

République Algérienne Démocratique et Populaire
Ministère de l'Enseignement Supérieur et de la Recherche
Scientifique

École Normale Supérieure de l'Enseignement Technologique de
Skikda



Département de : Physique et chimie

THÈSE

Présentée en vue de l'obtention du diplôme de

Doctorat

Domaine : Sciences de la matière

Filière : Physique

Spécialité : Physique des matériaux

Présentée par

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Thème :

Élaboration des composites à base de polyaniline et étude de
leurs propriétés physico-chimiques

Soutenue publiquement le : 20/05/2026

devant le jury composé de :

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Année Universitaire : 2025/2026

People's Democratic Republic of Algeria
Ministry of Higher Education and Scientific Research
Higher Normal School of Technological Education of Skikda



Department of : Physics and Chemistry

THESIS

Submitted in fulfillment of the requirements for the degree of

Doctorate

Domain: Materials Sciences

Field of study : Physics

Speciality: Materials Physics

Presented by :

Mr. DJEDID NABIL

Title:

**Elaboration of polyaniline-based composites and study of their
physicochemical properties**

Publicly defended on: 20/05/2026

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Academic Year : 2025/2026

Acknowledgments

First and foremost, I would like to express my deepest gratitude to my supervisors, **Dr. BOUBEKRI Hani** and **Professor BENDJEFFAL Hacene**, for their invaluable guidance, patience, and continuous support throughout this research. Their scientific expertise and insightful suggestions were fundamental to the completion of this work.

I would like to sincerely thank **Professor KHORIEF NACEREDDINE Abdelmalek** for honoring me by presiding over the jury. My gratitude also extends to **Professor BOUHADIBA Abdelaziz**, **Professor RAHMOUNI Salah**, and **Dr. CHEBLI Abdelhak** for accepting the task of examining this thesis.

I am also grateful to the technical and administrative staff at the **Higher National School of Technical Education (ENSET) of Skikda** for providing the facilities and the environment necessary to conduct my experiments.

Dedication

I dedicate this work:

To the memory of my beloved Father.

Though you are no longer with us to see this achievement, your spirit has guided every step I have taken. I pray that God grants you eternal peace and **blesses the soil where you rest**. This work is a tribute to the values of hard work and perseverance you taught me.

To my dear Mother.

For her endless love, her sacrifices, and her constant prayers. You are the pillar of my life, and I am forever grateful for your presence.

To my **Brothers and Sisters**, for their constant encouragement and for always being by my side.

To my **Spouse and Children** for their patience, understanding, and for being my source of strength during the long hours of work.

And finally, to all those who strive for knowledge and contribute to the advancement of science.

Abstract

In this work, thin polyaniline layers were prepared by chemical deposition, a simple, cost-effective, and eco-friendly method. To ensure proper film deposition on glass substrates, the effects of four main factors were examined, including aniline concentration, ammonium persulfate concentration, medium temperature, and reaction time. The optimization process employed a multivariate approach using the Box-Behnken design to identify the optimal conditions for these variables with the response surface method and the composite desirability function. Results indicated that the optimal precipitation conditions were aniline concentration (0.10 mol/L), ammonium persulfate concentration (0.0427 mol/L), medium temperature (55°C), and reaction time (52.42 minutes), resulting in an expected band gap energy of 1.693 eV. The deposited polyaniline thin films were characterized to analyze their morphological, structural, optical, and electrical properties. Techniques such as infrared spectroscopy, X-ray diffraction, optical microscopy, scanning electron microscopy, and visible and ultraviolet spectroscopy confirmed successful polymerization of aniline on the glass surface. These findings demonstrated the formation of amorphous, hydrophilic polyaniline layers under optimal conditions, with the films exhibiting semiconducting behavior and an energy gap of 1.735 eV. Electrical property analysis showed that the polyaniline layers have a room-temperature conductivity of 4.30 S/cm, an absolute conductivity of 0.52 S/cm, and a thermal activation energy of 2.2×10^{-3} eV.

Keywords: Thin films; Polyaniline; Box-Behnken; Chemical bath deposition; Conductive polymer; Optical properties.

