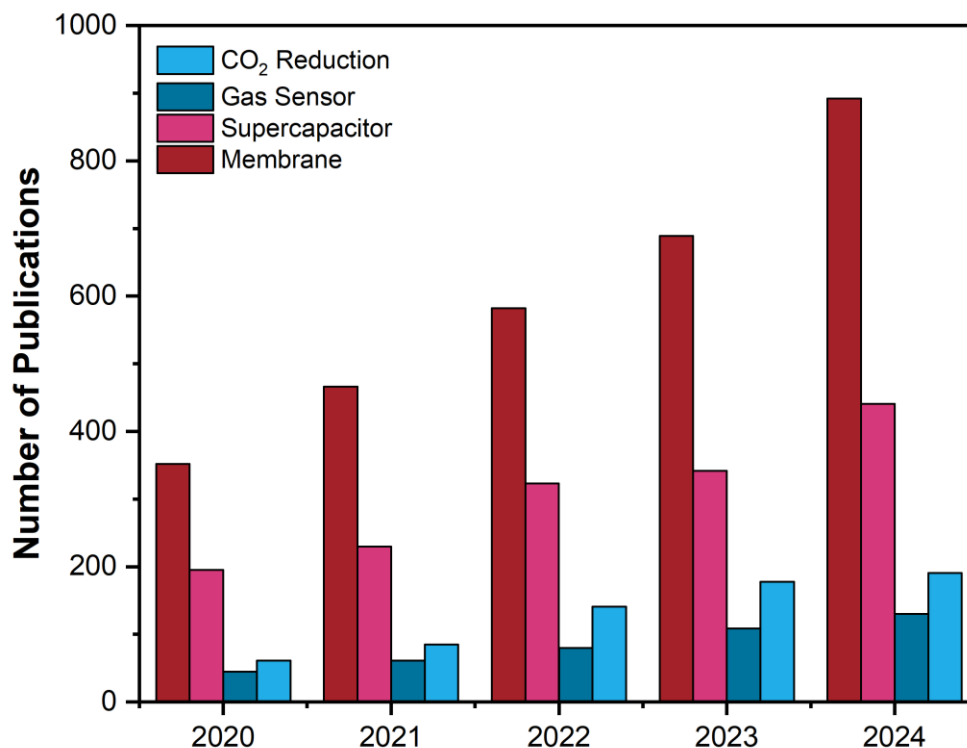


Figure 1.2: Number of publications in MOFs across different fields in the last five years (Source: Scopus Database)

1.2 MOFs Challenges: Commercialization

Nowadays, researchers around the globe are interested in the commercialization of MOFs at a large scale, with a focus on their practical application. Previously, MOFs have been synthesized as powder material, facing major problems related to their scalability at the industrial level due to their poor processability [10]. Other issues are related to its recyclability, poor handling properties, limited mass transfer, and risk of powder contamination [11], [12]. Aside from that, powder MOFs lack high mechanical strength and do not demonstrate good thermal as well as chemical stability at relatively high temperatures under reactive conditions, especially in the field of catalyst and gas separation [13]. Moreover, applications such as hydrogen storage require high thermal conductivity, packing densities, good stability levels in humid and reactive environments, and high

volumetric density, which could not be achieved by synthesizing powder materials [14]. Additionally, powder MOFs further require shaping, which adds additional cost. Moreover, this processing results in a loss of properties, a decrease in crystallinity, and an increased risk of contamination [10]. In this regard, synthesizing MOFs as a thin film opens many doors for their potential application in diverse fields.

1.3 What to Consider for MOF Commercialization?

From a commercialization perspective, the following key aspects need to be considered [15]:

- 1) The selection of a technique that could be adopted for the synthesis of diverse kinds of MOF by using the same processing equipment
- 2) Developing a process based on sustainability that creates fewer/or no environmental concerns
- 3) Working of synthesis technique at mild conditions with reproducibility of results with high purity
- 4) Potential of the process to switch from batch scale to continuous production

In terms of MOF component selection, it should adhere to green chemistry, and one should avoid the use of toxic chemicals like N, N-dimethylformamide and instead prefer the use of water, alcohol, or a more sustainable solvent. The selection of metal sources based on nitrides and chlorides is also highly discouraged because of their potential hazards, such as their explosive and highly corrosive nature. Switching such sources with oxides, carbonates, acetates, and sulfates is recommended. As far as ligand selection is concerned, it is recommended to use cost-effective, widely available, and

less toxic ligands, for instance, terephthalic acid ($\text{C}_6\text{H}_4(\text{CO}_2\text{H})_2$), trimesic acid ($\text{C}_9\text{H}_6\text{O}_6$), fumaric acid ($\text{C}_4\text{H}_4\text{O}_4$), and isophthalic acid ($\text{C}_8\text{H}_6\text{O}_4$) [16].

1.4 Advancing MOF Applications: From Powder to Thin Film Technologies

The dominant powder-based techniques that have been successfully employed for the upscaling of MOFs include solvothermal, sonochemical, microwave, mechanosynthesis/mechanochemical, and electrochemical deposition. Although all these techniques are suitable for large-scale applications, they also have some significant limitations. Solvothermal requires harsh conditions, i.e., high temperature and pressure, sophisticated reactors, and employs toxic metal salts and solvents for MOF synthesis. Sonochemical synthesis is found to be successful for limited types of MOFs. Microwave-assisted synthesis results in extremely small particles that further create complications in the purification and shaping processes. Mechanosynthesis is also not applicable to all kinds of MOFs and imposes some potential problems related to MOF contamination due to the wearing of metallic balls. Electrochemical synthesis has so far only been employed for HKUST-1 and is not very sustainable because of the usage of toxic solvents during cathodic deposition [17], [18]. The main advantages and disadvantages of each technique is displayed in more detail in Table 1.1.

Table 1.1: Prominent techniques utilized for the MOFs thin film synthesis.

Technique	<i>Solvothermal</i>	<i>Electrochemical Deposition</i>	<i>Mechanosynthesis</i>	<i>Sonochemical</i>	<i>Microwave</i>
					
Advantages	✓ High purity & crystallinity ✓ Higher reaction rate ✓ Discovery of new structures	✓ Good quality coatings ✓ Low-temperature requirement ✓ Short reaction interval ✓ Non-specialized equipment	✓ Solvent-free conditions ✓ Pressure and temperature are not required ✓ Faster and more efficient synthesis	✓ Short reaction time ✓ Simple equipment - High efficiency ✓ Ideal for nano-sized MOFs	✓ Simple and energy-efficient approach ✓ Simple approach ✓ Less hazardous solvents
Disadvantages	✗ Harsh conditions ✗ Use of toxic metal salts and solvents ✗ Not applicable to all MOFs	✗ Conductive substrate only ✗ Low yield ✗ Easy to produce byproducts ✗ Limited types of MOFs	✗ Limited types of MOFs ✗ Problems related to MOF contamination	✗ Secondary phases - Toxic metal salts ✗ Small scale ✗ Limited types of MOFs	✗ Purification and shaping ✗ Large-scale adaptability challenges ✗ Poor adhesion

To overcome the challenges of the aforementioned techniques, it is crucial to develop and design a technique that solves the above-stated problems. Additionally, moving from powder to thin film-based MOFs is also an attractive choice as it not only increases the application perspective of MOFs but also solves many problems related to powder MOFs. Furthermore, preparing MOF nanocomposites with metal or metal oxide is also considered an emerging trend in the field as it helps to improve physical-chemical properties and broaden their application in diverse fields.

Several thin film techniques have been employed for MOF syntheses, such as ALD, CVD, electrochemical deposition (ECD), and dip coating [19]. Previously, Drobek et al., employed ALD ZIF-8 synthesis by modifying the ZnO layer. In this investigation, the ZnO layer was synthesized using ALD on the surface of macroporous α -Al₂O₃ support, which was later transformed into ZIF-8 under solvothermal conditions by using 2-methylimidazole and methanol solution [20].

Sungmin Han and his coworker employed both PVD and CVD for the synthesis of HKUST-1 thin film. In this work, HKUST-1 was synthesized on a SiO₂/Si(100) surface. PVD was employed as a source of metal ions through an e-beam evaporator, Cu, and CVD for the organic linker using a thermal evaporator, H₃BTC. After completing the deposition of both layers, the thin film was subjected to annealing treatment [21]. Stassen et al., synthesized ZIF-8 via the CVD approach for microelectronics applications with high thin film quality, uniform layer, and controllable thickness. This process consists of two major steps: the deposition of metal oxide vapor and its conversion into MOF through vapour–solid reaction [22].

Assche et al. synthesized the dense layer of HKUST-1 using electrochemical synthesis. The electrolyte solution was a mixture of water, ethanol, and trimesic acid. Additionally, methyltributylammonium methyl sulfate (MTBS), was also added to increase the synthesis efficiency of HKUST-1 and solve the problem related to the electrical resistance of the solvent. In this investigation synthesis, HKUST-1 was synthesized at block wave voltages from 0 to 5 V at the frequencies of 0.05 Hz, 0.25 Hz, and 0.5 Hz, respectively. The actual time of synthesis was half of the total time of the synthesis process. Optimization of parameters such as voltage, time, and electrolyte solution resulted in the formation dense HKUST-1 layer at a short time [23].

Chernikova et al. reported a novel spin coating/LPE method for synthesizing HKUST-1 and ZIF-8 thin films. This approach consists of four micro-syringes (metal, solvent, ligand, solvent = one cycle) through which certain amounts of solution are dropped on the substrate under a specific duration while spinning at the rate of 500 rpm, which results in a homogenous layer of solution through centrifugal force. Here, they reported the fabrication of HKUST-1 thin film on an alumina substrate. The specimen was held on a rotating chuck and, after that, coated with the solution of $\text{Cu}_2(\text{CH}_3\text{COO})_4 \cdot x\text{H}_2\text{O}$ -ethanol for 5 sec, and then BTC-ethanol coating was applied for 10 sec. After each step, the substrate was cleaned with pure solvent [24].

Nevertheless, there are still many challenges that need to be addressed related to these techniques for the commercialization of MOF thin films. The demand for high capital cost and slow processing rate limits the adoption of ALD at the industrial scale. On the other hand, the requirement for expensive and sophisticated equipment creates constraints on CVD applications. The requirement of conducting substrate is the main disadvantage of

ECD. The other drawback of this technique includes the oxidation of the linker and the separation of metal ions on the cathode surface because of high inertness. Dip coating is widely utilized at the industrial level for thin film fabrication, but has the main drawback of synthesizing film defects like cracks and pinholes. Another problem with this technique is heterogeneity in film thickness [19], [25].

1.5 Advantages of Magnetron Sputtering for MOFs Synthesis

The utilization of PVD techniques such as magnetron sputtering is new to the MOF field and has the potential to address the drawbacks of previous synthesis techniques. Magnetron sputtering is a form of PVD technique in which the target acts as a cathode while the specimen material acts as an anode. The thin film is developed under a specific voltage through the collision of high-energy ions of inert gas with the target surface, which subsequently results in the ejection of atoms that are deposited on a substrate. The synthesis of MOF thin film via this technique has many advantages [26], [27], [28], [29]:

- 1) Cost-effectiveness and green nature
- 2) Coating uniformity with great control over thickness and morphology
- 3) Fast deposition rate with high purity
- 4) High scalability and repeatability
- 5) Excellent adhesion strength

In comparison to other vacuum-based techniques, the use of DC magnetron sputtering has many advantages. Hexagonal comparison graph of thermal evaporation, DC magnetron sputtering, PLD, ALD, and CVD displayed in Figure 1.3, showing the importance of using DC magnetron sputtering in the field of MOFs synthesis.

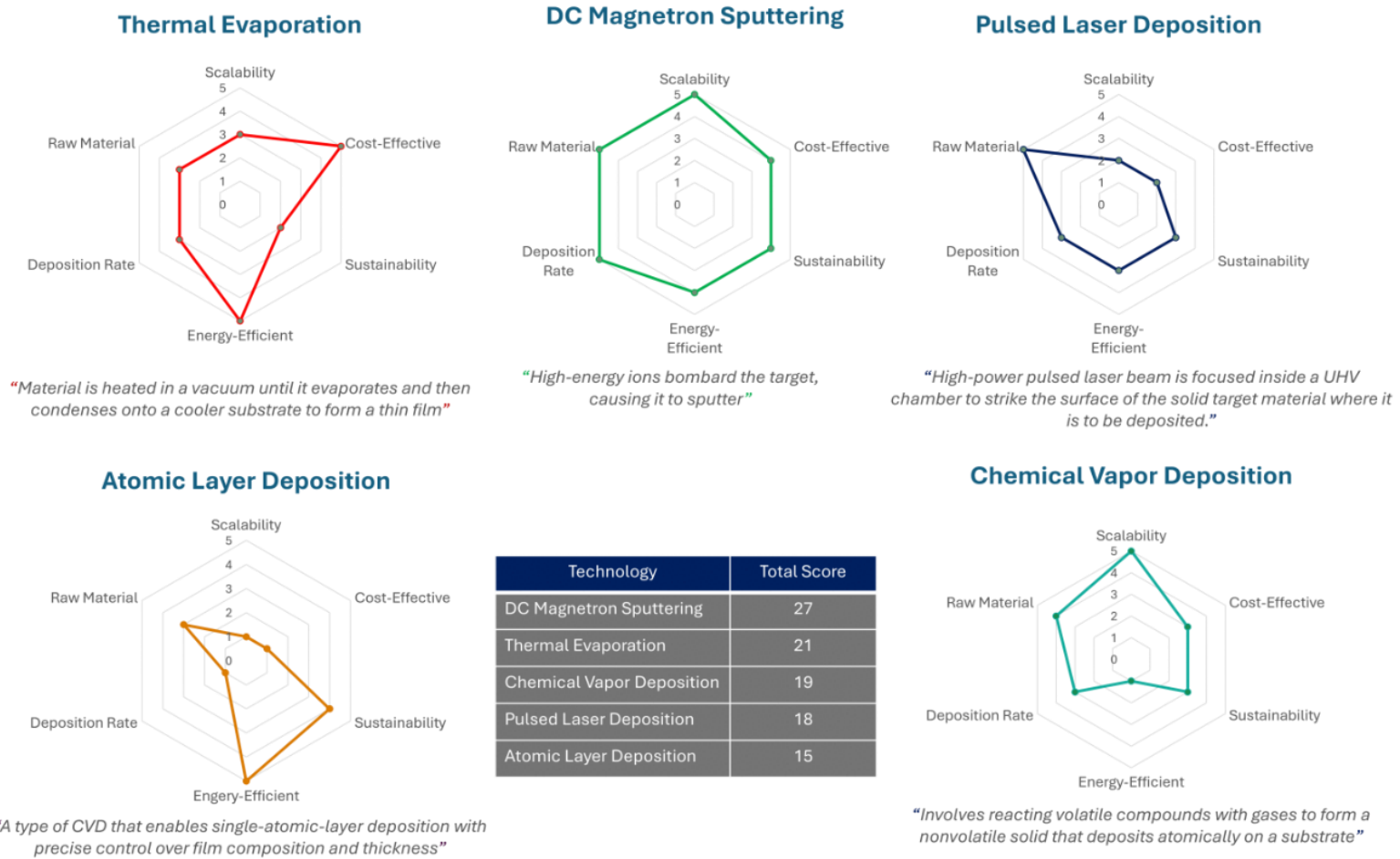


Figure 1.3: Hexagonal comparison graph of thermal evaporation, DC magnetron sputtering, PLD, ALD, and CVD by considering the six features. The table shows the total score of each technique (scores are assigned on a 1 to 5 scale for each feature, where 1 is the least favourable and 5 is the most favourable for each technique).

1.6 Magnetron Sputtering

The basic sputtering system consists of target materials that serve as a cathode while the substrate functions as an anode. The most commonly employed ionization gas in this process is Ar because of its cheapness and inertness. In the traditional sputtering process, the target atom of the depositing material is removed by bombarding the energetic ions of Ar^+ , which subsequently condense on the substrate surface. During this process, secondary electrons are also emitted due to ion bombardment, which plays a potential role in stabilizing and maintaining plasma. The main drawbacks of this process are [30], [31]:

- 1) Low ionization rate
- 2) Low deposition rate
- 3) High heating effect on the substrate

Magnetron sputtering is an advanced form of sputtering system and is designed to overcome the above-mentioned disadvantage. It has a similar configuration to conventional sputtering with the addition of a magnetron device whose main purpose is to develop magnetic and electric fields around the target and confine the plasma [32]. This type of sputtering can be operated in two different modes:

- 1) Direct Current Magnetron
- 2) Radio Frequency Magnetron

RF magnetron sputtering utilizes a high-frequency alternating field of 0.5 to 30 MHz. The most acceptable range for the commercial system is 13.56 MHz. This field accelerates ions and electrons in both directions. Like DC magnetron sputtering, it also employs magnets and offers a fast deposition rate. The major difference in its working

contrast to DC magnetron sputtering, is its ability to develop a positive charge with time during the sputtering process, which further leads to sputtering failure for deposition. The main purpose of creating an alternating field is to remove or avoid the accumulation of charge on the cathode surface [33], [34].

In the positive cycle, the electron moved toward the target surface, creating a negative bias. Meanwhile, in the negative cycle, RF power is used for continuous sputtering, resulting in the ion bombardment of the target. To create an inert environment, usually, Ar gas is used due to its larger mass, which further results in higher energy of plasma, which is beneficial for removing atoms from the target surface [33], [34]. The major differences between these two modes are mentioned in Table 1.2 [30], [31].

Table 1.2: The main differences between DC and RF magnetron sputtering.

	Magnetron Sputtering	
	DC System	RF System
Power supply	-2 to -5 kV of DC	13.56 MHz of RF
Depositing material	Metal, alloy, and compound	Insulators, low-conducting materials, polymers, covalent, and ionic compounds
Cost	Low	High
Design	Simple	Very complex

DC magnetron sputtering utilizes DC as a power source. In this process, electrons are confined over the cathode (target) using magnets, placed behind the target, promoting a faster deposition rate. The DC power consumption of the target material depends on its size. This technique is known for its cost-effectiveness and simplicity in comparison to RF

magnetron sputtering. Additionally, in contrast to other types of magnetron sputtering, it is the cheapest process [35].

1.6.1 Working Principle of Magnetron Sputtering

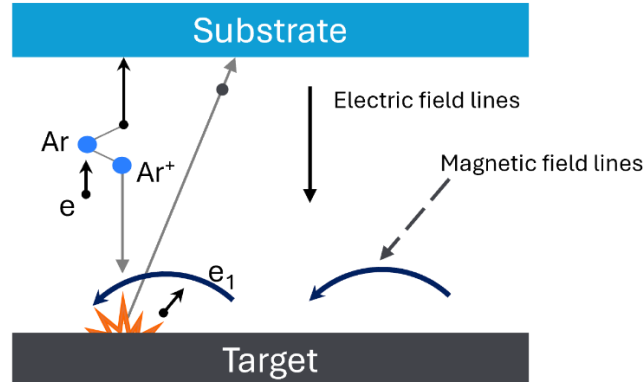


Figure 1.4: Working principle of magnetron sputtering [33].

Magnetron sputtering working principle can be understood by considering the Lorentz force equation:

$$F = -q(E + v \times B)$$

Where,

v is the velocity

B is magnetic induction intensity

E is the electric field

When the electric field is applied between the cathode and the anode, it leads to the interaction of electrons with Ar gas, causing ionization and resulting in the creation of new electrons. The ionized Ar^+ ions were projected towards the target materials while the new electrons moved towards the substrate. When Ar^+ ions bombard the surface of target materials, it results in the emission of neutral target atoms and secondary electrons, as shown in Figure 1.4.

These secondary electrons experience both electric and magnetic fields when ejected from the target surface. Firstly, secondary electrons experience an electric field in the “cathode dark region” and then experience a magnetic field in the negative glow zone (Figure 1.5) [33].

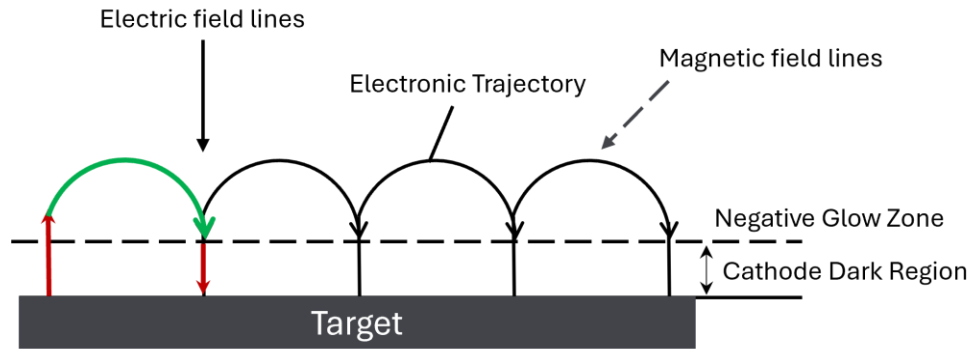


Figure 1.5: $E \times B$ drift of electrons under the action of orthogonal electromagnetic fields [33].

When an electron enters this zone, it has a certain speed and moves perpendicular to the magnetic field, where it experiences the Lorentz force and moves in a half-circle pathway. After completing half a circle pathway electron re-entered to electric field and experienced deceleration. Afterward, a new cycle will continue where electrons experience drift along the $E \times B$ direction. Because of the confinement of secondary electrons around the target deposition rate increased. At the same time, the number of collisions also increases with the gradual reduction of the electron energy. Because of the lower energy of the electron, it easily drifts from the target surface and moves toward the specimen under the influence of the electric field. Since electrons have very low energy, the amount of energy transferred by electrons to the substrate is also less. Due to this reason, the substrate experiences a reduced heating effect [33].

1.6.2 Magnetron Sputtering Configuration

Magnetron sputtering is classified into three different configurations that include:

- (a) Balanced magnetron
- (b) Unbalanced magnetron (**Type I**)
- (c) Closed field unbalanced magnetron (**Type II**)

In the *balanced magnetron*, the magnets' strength behind the target is equal, resulting in dense plasma formation at the cathode within a range of around tens of mm. Having this configuration has the advantage of achieving a higher sputtering rate of the cathode with stable plasma. In this type of magnetron configuration, sputtering takes place at lower pressure with higher current densities. Additionally, it also results in improved ionization efficiency because of increased collisions of gas molecules. However, also has some challenges related to poor production efficiency and limited transfer of bias current toward the substrate [36].

The balanced magnetron changed to an *unbalanced magnetron* when stronger magnets were placed on the outside, resulting in an unbalanced magnetic field. Because of such a configuration plasma extended right up towards the anode (substrate), which has the pros of increasing ion bombardment of the substrate with improved film quality, better adhesion, highly dense coating, and increased ion and electron current density of the substrate. The main disadvantage of this configuration is its ability to produce a non-uniform coating on complex parts [37].

To overcome the above disadvantage *closed field unbalanced magnetron (CFUMS)* configuration was introduced, which is an intermediate type of magnetron sputtering. In

comparison to Type I, where the inner magnetic flux is greater than the outer, in this case, the inner magnetic flux is weaker than the outer one. CFUMS is considered more versatile than an unbalanced magnetron. In this configuration, multiple magnets are used for the formation of a closed electron trap by generating multiple magnetic fields [38].

1.7 Main Objective of Study

This research aims to develop a novel approach to synthesize ZIF-8 and CAU-17 MOFs thin films, using DC/RF sputtering, followed by in situ. The specific objectives of this work are to:

- To synthesize metal oxide thin films such as ZnO and Bi₂O₃, using DC reactive sputtering.
- To transform the above metal oxide thin films to MOFs/metal oxide composites through an in-situ growth technique at different temperatures (from 25 to 150 °C) in different solvents such as water, DMF, etc.
- To investigate the structural, morphological, and compositional properties of the fabricated MOFs using different analytical techniques, including XRD, SEM, AFM, and XPS
- To investigate the influence of temperature and solvents on MOF growth and morphology evolution
- To explain the MOF growth mechanism

CHAPTER 2

LITERATURE REVIEW

Chapter 2

Literature Review

2.1 Zeolitic Imidazolate Frameworks

Zeolitic Imidazolate Frameworks (ZIFs) or Metal-Azolate Frameworks (MAFs) are a sub-class of MOFs because of their unique ability to utilize both features of zeolites and MOFs. Until now, ZIFs have been employed in diverse areas of research since their invention in 2006 [39]. Some of the prominent features of ZIFs include their remarkable stability in chemical and thermal conditions, high surface area, simplicity of synthesis, industrial scalability, permanent microporosity, and crystalline nature [40]. In ZIF, metal ions act as nodes that are connected to imidazole-based linkers that promote the formation of a 3-dimensional framework whose structure is closely comparable to conventional aluminosilicate zeolites [41].



Figure 2.1: Structure similarity between ZIFs and zeolites (a) Si–O–Si bonding in zeolites. (b) The M–Im–M linkage in ZIFs [42].

The angle between M-L-M (where M represents the metal node and L is the imidazolate linker) is 145° , resembling the angle found in Si-O-Si bonds that led to the large number of ZIFs synthesis, which consists of zeolite-like tetrahedral topologies as shown in Figure 2.1 [42], [43]. So far, in the literature, 105 ZIF topologies have been reported with 38 topological codes. Some of them consist of the same topology, however, differ in their pore shapes and sizes [44].

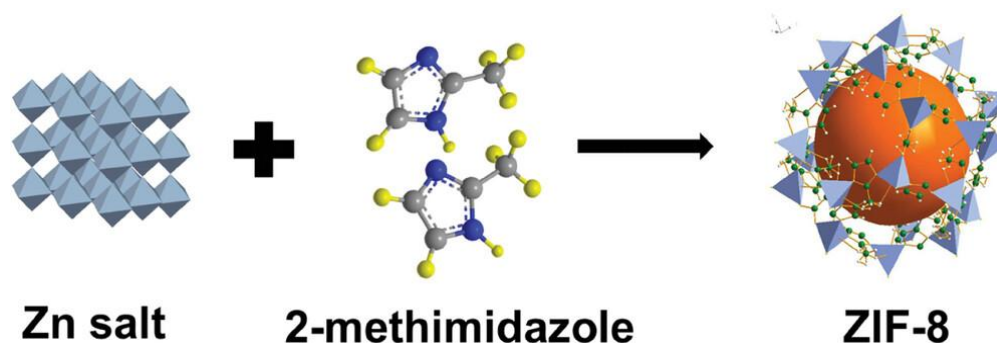


Figure 2.2 Chemical reaction representing the formation of the ZIF-8 framework [45].

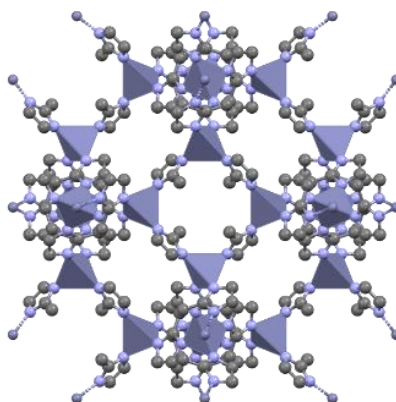


Figure 2.3: ZIF-8 Crystal structure (CCDC No. 602542)

Within the ZIF family, ZIF-8 is the most well-known and extensively investigated material due to its outstanding stability in chemical and thermal conditions (up to 500°C) [46]. The basic chemical reaction for the formation of ZIF-8 is shown in Figure 2.2. This material consists of a sodalite (SOD) structure, Figure 2.3, that comprises Zn^{+2} ions and 2-

methylimidzaolate ligands (Hmim) with 4 and 6-member ring Zn-N₄ clusters and results in the formation of nanocages of size 1.2 nm with a micropore of 11.6 Å, located at the center of ZIF-8 structure, which is accessible via apertures size of 3.4 Å [39], [41], [47], [48].

2.1.1 ZIF-8 Chemistry

2.1.1.1 Imidazole-Based Linker

Imidazole, C₃H₄N₂, falls under the class of N-heterocyclic group that comprises 5-membered rings. The imidazole ring consists of 2 N atoms with distinct properties. Nitrogen can deprotonate and coordinate with transition metals. While the other nitrogen has the protonation ability and usually takes part in hydrogen bonding. Considerable interest has been developed in metal ions' coordination with heterocyclic compounds, particularly for materials synthesis and characterization, using imidazole derivatives [49], [50]. 2-methylimidazole (2-mIm), C₄H₆N₂, is one of the most employed linkers for the synthesis of MOFs and is well-known for its affordable price at the industrial level [51]. Its structure is composed of nitrogen groups at the positions of 1 and 3, a kind of nitrogen-containing heterocyclic compound [52], [53]. 2-mIm is a substituted form of Imidazole (Im), and its complexes are less stable in contrast to Im because of steric hindrances raised due to substitution [50]. The Im ring in 2-mIm can be identified as an aromatic compound, with an interacting ability with other aromatic systems through π - π stacking interaction. The main reason behind it is the presence of two double bonds and a pair of electrons, originating from protonated nitrogen [54]. In terms of ZIF structure, it is composed of metal ions that are tetrahedrally coordinated with organic linkers, i.e., imidazolate, and its derivative, resulting in a distinct topology due to the selection of the linker [55]. Additionally, structure adoption depends on both the linker and solvent.