الملخص

في هذا العمل، تم تحضير طبقات رقيقة من البولي أنيلين باستخدام طريقة الترسيب الكيميائي، وهي طريقة سهلة، اقتصادية وصديقة للبيئة. لضمان الترسيب السليم للأغشية على ركائز زجاجية، تم دراسة تأثير أربعة عوامل مخبرية نذكر من بينها تركيز الأنيلين، تركيز بيرسلفات الأمونيوم، ودرجة حرارة الوسط، و مدة التفاعل ، تمت عملية التحسين باستخدام نهج متعدد المتغيرات يعتمد على تصميم بوكس-بهنكن، وهذا بغية تحديد الظروف المثلى لهذه المتغيرات باستخدام طريقة سطح الاستجابة (RSM) ووظيفة الرغبة المركبة (CDF). اظهرت النتائج المتحصل عليها ان أفضل شروط الترسيب هي تركيز الأنيلين (0.10 مول/لتر)، وتركيز بيرسلفات الأمونيوم (0.0427 مول/لتر)، ودرجة حرارة الوسط (55°م)، ووقت التفاعل (52.42 min)، مما أدى إلى طاقة فجوة نطاق متوقعة تبلغ 1.693 إلكترون فولت. تم توصيف الأغشية الرقيقة من البوليأنيلين المودعة لتحليل خصائصها المورفولوجية والهيكلية والبصرية والكهربائية. أكدت تقنيات مثل الشعبة تحت الحمراء، الأشعة السينية، المجهر الضوئي، المجهر الماسح الإلكتروني، مطيافية المجال المرئي و فوق البنفسجي، نجاح بلمرة الأنيلين على سطح الزجاج. أشارت هذه النتائج إلى تكوين طبقات بوليأنيلين غير متبلورة ومحبة للماء في ظل الظروف المثلى، حيث أظهرت الأغشية سلوكًا شبه موصل وفجوة طاقة تبلغ 1.735eV، اظهرت دراسة الخصائص الكهربائية ان طبقات البولي الانلين المحضرة تتميز بناقلية عند درجة حرارة عادية تقدر بـ 4.30 S/cm ، ناقلية مطلقة (0.52 S/cm) و طاقة التنشيط الحرارية في حدود 2.2×10^{-3} إلكترون فولت.

الكلمات المفتاحية: الأغشية الرقيقة؛ البولي أنيلين؛ بوكس-بهنكن؛ الترسيب الكيميائي؛ البوليأمر الموصل؛ الخصائص البصرية.

Résumé

Dans ce travail, des couches minces de polyaniline ont été préparées par dépôt chimique, une méthode simple, économique et respectueuse de l'environnement. Afin de garantir la bonne précipitation des membranes sur des supports en verre, l'effet de quatre facteurs expérimentaux a été étudié, parmi lesquels la concentration en aniline, la concentration en persulfate d'ammonium, la température du milieu et la durée de la réaction. L'optimisation a été réalisée à l'aide d'une approche multivariée basée sur le plan Box-Behnken afin de déterminer les conditions optimales pour ces variables, à l'aide de la méthode de la surface de réponse et d'une fonction de désirabilité composite. Les résultats obtenus ont montré que les meilleures conditions de déposition sont une concentration d'aniline de 0,10 mol/L, une concentration de persulfate d'ammonium de 0,0427 mol/L, une température du milieu de 55 °C et un temps de réaction de 52,42 min, ce qui a conduit à une énergie de bande interdite prévue de 1,693 eV. Les films minces de polyaniline déposés ont été caractérisés afin d'analyser leurs propriétés morphologiques, structurales, optiques et électriques. Des techniques telles que la FTIR, la DRX, le microscope optique, la MEB et la spectroscopie UV-Vis ont confirmé le succès de la polymérisation de l'aniline sur la surface du verre. Ces résultats ont indiqué la formation de couches de poly(aniline) non cristallines et hydrophiles dans des conditions optimales, les membranes présentant un comportement semi-conducteur et un gap énergétique de 1,735 eV. L'étude des propriétés électriques a montré que les couches de polyaniline se caractérisent par une conductivité à température ambiante estimée à $4,30 \times 10^{-3}$ S/cm, une conductivité absolue de $0,52 \times 10^{-3}$ S/cm et une énergie d'activation thermique de l'ordre de $2,2 \times 10^{-3}$ eV.

Mots-clés : Couches minces ; Polyaniline; Box-Behnken ; Dépôt chimique en bain ; Polymère conducteur ; Propriétés optiques.

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LIST OF ABBREVIATIONS

PANI	Polyaniline
PPy	Polypyrrole
PVC	Polyvinyl Chloride
ICP	Intrinsically conductive polymer
PAC	polyacetylene
PEO-LiTFSI	Polyethylene oxide-Lithium bis(trifluoromethanesulfonyl)imide
PVDF-HFP/EMIM-TFSI	Poly(vinylidene fluoride-co-hexafluoropropylene)/-Ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide
ECPs	Extrinsically conductive polymers
PEDOT	Poly(3,4-ethylenedioxythiophene)
PSS	(Poly(styrene sulfonate))
LED	light-emitting diodes
OLED	Organic Light-Emitting Diode
HOMO	Highest occupied molecular orbital
LUMO	Lowest unoccupied molecular orbital
CB	Conduction Band
VB	Valence Band
IP	Ionization potential
CPs	Conductive polymers
EA	Electron affinity
PANi-EB	Polyaniline-(Emeraldine Base)
PANi-ES	Polyaniline- (Emeraldine Salt)
NMP	N-Methyl-2-pyrrolidone
UV-Visible	Ultraviolet-Visible Spectroscopy
ITO	Indium Tin Oxide
LbL	layer-by-layer
CVD	Chemical Vapor Deposition
CBD	Chemical Bath Deposition Method
SILAR	Successive Ionic Layer Adsorption and Reaction
PVD	Physical Vapor Deposition
PLD	Laser Ablation Deposition
VTE	Vacuum thermal evaporation
ALD	Atomic Layer Deposition
LB	Langmuir–Blodgett
LPCVD	Low-Pressure Chemical Vapor Deposition
PACVD	Plasma-Assisted Chemical Vapor Deposition
LCVD	Laser Chemical Vapor Deposition
SILAR	Successive Ionic Layer Adsorption and Reaction
APS	Ammonium persulfate
TCR	Temperature Coefficient of Resistance
LCD	Liquid-Crystal Display

CD	Compact Disc
DVD	Digital Versatile Disc
OFAT	One factor at a time
DoE	Design of Experiments
QbD	Quality by Design
DF	Desirability function
BBD	Box-Behnken Design
FTIR	Fourier Transform Infrared Spectroscopy
<i>XRD</i>	X-ray Diffraction
RSM	Response Surface Methodology
ANOVA	Analysis of Variance
DF	Desirability function
Adj SS	Adjusted Sum of Squares
Adj MS	Adjusted Mean Squares
<i>F</i> -Value	Fisher Value
<i>P</i> -Value	Probability Value
R-sq	R-Squared
R-sq(adj)	Adjusted R-Squared
R-sq(pred)	Predicted R-Squared
PROMPD	Professional Multi-Purpose Diffractometer
FWHM	Full Width at Half Maximum
DC	Direct Current
<i>OFAT</i>	One Factor At a Time
<i>ANN</i>	Artificial Neural Network
OM	Optical Microscopy

List of Symbols

T°	Temperature
t	Time
C_{An}	Aniline concentration
$C_{S_2O_8^{2-}}$	Ammonium persulfate concentration
E_g	Gap energy
Q	<i>Stone-Geisser</i> coefficient
SSE	Sum of squared errors
SSO	Sum of squares of observed
α	Absorption coefficient
h	Planck's constant
ν	Frequency
A	Constant transition probability
R	Reflectance
D	Crystallite size
λ	Wavelength
β	Angular width at half maximum intensity
θ_{β}	Bragg's law angle
k	Dimensionless constant
σ	Conductivity
E_a	Activation energy
K_B	Boltzmann constant
MW	Molecular Weight