2.1.1.2 Metal Ions

ZIF structure construction is based on bivalent metal ions (M^{2+}). In this regard, the most employed M^{2+} are Zinc (Zn) and Cobalt (Co) [56]. These transition metals develop by connecting with nitrogen atoms of deprotonated Im molecules, resulting in tetrahedral frameworks [57]. It is important to note that not all metal ions have the ability to form the ZIF structure, however, metal ions like Iron (Fe), Copper (Cu), Cadmium (Cd), or Manganese (Mn) can form ZIF materials. The M^{2+} ions in ZIFs do not result in the formation of clusters as they are isolated. Because of this reason, metal-metal, metal-oxygen-metal, or metal-nitrogen-metal bonds do not take place; instead, it singular $[M^{II}(\text{linker})_4]^{2-}$ environments develop [58]. ZIF has a four-connected framework, meaning ZIFs adopt zeolitic topologies where metal ions substitute tetrahedral Si atoms, and the linker substitutes with O atoms in the building block of SiO_2 [59].

2.1.1.3 Pearson's Principle

According to the hard and soft acids and bases (HSAB) principle, the ZIF structure is based on soft-soft interaction. Such interaction results in the formation of a stronger bond between divalent transition metals and N-donor ligands. Additionally, MOFs constructed using soft acid and soft base result in increased hydrothermal stability because of increased charge transfer between them, with higher correlation energy in the framework [60].

In the ZIF-8 structure, azolate ligands like 2-mIm (soft Lewis's base) develop strong bonds with metal ions, i.e., Zn^{2+} (soft Lewis's acid), resulting in a stable structure along with superior thermal and chemical stability due to strong coordination bonds [61], [62]. The use of the HSAB principle has the benefits of understanding ZIF-8 stability in an

aqueous medium and predicting the bond strength formation, chemical reactivities, and designing stable MOFs [63].

2.1.2 Synthesis of ZIF-8 Thin Film

2.1.2.1 Atomic Layer Deposition

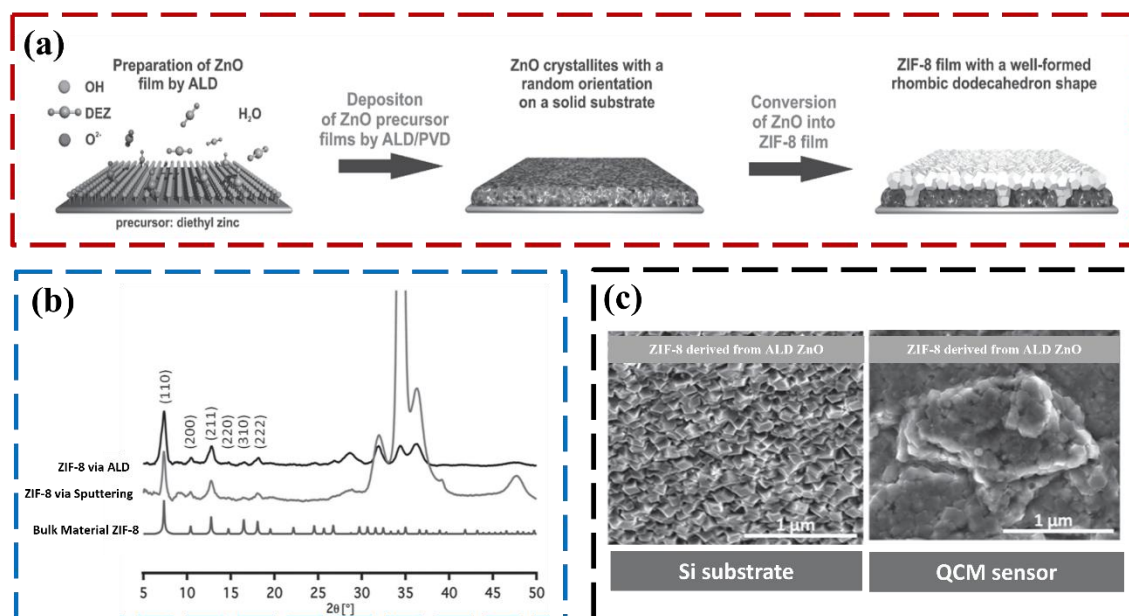


Figure 2.4: (a) Schematic diagram of synthesizing ZIF-8 films using the ALD technique; (b) XRD analysis of synthesized ZIF-8 thin film via ALD and sputtering; (c) SEM images of derived ZIF-8 on the surface of Si substrate and QCM sensor [64].

Khaletskaya et al., synthesised ZIF-8 thin film via ALD techniques. The main concept of this technique was using the ZnO layer as a source of Zn^{2+} ions and further reacting it with an organic linker for ZIF-8 formation, as shown in Figure 2.4 (a). In this investigation, the ZnO layer of 47 nm thickness was deposited on the Si or QCM substrates using the ALD technique with a wurtzite structure. The prepared ZnO substrate was then converted into ZIF-8 through microwave-assisted treatment, where the coated substrate was immersed in the solvent mixture of DMF/H₂O and subjected to heating at 80 °C for 1 hr. The XRD analysis confirmed the formation of ZIF-8 over the surface of ZnO Figure 2.4 (b). This work highlights the direct synthesis of ZIF-8 from metal oxide using cheap raw

materials with a dense and uniform coating (Figure 2.4 (c)), finding potential applications in microelectronics and miniaturized devices [64].

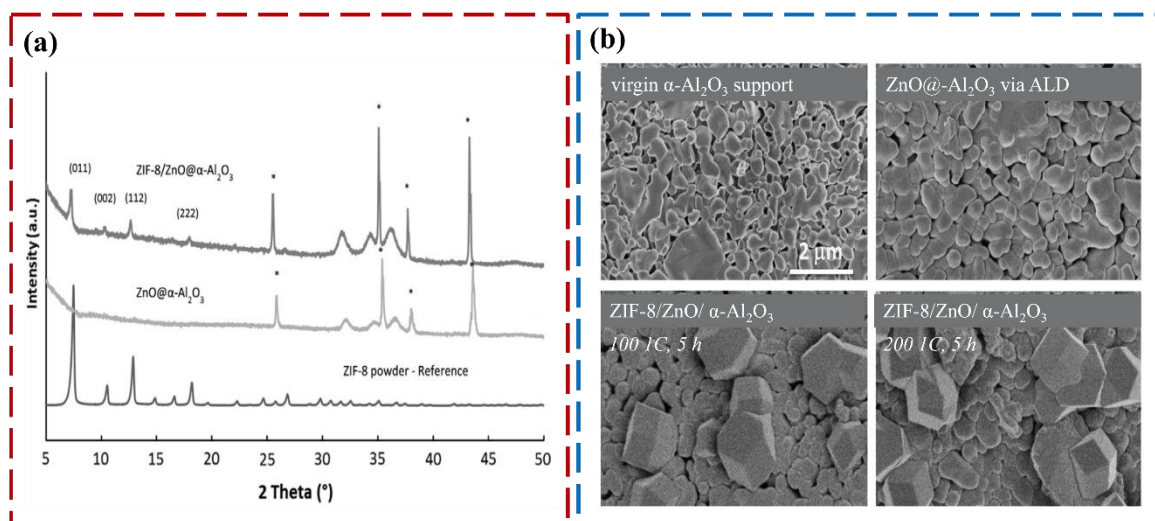


Figure 2.5: Surface modification of ZnO into ZIF-8 using ALD technique (a) XRD analysis (b) FESEM images of ZIF-8 [20].

Drobek et al., employed ALD ZIF-8 thin film fabrication through the conversion of the ZnO layer. In this study, the ZnO layer deposited by ALD on the surface of α -Al₂O₃ support was subsequently transformed into ZIF-8 using a solvothermal technique by immersing the coated substrate in the solution of 2-mIm and methanol for 5 hrs at 100°C. The XRD analysis showed the synthesis of ZIF-8 on α -Al₂O₃ as displayed in Figure 2.5 (a). The surface morphology of the converted layer is shown in Figure 2.5 (b). The optimal thickness of ZnO in this investigation was 50 nm [20].

2.1.2.2 Chemical Vapor Deposition

Stassen et al., synthesized ZIF-8 via the CVD approach for microelectronics applications with high thin film quality, uniform layer, and controllable thickness. This process consists of two major steps: the deposition of metal oxide vapor and its conversion into MOF through a vapor–solid reaction, as illustrated in Figure 2.6 (a).

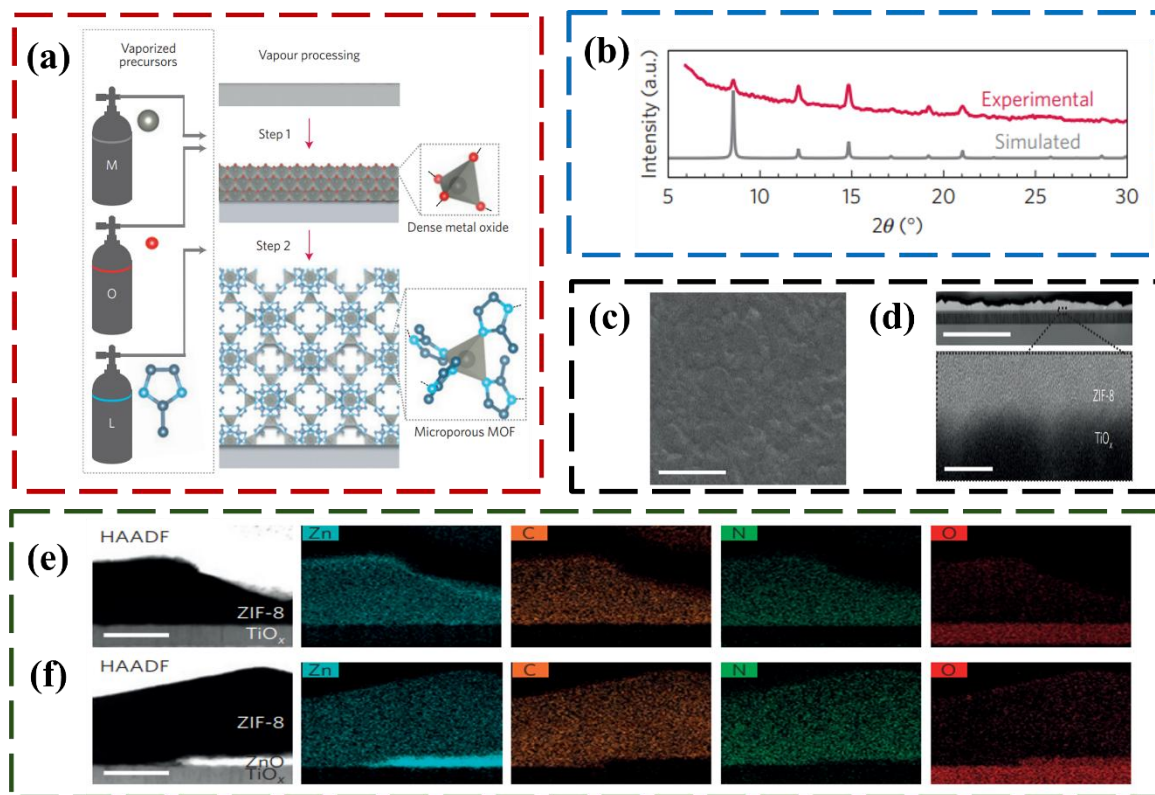


Figure 2.6: ZIF-8 formation using CVD technique (a) schematic diagram; (b) XRD analysis of ZIF-8; (c) SEM analysis of thin film; (d) TEM cross-sectional analysis; HAADF and EDS cross-section maps of the (e) completely and (f) partially transformed film [22].

In this investigation, metal oxide was deposited on a silicon wafer via ALD to a thickness between 3 to 15 nm. The ZIF-8 synthesis on the surface of the as-deposited substrate takes place in three steps: (1) pre-heating ZnO coated substrate and 2-mIm at 100°C, separating; (2) placing coated substrate and organic linker inside the CVD chamber for ZIF-8 formation and heating them for 30 min at 100°C; and (3) activating ZIF-8 at 110°C for 10 mins under nitrogen flow. XRD analysis confirmed the existence of highly crystalline and continuous thin film ZIF-8 formation with a crystallite size of 500nm (Figure 2.6 (b)). Cross-sectional analysis showed the complete conversion of the ZnO into ZIF-8 when the ZnO precursor thickness was >10nm (Figure 2.6 (c-d)). The original thickness of the thin film was determined through a HAADF and high-magnification TEM, which shows

the influence of thickness on partial and complete transformation of ZnO thin film into ZIF-8 (Figure 2.6 (e-f)) [22].

Cruz et al., analyzed the effect of different precursor layers on the formation of ZIF-8. In this research, common microfabrication techniques were used for synthesizing ZnO, such as sputtering, ALD, and molecular layer deposition. The synthesized ZnO layer was subsequently transformed into the ZIF-8 thin film via vapor phase reaction inside the CVD reactor, using 2-methylimidazole as a linker. This study highlights the advantage of having a defective and reactive nature of the precursor in the synthesis of MOF thin films [65].

2.1.2.3 RF Magnetron Sputtering

Neelakanda et al., synthesized ZIF-8 at room temperature using RF sputtering, displaying a very dense thin film without any defect formation. The synthesis process of ZIF-8 thin film is displayed in Figure 2.7 (a). This approach used a polyacrylonitrile (PAN) porous membrane as a support material. The ZnO layer was deposited using RF sputtering and subsequently transformed into ZIF-8 by two methods: (A) directly immersing PAN-ZnO substrate in the solution of 2-mIm and (B) dip coating of PAN-ZnO substrate in 2-mIm solution for few seconds and then immersing into the new solution, consists of zinc nitrate and 2-mIm solution, for secondary growth. *Method B* displayed better results in contrast to *Method A* in terms of dense layer formation, smaller crystal size, and a very thin film of thickness around 900 nm, Figure 2.7 (b-c) [66].

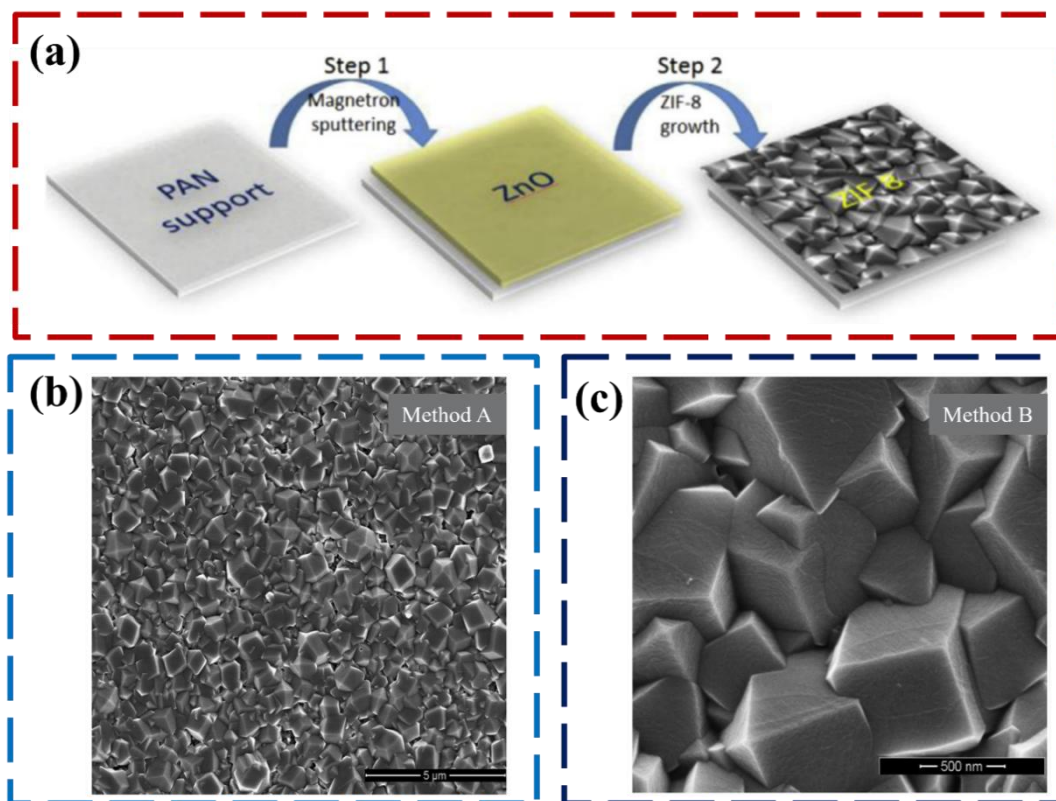


Figure 2.7: (a) Synthesis diagram of ZIF-8 on the membrane; (b-c) SEM images thin film synthesized via methods A and B [66].

Similarly, Yu et al., partially converted the ZnO layer, synthesized by RF sputtering, into ZIF-8 on the surface of the alumina substrate. The technique consists of three main steps: (a) deposition of the ZnO layer, (b) transformation of the ZnO into ZIF-8 through hydrothermal synthesis, and (c) secondary growth of ZIF-8. The primary aim of that work was to improve the reproducibility of ZIF-8 membranes compared to the traditional sol-gel technique. Partial transformation of the ZnO into ZIF-8 demonstrated the ability to achieve heterogeneous nucleation, improvement in adhesion strength between MOF and support materials, and significantly improved reproducibility [67].

2.1.2.4 Electrochemical Deposition

Worrall et al., successfully synthesized five different types of ZIFs through an anodic dissolution method for supercapacitor electrodes. ZIFs coating was synthesized by immersing metal foil in the heated electrolytic bath made of different linkers (2-mIm, mI, bIm, and emI), selected according to the type of ZIF-8. A 2.5 V was applied between the electrodes for synthesizing the ZIF on an anodic surface, and subject to post-cleaning in a methanol solution. The study highlighted the ability of anodic dissolution to synthesize various kinds of ZIFs, such as ZIF-4, ZIF-7, ZIF-8, ZIF-14, and ZIF-67, and the dependence of materials crystallinity on reaction interval and concentration of linker [68].

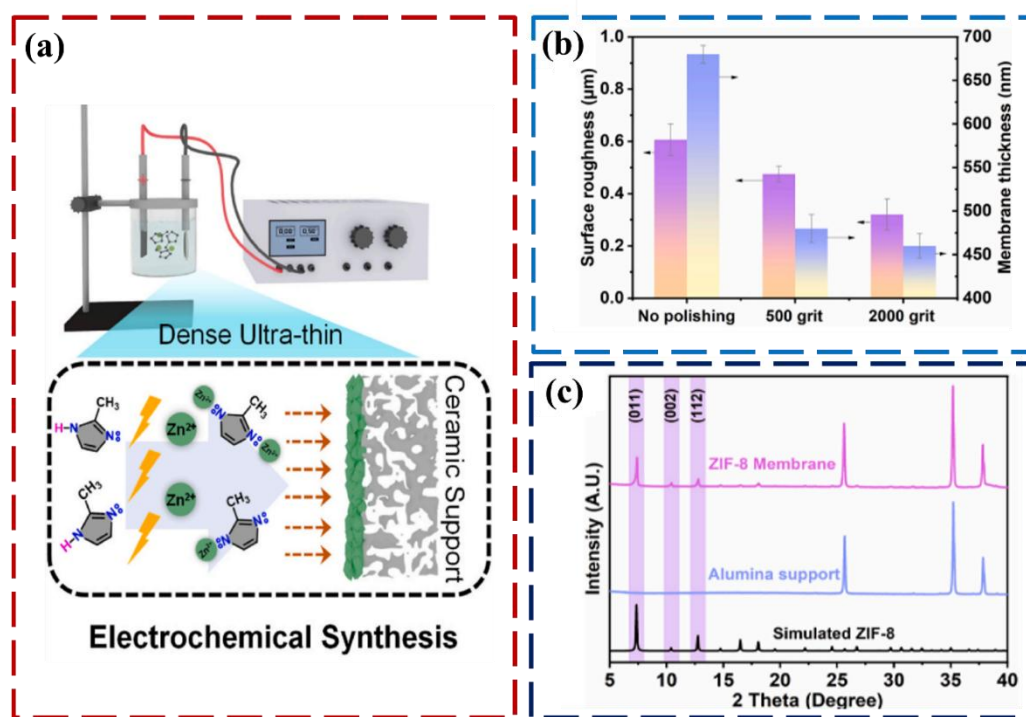


Figure 2.8: (a) ZIF-8 synthesis scheme using electrochemical synthesis strategy, (b) Influence of polishing on surface roughness and membrane thickness, (c) XRD patterns of ZIF-8 [69].

Lian et al., synthesized ZIF-8 on the non-conducting material surface using electrochemical deposition (Figure 2.8 (a)). The α -Al₂O₃ was used as substrate material, fabricated by sintering the compacted powder after hydraulic pressing. To make the surface conductive, a gold layer was deposited on the support surface. This process consists of 2-mM and zinc acetate as an electrolytic solution, α -Al₂O₃ substrate as a working electrode, and graphite electrode as a reference electrode. ZIF-8 synthesis takes place by applying a constant current of 0.5 mA for 20 to 150 minutes. The results demonstrated the stable ZIF-8 crystal formation by optimizing the substrate roughness, Au sputtering time, metal/ligand ratio, and electrochemical deposition interval [69].

For the formation of a uniform layer of ZIF-8, the surface of α -Al₂O₃ was subjected to grinding is sandpaper of different grit sizes, significantly reducing the surface roughness as shown in Figure 2.8 (b). The surface roughness of 0.32 μ m was considered the optimal value for the synthesis of ZIF-8. It was also observed that decreased roughness resulted in the dense formation of ZIF-8. XRD analysis confirmed that ZIF-8 was successfully synthesized with a highly crystalline peak over the surface of α -Al₂O₃, Figure 2.8 (c) [69].

2.1.2.5 Dip Coating

Cookney et al., utilized dip coating for ZIF-8 nanofilms synthesis that exhibits highly dense thickness, homogenous morphology, and accessibility to small penetrants. This technique consists of four steps, which involve immersion of the substrate into Zn²⁺ solution, washing with a solvent, then dipping into the solution rich in 2-methylimidazole, and subsequently again washing in a solvent. This whole process is considered a full cycle for ZIF-8 formation, and by controlling the withdrawal speed, ZIF-8 coating thickness could be modified [70]. Figure 2.9 (a) confirms uniform thin film formation without any

cracks or pinholes in the ZIF-8 thin film. The SEM higher magnification results related to the ZIF-8 do not exhibit its conventional rhombic dodecahedral structure. The XRD results showed the directional growth of ZIF-8 crystals along the $\{112\}$ plane (Figure 2.9 (b)).

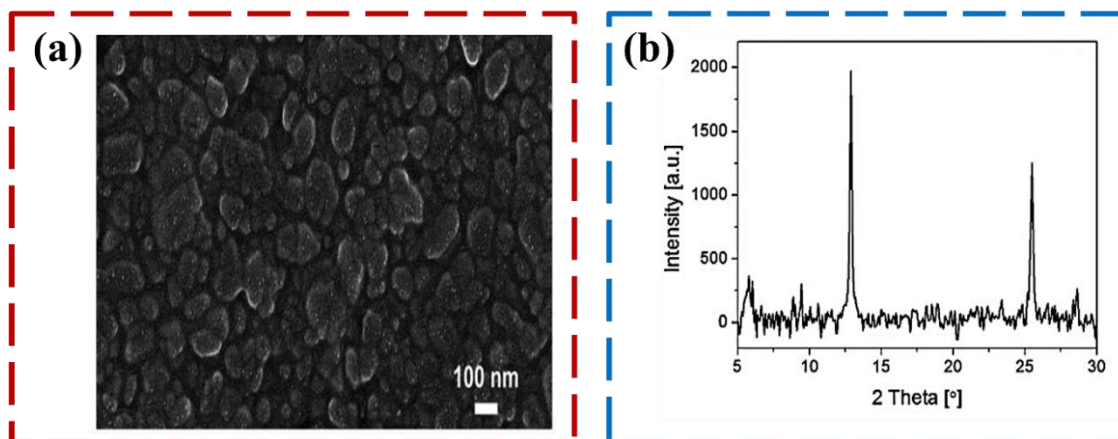


Figure 2.9: (a) Synthesis scheme of ZIF-8 thin film using dip-coating technique; (b) SEM images ZIF-8 nanofilms; and (d) XRD pattern of ZIF-8 thin film.

Kong et al., described a simple, effective, and low-cost technique for the ZIF-8 synthesis through the conversion of ZnO layer with reproducible results. In this approach, ZnO nanoparticles were deposited on α -Al₂O₃ tubes through a manual rubbing process as illustrated in Figure 2.10 (a). The SEM analysis revealed the uniform coverage of α -Al₂O₃ tubes with ZnO nanoparticles, as shown in Figure 2.10 (c). The coated tube was then air calcined at 973 K for 3 hours. Before ZIF-8 growth, the calcined surface of the ZnO layer was activated by immersing in the solution of 2-mIm and methanol for 2hr to promote nucleation sites. The synthesis of ZIF-8 takes place via a solvothermal approach where the activated substrate is transferred to an autoclave, containing the solution of 2-mIm, zinc chloride, sodium formate, and methanol, and heated at 373 K for 5hrs. The XRD analysis verified the successful synthesis of ZIF-8 as shown in Figure 2.10 (e) [71].

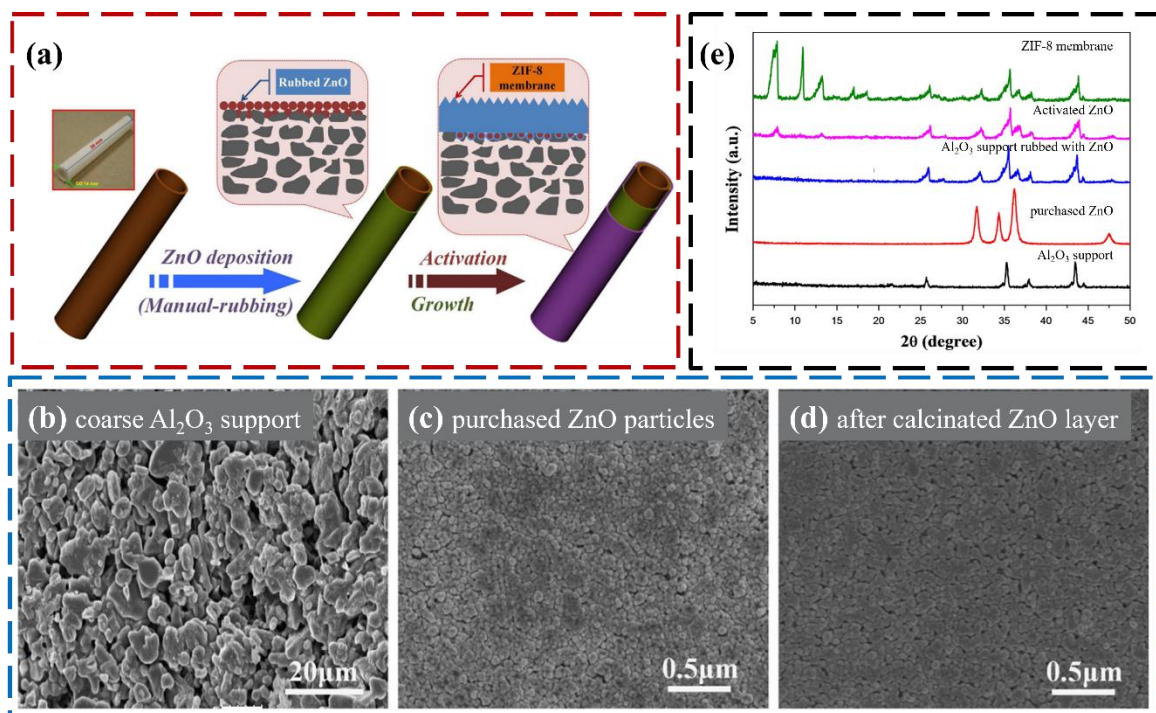


Figure 2.10: (a) preparation procedure of ZIF-8 thin film; (b-d) SEM images of support, ZnO particles; and calcinated ZnO layer; and (e) XRD pattern of ZIF-8 [71].

2.1.2.6 Solvothermal/Hydrothermal

Wang et al., growth ZIF-8 on the zinc substrate using solvothermal approach. Figure 2.11 (a) shows the synthesis steps of ZIF-8 thin film. In that work, the zinc substrate was immersed in the solution containing 2-mIm, DMF, and zinc nitrate. The synthesis takes place in an autoclave where the solution, along with the zinc substrate subjected to heat at 150°C for 24 hours. The resultant thin film displayed well-formed ZIF-8 crystal facets with a coating thickness of 40 to 50 μm . The XRD pattern confirmed the formation of ZIF-8 and showed the presence of ZnO due to the oxidation of the metal substrate on the zinc substrate using a solvothermal approach (Figure 2.11 (b)). Another reason for ZnO formation is the competitive interaction of Zn ions towards hydroxyl groups and ligands. For determining the strong bonding of ZIF-8 with the zinc substrate, an adhesion test was performed using the sonication method. In that test, the substrate was immersed in CH_3OH

solution and subjected to sonication for 30 minutes. SEM results showed strong adhesion of ZIF-8 to the substrate without any damage (Figure 2.11 (c)). This work highlights the direct synthesis of ZIF-8 using the solvothermal technique with dense coating and stronger adhesion for sensing and electronic devices [72].