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Introduction

Conductive polymers, once considered insulating organic materials, have played a major role in advancing optoelectronic technologies due to their remarkable electrical and physicochemical properties [1–6]. Since the discovery of electrical conductivity in polyacetylene by Shirakawa and co-workers, materials science has undergone a significant transformation [1–8]. This breakthrough led to the development of several conducting polymers, including poly(3,4-ethylenedioxythiophene), polyaniline (PANi), and polypyrrole. Compared with conventional inorganic conductors, these polymers offer advantages such as mechanical flexibility, low density, and reduced production costs [2–8]. Consequently, they have been widely investigated for applications in organic photovoltaics, flexible electronics, sensors, and energy storage devices [3–9]. Still, their large-scale use remains limited by environmental instability and complex synthesis processes. To address these challenges, recent studies have focused on hybrid systems that combine conducting polymers with nanomaterials to enhance performance and expand application potential [8–10].

Among conducting polymers, polyaniline (PANi) has attracted particular interest because of its simple chemical structure, low cost, ease of synthesis, and unique redox properties [10–11]. These features make PANi suitable for diverse applications, including batteries, supercapacitors, sensors, and anticorrosion coatings. PANi exists in several oxidation states, namely leucoemeraldine (fully reduced), emeraldine (partially oxidized), and pernigraniline (fully oxidized), enabling tunable electrical properties depending on its oxidation level [11–12]. Furthermore, protonic acid doping significantly enhances its electrical conductivity, making PANi attractive for electronic and optoelectronic devices [13–14]. Despite these advantages, PANi suffers from limited thermal and mechanical stability, which restricts its performance under harsh conditions [15]. As a result, extensive research has focused on improving PANi properties through structural modification and thin-film fabrication.

PANi thin films are particularly appealing due to their adjustable conductivity, chemical stability, and cost-effectiveness. These characteristics make them promising materials for electronic devices, electrodes, sensors, and energy storage systems. Several techniques have been developed to fabricate PANi thin films, each offering control over morphology and physical properties [16–17]. Chemical oxidative polymerization involves the reaction of aniline with an oxidizing agent, such as ammonium persulfate, in an acidic medium and is suitable for producing large-area films. Electrochemical polymerization allows precise control of film thickness and uniformity through anodic oxidation of aniline on conductive substrates [18–20]. Other methods, including spin coating, successive ionic layer adsorption and

reaction (SILAR), and Langmuir–Blodgett deposition, can yield well-organized films for specialized applications [2–4,21]. Still, many of these techniques require expensive equipment, high energy consumption, and complex operations, which limit their scalability and industrial applicability.

In contrast, the chemical bath deposition (CBD) method offers a simple, economical, and environmentally friendly alternative for thin-film fabrication. This technique allows easy control of film thickness, compatibility with large-area substrates, and operation at relatively low temperatures while generating minimal waste [9]. These advantages make CBD a promising approach for the large-scale preparation of PANi thin films.

The properties of PANi thin films synthesized by CBD strongly depend on several operational parameters, including aniline concentration, oxidant concentration, temperature, solution acidity, and number of deposition cycles. Traditionally, optimization has been carried out using the “one factor at a time” (OFAT) approach, where each parameter is varied independently. Although simple, this method is time-consuming, costly, and incapable of identifying interactions between variables. Full factorial designs are also impractical due to the large number of experiments required. In contrast, chemometric optimization techniques enable simultaneous evaluation of multiple parameters, improving accuracy while reducing experimental effort and cost. Experimental design methods such as Taguchi, Doehlert, central composite, and Box–Behnken designs are widely used to optimize synthesis conditions and investigate variable interactions [25–30].

This work focuses on the synthesis of polyaniline thin films, aiming to produce light-sensitive films with uniform thickness and height. The deposition of thin films has been studied under the influence of several factors, including aniline concentration C_{An} , ammonium persulfate concentration $C_{S_2O_8^{2-}}$, medium temperature T° , and reaction time t . The optimization process employed a multivariate approach using the Box-Behnken design (DDB) to identify the optimal conditions for these variables with the response surface method (RSM) and the composite desirability function (CDF). The influence of these factors and their interactions on the optical energy gap was evaluated to determine optimal conditions for producing high-quality PANi thin films with a reduced energy gap. Various techniques, including FTIR spectroscopy, UV-Vis spectroscopy, optical microscopy, X-ray diffraction, and scanning electron microscopy, were used to study the morphological, optical, and electrical properties of Polyaniline thin films prepared under optimal conditions.

This thesis is structured around two main parts and four interdependent chapters:

The first chapter presents a bibliographical study that will begin with a general introduction to conductive polymers, focusing more specifically on polyaniline, and then on the technological applications of this polymer.

The second chapter, entitled "Methods of Preparing Thin Films," covers a historical overview of thin films, their concept, stages of formation and growth, the principle of their deposition, as well as physical and chemical deposition techniques.

The third chapter focuses on the study site, sampling strategies, materials, and methodologies employed. I.

The fourth chapter presents the results and discussion

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Chapter I: General Overview of Conductive Polymers

I.1. Introduction

The use of materials spans all areas of human activity, dating back to prehistoric times. They serve as essential tools for meeting mankind's core needs. Materials can be grouped into three main categories based on their properties: ceramics, glass, metals and their alloys, and polymers. In fact, polymers have played a crucial role in human societal development. They are among the most widely used materials and have significantly helped solve major challenges in various fields in recent decades [1,2]. This chapter provides a detailed overview of existing conductive polymers, with a particular focus on polyaniline (PANI). We also discuss the latest advancements regarding their applications, electrical properties, doping mechanisms, and other important features [3,4].

I.2. Polymers

A polymer is a natural or synthetic macromolecule composed of many covalently bonded repeating units called monomers, derived from Greek "poly" (many) and "mer" (parts). Natural examples include cellulose, wool, silk, and rubber, while synthetic examples include PVC, nylon, polyethylene, polypropylene, polyamides, and polycarbonates, all produced via polymerization reactions [5-7]. In materials science, polymers are evolving rapidly, with applications spanning traditional plastics, rubber, fibers, paints, and adhesives to advanced uses in aircraft, bulletproof vests, and artificial joints. Unlike small molecules with fixed molecular weights, polymers exhibit polydispersity in chain length, with chains of equal mass differing in dimensions or shape due to conformational isomerism [7-8]. Chains are rarely perfectly linear; branching is common, and in extreme cases, they form three-dimensional networks via intersecting branches (Figure I.1).

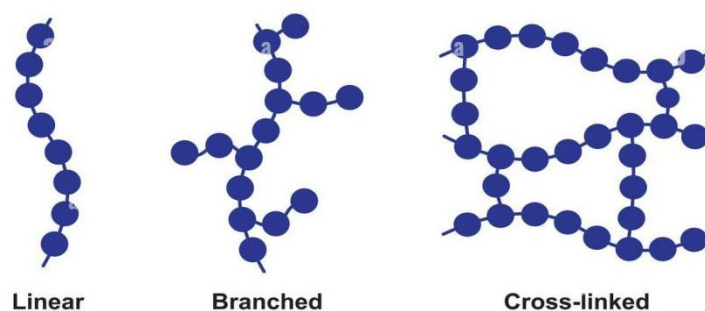


Figure I.1: Representation of fundamental polymer chain structures, a) Linear, b) Branched, c) Crosslinked.

Polymers composed of two distinct types of monomers are classified as copolymers which fall into four primary categories based on their structural arrangement: alternating

copolymers featuring regular, sequential repetition of the two monomer units along the chain; random copolymers with irregularly sequenced monomer units lacking any specific order; block copolymers comprising extended, continuous segments (blocks) of one monomer type followed by blocks of the other; and graft copolymers consisting of a primary backbone chain of one monomer with side chains or branches of the second monomer attached at various points along the main chain.

Since the 1960s, specific technological applications have driven the need for new materials that combine the mechanical properties of conventional polymers with the electrical features of conductive materials. These advanced systems, made of highly conductive organic polymers, are scientifically classified as 'conductive polymers'.