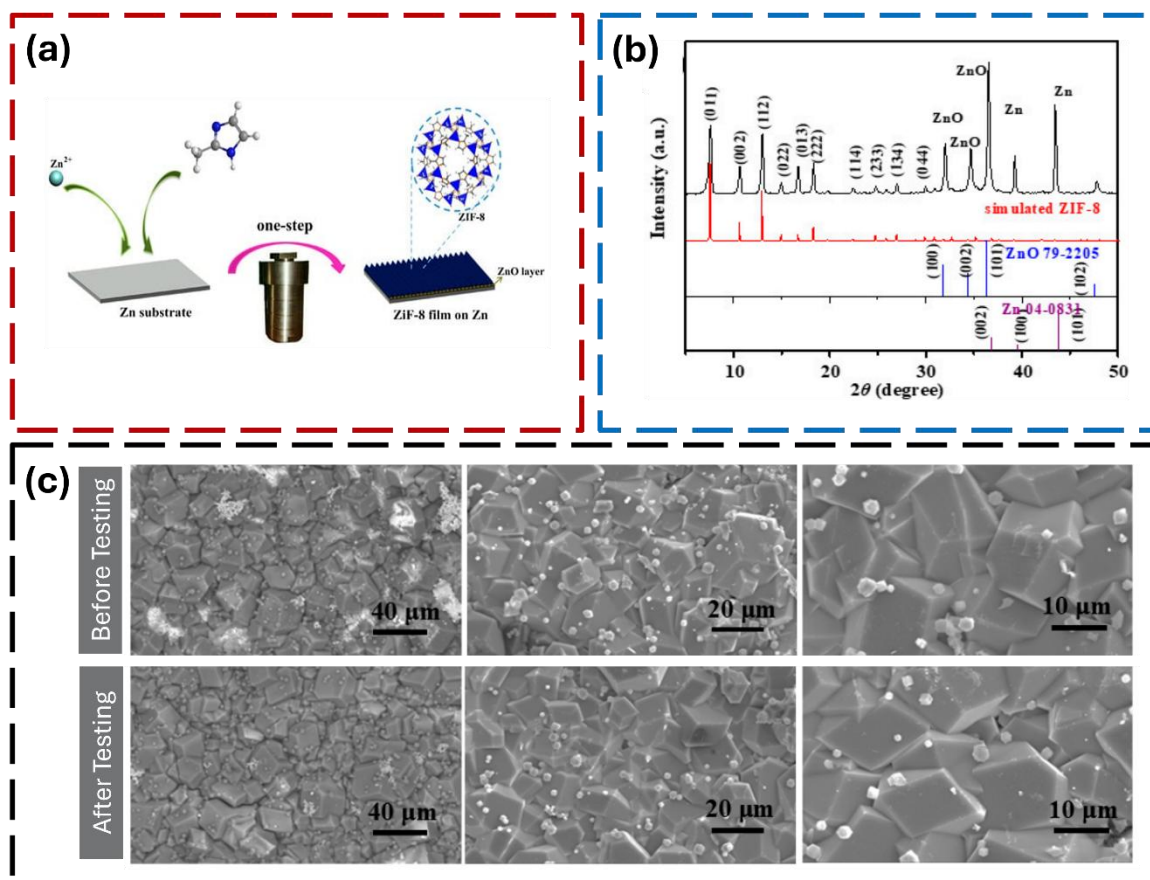


Figure 2.11: (a) in situ synthesis approach of ZIF-8 on zinc specimen, (b) XRD analysis of ZIF-8 thin film, and (c) adhesion test of thin film before testing, and after testing at different magnifications [72].

Table 2.1 and Table 2.2 display the main advantages and disadvantages of each technique that has been employed so far for the synthesis of ZIF-8 thin films using powder and vacuum-based technology.

Table 2.1: Advantages and disadvantages of conventional techniques for the synthesis of ZIF-8 thin films

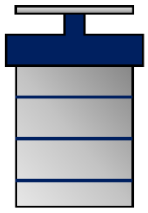
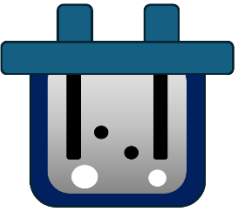
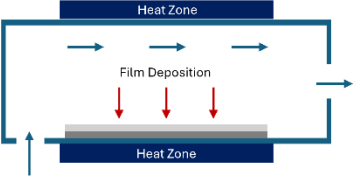
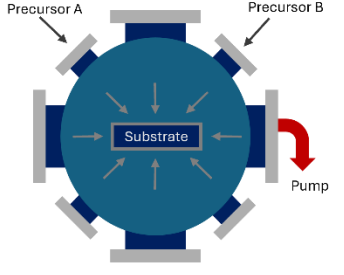
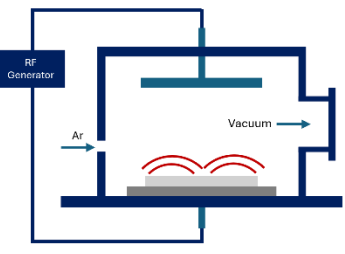
Solvothermal	Electrochemical Deposition	Dip Coating
		
Advantages: ✓ High purity & crystallinity ✓ Higher reaction rate ✓ Dense coating ✓ Stronger adhesion	Advantages: ✓ High-quality coatings ✓ Low-temperature process ✓ Short reaction time ✓ No specialized equipment	Advantages: ✓ Simplicity ✓ Cost-Effective ✓ Environmentally friendly ✓ No excess MOF waste
Disadvantages: ✗ Incomplete coverage ✗ Pinholes ✗ High energy use ✗ Long reaction times	Disadvantages: ✗ Requires conductive substrate ✗ Low material yield ✗ Prone to by-product formation	Disadvantages: ✗ Defects or cracks ✗ Small-scale production ✗ Time-consuming process ✗ Limited to paddlewheel MOFs

Table 2.2: Advanced vacuum-based technology advantages and disadvantages for ZIF-8 thin film synthesis

Chemical Vapor Deposition	Atomic Layer Deposition	RF Magnetron Sputtering
		
Advantages: ✓ High film quality ✓ Uniform layers ✓ Scalable process	Advantages: ✓ Precise composition control ✓ Tunable film thickness ✓ Excellent conformality	Advantages: ✓ Uniform coatings ✓ Excellent templating ✓ Efficient chemical conversion
Disadvantages: ✗ Expensive equipment ✗ Toxic precursors ✗ High operating temperature	Disadvantages: ✗ Slow deposition rate ✗ High system cost ✗ Limited precursor options	Disadvantages: ✗ Expensive equipment ✗ Scaling limitations ✗ Low deposition rate

2.1.3 Factors Affecting ZIF-8

2.1.3.1 2-Methylimidazole Influence

Kida et al., investigated the effect of the molar ratio of Hmim/Zn on ZIF-8 formation. In the first part of that study, they determined the impact of 2-mIm on the formation of ZIF-8 by keeping water and Zn amounts constant. They determined that a lower concentration of 2-mIm results in by-product formations such as zinc nitrate and zinc hydroxide with relatively low crystallinity of ZIF-8. Additionally, the average crystal size was determined to decline with the increase of Hmim/Zn molar ratios. In the second part of their work, they investigated the effect of the Hmim/Zn molar ratio on the ZIF-8 formation by modifying the water content. They determined that as the water content reduced, the formation of by-products also decreased. The study also suggested that the formation of highly crystalline ZIF-8 is achievable when an excess amount of 2-mIm was used, in contrast to an inorganic solvent such as DMF and methanol. Furthermore, they also investigated the influence of time interval on ZIF-8 formation and determined that in water, the formation of ZIF-8 is similar at all intervals, indicating faster synthesis in an aqueous medium [73].

2.1.3.2 Role of Different Solvents

Pan et al., reported ZIF-8 rapid synthesis in aqueous medium with excellent chemical and thermal stability. In this investigation, zinc nitrate hexahydrate was used as a Zn^{2+} source, 2-mIm as an organic linker, and DI water as a solvent with the molar ratio of 1: 70: 1238. As-synthesized ZIF-8 displayed a pure phase with peak broadening, indicating the formation of nanosized crystals (Figure 2.12 (a)). For thermal properties determination, ZIF-8 was heated at 200°C with no modification in the XRD pattern (Figure 2.12 (b)).

Heating at 300°C showed a significant change in the XRD spectra. The ZIF-8 structure was destroyed completely at 400°C and displayed only ZnO peaks in the spectra. The stability of ZIF-8 in chemicals was analyzed by heating it in the boiling solution of water and methanol for 5 days without any change in SEM morphology and XRD results (Figure 2.12 (c)) [74].

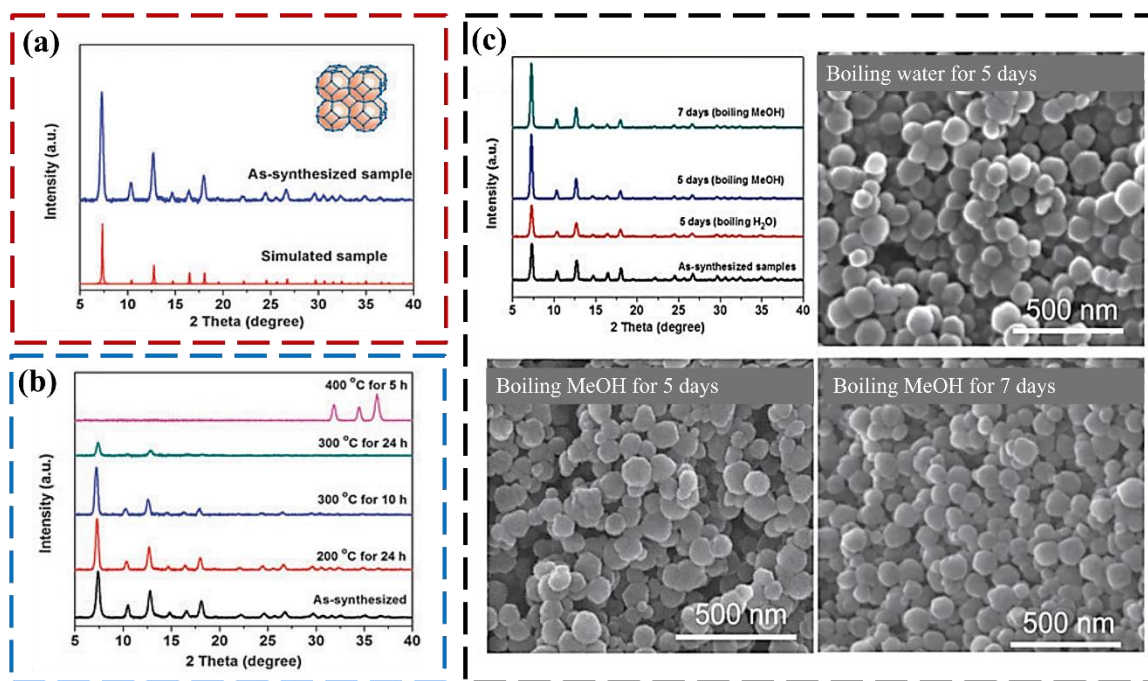


Figure 2.12: (a) XRD analysis of ZIF-8 thin film; (b) thermal stability analysis of ZIF-8 thin film; (c) chemical stability testing; and (d-e) influence of solvent on the morphology of ZIF-8 during chemical stability testing [74].

2.1.3.3 Zn Sources Influence

Jian et al., synthesized ZIF-8 in H₂O by using six different Zn salts under varying synthesis conditions at 25°C (zinc acetate, zinc sulfate, zinc nitrate, zinc chloride, zinc bromide, and zinc iodide). Their findings display that the selection of Zn salts has a great impact on the ZIF-8 morphology and crystallinity, as shown in Figure 2.13 (a-f). The molar ratio of Hmim/Zn $\geq$ 35 results in pure ZIF-8 formation; this behavior was observed in all

ZIF-8 samples synthesized with different zinc salts. Additionally, they also determined that particle size reduces as the concentration of Hmim increases, indicating the dependence of ZIF-8 on both zinc source and linker concentration (Figure 2.13 (g)). The effect of water content was also investigated, and their results show that using lower content results in the disappearance of unknown phases and increased nucleation rate (Figure 2.13 (h)) [75].

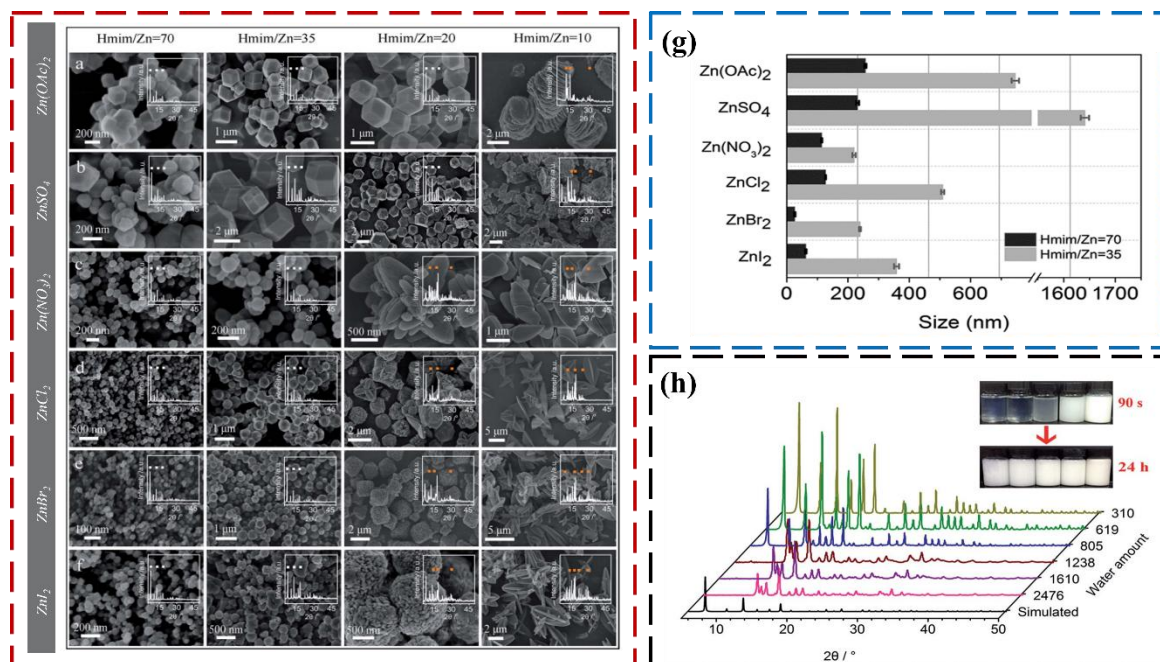


Figure 2.13: (a-f) Influence of metal salts on ZIF-8 morphology; (g) obtained average particle size using different metal precursors; and (h) XRD analysis under the varied water content at a constant molar ratio of Hmim/Zn [75].

2.1.3.4 Role of Time

Lee et al., examined the impact of time on ZIF-8 formation. In this work, ZIF-8 thin film was synthesized by dip coating, where the ZnO surface was modified into the MOF layer. ZIF-8 synthesis took place in three different solvents, i.e., DMF, methanol, and DI water at room temperature. During the time-dependent study, it was determined that ZIF-8 formation was faster in DI water in contrast to DMF and methanol, with a larger grain size because of the fast dissolution of ZnO and increased basicity of 2-mIm in DI water,

leading to fast nucleation, conversion, and ZIF-8 formation. In addition, the effect of mixed solvent was also studied where ZIF-8 formation was investigated in the solvent mixture of methanol and DI water, using different ratios (water/MeOH= 1/3, 1/1, and 3/1) for 12 hrs at 30°C. The most significant results were obtained at the 3/1 ratio with fast conversion of ZnO into ZIF-8 [76].

2.1.3.5 Role of Temperature

Tsai et al., analyzed the influence of temperature (-15 to 60 °C) on ZIF-8 formation in a methanol solution. They reported that the average particle size and minimum particle size, calculated from TEM and SEM, dropped with the temperature increase. In that research, they conclude that the nucleation of ZIF-8 relies on the synthesis temperature. The lower temperature displayed a slower nucleation rate and a bigger particle size, and vice versa [77].

2.1.3.6 Role of pH

Lai et al., investigated the impact of time, molar ratio, and pH on ZIF-8 formation in methanol solution. Under the influence of time (5, 60, and 1440 minutes), they observed that the plane intensity of (110) increased with time, indicating ZIF-8 formation with a stable rhombic dodecahedron shape with increased crystallinity because of the Ostwald ripening growth mechanism. Increased molar ratio of methanol (Zn^{2+} : Hmim: MeOH = 1:7.9:86.7 to 1:7.9:1002) resulted in a decrease of crystallinity. The lower content of methanol resulted in the highest crystallinity because of the presence of higher concentrations of Zn^{2+} and deprotonated meIm⁻ in the solution. The influence of pH on ZIF-8 synthesis was also investigated, and the results demonstrate pH of 7.4 displayed higher crystallinity than a pH of 8.2. These results differ from previously reported work, most

likely due to turbulence created during stirring, resulting in particle aggregation and inter-growth. The lower crystallinity takes place because of the strong deprotonation of NaCOOH. At the pH of 6.8 in the presence of HCl, ligand deprotonation becomes limited with hindrance in growth due to the competition of protons in HCl, and Zn^{2+} for negatively charged meIm^- ion [78].

2.2 Bismuth-Based Metal-Organic Framework

To date, there are only four types of permanent microporosity Bi-based MOFs that have been successfully synthesized within the last five years, which include CAU-7, NOTT-220, CAU-17, and CAU-35. Among them, CAU-17 {CAU = Christian Albrecht University} is the only one that can be synthesized cheaply presently by using trimesic acid (H_3BTC) {also known as 1,3,5-benzenetricarboxylic acid (BTC)}. Additionally, it has a more complicated structure in contrast to other Bi-based MOFs. In terms of its topology, so far, 54 unique nodes with 135 edges have been reported. Its structure consists of linear chains of infinite Bi-oxo rods with edge-sharing helical BiO_9 polyhedra. The crystal structure of CAU-17 is displayed in Figure 2.14 below [79], [80].

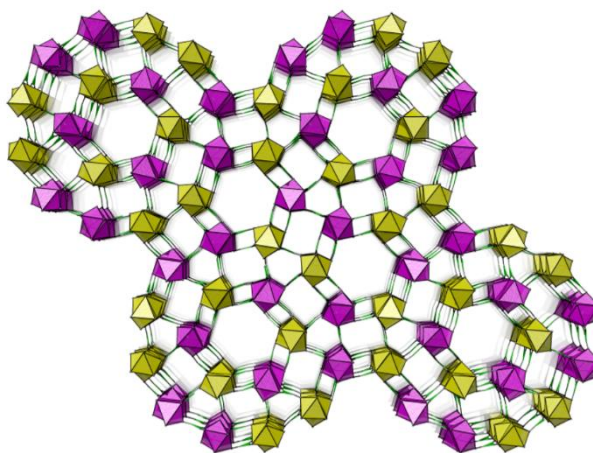


Figure 2.14: Crystal structure of CAU-17 [81].

In CAU-17, many framework species take part in asymmetric units, i.e., 9 Bi^{3+} cations, 9 BTC^{3-} anions, and 9 coordination water units, where each cations of the nodes create a bond with the cations of the metal node and the anions of the linker. 9 metal nodes connect with 8 O anions of the linker and 1 O anion of coordinated water molecules. Each Bi-cations shares 4 O anions with adjacent cations, forming helical/spiral rods. These rods

develop joints with BTC^{3-} anions, resulting intricate 3D framework of CAU-17 [81], [82]. In short, its crystal structure consists of left- and right helical/spiral edge-sharing BiO_9 polyhedra linked with BTC^{3-} ions (1,3,5-benzenetricarboxylate or trimesate), forming channels of hexagonal, rectangular, and triangular [80].

2.2.1 Bismuth MOFs Structure

2.2.1.1 Carboxylate Ligands – Linker Chemistry

This type of ligand is classified into three groups: di-, tri-, and tetra-topic carboxylic ligands. The unique aspect of carboxylate ligands is the ease of their synthesis and commercial availability. For the formation of Bi-MOFs, there are two widely utilized ligands, i.e., di-topic carboxylic ligands and pyridine dicarboxylic acid. Additionally, the heterocyclic di-carboxylate ligand was also used for the design and construction of it [83].

The versatility of tri-topic carboxylate ligands was also explored for Bi-MOFs synthesis. In this regard, 1,3,5-tricarboxylic acid, H_3BTC , is widely employed. H_3BTC is known as trimesic acid (TMA) and is sometimes designated as BTC in the literature. Its basic structure is shown in Figure 2.15. H_3BTC consists of three carboxylic acid groups that allow it to interact with metal ions in multiple coordination modes that possess a high surface area, porous nature, chemical stability, and enhanced properties such as thermal and electrical properties [84], [85]. Bi-MOF synthesis by using trimesic acid is described as BTC-based MOFs, for instance, CAU-17. Other types of ligands in this category include: 1,3,5- benzenetrisbenzoic acid, which led to the formation of CAU-7. The modified form of CAU-7 is CAU-35 which consists of a similar structure crystal, however, synthesized using triazine-2,4,6-triyltribenzoic acid.

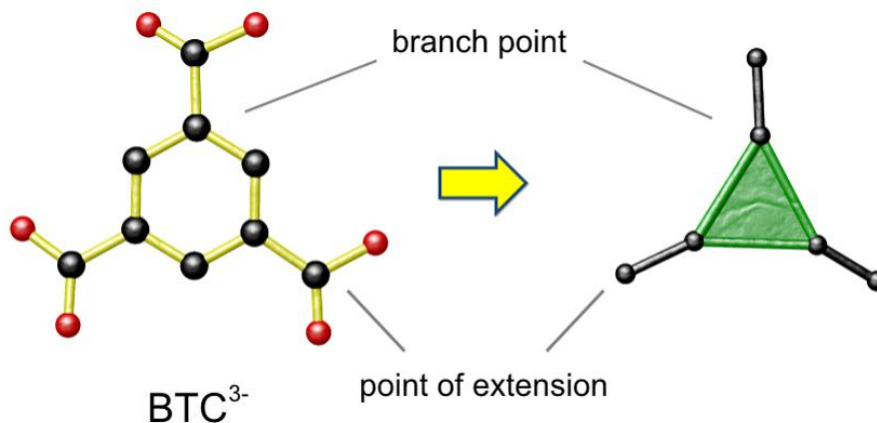


Figure 2.15: Deconstruction of the organic linker of CAU-17, where the point of extension indicating carbon atoms and benzene ring represents the branch point as nodes in the BTC^{3-} linker [81].

The unique characteristics of using tetra-carboxylate ligands are rich coordination modes and a large steric hindrance space, useful for effectively avoiding framework interpenetration. The synthesis of NOTT-220 is based on H_4BPTC , resulting in a non-interpenetrated framework [83]

2.2.1.2 Chemistry of Bi cations

Bismuth's electronic configuration is $[\text{Xe}] 4f^{14}5d^{10}6s^2p^3$ and classified under group 15 of the periodic table. In terms of its oxidation states, it exists as 0, +1, +2, +3, and +5 due to its outer valence electrons 6s and 6p, where usually three 6p electrons play a major role in bond formation during coordination [86], [87], [88]. Among them, two major states are +3 and +5, in which +3 represents the most frequent occurrence and stable form [89]. The coordination number of Bi^{+3} exists between 3 to 10 and shows irregular coordination geometry [90]. The unique feature of this element is its lower toxicity and earth abundance (64th most abundant element) [82]. Additionally, Bi and its compounds are regarded as safe and non-toxic for biomedical applications.

A typical choice of Bi source for Bi-MOF synthesis is bismuth (III) nitrate pentahydrate $[\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}]$ due to its cost-effectiveness, relatively lower toxicity, and commercial availability [91], [92], [93]. In the context of green chemistry, the use of metal nitrate salts is not desirable instead, metal salt precursors based on oxide, hydroxide, carbonate, sulfate, and acetates are recommended [16]. Bismuth oxide could be a potentially desirable option for the synthesis of Bi-MOFs, such as Bi_2O_3 , comprised of six main polymorphs, i.e., α , β , γ , δ , ω , and ϵ . Of these phases, only α -monoclinic and δ -face-centered cubic phases are stable at low and high temperatures, respectively [94], [95], [96].

By the Hard-Soft Acid-Base Principle (HSAB), Bi^{+3} is a borderline Lewis acid. It exhibits higher affinity towards negatively charged multidentate ligands consisting of O- and N-donor atoms, due to the polycarboxylate anions being considered a preferred ligand for constructing Bi-MOFs because of strong chelating effects [97]. However, there are certain obstacles to the use of Bi^{+3} ions for the Bi-MOF synthesis, such as large ion radius, low electronegativity, strong polarization, and easy hydrolysis, resulting in limited research on it [98].

2.2.2 Synthesis of CAU-17

2.2.2.1 Solvothermal Method

The solvothermal method is a widely utilized method for synthesizing CAU-17. The typical synthesis process consists of a reaction mixture of the linker, metal salt, and solvent. The resulting mixture was then sealed in an autoclave and subjected to heating at a specific temperature and duration. The resulting product was then thoroughly rinsed with DI water and dried under a vacuum overnight [99]. The reported solvent for the synthesis of CAU-17 includes methanol [100], DMF/methanol [101], and methanol/deionized water [102]

Zhao et al., employed the solvothermal method for CAU-17 synthesis, wherein they prepared two solutions separately, one solution consisting of H₃BTC in methanol and the other one Bi(NO₃)₃·5H₂O in DMF. Both solutions were then subjected to 20 mins of ultrasonication separately and subsequently combined by transferring the solution to ultrasonication, where it was heated at 120 °C for 1 day. The solid powder was then subjected to centrifugation, washed with MeOH and deionized water three times, and subsequently dried at 60 °C [103].

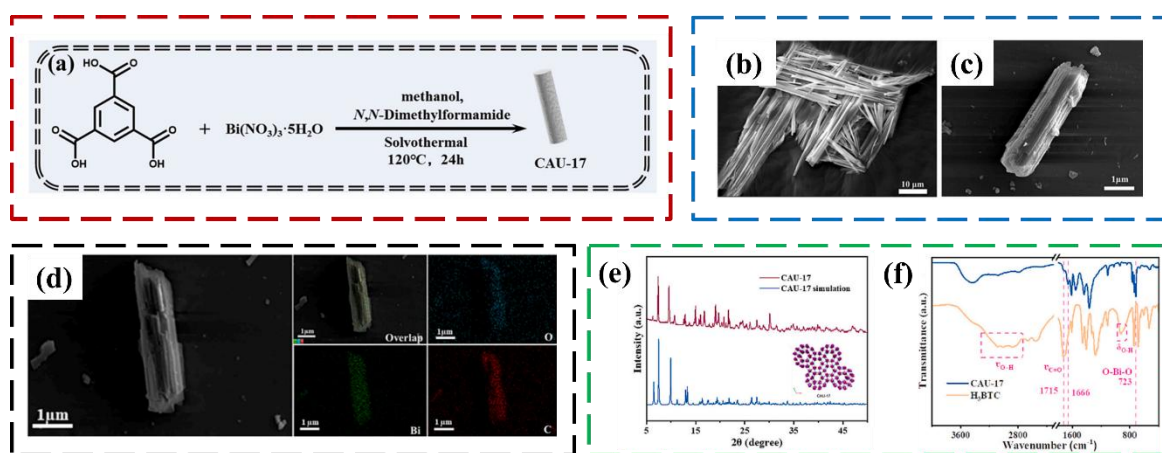


Figure 2.16: (a) Chemical reaction for CAU-17 synthesis; (b-c) FESEM analysis; (d) EDX mapping; (e) XRD pattern; and (f) FTIR results of CAU-17 [103].

The reaction scheme for the formation of CAU-17 is depicted in Figure 2.16 (a). The SEM results confirmed the nanorod morphology of CAU-17 with a uniform distribution of bismuth, carbon, and oxygen (Figure 2.16 (b-d)). The XRD results of the as-prepared sample highly correspond with the simulated results (Figure 2.16 (e)). The CAU-17 FT-IR spectra showed the existence of new characteristics belonging to O-Bi-O bonding and the disappearance of H₃BTC peaks at 3400 to 2200 cm⁻¹ (Figure 2.16 (f)) [103].

2.2.2.2 Ultrasonic Method

Ultrasonic synthesis is based on sound waves (20 kHz to 15 MHz) that induce chemical reactions for the synthesis of materials. In this technique, the direct interaction of chemical species and sound waves does not take place directly rather than through acoustic cavitation that consists of three steps: bubble formation, its growth, and collapse. During the collapsing stage, intense heat is generated, resulting in sufficient energy for the completion of the reaction at room temperature [104], [105].

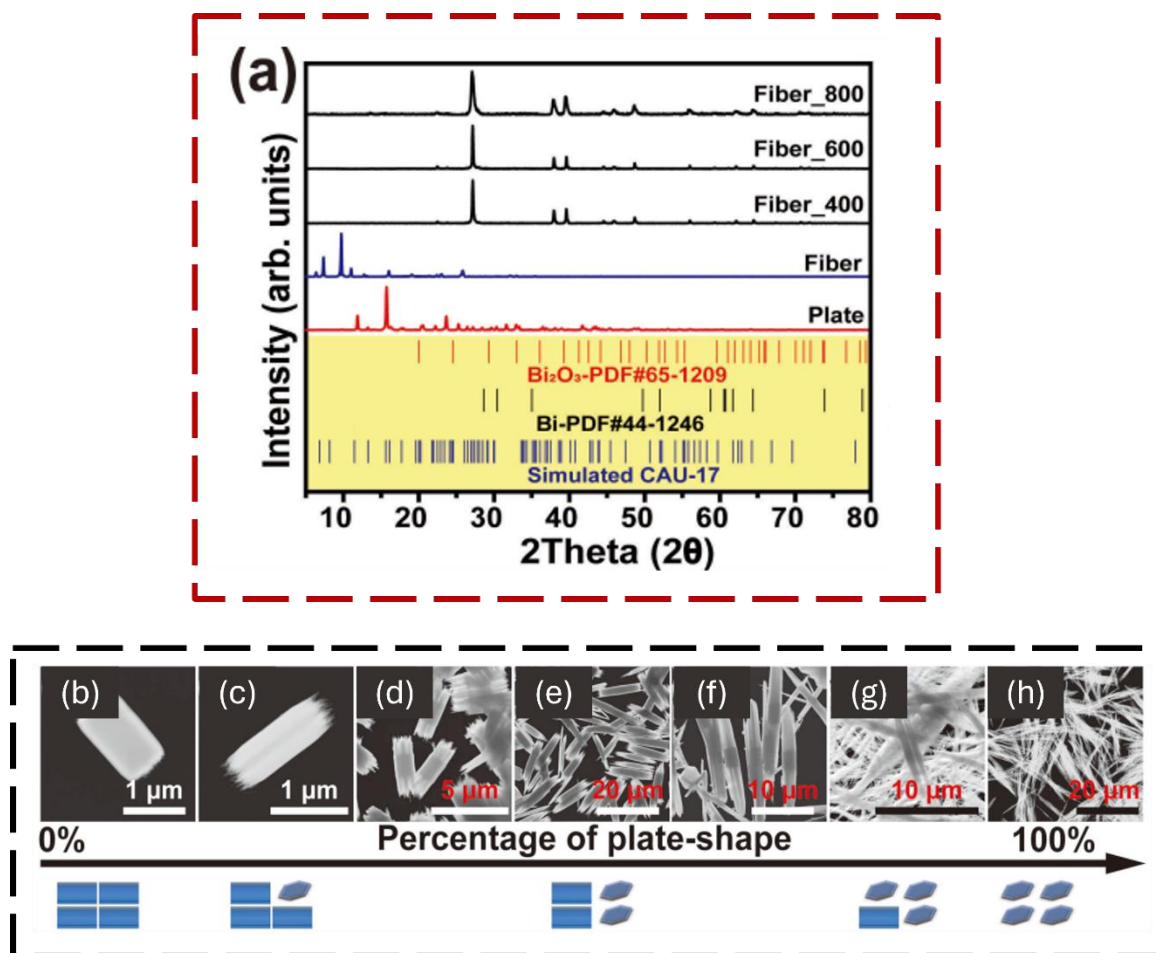


Figure 2.17: XRD analysis of CAU-17 under the influence of synthesis condition (b) Schematic diagram showing the impact of increased content of surfactant on CAU-17 formation; and (c-i) representing FESEM images as the amount of plate content increases [106].

One innovative approach to the synthesis of CAU-17 at room temperature is through ultrasonics reported by Ying et al. In this technique, firstly, the mother mixture of H_3BTC , $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$, and CTAB was prepared. Afterward, MeOH solution was inserted rapidly into the prepared solution and subjected to ultrasound treatment for 40 minutes, resulting transparent solution with the formation of white precipitates, which were later collected by centrifugation and subjected to post-cleaning with MeOH, and subjected to drying at 60°C for 3 hrs.

In this investigation, they obtained the hexagonal and plate-like morphology of CAU-17. The hexagonal-like shape of CAU-17 was achieved through the addition of CTAB, strongly corresponding with the reported diffraction pattern without any impurity peaks (Figure 2.17 (a)). The plate-like morphology of CAU-17 was obtained without the addition of CTAB, displaying distinct diffraction patterns and indicating sensitivity toward the synthesis parameters. Additionally, it is also found that modifying reagent concentration (linker, metal ions, and surfactant) significantly influences the particle size as well as the nucleation and growth mechanism. Adding a minor concentration of CTAB of 25 mg changed the plate-like morphology into hexagonal. Further increasing the concentration to 200 mg resulted in a completely new shape of the nanowire with a diffraction pattern consistent with the reported one Figure 2.17 (b-h)) [106].

2.2.2.3 Green Synthesis

To reduce environmental concerns related to the synthesis of CAU-17, researchers nowadays are working to develop a sustainable process for its synthesis. Adhering to green principles, Yang et al. reported a novel technique for synthesizing CAU-17 without using toxic solvents and harsh conditions such as high temperatures. In that investigation, they

used an amphiphilic molecule, i.e., cetyltrimethylammonium bromide (CTAB), for CAU-17 at 25°C using H₂O as a solvent. The reaction solution consists of H₃BTC, Bi(NO₃)₃·5H₂O, and CTAB in H₂O, subjected to ultrasonication for 10 mins. The obtained solid materials were then cleaned with MeOH. The material activation was performed in the vacuum-drying oven at 110 °C for an overnight period [107].

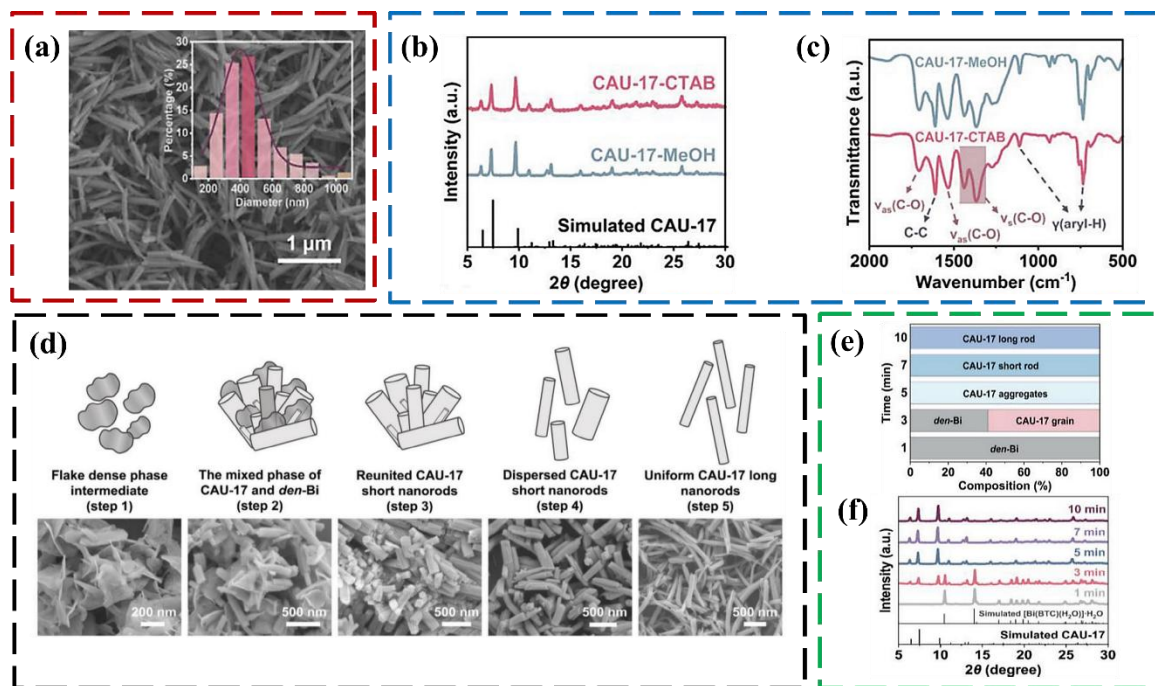


Figure 2.18: (a) SEM analysis of CAU-17 with the addition of CTAB; (b) XRD analysis of CAU-17; (c) FTIR results of CAU-17; (d) Schematic diagram showing the formation of secondary phases in CAU-17 synthesis at different reaction times along with corresponding SEM images (e) formation of different phase during synthesis of CAU-17. (f) XRD patterns of CAU-17 at different reaction times [107].

The SEM analysis revealed the nanorod shape of CAU-17 (Figure 2.18 (a)), in contrast to the reported morphology, it was noticed that the size of the nanorod was smaller. The XRD results confirm the successful synthesis of CAU-17 using CTAB; those diffraction patterns highly match the reported results (Figure 2.18 (b)). The FT-IR results displayed the symmetric and asymmetric stretching vibrational modes of carboxylate groups in CAU-17 spectra (Figure 2.18 (c)). During the CAU-17 formation in CTAB, the secondary phase den-

Bi also took place. SEM results revealed the transformation of den-Bi from sheet-like morphology to nanorods (Figure 2.18 (d)). It was determined that increasing synthesis time results in its disappearance and results in CAU-17 formation only. The XRD analysis also confirmed this behavior as shown in Figure 2.18 (e-f) [107].

2.2.2.4 Microwave Method

This technique is based on electromagnetic waves ranging from 300 MHz to 300 GHz. In this synthesis approach, two basic mechanisms are involved: dipole rotation and ionic conduction that transfer energy to the substance being heated directly without heating the container [108], [109], [110]. Microwave synthesis is a unique approach to the synthesis of CAU-17, initially introduced by Inge et al. in 2016. In this approach, a solution of H₃BTC and Bi(NO₃)₃·5H₂O was prepared in methanol solution in a sealed glass vial. The solution was then heated at a temperature of 120 °C for 20 mins inside the microwave with an rpm of 600. The resulting single crystal of CAU-17 was then obtained by filtration [81].

2.2.3 Factors Affecting CAU-17

Generally, the synthesis of CAU-17 and other Bi-based MOFs is highly dependent on synthesis conditions such as the nature of the solvent, reaction duration, and synthesis temperature. Previously, it has been reported that CAU-17 forms unknown impurities at lower temperatures (<120°C) when synthesized at relatively shorter reaction intervals [81], [111].

2.2.3.1 Effect of Solvent

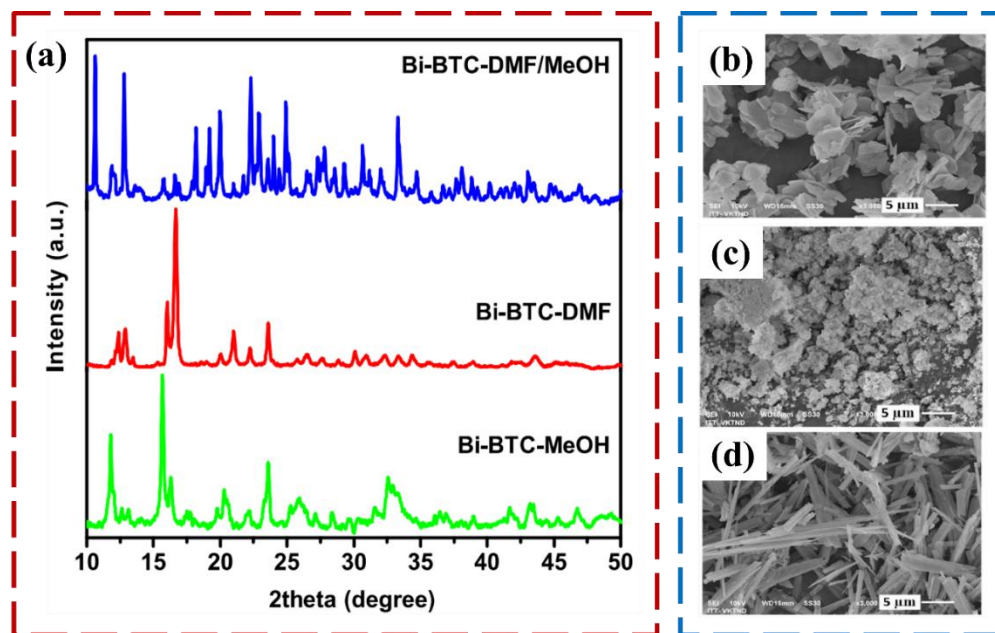


Figure 2.19: (a) XRD analysis of Bi-BTC formation under different solvents; (b-d) SEM analysis of prepared Bi-BTC in MeOH, DMF, and DMF/MeOH, respectively [112].

Nguyen et al., studied the impact of solvent on the structure and morphology of CAU-17. In that work, CAU-17 was fabricated via a traditional solvothermal route using different solvents, i.e., methanol (MeOH), dimethylformamide (DMF), and the mixture of DMF/MeOH. They determined that the solvent choice has a huge influence on the CAU-17 structure. The use of MeOH and DMF for the synthesis of CAU-17 resulted in different diffraction patterns (Figure 2.19 (a)) in comparison to the reported one, indicating the formation of the bismuth carboxylate $\text{Bi}_2(\text{O})(\text{OH})(\text{HBTC})(\text{NO}_3)$ compound. CAU-17 synthesizing using the mixture of DMF/MeOH resembles Bi-based MOF $[\text{Bi}(\text{BTC})(\text{H}_2\text{O})]$ (CAU-17). SEM analysis of CAU-17 in DMF results in an irregular block structure, indicating a fast growth rate and promoting unidirectional growth of one face (Figure 2.19 (b)). Using polar protic solvents like MeOH results in the decrease of nucleation rate and prevents anisotropic growth, forming plate-like morphologies (Figure 2.19 (c)). The

combination of both polar aprotic and protic solvents results in the formation of rod-like morphologies (Figure 2.19 (d)). Such morphologies were achieved due to the role of DMF's increased growth rate and MeOH in inhibiting anisotropic growth [112].

2.2.3.2 Effect of Temperature

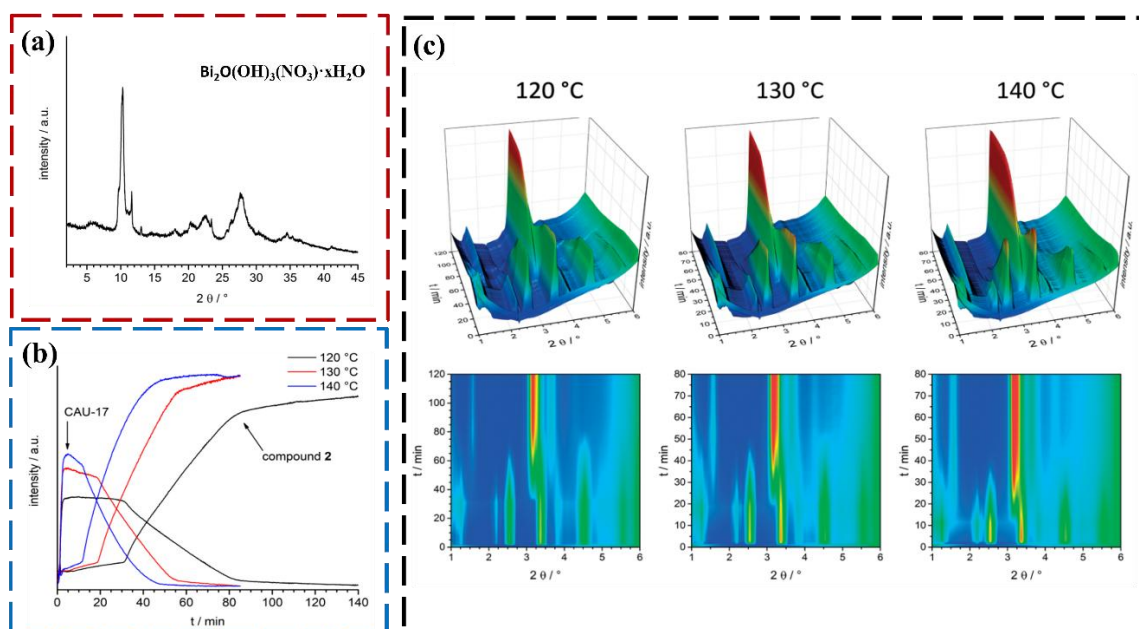


Figure 2.20: (a) XRD analysis of secondary phase; (b) influence of time on the formation of different secondary phases in CAU-17; and (c) In-situ XRD analysis of CAU-17 [80].

Köppen et al., investigated the formation of CAU-17 via in-situ PXRD, where they determined the formation of an unknown impurity (i.e., $\text{Bi}_2\text{O}(\text{OH})_3(\text{NO}_3) \cdot x\text{H}_2\text{O}$) after a short reaction interval. In this investigation mother solution of H_3BTC and $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ in the methanol solution in a glass vial and heated in a microwave oven for 20 mins while stirring the solution at 600 rpm. The in-situ PXRD investigation takes place in a homemade SynRAC setup. It was observed in PXRD that in a few minutes, the formation of CAU-17 occurs before reaching the intended temperature, Figure 2.20 (b). An unknown dense phase formation takes place after the short reaction interval. Such impurities corresponding to $\text{Bi}_2\text{O}(\text{OH})_3(\text{NO}_3) \cdot x\text{H}_2\text{O}$ are denoted as compound (2); the diffraction pattern is given in

Figure 2.20 (a). Additionally, it was determined that increased temperature results in the fast formation of compound (2), appearing after 31 minutes at 120°C, 18 minutes at 130°C, and 11 minutes at 140°C, as shown in Figure 2.20 (c), indicating the sensitivity of CAU-17 towards synthesis parameters. Additionally, it is also determined that shorter reaction intervals and temperatures less than 120 °C result in the formation of an unknown. The pure phase of CAU-17 was achieved at the optimal conditions, i.e., 120°C and 20 minutes [80].

2.2.4 Factor Affecting CAU-17 Morphology

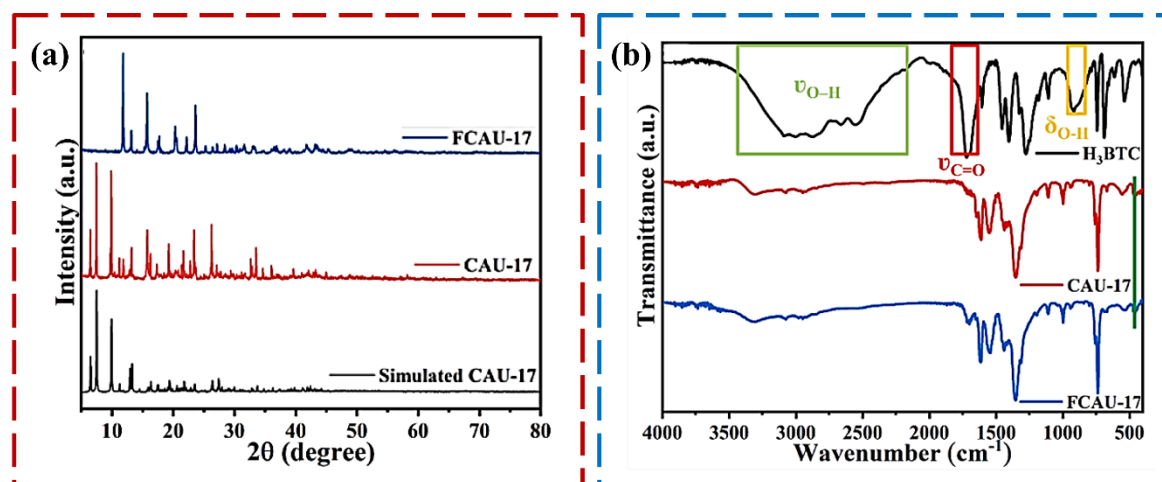


Figure 2.21: CAU-17 and FCAU-17 (a) XRD analysis; (b) FT-IR analysis [113].

Dong et al., reported the influence of synthesis techniques on CAU-17 morphology. In that work, they employed a conventional solvothermal technique and sonication approach, resulting in microrods and microflakes-like morphology, respectively. The obtained diffraction pattern of microrods highly resembles the reported CAU-17 pattern, however, microflakes displayed a unique pattern (Figure 2.21 (a)). To further confirm whether this material belongs to CAU-17 or not, FTIR analysis was performed (Figure 2.21 (b)), whose results indicate the presence of a similar function in CAU-17, emphasizing that the microflakes-like morphology belongs to CAU-17 [113].

2.2.4.1 Agitation-Free Method

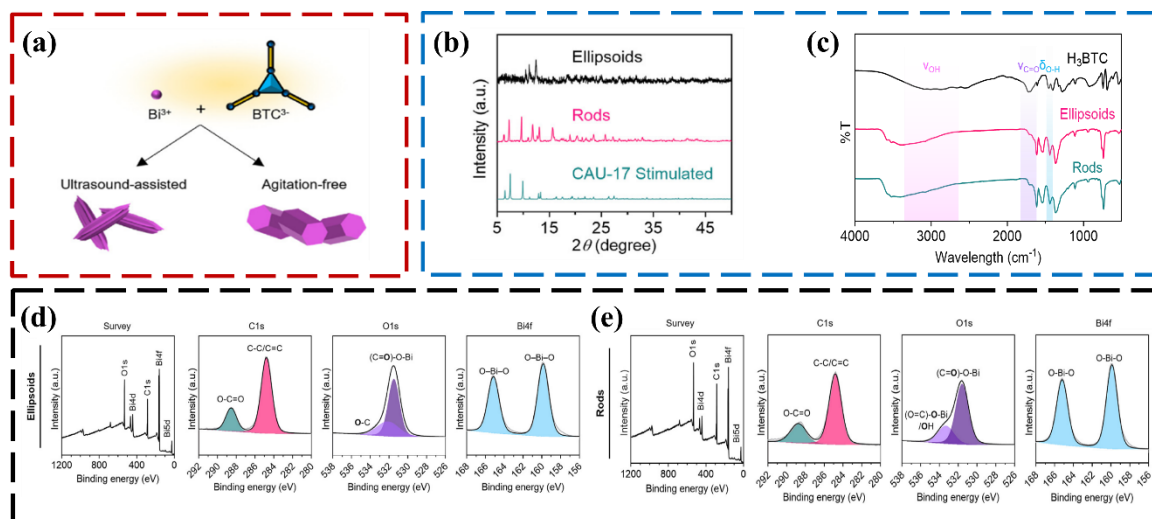


Figure 2.22: (a) Schematic diagram of forming Ellipsoids and Rods morphology of CAU-17; (b) XRD results; (c) FT-IR analysis; and (d-e) XPS analysis of Ellipsoids and Rods [114].

Huang et al., reported a new approach for the CAU-17 synthesis through an agitation-free method for promoting the rod-like morphology. In this process reaction takes place in the mixture of H_3BTC and $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ in the methanol solution for 30 mins. Two interesting morphologies were observed during this synthesis approach. If no agitation is applied, the process results in the formation of rod-like morphology; otherwise results in almond-flakes-like morphology. The diffraction pattern of almond-flakes-like morphology displayed a unique pattern than the reported CAU-17 (Figure 2.22 (b)). FTIR and XPS results revealed that this unique morphology consists of similar functional groups and element composition as previously reported, confirming the successful synthesis of CAU-17 (Figure 2.22 (c-e)) [114].

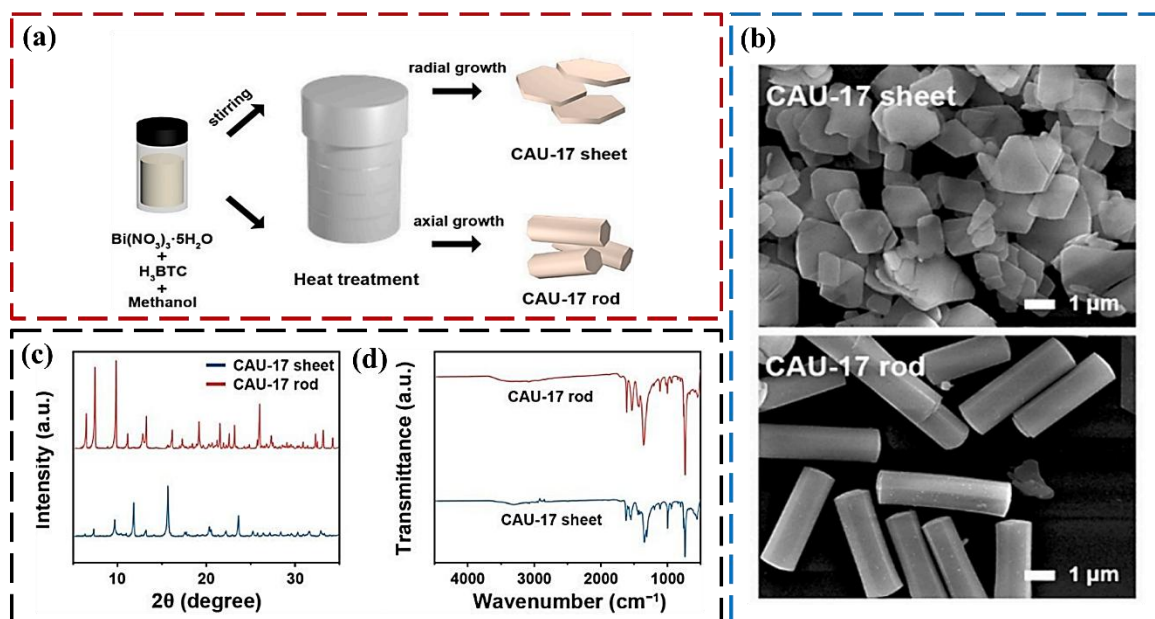


Figure 2.23: (a) Schematic diagram of synthesizing CAU-17 sheets and rods; (b) FESEM results (c) XRD patterns; and (d) FT-IR analysis [115].

Lee et al., synthesized rod and sheet-like morphology of CAU-17 using the conventional solvothermal approach under the influence of stirring time (Figure 2.23 (a)). The synthesis of rod-like morphology took place without stirring, promoting the axial growth of CAU-17. Whereas sheet-like morphology occurs when the reaction solution is subjected to stirring for 20 minutes until the sediment forms, resulting in radial growth due to fast nucleation of CAU-17 precursor in MeOH solution. Both morphologies displayed similar crystal structures and functional groups during XRD and FTIR analysis (Figure 2.23 (b-d)) [115].

2.2.5 Secondary Phases in CAU-17

In hydrothermal synthesis, the interaction of trimesic acid (H_3BTC) with $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ results in the formation of a phase-pure product, i.e., $\text{Bi}_2(\text{O})(\text{OH})(\text{HBTC})(\text{NO}_3)$ (**compound 1**), when the molar ratio of $\text{Bi}^{3+}:\text{H}_3\text{BTC}$ is 2:1 without the addition of nitric acid (HNO_3). Decreasing the molar ratio from 2:1 to 0.5:1

results in forming a secondary side product, i.e., $\text{Bi}_6\text{O}_5(\text{BTC})_2(\text{HBTC})$, as shown in Figure 2.34. The addition of 5 moles of HNO_3 in the solution of $\text{Bi}^{3+}:\text{H}_3\text{BTC}$ prevents the formation of side products at all molar ratios except 0.5:1, where a complete amorphous phase forms. High throughput analysis indicates $\text{Bi}^{3+}:\text{H}_3\text{BTC}$ molar ratio greater than 2:1 results in the formation of a structure that consists of the Bi-O layer, i.e., **compound 1**. Decreasing the 2:1 molar ratio results in $\text{Bi}_6\text{O}_5(\text{BTC})_2(\text{HBTC})$, forming the chains of BiO_x polyhedral [116].

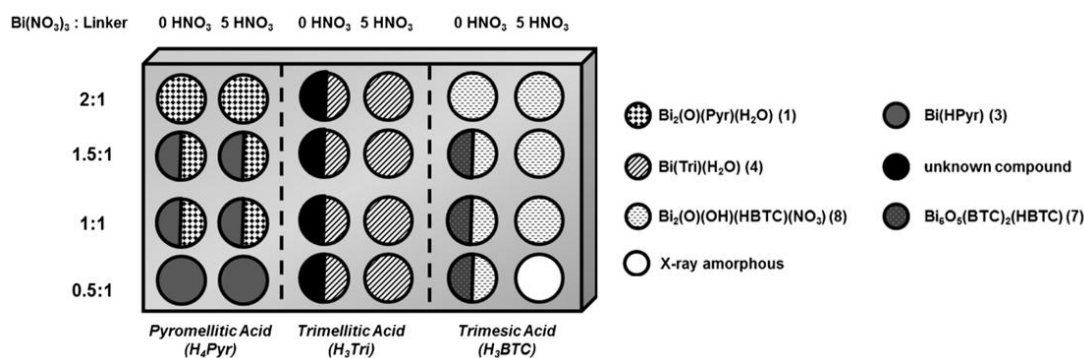


Figure 2.24: Formation of secondary phases under different metal ion and linker ratios [116].

$[\text{Bi}(\text{BTC})(\text{H}_2\text{O})] \cdot \text{H}_2\text{O}$ consists of a monoclinic structure, having a space group of $\text{P}2_1/\text{c}$, where the Bi^{3+} ion has an eightfold coordination. Its structure is composed of 1 crystallographically independent Bi^{3+} ion, 1 BTC^{3-} ion, 1 coordinated, and 1 uncoordinated H_2O molecule. The formation of Bi_2O_{14} dimers takes place when two BiO_8 polyhedra share an edge, where 12 O atoms come from carboxylate groups and 2 O atoms from coordinated H_2O molecules. A three-dimensional network forms when dimers connect with the trimesate ion's aromatic ring along the b-axis. The coordinated and uncoordinated H_2O molecule forms hydrogen bonding with carboxylate groups [116].

Bi₆O₅(BTC)₂(HBTC) consists of a similar crystal structure and space group to **[Bi(BTC)(H₂O)]·H₂O**. Its structure is made of 6 crystallographically independent Bi³⁺ ions, 5 O²⁻ ions, and 2 fully deprotonated and 1 single protonated BTC³⁻ ions. The coordination number of Bi³⁺ ions is between 7 and 9, where it is surrounded by O atoms from carboxylate groups and O²⁻ ions forming Bi₆O₃₁ units along the a-axis. Pseudo-hexagonal arrangement takes place when it connects with trimesate ions of aromatic rings [116].

CHAPTER 3

EXPERIMENTAL PROCEDURE

Chapter 3

Experimental Procedure

3.1 Chemicals and Materials

All chemicals were used as they were, without any further purification.

- 99.99% pure zinc sputter target
- 2-methylimidazole (2-mIm; 99.99%)
- Ethyl alcohol (absolute; $\geq 99.8\%$)
- 99.99% pure bismuth sputter target
- 1,3,5-benzenetricarboxylic acid (BTC; 98.0 % purity)
- N, N-dimethylformamide (DMF; 99.5% purity)
- Hydrochloric acid (0.01M)

3.2 ZIF-8 Thin Film Synthesis

3.2.1 ZnO Thin Film Deposition

The synthesis of ZnO thin film in this work took place by DC reactive magnetron sputtering on different substrates. Accordingly, a chamber was evacuated to a pressure of 8.69×10^{-5} torr for the synthesis of ZnO thin film. Then, the chamber was supplied with an inert gas, Ar gas (99.9% purity), and oxygen (99.9% purity), wherein the pressure of the sputtering chamber was raised to 5.28×10^{-3} Torr. Ar and O₂ were supplied into the chamber at a flow rate of 35:35 sccm. The sputtering power was set to 100W, and deposition was

carried out for 1 hour. While sputtering, the substrate was rotated to achieve homogeneous deposition. The complete deposition parameters are mentioned in Table 3.1. The substrate was acid-washed before depositing the metal oxide thin film, e.g., acetone and/or ethanol for 10 minutes. After the acid treatment, the substrate was rinsed with DI water and dried on the hot plate. The synthesis scheme of ZnO thin film is illustrated in Figure 3.1 (Steps 1-2).

Table 3.1: ZnO thin film synthesis parameters deposited by DC reactive magnetron sputtering.

Parameters	Conditions
Working pressure	5.28×10^{-3} torr
DC Power	100 W
Duration	1 hr
Ar/O ₂ flow rate	35/35 sccm
Substrate Temperature	25 °C
Target to Substate Distance	18 cm
Rotation	1.55 rpm

3.2.2 ZnO Conversion into ZIF-8 Thin Film

ZIF-8 thin film synthesis on ZnO-coated substrate via in situ approach as shown in Figure 3.1 (Steps 3 and 4). The reaction solution was prepared by dissolving 100 mg of 2-mIm in 5 mL of deionized water and subjected to sonication until the linker completely dissolved in the solution. As-deposited ZnO thin film was immersed in the reaction mixture and heated at 25°C, 50°C, 75°C, and 100°C for 24 hours. The synthesized ZIF-8@ZnO substrate was then washed with ethanol and dried in the oven until the solvent was completely evaporated.

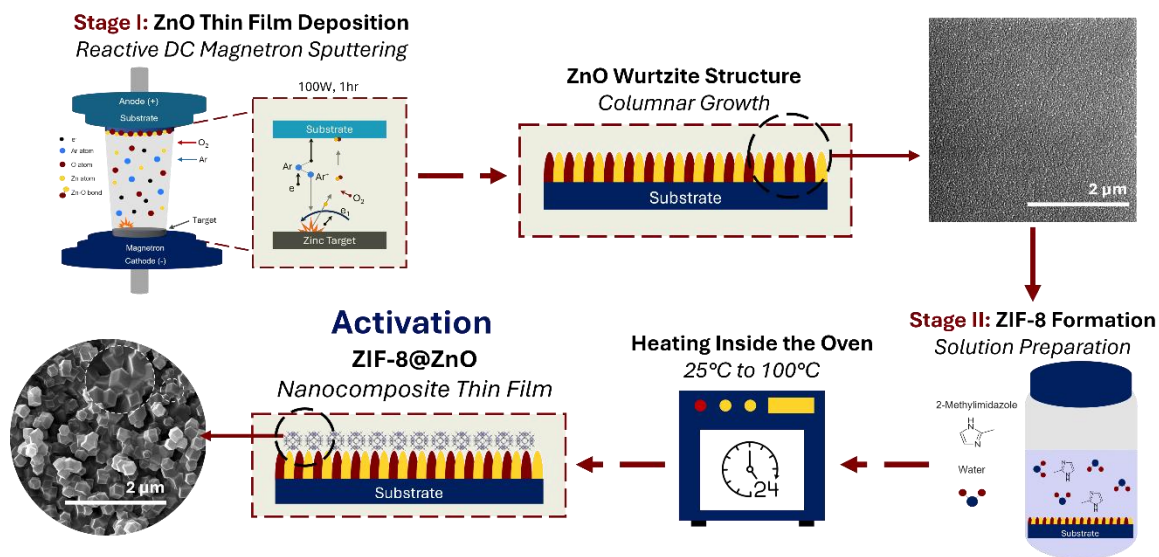


Figure 3.1: Synthesis scheme of ZIF-8 thin films.

3.3 CAU-17 Thin Film Synthesis

3.3.1 Bi₂O₃ Thin Film Formation

The Bi₂O₃ films were synthesized on different substrates. Before deposition, the substrates were ultrasonicated in acetone, ethanol, and DI water separately for 10 mins and then dried on the hotplate (100 ± 5°C). Bismuth targets of 99.99% purity were sputtered by DC magnetron sputtering (NSC-4000 sputter coater) by using Ar and O₂ as sputtering gases, respectively. After cleaning, the substrates were mounted on the substrate holder, and the deposition chamber was evacuated to a base pressure of 4.14x10⁻⁵ torr. Bi₂O₃ films with a cathode power of 50 W were deposited on different substrate for 15 mins under an Ar:O₂ flow rate (sccm) of 35:35 at room temperature. During synthesis, the substrate table was rotated to achieve uniform thickness. The complete synthesis steps and deposition conditions of Bi₂O₃ thin films are shown in Figure 3.2 and Table 3.2, respectively.

Table 3.2: Bi_2O_3 thin film synthesis parameters deposited by reactive magnetron sputtering.

Parameters	Conditions
Working pressure	4.14×10^{-5}
DC Power	50 W
Duration	15 mins
Ar/ O_2 flow rate	35/35 sccm
Substrate Temperature	25 °C
Target to Substrate Distance	18 cm
Rotation	1.55 rpm

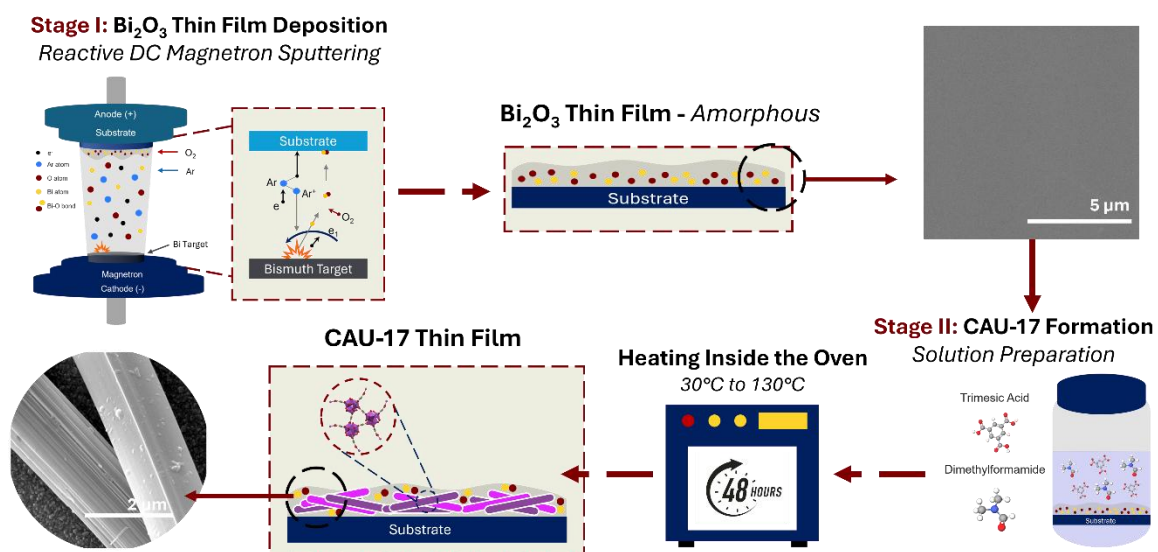


Figure 3.2: Synthesis scheme of CAU-17 thin films.

3.3.2 Bi₂O₃ Conversion into CAU-17 Thin Film

The Bi₂O₃ coated substrate was then immersed in a reaction medium that consisted of dimethylformamide (DMF) as a solvent (5 mL), a 3,5- benzenetricarboxylic acid (BTC) as an organic linker (100 mg), and 0.01M HCl as a modulator (1 mL). The reaction was carried out at different temperature ranges (30°, 55°, 80°, 105°, & 130°C) for 2 days, and then the synthesized CAU-17 thin film was dried in ethanol solution inside the oven (100°C) until it completely vaporized. Steps 3 and 4 in Figure 3.2 belong to the CAU-17 formation.

3.4 MOFs Thin Films Characterization

3.4.1 X-Ray Diffraction

X-ray diffraction (XRD) analysis was conducted on a Rigaku Mini X-ray diffractometer operating at a tube voltage of 30 kV and current of 15 mA with a Cu K α wavelength of 1.54 Å. The 2 θ range was set to 5 to 65° with a scan rate of 1°/min.

3.4.2 Field Emission Scanning Electron Microscopy

The surface morphology of thin films was characterized by Field Emission Scanning Electron Microscopy (FESEM, Tescan Lyra 3) operating at 20 kV. The sputtering coater machine was used to deposit a gold layer on the surface of thin films, operating at a voltage of 20V with a set time of 45 seconds.

3.4.3 Raman spectroscopy

To determine the chemical bonding characteristics of the MOF thin film, Raman spectroscopy was performed using a DXR Raman microscope (Thermo Fisher, Wisconsin, USA). The analysis was performed using a 10X confocal microscope objective equipped with 1200 lines/mm diffraction. The system was operated at a laser power and wavelength

of 3 mW and 455 nm, respectively. Raman signals were acquired in 5 accumulations of 50 sec from 400 to 2000 cm^{-1} .

3.4.4 Fourier-Transform Infrared Spectroscopy

The FT-IR analysis was performed on a PerkinElmer Spectrum 3 to determine the characteristic functional groups present in the MOF thin film. The analysis was recorded between the wavelengths of 400 to 4000 cm^{-1} with a spectral resolution of 4 cm^{-1} .

3.4.5 X-Ray Photoelectron Spectroscopy

The elemental composition of the thin films was examined using the X-ray photoelectron spectroscopy technique (XPS, Thermo Scientific, ESCALAB 250Xi) equipped with an Al $K\alpha$ X-ray source. Thermo Advantage software was used for analyzing and processing the XPS spectrum.

CHAPTER 4

Results and Discussion

Chapter 4

Results and Discussion

Section I

4.1 Results and Discussion: ZIF-8 Thin Films

4.1.1 X-Ray Diffraction: Verifying ZIF-8 Structure

The XRD analysis confirmed the crystal structure, phase purity, and crystalline nature of the ZIF-8 thin film. Figure 4.1 shows XRD patterns of ZnO and ZIF-8@ZnO thin film on a glass substrate synthesized at room temperature for 24 hrs. As-deposited ZnO thin film confirmed XRD peak at 33.83° , indicating (002) hexagonal wurtzite structure of ZnO. As for ZIF-8@ZnO thin film, sharp intense diffraction peaks of ZIF-8 were observed at 7.6° , 10.49° , 12.80° , 14.80° , 16.73° , and 18.14° corresponding to (011), (002), (112), (022), (013), (222) planes, respectively [117]. All the peaks of the synthesized ZIF-8@ZnO strongly correspond to the simulated powder ZIF-8 pattern and confirm its sodalite structure. A slight peak shift of ~ 0.4 toward a higher angle was observed in all peaks compared to reported values in the literature. As per Bragg's Law ($n\lambda = 2d \sin\theta$), change of d-spacing (d) results in the shift of the diffraction angle (θ) when λ is constant [118]. The positive shift of peaks here represents the presence of compressive stress in the ZIF-8@ZnO thin film.

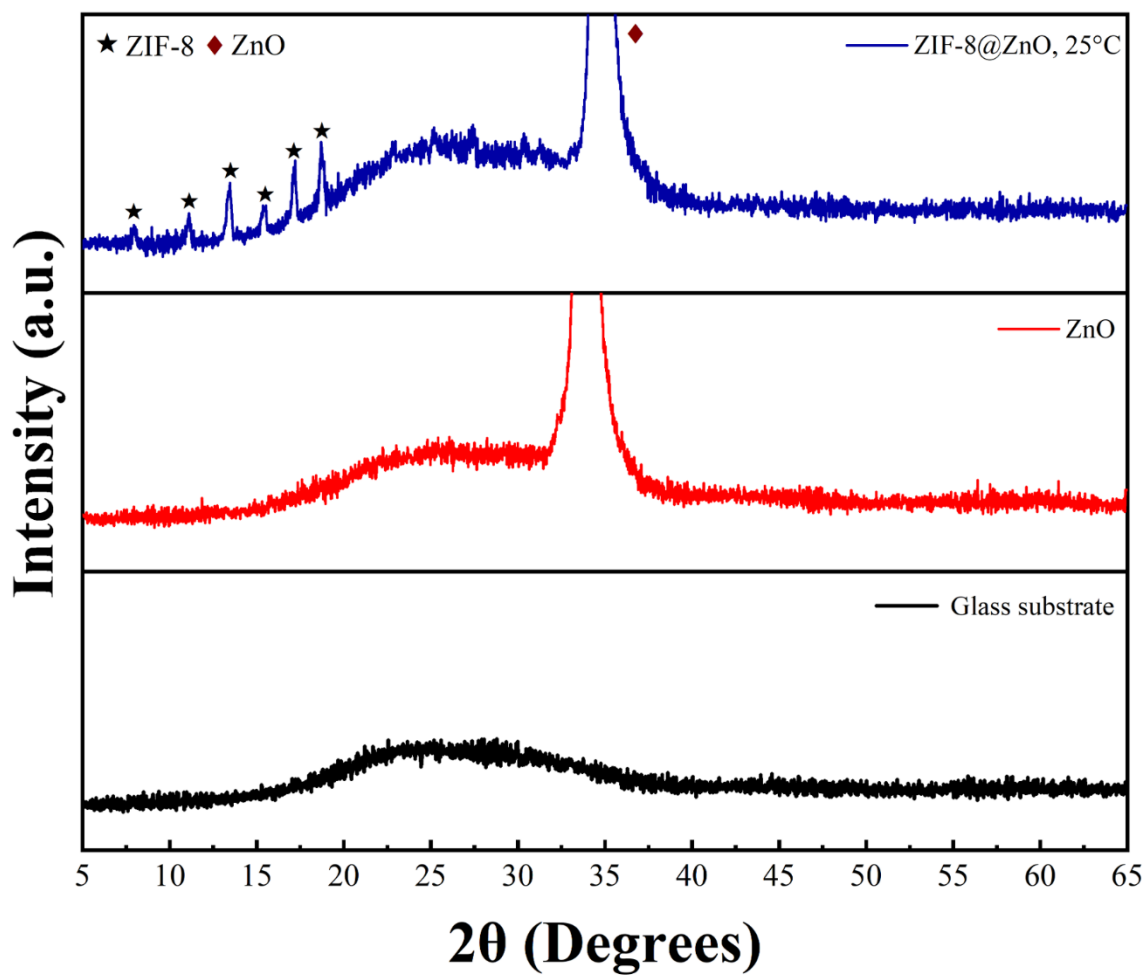


Figure 4.1: XRD analysis of glass substrate, as-deposited ZnO thin film, and ZIF-8@ZnO thin film.

4.2 X-Ray Photoelectron Spectroscopy: Verifying ZIF-8 Functional Groups

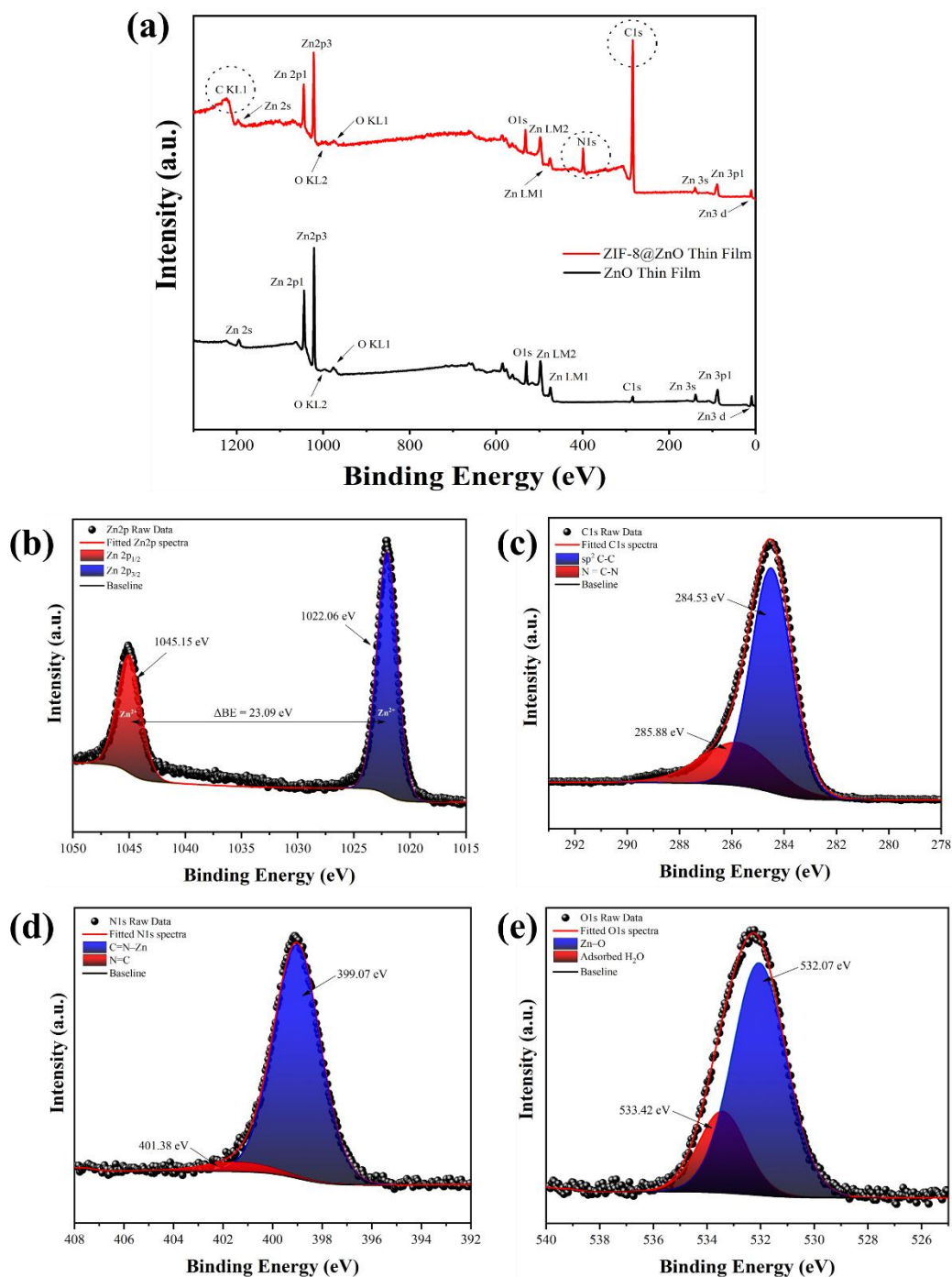


Figure 4.2: Illustrates the XPS analysis: (a) the full survey spectra of sputtered ZnO thin film and ZIF-8@ZnO thin film prepared at 25°C for 24 hrs. High-resolution spectra of ZIF-8@ZnO thin film are shown for (b) Zn2p, (c) C1s, (d) O1s, and (e) N1s.

The surface composition of the synthesized ZIF-8@ZnO thin films was examined using the X-ray photoelectron spectroscopy (XPS) technique. Figure 4.2 (a) shows the complete XPS spectra of sputtered ZnO and ZIF-8@ZnO, confirming the existence of zinc, carbon, oxygen, and nitrogen elements. For the correction of binding energies, the C1 peak of carbon (BE = 284.6 eV) was used as a reference [21].

The high-resolution spectrum of Zn2p ZIF-8@ZnO thin film consisted of two peaks belonging to Zn2p_{1/2} and Zn2p_{3/2}, indicating the existence of Zn²⁺ in the synthesized ZnO@ZIF-8 thin films, as shown in Figure 4.2 (b) [119]. The Zn2p spectrum of ZIF-8@ZnO exhibits two peaks at 1045.15 and 1022.06 eV, with a spin-orbit splitting of 23.09 eV. A slight peak shift toward higher binding energy was determined, which could be attributed to a chemical interaction between ZnO and ZIF-8 [120]. Table 4.1 gives a quantitative analysis of XPS for ZnO and ZIF-8@ZnO thin film.

Figure 4.2 (c) shows the C1s spectrum of ZIF-8@ZnO, consisting of two peaks obtained via peak splitting. The dominant peak at 284.53 eV corresponds to the imidazole linker, indicating the presence of the sp²-hybridized C-C bond in imidazole rings. The small peak at 285.88 eV belongs to the sp² C bonded in the hetero-cycle N = C-N [121]. The peak at 533.42 eV is attributed to chemically adsorbed water [122], [123]. The N1s spectrum of ZIF-8@ZnO, shown in Figure 4.2 (d), consists of two peaks at 399.07 eV and 401.38 eV corresponding to C=N-Zn and N=C [119]. Figure 4.2 (e) shows the O1s spectrum of ZIF-8@ZnO, which is deconvoluted into two peaks. The peak at 532.07 eV is assigned to O²⁻ ions, coming from the ZnO structure, which indicates bonding between Zn-O in ZIF-8@ZnO [119], [120], [121].

Table 4.1: Quantitative XPS analysis of as-deposited ZnO and ZnO@ZIF-8 thin film.

Sample	Name	Peak BE	FWHM (eV)	Area (P) CPS.eV	Atomic %
ZnO	Zn 2p ³	1021.01	2.95	7587297.71	36.33
	O 1s	530.16	3.38	1700663.48	40.32
	C 1s	284.37	2.71	387819.58	23.36
ZnO@ZIF-8	Zn 2p ³	1021.86	2.97	393314.24	4.00
	C 1s	284.26	3.06	628231.13	80.34
	N 1s	398.88	3.04	121449.67	9.79
	O 1s	532.18	3.29	116312.24	5.86

4.3 Influence of Temperature on ZIF-8 Thin Films

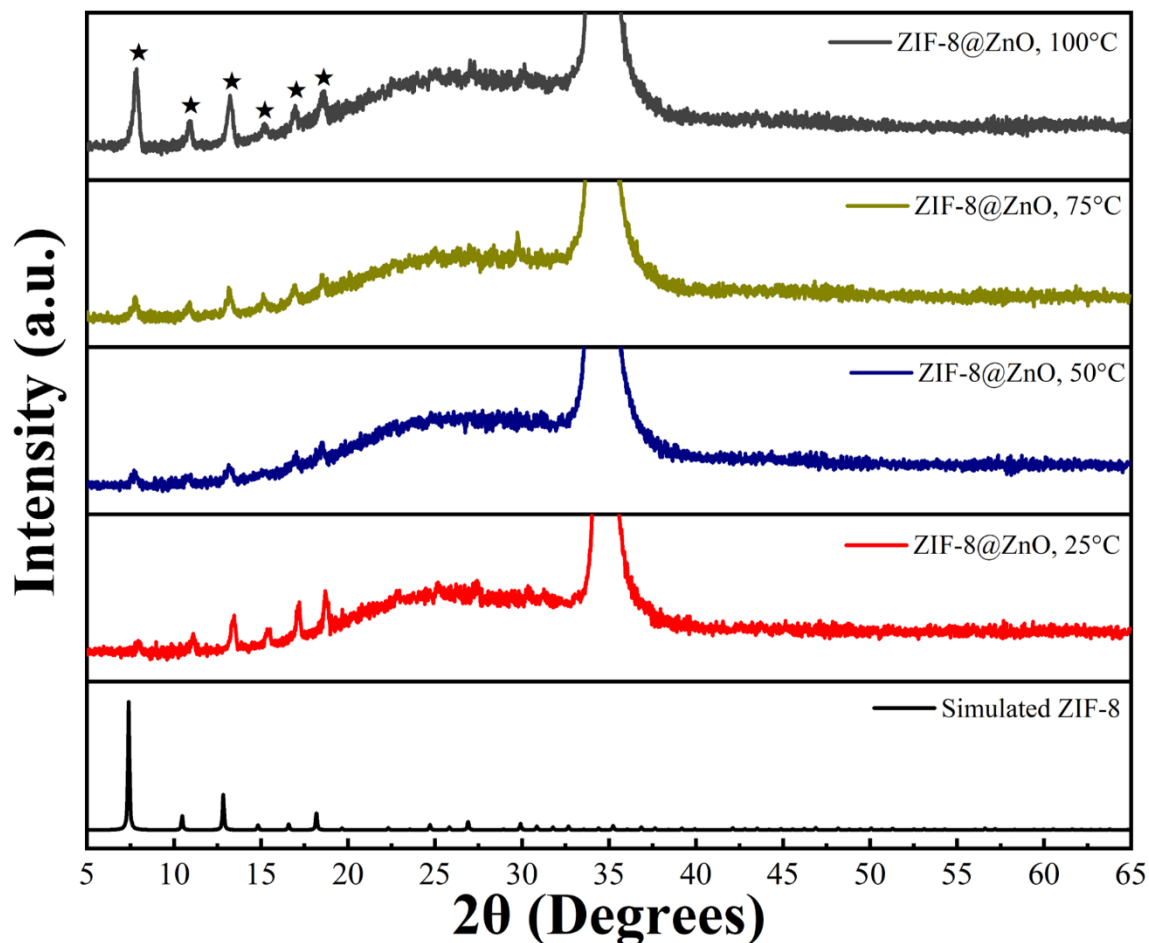


Figure 4.3: XRD spectra of ZIF-8@ZnO thin films prepared at different temperatures i.e., 25°C, 50°C, 75°C, and 100°C.

The influence of the temperature of ZIF-8 was investigated by increasing the synthesis temperature from room temperature to 100°C. The XRD results revealed that the crystallinity of ZIF-8 significantly increased by reaching higher temperatures as shown in Figure 4.3. The most intense and sharp peaks of ZIF-8 in ZIF-8@ZnO thin film were determined at 100°C, demonstrating improved crystallinity and a fast nucleation rate.

4.4 Effect of Synthesis Temperature on ZIF-8 Morphology

The morphology of the ZIF-8@ZnO thin films was observed by Field Emission Scanning Electron Microscopy (FESEM). It was determined that increasing the synthesis temperature

has a substantial impact on the formation of ZIF-8 morphology as well as on its nucleation and growth process. The FESEM images shown in Figure 4.4 (a-d) represent typical ZnO@ZIF-8 thin films that are synthesized at different temperatures, i.e., 25°C, 50°C, 75°C, and 100°C, for 24 hrs. All the synthesized thin films showed the uniform formation of ZIF-8 on the surface of ZnO. A highly uniform and homogenous distribution of ZIF-8 was obtained at room temperature. However, under the influence of temperatures from 50 to 75°C, the formation of ZIF-8 was significantly affected. In contrast to room temperature synthesized thin film, ZIF-8@ZnO prepared at 100°C displayed a bigger size of particle size.

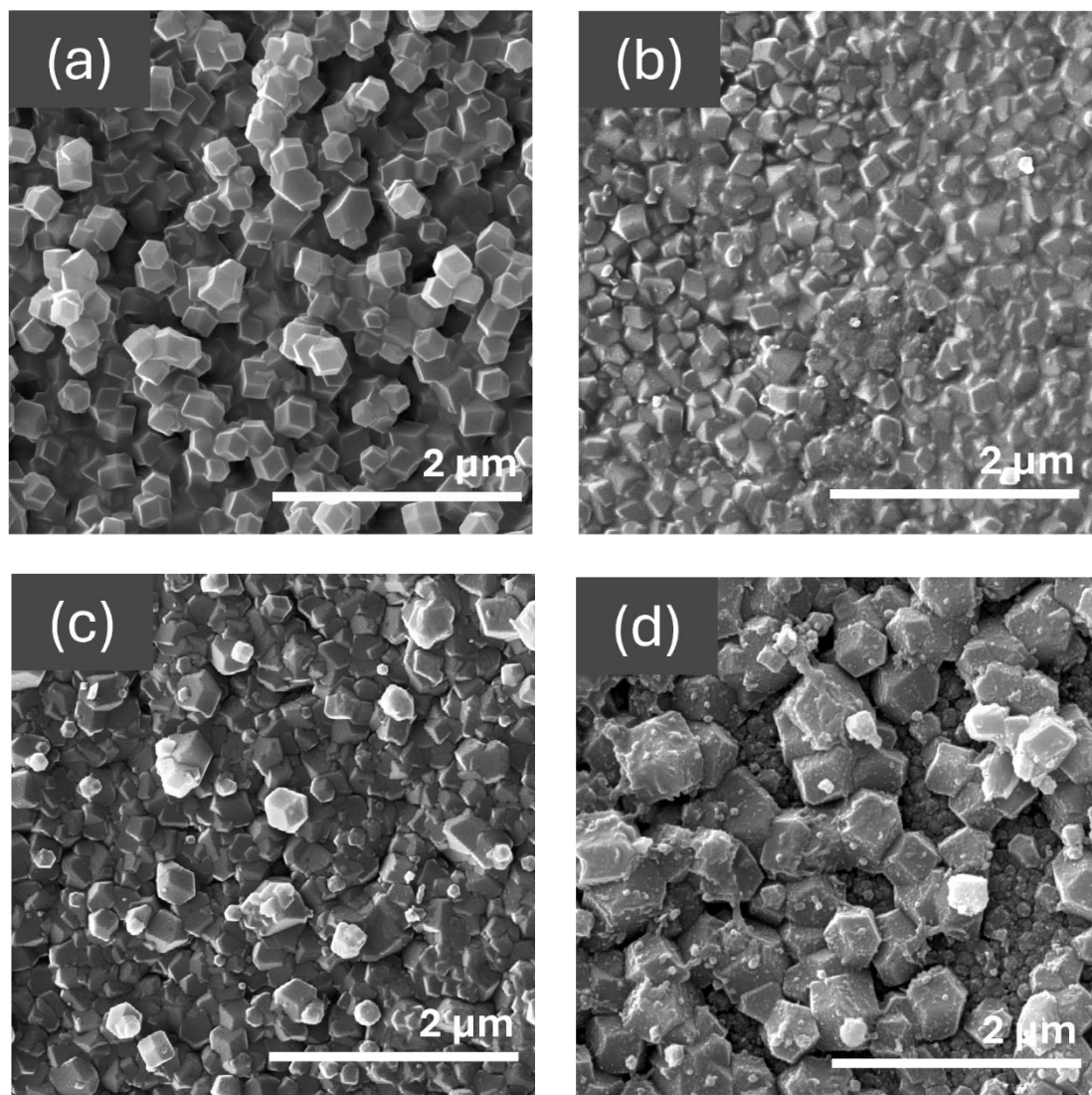


Figure 4.4: FE-SEM images of ZIF-8@ZnO thin films prepared at different synthesis temperatures: (a) 25°C, (b) 50°C, (c) 75°, and (d) 100°C.

4.4.1 Growth of ZIF-8@ZnO Thin Films on Different Substrates

4.4.1.1 ZIF-8@ZnO Synthesis on FTO Substrate

As-deposited ZnO thin film confirmed an XRD peak at 33.80° . As for ZIF-8@ZnO thin film, as shown in Figure 4.5. The sharp diffraction peaks of ZIF-8 were observed at 7.6° , 10.49° , 12.80° , 14.80° , 16.73° , and 18.14° which strongly corresponds to simulated powder ZIF-8 pattern while other peaks belong to FTO substrate at 26.68° , 33.72° , 37.88° , 51.61° , 54.58° , and 61.55° .

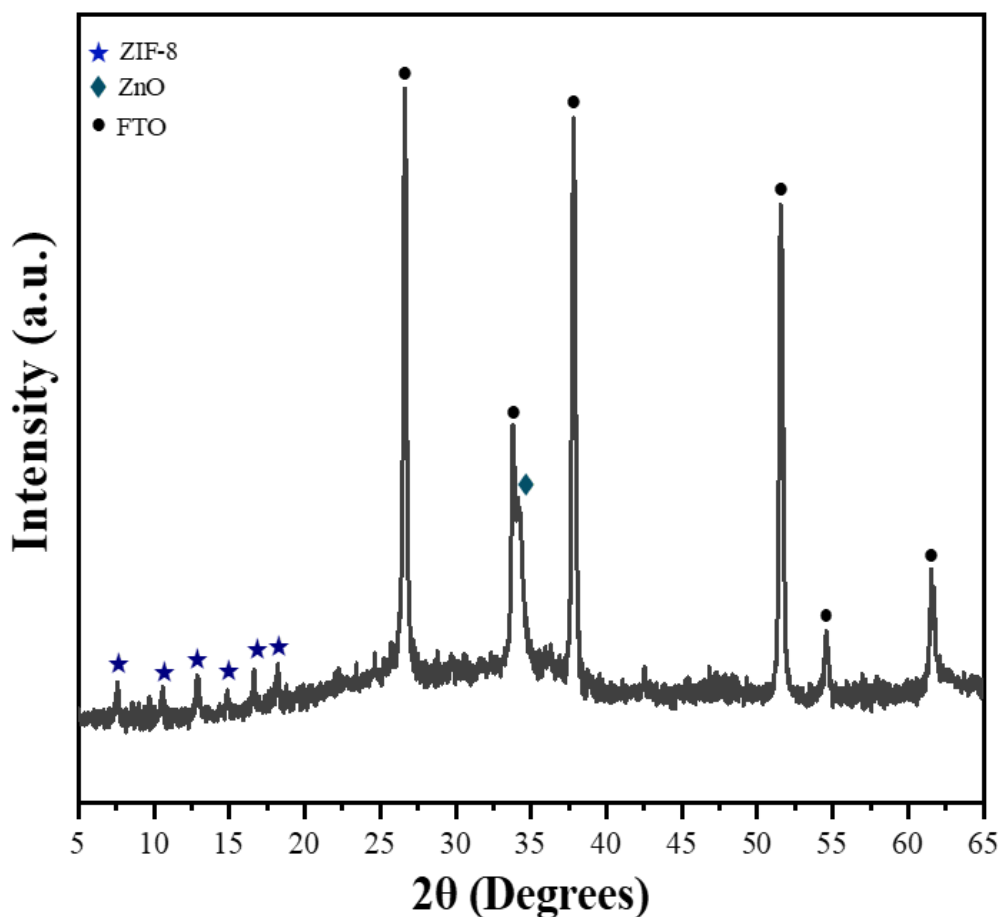


Figure 4.5: XRD of ZIF-8@ZnO thin film prepared at 100°C on the surface of FTO.

4.4.1.2 ZIF-8@ZnO Synthesis on Carbon Paper

Figure 4.6 shows the diffraction pattern of ZIF-8@ZnO on carbon paper where the ZIF-8 peaks belong to 7.09° , 10.05° , 12.43° , 14.34° , 16.21° , and 17.75° . Diffraction peaks at 17.85° , 26.25° , 36.72° , 42.40° , 44.23° , 50.41° , and 54.34° corresponds to carbon paper.

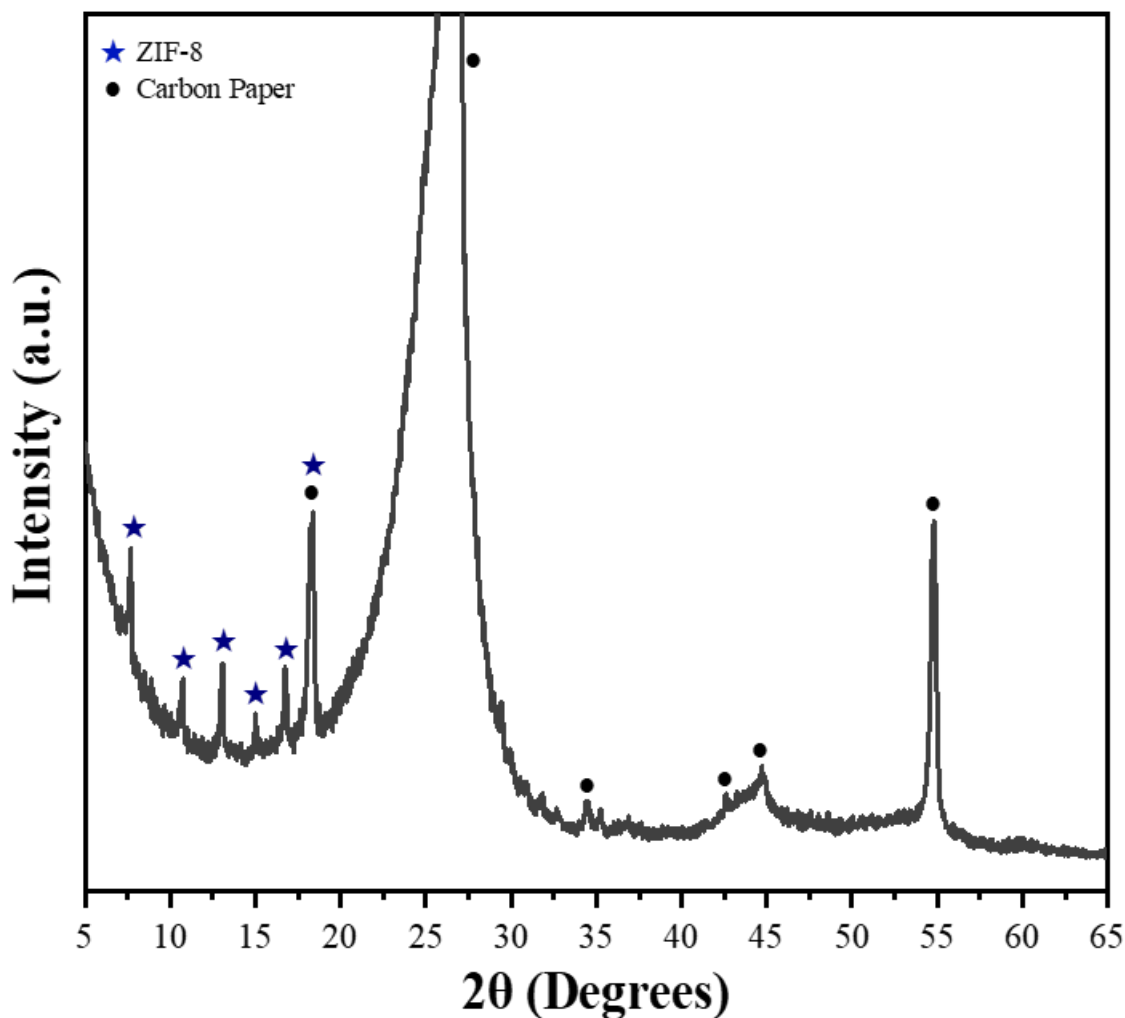


Figure 4.6: XRD pattern of ZIF-8@ZnO thin film prepared at 75°C on the surface of carbon paper.

4.4.1.3 ZIF-8@ZnO Morphology on FTO Surface

The surface morphology of ZIF-8@ZnO on the surface of FTO is displayed in Figure 4.7, showing homogenous coverage and formation of the cubic morphology.

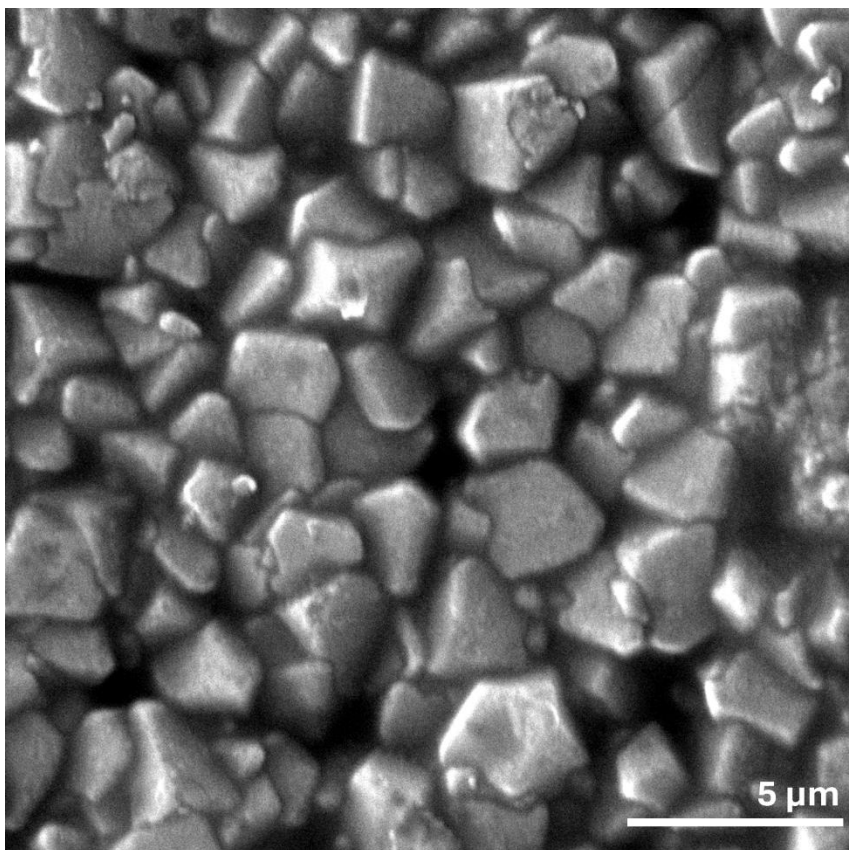


Figure 4.7: FESEM image of ZIF-8@ZnO thin film prepared at 100°C for 24 hrs on the surface of FTO.

4.4.1.4 ZIF-8@ZnO Morphology on Carbon Paper

The surface morphology of ZIF-8@ZnO on the surface of carbon paper is displayed in Figure 4.8, showing well-defined cubic morphology.

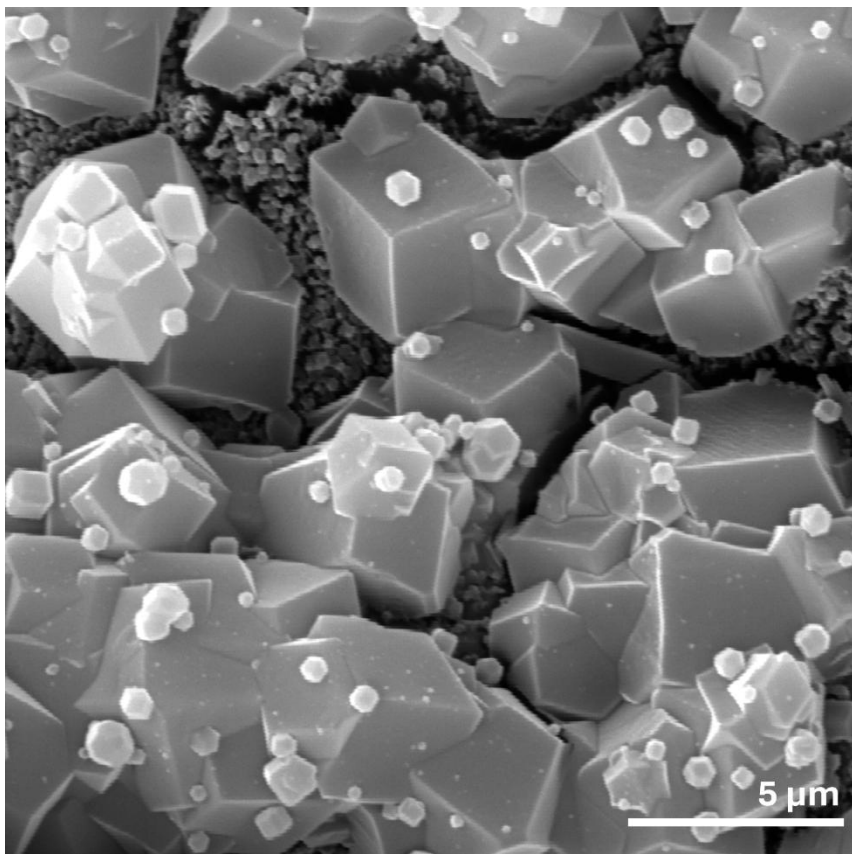


Figure 4.8: FESEM image of ZIF-8@ZnO thin film prepared at 75°C for 24 hrs on the surface of carbon paper.

4.5 ZIF-8 Thin Film Formation Mechanism

The following reactions (eq. 1-3) take place during the reactive DC magnetron sputtering for the synthesis of ZnO thin film, where pure zinc target reacts with the gas mixture of Ar/O_2 . First, the ionization of Ar takes place, generating Ar^+ ions and additional electrons. The energetic Ar^+ ions then projected toward the target material and bombarded its surface, resulting in the release of neutral zinc atoms (Zn^0) which subsequently reacts with O_2 gas. This interaction results in the formation of ZnO^0 neutral atoms, which further condense to the substrate surface and form a thin film of metal oxide as illustrated in Figure 4.9.

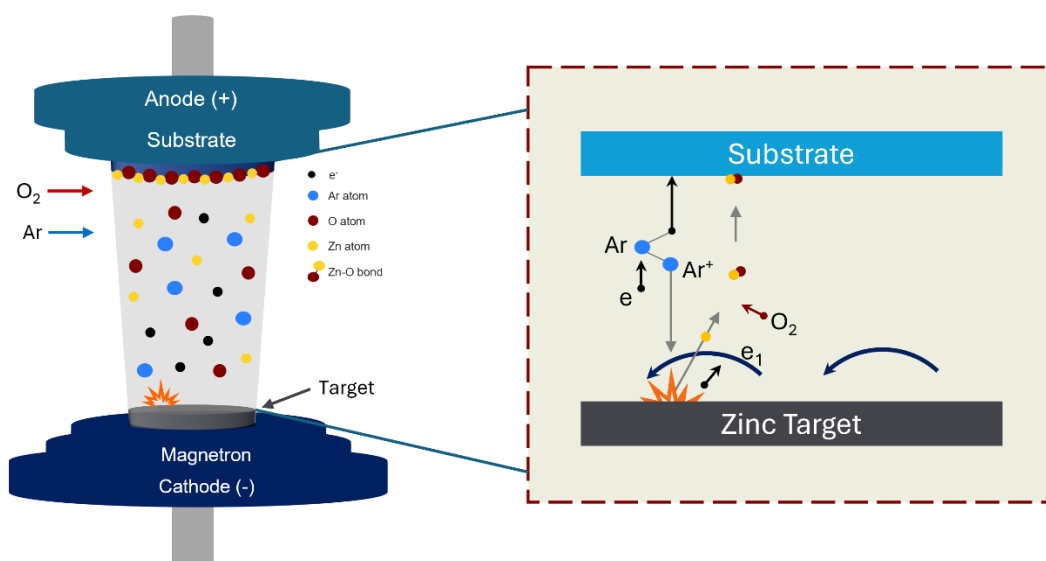


Figure 4.9: ZnO thin film formation in reactive DC magnetron sputtering.

The resulting thin film exhibits the formation of a highly crystalline ZnO wurtzite structure with columnar growth under high vacuum conditions, showing preferential orientation along the (002) plane. ZnO is a kind of semiconductor that belongs to the II-VI group, characterized by a wide band gap ranging from 3.2 to 3.37 eV [124]. It has sp^3 covalent bonding, where each zinc atom is surrounded by four oxygen atoms forming a tetrahedral coordination structure [125]. Furthermore, ZnO is a polar crystal composed of alternating stacking planes of Zn and O along the [0001] direction (c-axis), and it comprises four low-index surfaces: m-plane ($10\bar{1}0$), a-plane ($11\bar{2}0$), basal Zn plane (0001), and O plane ($000\bar{1}$), as shown in Figure 4.10 [126], [127], [128]. The ($10\bar{1}0$) and ($11\bar{2}0$) surfaces are parallel to the c-axis and are considered non-polar planes due to the same number of Zn and O atoms, which signifies their thermodynamic stability. The other two planes, (0001) and ($000\bar{1}$), are polar and exhibit metastable nature due to the electric dipole moment [129], [130].

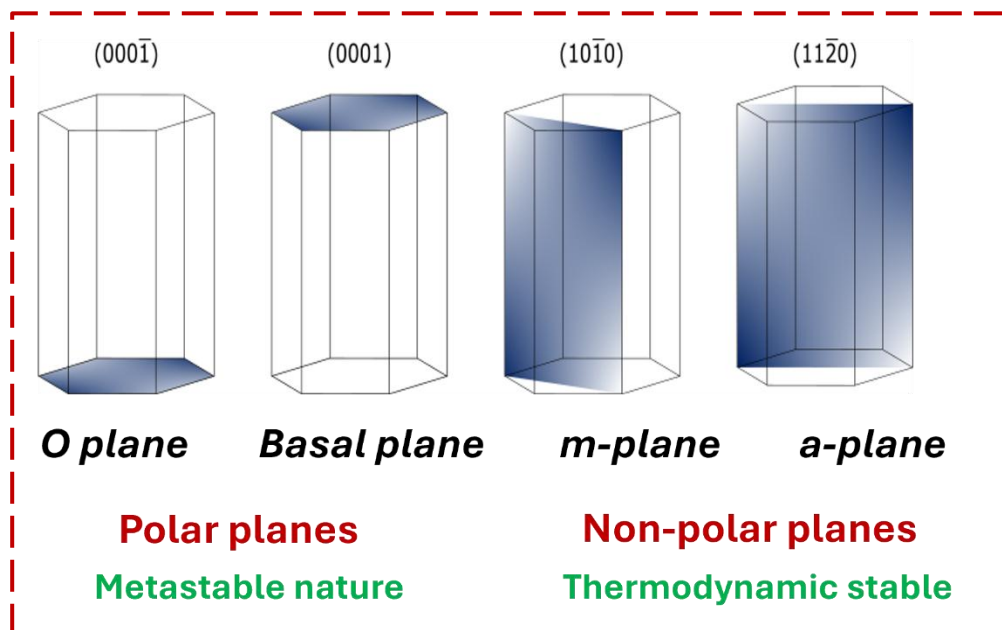


Figure 4.10: Crystallographic low-index surfaces of wurtzite ZnO.

In a hexagonal structure like the ZnO wurtzite structure, the sp^3 hybridized orbit spreads along the $[0001]$ direction because the surface free energy of the (0001) plane does not have a finite value [131]. To overcome the instability of such a plane, ZnO tends to grow along the c-axis in a columnar manner [126], [131], [132], [133]. From the surface energy perspective, the ZnO facet $\{0001\}$ has the lowest energy, then $\{01\bar{1}0\}$ and $\{2\bar{1}\bar{1}0\}$ facets. According to the lowest energy principle, the surface with the minimum energy tends to exhibit faster growth. Therefore, the growth rate will be faster on the (0001) plane than on other planes [134]. In comparison to the O plane $(000\bar{1})$, the Zn plane (0001) is more chemically active, promoting growth because of its higher activity, while the O plane $(000\bar{1})$ surface remains relatively inert [134], [135]. In terms of growth kinetics, neighbouring crystals compete based on their growth orientation, where fast-growing crystals overtake and terminate slow-growing crystals [136]. Due to this reason, ZnO growth along the (0001) is dominant compared to other planes.

This preferential growth of the ZnO plane is well-known on both single-crystalline and amorphous substrates [137]. Previous studies have also demonstrated that columnar growth is predominant under high vacuum conditions and leads to an improved crystalline nature of thin films [138], [139]. Such orientation could be understood by the Drift model (Figure 4.11), which states that during the initial stage of nucleation, various nucleus orientations emerge and compete for growth. Ultimately, those nuclei with faster growth rates prevail, promoting c-axis orientation [140].

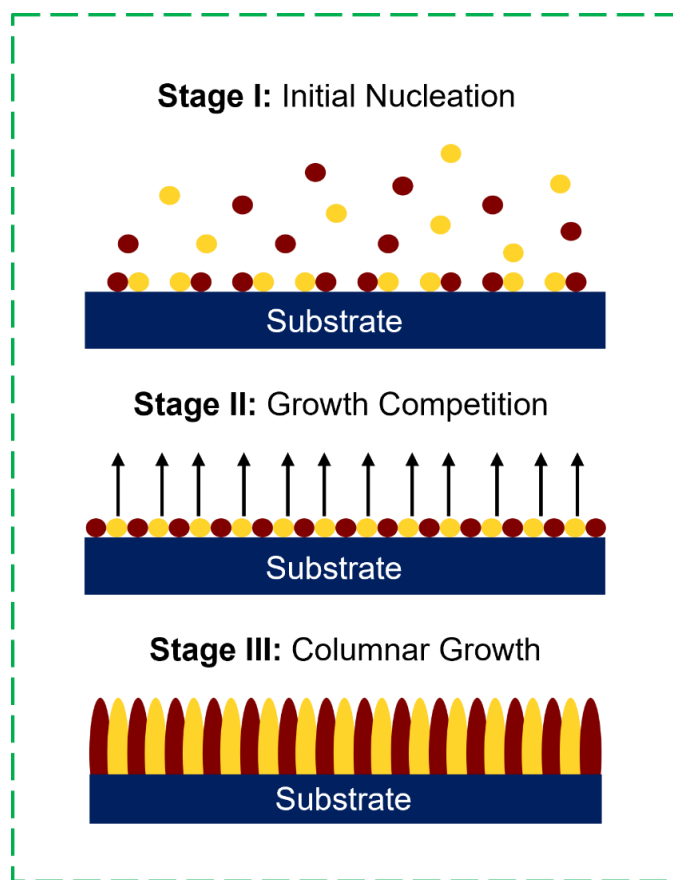
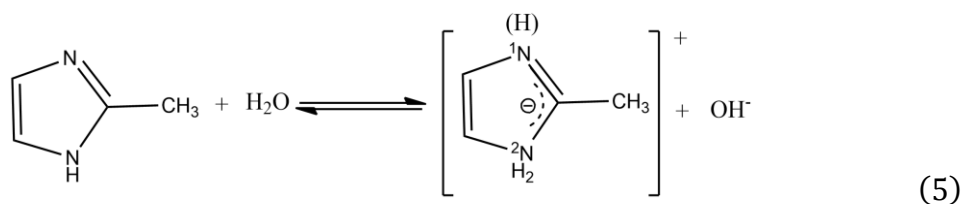


Figure 4.11: Columnar growth mechanism of sputtered ZnO along the (0001) plane.

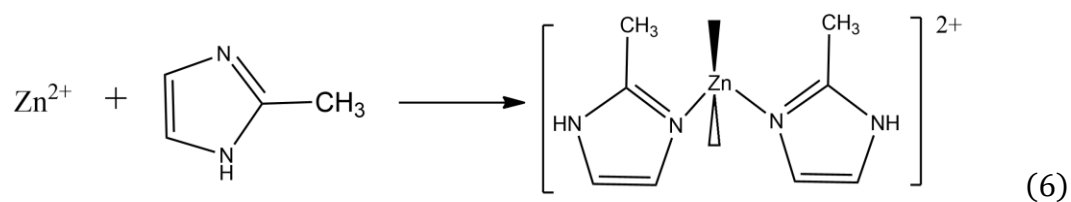
As-deposited ZnO thin film is then used as a source of Zn^{2+} ions for forming ZIF-8 thin film by providing nucleation sites. Generally, the dissolution of ZnO into Zn^{2+} ions tends to occur readily in both acidic and basic media [64]. It has also been reported that direct synthesis of MOFs from metal oxide is a simple and effective approach, resulting in strong adhesion between metallic substrate and MOF, while providing admirable structural stability [141], [142].

In situ growth of ZIF-8 directly from Zn/ZnO-coated substrate promotes the effective growth of high-quality ZIF-8 thin film, as their surface promotes numerous homogenous nucleation sites for the formation of ZIF-8 [64], [143], [144], [145]. Moreover, the utilization of ZnO for the preparation of ZIF-8 thin film has an advantage over zinc salts, particularly in terms of environmental sustainability due to its non-toxic nature [146]. Additionally, the transformation of ZIF-8 at low temperatures is achievable due to enhanced reaction activity of the nanosized ZnO, which has the potential to address problems related to spatial localization of ZIF-8 growth [147]. In this work, the dissolution of ZnO occurs in a reaction medium composed of an aqueous solution and the organic linker 2-methylimidazole (Hmim). The pH of the solution ranged from 9.81 to 10.32 in this investigation.

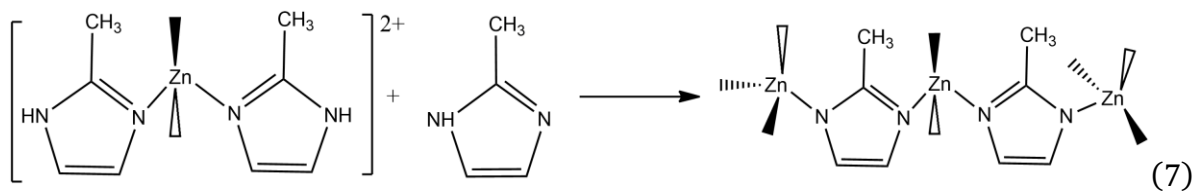
Usually, in the water-based system, the formation of ZIF-8 thin film takes place via hydrolysis of the Hmim and zinc source, followed by the coordination of Zn^{2+} with the Hmim, and a deprotonation reaction between the Hmim and intermediate complex $(\text{Zn}(\text{Hmim})_n)^{2+}$. However, in the case of the aqueous medium, deprotonation of Hmim does not take place due to its high pK_a value ($\text{pK}_a [\text{Hmim}] = 14.2$). Hence, only hydrolysis of the ligand occurs, where Hmim exhibits two forms: Hmim and H_2mim^+ . Due to this reason, the nature of the Hmim solution is highly basic ($\text{pH} > 7$) and possesses higher electron density, which is beneficial for the ease of coordination with transition metal ions [75], [148]. During the hydrolysis stage, the water interacts with Hmim and leads to the formation of protonated Hmim (H_2mim^+) and OH^- ions (eq. 5) [75].



Past studies also have emphasized that during the formation of ZIF-8, the Hmim has multiple roles, such as its ability to act as an etching agent to release Zn^{2+} ions by dissolving ZnO and coordinating with Zn^{2+} ions, depending on the composition of the solvent [64]. In our reaction system, Hmim interacts with Zn^{2+} ions, forming a three-dimensional porous network resembling a zeolite structure [149]. The coordination of Zn^{2+} ions with nitrogen atoms of Hmim results in the $\text{Zn}(\text{Hmim})_n^{2+}$ formation, indicating the early formation of ZIF-8 taking place (eq. 6) [75], [150].



After this stage, Hmim reacts with $\text{Zn}(\text{Hmim})_n^{2+}$, acting as a deprotonation agent by consuming the H^+ ion from $\text{Zn}(\text{Hmim})_n^{2+}$ and resulting in the formation of the ZIF-8 structure (eq. 7). This reaction takes place because of the higher pK_a value of Hmim compared to that of the complex intermediate ($\text{pK}_a [\text{Zn}(\text{Hmim})_n^{2+}] = 10.3$).



Chapter 4

Results And Discussion

Section II

4.6 Results and Discussion: CAU-17 Thin Films

4.6.1 XRD: Verifying CAU-17 Structure

XRD analysis of the as-deposited Bi_2O_3 thin film and CAU-17 thin film prepared at 105°C for 2 days is shown in Figure 4.12. No peaks were observed in the diffraction pattern of Bi_2O_3 , indicating the amorphous nature of the thin film. Previous literature also highlights that the synthesis of Bi_2O_3 at room temperature via magnetron sputtering results in an amorphous phase [151], [152]. The most intense peaks of CAU-17 were determined at 8.35° , 10.49° , 12.68° , 16.51° , 24.75° , and 33.13° . The crystallite size of the CAU-17 was 62 nm, calculated by applying Scherrer's equation to the most intense peak. The XRD pattern of CAU-17 displayed distinct peaks in comparison to the reported simulated pattern of CAU-17. The main reason for obtaining such diffraction is the high sensitivity of CAU-17 towards synthesis conditions and preparation approaches.

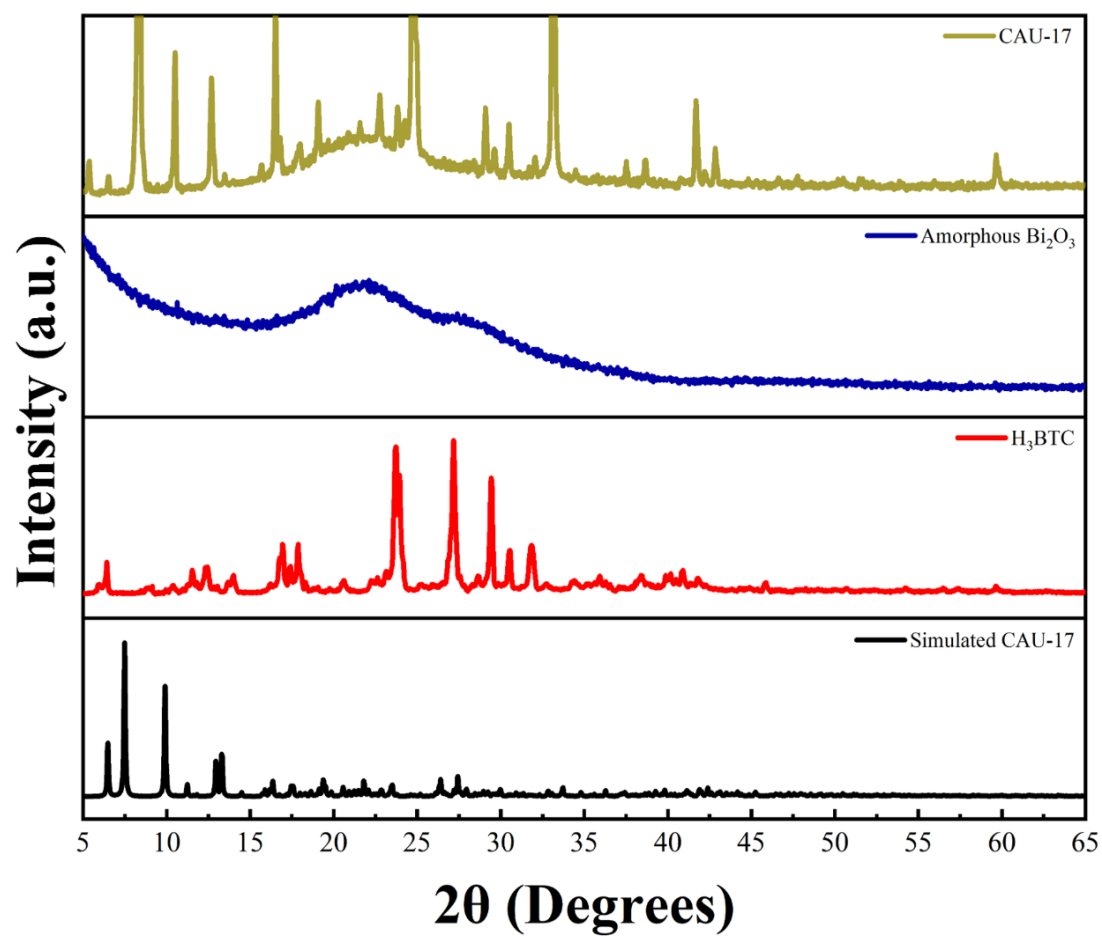


Figure 4.12: XRD of H₃BTC, amorphous Bi₂O₃, and CAU-17 thin film.

4.7 FESEM: Confirming CAU-17 Morphology

To further confirm whether CAU-17 was successfully formed or not, FESEM was employed. FESEM results revealed that CAU-17 exhibits a nanorod-like morphology, as shown in Figure 4.13, consistent with the reported morphology in the literature[103].

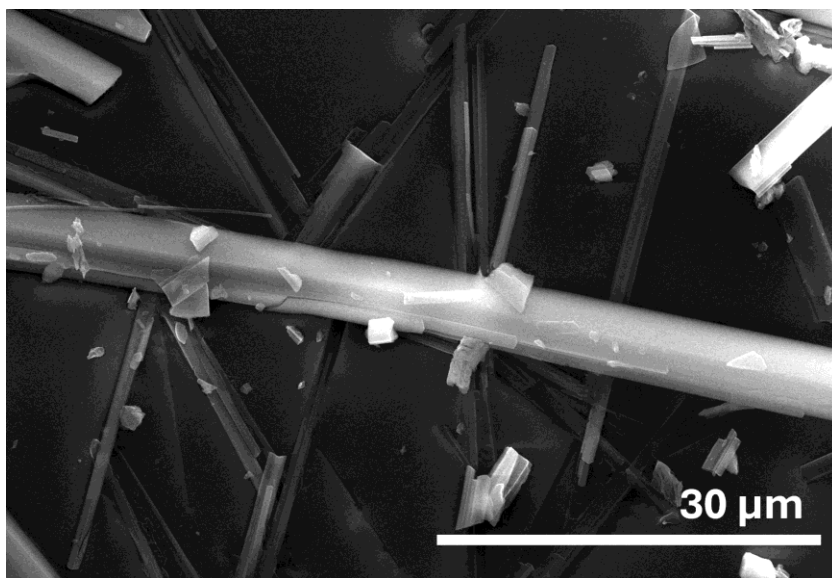


Figure 4.13: FE-SEM image of CAU-17 thin film.

4.8 CAU-17 Identification via Spectroscopy Techniques

4.8.1 EDX Analysis: Elemental Composition Confirmation

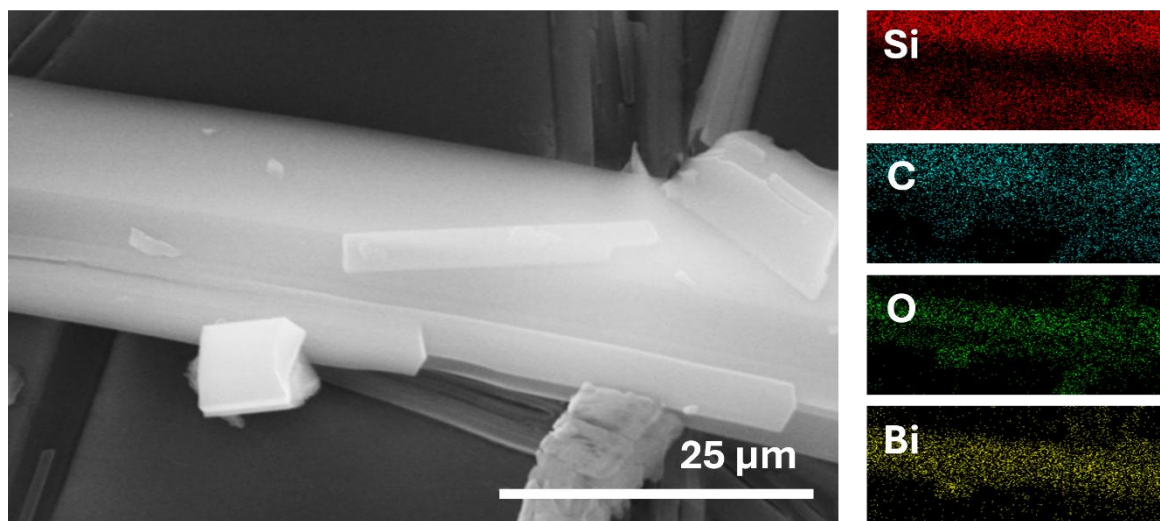


Figure 4.14: EDX mapping of CAU-17 thin films.

EDX elemental mapping of CAU-17 nanorod, shown in Figure 4.14, confirms the existence of bismuth (Bi), carbon (C), and oxygen (O). The homogenous distribution of these elements throughout the nanorods represents the well-formed structure of CAU-17. Additionally, it was also observed that nanorod morphology consists of a high bismuth content, indicating a nearly complete transformation of the Bi_2O_3 thin film into CAU-17 formation.

4.8.2 Raman Spectroscopy: Identification of Vibrational Modes

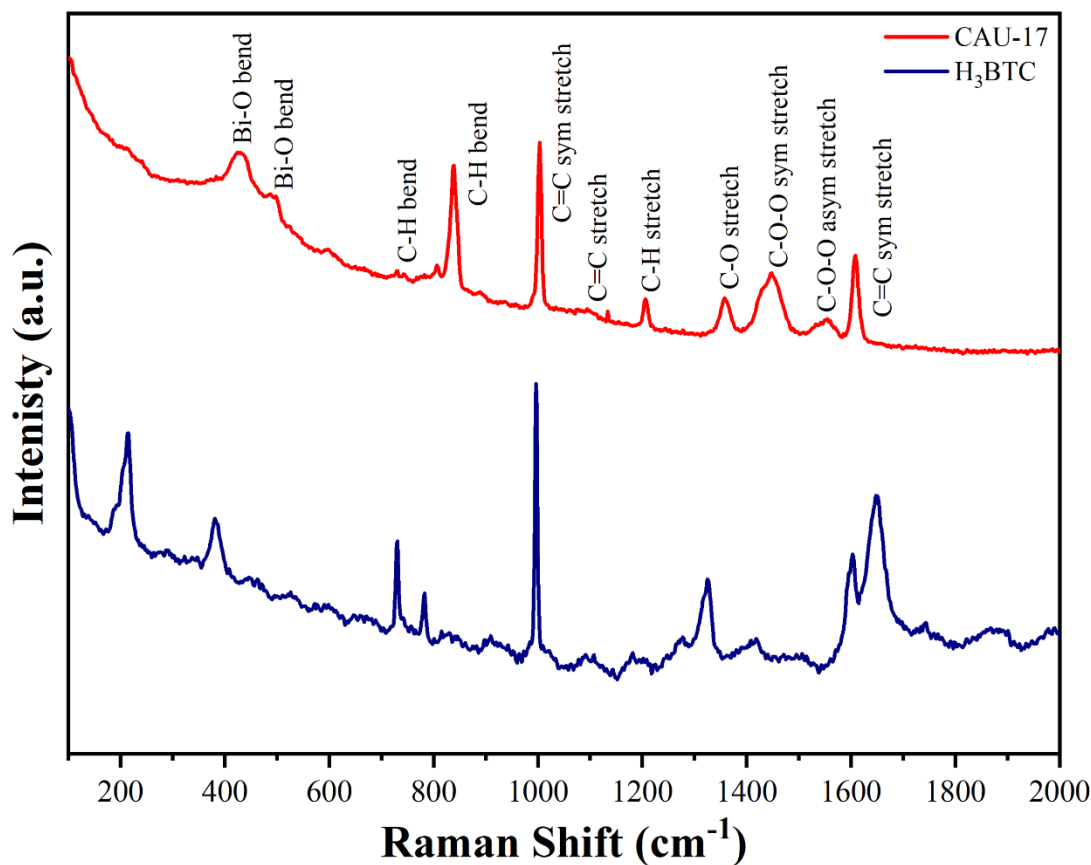


Figure 4.15: Raman spectra of H₃BTC and CAU-17 of thin film.

To confirm the molecular structure of the CAU-17 thin film, Raman spectroscopy was used. The Raman spectra of H₃BTC and CAU-17 are shown in Figure 4.15, which exhibits multiple peaks corresponding to their respective functional groups. The Raman spectrum of the CAU-17 MOF thin film was highly consistent with the reported literature [153]. The CAU-17 spectrum showed the characteristic peaks of H₃BTC within the range of 700-2000 cm⁻¹ and Bi-O-related bonds at 50-600 cm⁻¹ [106]. The characteristic bands at 425.73 and 490.33 cm⁻¹ belong to the Bi-O bond stretching modes. The stretching and bending modes of C-H bonds were observed at 731.39, 838.42, and 1205.79 cm⁻¹. The C-O-O symmetric and asymmetric stretching vibration modes were determined at 1448.78 and 1554.85 cm⁻¹,

respectively [154]. The peaks at 1003.30, 1133.48, and 1608.84 cm^{-1} represent the symmetric stretching of C=C bonds from the aromatic ring of H₃BTC [154], [155], [156]. The band at 1358.14 was assigned to the in-plane vibration of the C-O bond [157]. The presence of C-O-O and Bi-O bonds in CAU-17 spectra indicates the existence of required functional groups and confirms metal-linker coordination.

4.8.3 FT-IR Spectroscopy: Verifying Functional Groups

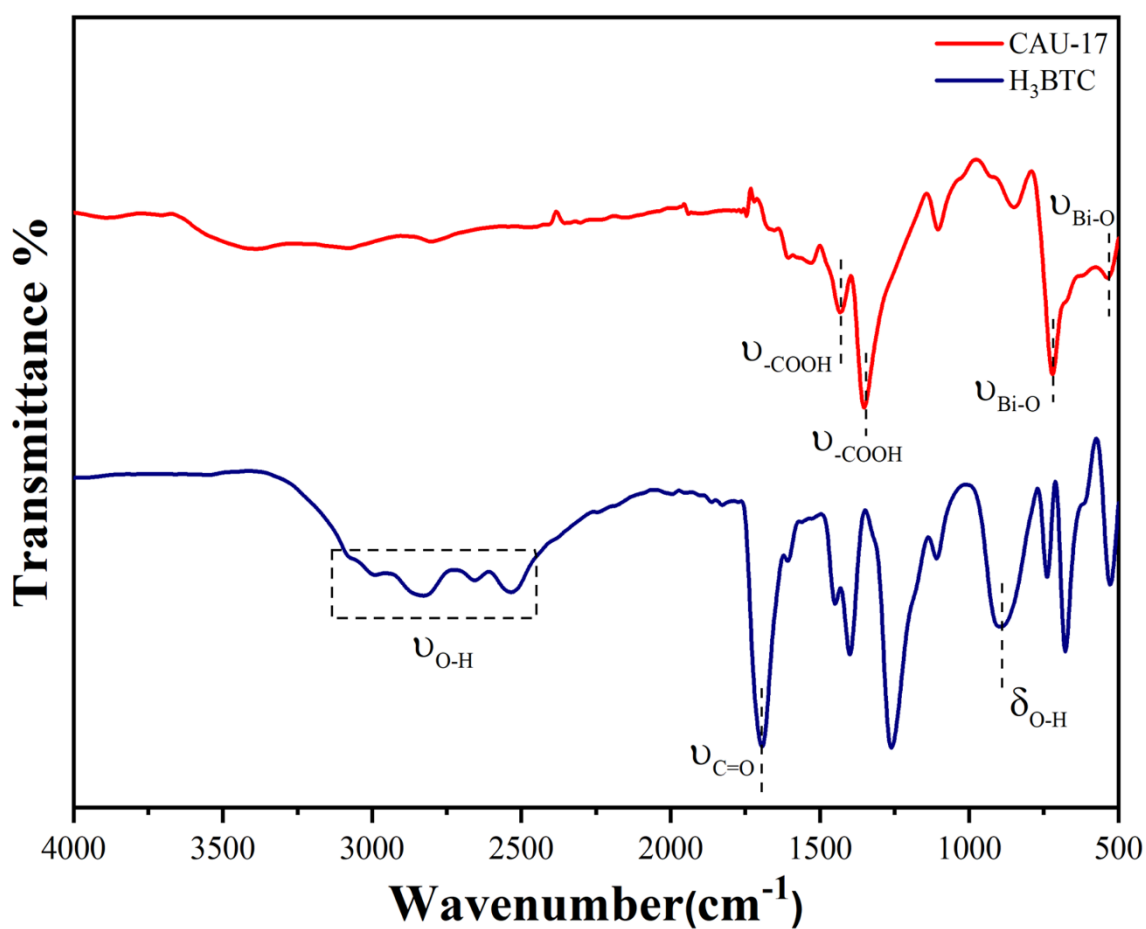


Figure 4.16: FT-IR of H₃BTC and CAU-17 of thin film.

The FT-IR spectroscopy was applied to determine the existence of intended functional groups in the structure of the CAU-17 thin film. Figure 4.16 shows the FT-IR results of H₃BTC and CAU-17 thin film. The FT-IR spectrum of H₃BTC, shows the characteristic

peaks of O–H stretching, C=O stretching, and O–H bending groups at 3000-2500 cm^{-1} , 1763-1569 cm^{-1} , and 996-764 cm^{-1} , respectively [113]. In the FT-IR spectrum of the CAU-17, both characteristic peaks of the Bi–O and carboxylate group were observed. The new peaks appeared within the range of 500 to 700 cm^{-1} , corresponding to the Bi–O group, indicating the coordination of the COOH group of the organic linker with the Bi^{3+} ions through electrostatic interaction [158]. The characteristics peak at 536 and 720 cm^{-1} , corresponding to Bi–O stretching [159]. The carboxylate groups were observed at 1352 and 1432 cm^{-1} , attributed to asymmetric vibration of the -COOH group [113]. The disappearance of the characteristic peaks of H_3BTC linker, along with the appearance of new bands corresponding to the coordination between the linker and Bi^{3+} ions, confirms the successful formation of the CAU-17 thin film.

4.8.4 XPS: Verification of Surface Composition and Functional Groups

XPS analysis was performed to determine the surface composition, chemical states, and functional groups of the CAU-17 MOF thin film. Figure 4.17 (a) shows the survey scan that confirms the existence of the main constituents of CAU-17, i.e., Bi, C, and O elements in the synthesized thin film, consistent with the aforementioned EDX mapping results. The presence of Sn is due to the synthesis of CAU-17 thin film on the surface of the FTO substrate. While the existence of N may be due to atmospheric nitrogen. For the correction of binding energies, the C 1s peak of carbon (BE = 284.6 eV) was used as a reference [21]. The high-resolution Bi 4f spectrum of CAU-17 is shown in Figure 4.17 (b), which consists of two binding energy peaks at 158.08 eV and 163.18 eV corresponding to Bi^{3+} 4f_{7/2} and Bi^{3+} 4f_{5/2}, respectively [113], [160]. These peaks confirm the existence of Bi^{3+} ions in the CAU-17 thin film [161]. The O 1s spectrum displayed three peaks (Figure 4.17 (c)), where

the intense peak at 530.08 eV corresponds to Bi-O bonding, while the low intensity peaks at 531.68 eV and 532.98 eV belong to the O-H bond in H₂O and O in bismuth-oxo clusters of CAU-17 thin film, respectively [103], [113], [162]. The C 1s spectrum of CAU-17, shown in Figure 4.17 (d), consists of three peaks at 284.38, 286.28, and 287.68 corresponding to C=C, C-C, and O-C=O of the H₃BTC linker in the CAU-17 framework, respectively [113], [163], [164]. These findings were also consistent with the aforementioned Raman and FT-IR spectra.

By considering the spectra of Bi 4f and O 1s, and also the structure of CAU-17 {9 Bi³⁺, 9 BTC³⁻ and 9 H₂O}, it was observed that the Bi³⁺ ions are coordinated with 9 O atoms in the prepared CAU-17 thin film [82], [162]. In this coordination system, 8 O atoms belong to the BTC³⁻ ligands and 1 O atom from water molecules, resulting in the formation porous framework of CAU-17 [158].

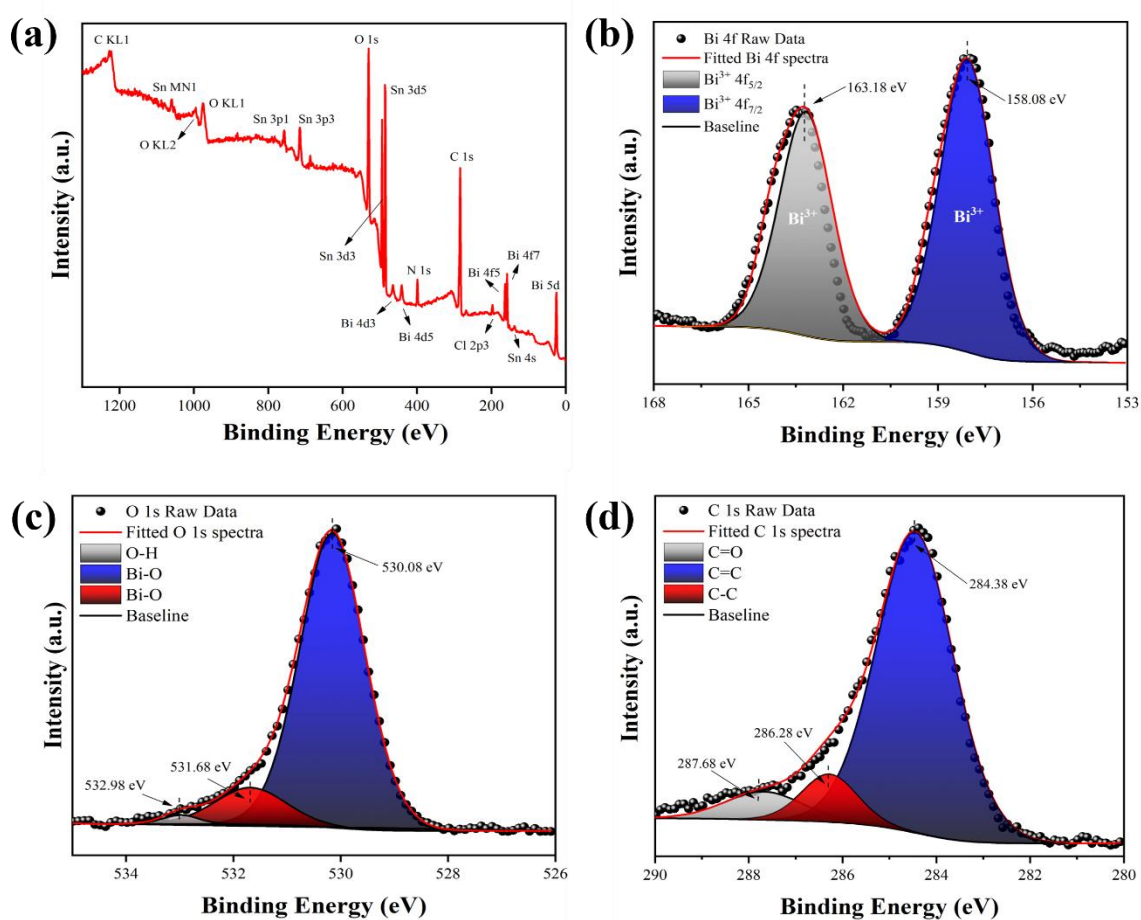


Figure 4.17: XPS results of CAU-17 thin film (a) survey spectra (b) Bi4f (c) O1s and (d) C1s.

4.9 Influence of Temperature on CAU-17 Formation

Many researchers previously confirmed that temperature plays a major role in the synthesis of MOFs and has a great influence over their structure and morphology [165], [166], [167]. Additionally, temperature significantly influences thermodynamics, reaction kinetics, and coordination chemistry of MOFs [168]. The influence of synthesis temperature on CAU-17 formation was investigated by heating at 30°C, 55°C, 80°C, 105°C, and 130°C, and the corresponding XRD results are depicted in Figure 18. The synthesis of CAU-17 at 30°C displayed two weak XRD signals at 8.66° and 12.98°, indicating a poor crystalline nature and an early stage of nucleation. Increasing the synthesis temperature to 55°C results in improved peak intensity; however, the CAU-17 thin film still exhibits low crystallinity, displaying a sharp peak at 8.58° along with a weak signal at 10.69°, 13.15°, 25.08°, and 33.46°. The main reason behind this is that Bi³⁺ ions belong to the group of metal ions that possess high valence. It has previously been reported that synthesizing MOF using trivalent-metal ions at room temperature is challenging and usually requires external energy for its formation [169], [170]. Due to this reason, the synthesized CAU-17 at the lower temperature displayed weak signals. Further increasing the temperature from 80 °C to 130 °C displayed the formation of several XRD peaks, suggesting a strong temperature-dependent formation of CAU-17 thin film. Under this temperature range, all three spectra of CAU-17 were highly consistent with each other and displayed the most intense peaks of CAU-17 at 8.35°, 10.49°, 12.68°, 16.51°, 24.75°, and 33.13°.

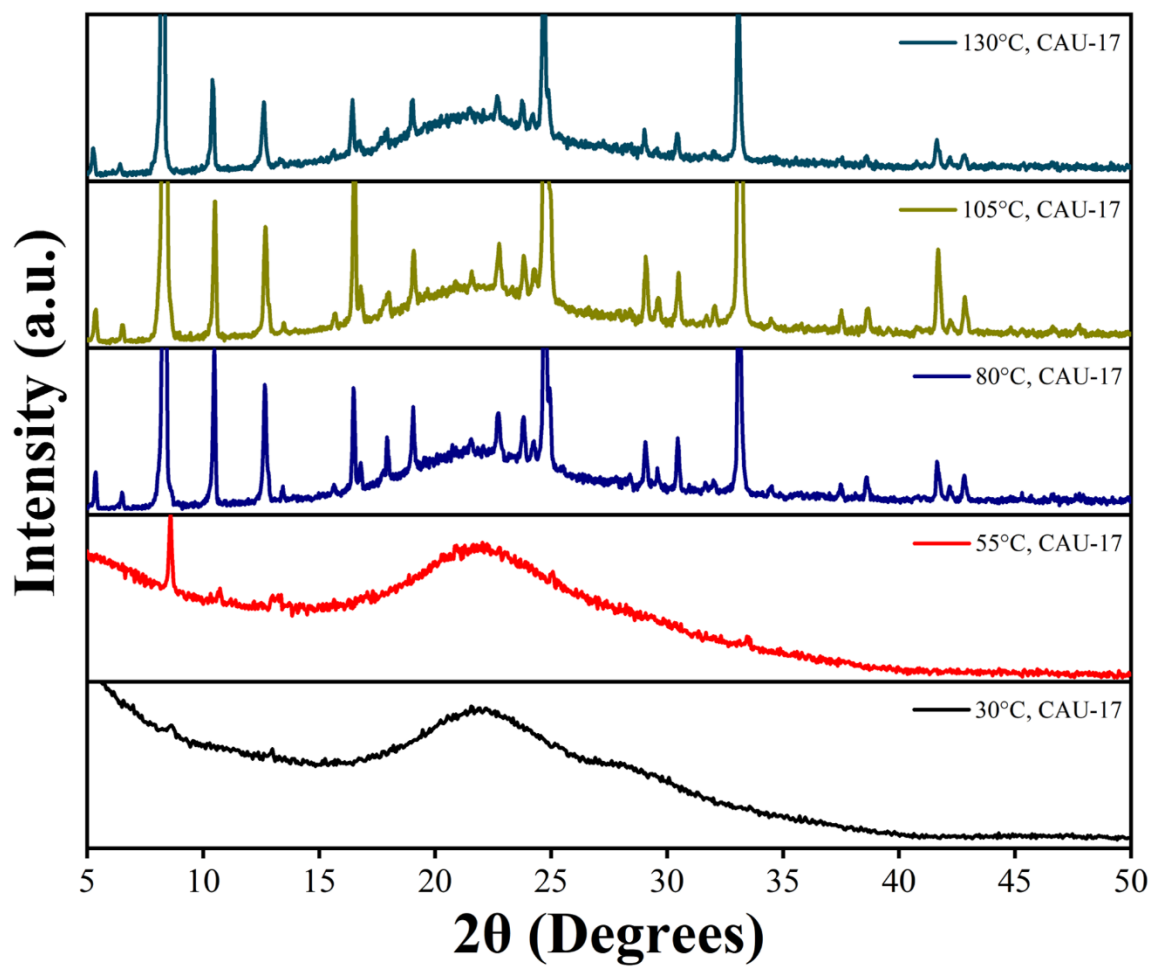


Figure 4.18: XRD of CAU-17 thin films prepared at different temperatures i.e., 30°C, 55°C, 80°C, 105°C, and 130°C.

4.10 Influence of Fabrication Temperature on CAU-17 Thin Film Morphology

The FESEM images of CAU-17 thin films fabricated at different temperatures are shown in Figure 4.19, which reveals that temperature has a significant impact on the formation of CAU-17 morphology. An increase in the temperature from 30°C to 130°C resulted in the transformation of small nanorods into larger nanorods. Figure 4.19 (f) shows the influence of temperature on the CAU-17 nanorods' diameter, measured using ImageJ software. For the samples prepared at 30 to 80°C, individual nanorods were analyzed. However, for samples synthesized at higher temperatures (105°C to 130°C), only one single nanorod was considered, where multiple measurements were taken for improving accuracy. With the increase in temperature from 30°C to 130°C, the diameter of nanorods was found to increase from 0.15 to 6.86 μm . Moreover, it was also observed that the growth of CAU-17 nanorods was random and non-directional.

The synthesis of CAU-17 at 30°C displayed the formation of multiple nanorods, as shown in Figure 4.19 (a). Additionally, it was also observed that multiple nanorods arranged themselves in one specific crystallographic direction. At the intermediate temperature range of 55 to 80°C, it was observed that multiple nanorods grew along the same direction, which further fused into large single nanorods at higher temperatures, as observed in Figure 4.19 (b-e). Such growth behavior belongs to “oriented attachment,” conceptualized by Penn and Banfield et al [171]. According to this model, the same crystallographic-oriented nanoparticles (i.e., one-, two-, three-dimensional) undergo fusion to form a single crystal [172]. This process consists of three stages: (1) adjacent nanoparticles self-organize themselves towards a specific crystallographic direction; (2) the fusion of nanoparticles and formation of a smooth and continuous interface; and (3) maintaining nanoparticle alignment

during the entire growth process [173], [174]. Similarly, the same trend was observed in the CAU-17 nanorods formation, as evidenced by the FESEM image shown in Figure 4.19 (a), where smaller nanorods aligned themselves towards the specific crystallographic direction at relatively low temperature. The interaction between nanorods takes place via Van der Waals forces, and due to their thermal energy, they try to arrange themselves towards a specific crystallographic direction to find the lowest energy configuration [172]. As the thermal energy of the material increases with temperature, the nanorods align more quickly and gain more freedom to form larger-sized nanorods at higher temperatures (80°C to 130°C). Herein, the oriented attachment growth mechanism takes place due to the in-situ growth of CAU-17 on the quartz substrate.

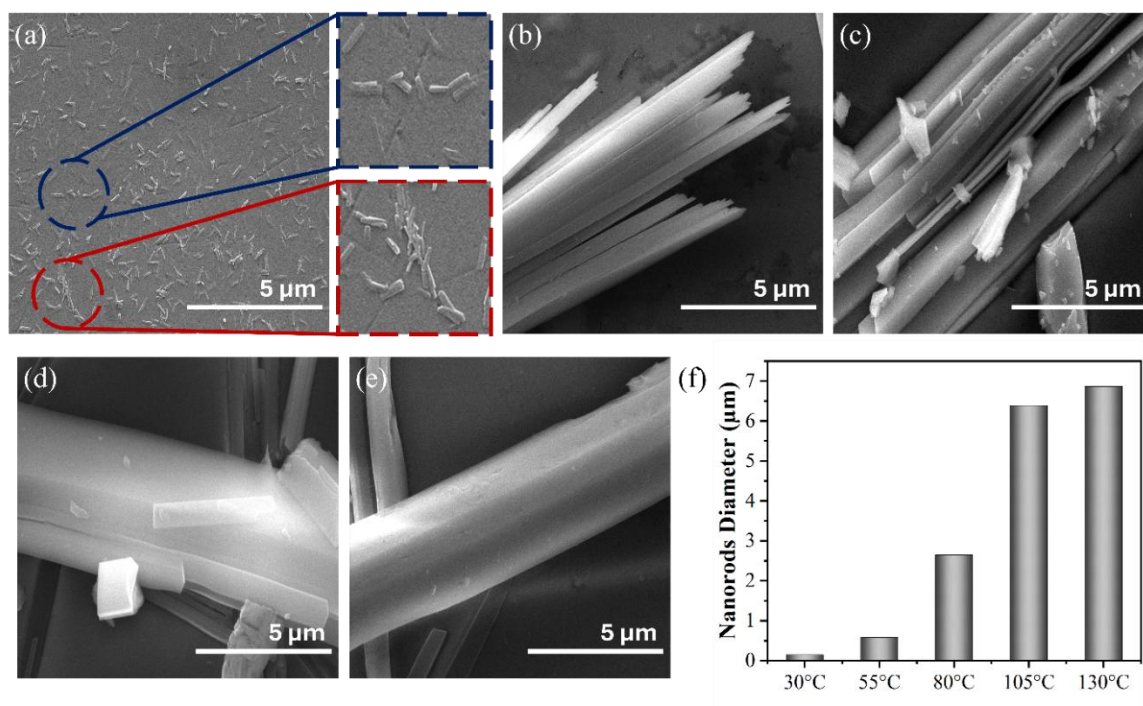


Figure 4.19: FESEM images of CAU-17 thin films synthesized at different temperatures: (a) 30°C, (b) 55°C, (c) 80°C, (d) 105°C, and (e) 130°C. (f) Influence of synthesis temperatures on CAU-17 nanorods diameter.

4.11 Formation of CAU-17 on Different Surfaces

4.11.1 CAU-17 synthesis on FTO substrate

Figure 4.20 confirms the formation of CAU-17 on the FTO surface. The sharp intense peaks of CAU-17 displayed at 8.64° , 10.8° , 13° , 16.84° , 25.08° , and 33.48° .

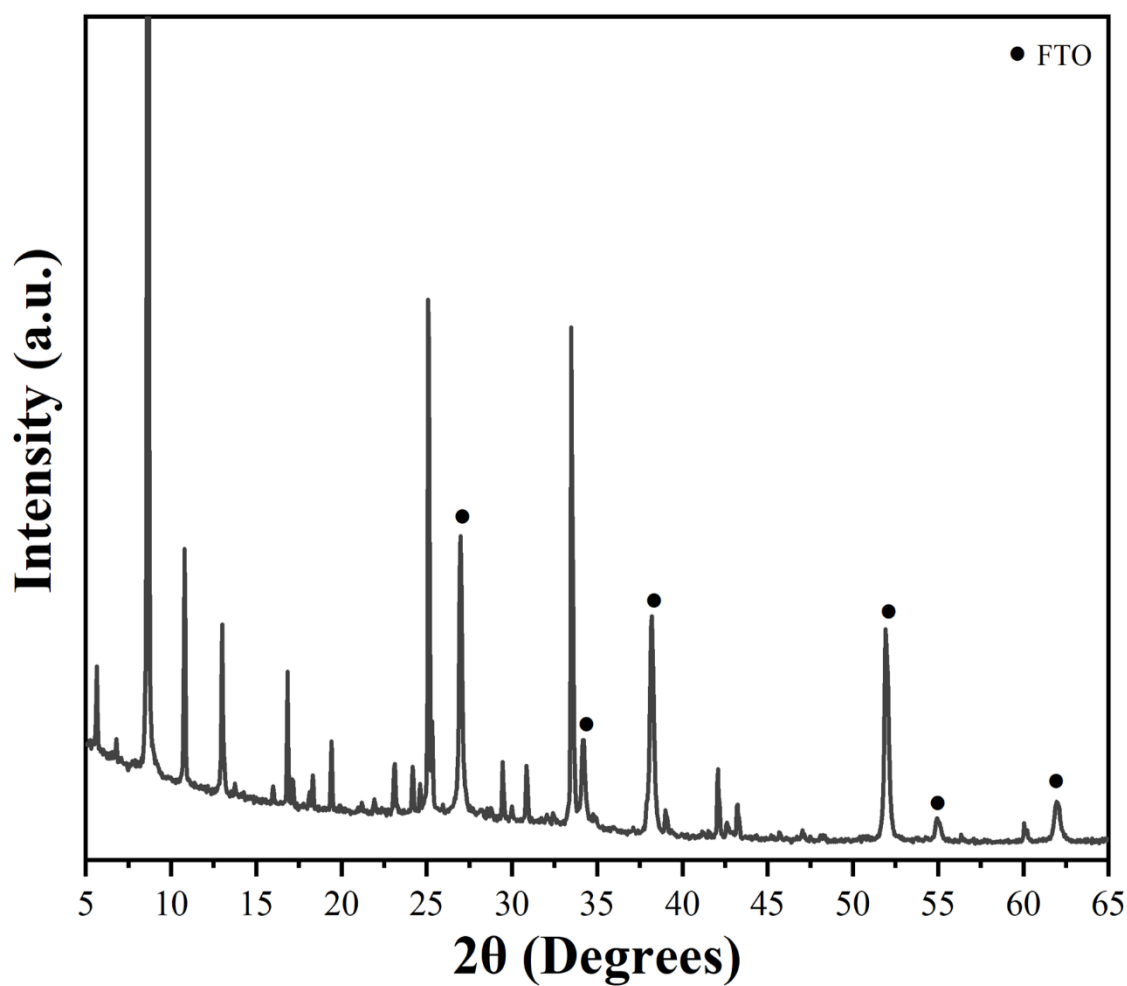


Figure 4.20: XRD pattern of CAU-17 thin film prepared at 130°C for 2 days on the surface of FTO.

4.11.2 CAU-17 synthesis on Carbon Paper

Figure 4.21 represents the XRD results of CAU-17 on the surface of carbon paper, displaying intense peaks at 8.31° , 10.5° , and 12.7° .

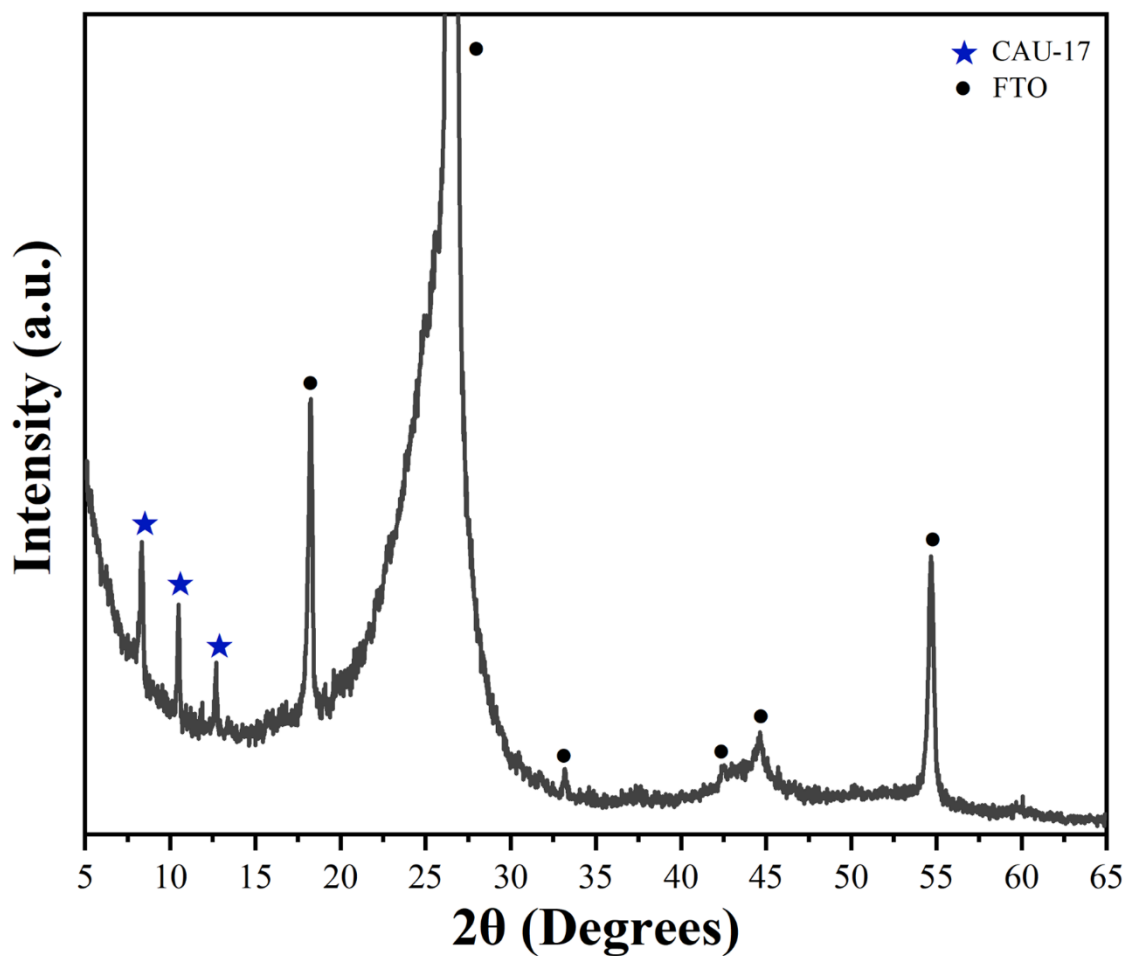


Figure 4.21: XRD pattern of CAU-17 thin film prepared at 130°C for 2 days on the surface of carbon paper.

4.11.3 CAU-17 morphology on FTO surface

The surface morphology of the CAU-17 on the FTO substrate is displayed in Figure 4.22, showing well-defined nanorod formations.

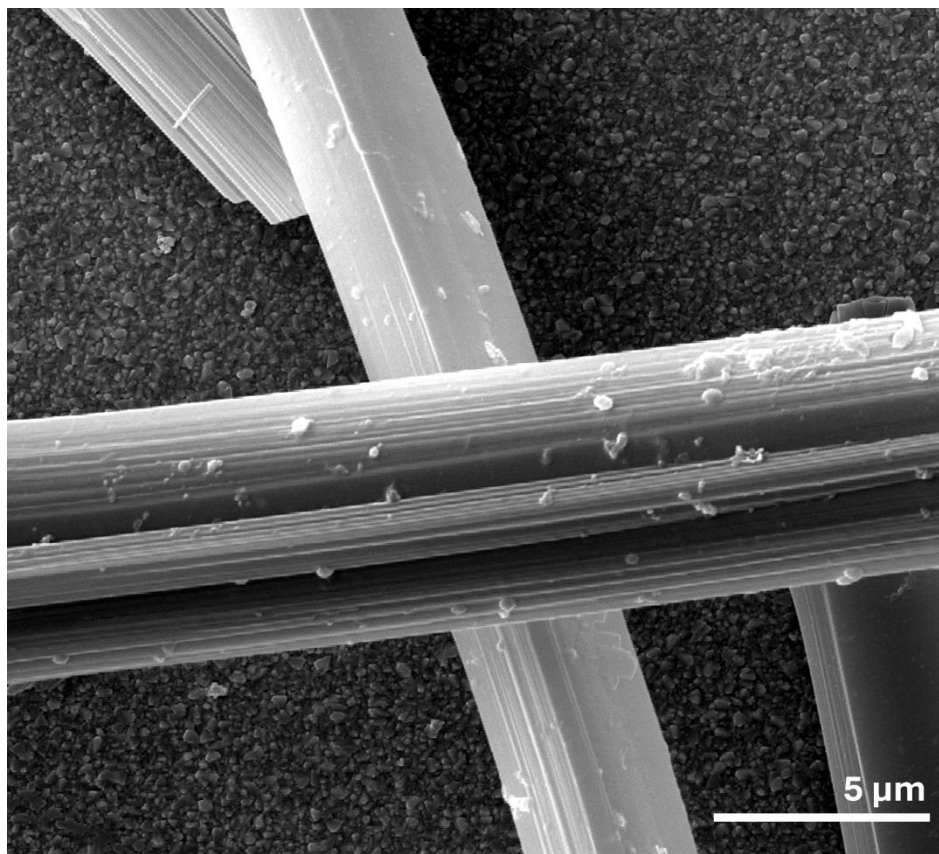


Figure 4.22: FESEM image of CAU-17 thin film prepared at 130°C for 2 days on the surface of FTO.

4.11.4 CAU-17 morphology on Carbon Paper

The surface morphology of the CAU-17 on the carbon paper is displayed in Figure 4.23, showing well-defined nanorod formations.

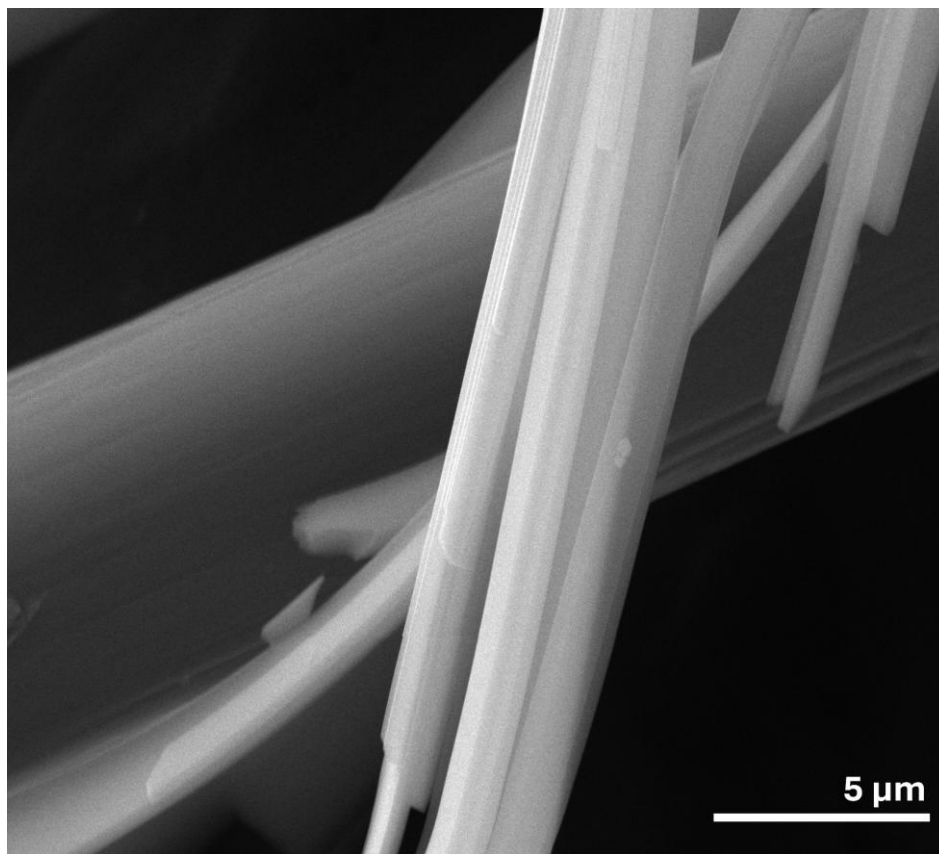


Figure 4.23: FESEM image of CAU-17 thin film prepared at 130°C for 2 days on the surface of carbon paper.

4.12 CAU-17 Thin Film Formation Mechanism

The formation of Bi_2O_3 takes place via the following reaction (eq. 8 to 10). Firstly, the ionization of argon ions takes place, which results in the formation of Ar^+ ions. These ionized Ar^+ ions further bombarded the surface of the pure bismuth target, resulting in the formation of bismuth atoms (Bi^0). These atoms further interact with the oxygen and result in the formation of Bi_2O_3 by consolidating on the surface of the substrate as illustrated in Figure 4.24.

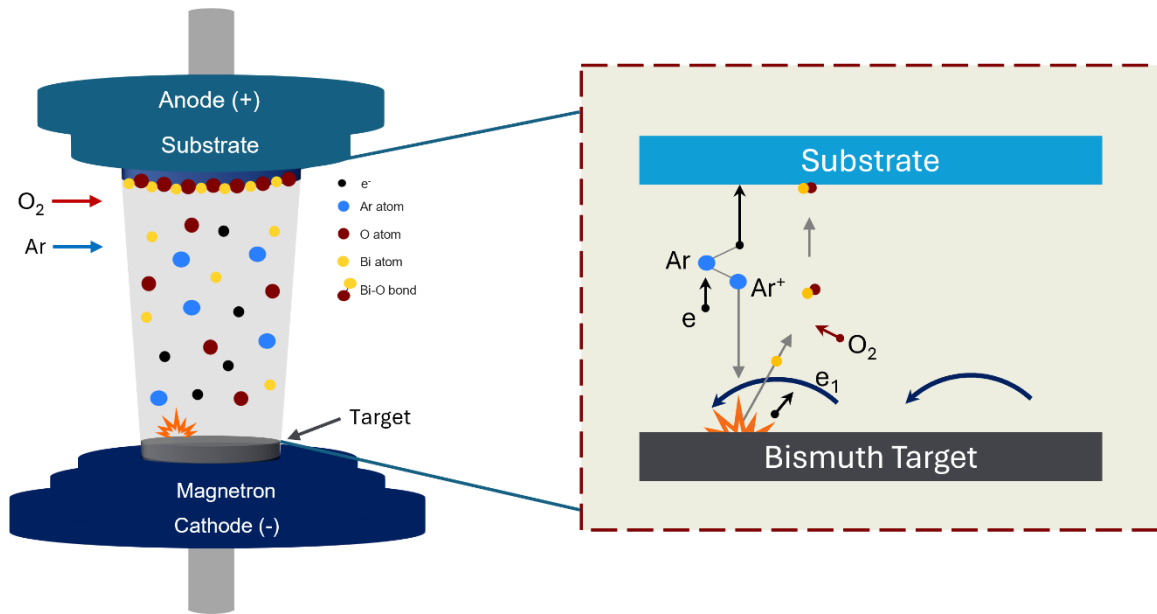


Figure 4.24: Bi_2O_3 thin film formation in reactive DC magnetron sputtering.

In this investigation, it is determined that the formation of Bi_2O_3 is amorphous. The main reason for its formation is the use of low working gas pressures, room temperature synthesis, and low power utilization. Previously reported literature also indicates that using such conditions in reactive magnetron sputtering results in the formation of amorphous Bi_2O_3 thin film [151], [152], [175].

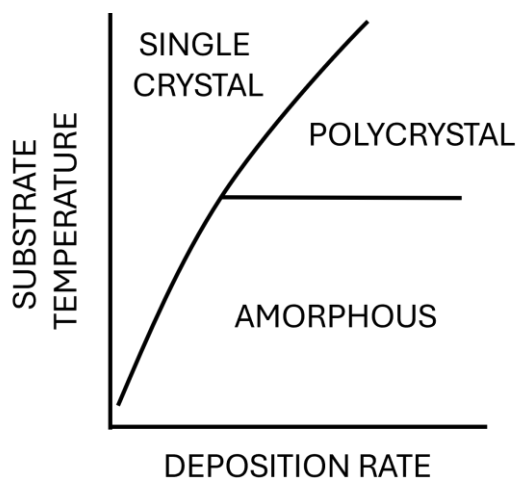


Figure 4.25: Relationship between deposition rate and substrate temperature [176].

Such formation can be understood by considering the relationship between substrate temperature and deposition rate on the formation of thin film, as shown in Figure 4.25. Low substrate temperature and high growth rates favor the formation of the amorphous phase. Such formation takes place because of the relatively low time availability between each deposited atom layer to relax into a crystalline lattice before being covered by subsequent layers, and the lower mobility of atoms over the surface. The mobility of atoms partly depends on the kinetic energy of the incident atom. Higher kinetic energy of the incident atom may also result in surface migrations even though the surface temperature is lower. The formation of the amorphous phase occurs during sputtering when both the substrate's temperature and the incident atom's kinetic energy are low, resulting in a limited number of

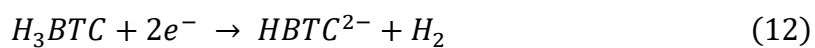
surface migrations. Under such conditions, amorphous layer formation occurs as individual atoms will not get enough energy to arrange themselves in an orderly manner to have an equilibrium crystalline structure [176].

The formation of CAU-17 consists of three primary reactions: (1) dissolution of Bi^{3+} ions; (2) deprotonation of H_3BTC ; and (3) coordination reaction for the development of the framework. In this investigation, CAU-17 $\{\text{Bi}(\text{BTC})(\text{DMF})\}$ is formed in dimethylformamide (DMF) and trimesic acid (H_3BTC). The ligand H_3BTC is a structure-directing agent and acts as a hard base because of its carboxyl groups ($-\text{COOH}$) that bind with Bi^{3+} ions, resulting in the formation of a stable structure [114]. The DMF solution was used as an aprotic polar solvent and functioned as a deprotonation agent [177]. A previous study also highlighted DMF's importance for obtaining MOF structure stability [178]. The formation of CAU-17 occurs when deprotonation of H_3BTC takes place in the DMF solution [179]. In this process, the $-\text{COOH}$ group of H_3BTC lost its three protons (H^+), resulting in the formation of a negatively charged carboxylate ion ($-\text{COO}^-$) [179], [180].

H_3BTC is a type of multifunctional ligands that consist of a benzene ring with three carboxylate groups at the positions of 1,3,5, and is known for its ability to construct the coordination architecture with metal ions through adopting different coordination modes due to its fully or partially deprotonation ability [181]. Depending on the pH of the solution, H_3BTC can be either fully or partially deprotonated [182]. Past investigation indicates that partially deprotonated BTC takes place at the pH of 5, and fully deprotonated at the pH of 7 and 9 [183]. In this work, the pH of the mother solution was between 4.80 and 7.48.

The deprotonation of H₃BTC is a two-step reaction (eq. 12 and 13). Firstly, partial deprotonation of H₃BTC occurs where HBTC²⁻ ions form, and further deprotonation results in the formation of BTC³⁻ ions.

Partial Deprotonation Reaction:



Full Deprotonation Reaction:



The charge difference of Bi³⁺ and BTC³⁻ ions encourages the formation of the CAU-17 framework, where Bi³⁺ serves as a central metal ion that coordinates with the -COO⁻ group of deprotonation of H₃BTC to form a coordination bond (eq. 14) [180]. 0.01M HCl was added to the solution of H₃BTC and DMF as a pH modulator. Prior studies also revealed that the addition of HCl results in a speed-up of the reaction, ensuring phase-purity and reproducibility of results [184], [185].



CHAPTER 5

Conclusion & Final Remarks

Chapter 5

Conclusion And Final Remarks

5.1 Conclusion

The main objective of this research is to bring novelty and innovation to the MOFs community in terms of thin film synthesis and further extend its research area in advanced nanotechnology applications. In the past, MOFs' thin film synthesis was based on powder techniques, which usually required harsh synthesis conditions, applicable to limited substrates, susceptible to secondary phases or impurities during the synthesis, and employed toxic metal salts for their synthesis. Moreover, the major drawbacks of pervious techniques were their inability to be adopted at an industrial scale for several applications and the formation of limited kinds of MOFs. In this regard, designing a technique that offers a wide range of MOFs synthesis, driven by green chemistry, that works under mild conditions, and is adaptable to large-scale production is the main concern of today's MOFs researcher.

The concept of using “*Reactive DC Magnetron Sputtering*” for the synthesis of MOF thin films is relatively new and has not previously been explored. This technique has great potential in opening the doors to its commercialization at an industrial level and offers many advantages over conventional techniques and presently employed vacuum-based technologies. The advantages, like its suitability for large-scale synthesis, cost-

effectiveness, and adherence to the green chemistry principles, are starting a new age of advancement in this field.

In this research work, an idea for developing MOF thin films through a surface modification technique was presented, where a layer of metal oxide is fabricated using reactive DC magnetron sputtering on the surface of the specimen that acts as a metal ion source for MOF synthesis. The nature of the specimen could be conductive, non-conductive, or any flexible material. These ions further interact with the organic linker in a solvent under very mild conditions. Such interaction results in the formation of the MOF thin films.

The research findings in this thesis work predominantly focus on MOFs synthesis and characterization techniques. Herein, two distinct classes of MOFs were synthesized, one belonging to the special sub-category of MOFs, i.e., Zeolitic Imidazolate Framework. In this category, ZIF-8 was synthesized, the most renowned type of ZIF. The other class of MOFs belongs to bismuth-based MOFs, where CAU-17 was synthesized. This type of MOF is known for its permanent porosity and cost-effective synthesis using cheap organic linkers, i.e., H₃BTC linker.

Reactive DC magnetron sputtering demonstrated its ability to synthesize MOF thin films via surface modification based on an in-situ technique. The biggest advantage of using this technique is eliminating metal salt requirements and converting of metal oxide layer into an MOF thin film under mild conditions. So far, two MOFs have been synthesized with the help of this technique, where the ZIF-8 structure was easiest to identify and verify. For the complicated and complex structure like CAU-17 wide range of spectroscopy techniques has been employed for MOFs identification of main functional groups and characteristic peaks. Additionally, the influence of temperature on ZIF-8 and CAU-17 thin films was also

investigated; those results showed that the crystalline nature and framework of both MOFs depended on it. An increase in synthesis temperature resulted in the formation of highly crystalline thin films with the desired morphology. Furthermore, the ability of DC reactive magnetron sputtering to synthesize thin films on different surfaces of different materials further increased the prospective of MOFs thin films for advanced applications such as gas sensors, CO₂ reduction, batteries, and supercapacitors.

5.2 Project Achievements

ZIF-8: Prominent Accomplishments

- 1st study that conceptualized the use of reactive DC magnetron sputtering for ZIF-8 thin film synthesis
- 1st study that emphasizes the importance of temperature on the crystalline nature of ZIF-8 thin film in aqueous solution

CAU-17: Prominent Accomplishments

- 1st study that stated the use of a vacuum-based technique for the synthesis of CAU-17 thin film
- 1st study that prove the synthesis of CAU-17 at lower/higher temperature than 120°C without any formation of secondary phases or impurities
- 1st study that gives the concept of “Oriented attachment” in CAU-17 formation

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Publications

Muhammad Zain Azeem, Khaled Hassanein Sayed, Badriah Sultan, Abduljabar Alsayoud, S. B. Qadri, Qasem A. Drmish. "Vacuum-Driven Approach for Synthesizing CAU-17 MOF Thin Films." (In preparation for submission)

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