I.2.1. Conductive Polymers

In 1974, chemist Hideki Shirakawa serendipitously discovered the first intrinsically conductive polymer (ICP) - a silvery polyacetylene (PAC) film - while using a catalyst concentration 1,000 times higher than needed. This important discovery led to a key collaboration among Shirakawa, Alan G. MacDiarmid, and physicist Alan J. Heeger to develop synthetic methods for ICPs [1].

In 1977, the research team achieved a remarkable increase in doped polyacetylene (PAC) conductivity from around 10^{-9} S/cm to 10^2 S/cm - an impressive 11-order-of-magnitude improvement. This breakthrough sparked widespread research aimed at optimizing conductivity performance, eventually earning the three scientists the Nobel Prize in Chemistry 25 years later [9,10]. Conjugated polymers mainly consist of alternating carbon single (σ) and double (π) bonds, with σ -bonds providing structural support and π -bonds allowing electron delocalization along the macromolecular chain. Although this setup produces extended electronic states, the inherent conductivity remains relatively low (10^{-12} to 10^{-7} S/cm). However, doping can boost conductivity by about ten orders of magnitude, reaching near-metallic levels. The term 'conductive polymers' encompasses both ionically conductive polymers (charge transport via ions) and electronically conductive polymers (charge transport via electrons) [11-13].

I.3.Types of conductive polymers

The conductive polymers can be classified into three categories:

I.3.1. Ionic conductive polymers

The conductivity of this polymer class originates from mobile ions distributed within the polymeric matrix. Primarily utilized as solid electrolytes and separator membranes in fuel cells [13,14,17].

Table I.1: Some examples of ionic polymers:

Polymer	Composition	σ (S/cm)	T° (°C)	Applications
PEO-LiTFSI	Polyethylene oxide + Li salt	10^{-4} – 10^{-3}	60–80	Solid-state lithium batteries
PVDF-HFP/EMIM-TFSI	Fluoropolymer + ionic liquid	10^{-3} – 10^{-2}	25–100	Flexible supercapacitors
Nafion®	Perfluorosulfonic acid	10^{-2} – 10^{-1}	50–90	Fuel cell membranes
Chitosan-LiClO ₄	Biopolymer + Li salt	10^{-5} – 10^{-4}	20–50	Biodegradable batteries

I.3.2. Electronically Conductive Polymers:

Electronically conductive polymers are divided into two categories: extrinsically conductive polymers (ECPs) and intrinsically conductive polymers (ICPs). ECPs are polymer materials that become conductive only after doping with specific additives. Unlike intrinsically conductive polymers such as PEDOT, the conductivity of these polymers depends solely on the presence of doping agents [12]. The conductivity in this class arises from a π -conjugated system (alternating single and double bonds) along the polymer backbone. In their neutral state, ICPs act like traditional insulating polymers (Table I.2). However, their conductivity increases significantly through oxidation (p-doping) or reduction (n-doping) of the polymer matrix—a process called polymer doping. Because polyacetylene is unstable, researchers shifted their focus to more stable polycyclic aromatic molecules, including polythiophene, polypyrrole, poly(p-phenylene vinylene), and polyaniline [15,16].

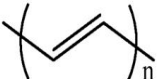
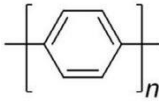
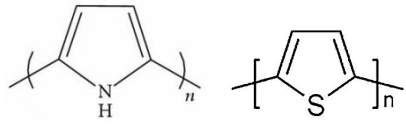
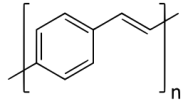
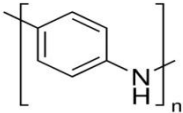
Table I.2: Some examples of Electronically Conductive Polymers

Polymer	Doping Type	T (°C)	σ_{Max} (S/cm)	Primary Applications
PEDOT:PSS	Self-doped	-20 to 100	10^3	Flexible displays, OLEDs, bioelectronics
Polypyrrole (PPy)	p-doped (FeCl ₃)	-10 to 80	10^2	Chemical sensors, antistatic coatings
Polyaniline (PANI)	Acid-doped (HCl)	0 to 70	10^2	Corrosion protection, conductive textiles
Polyacetylene	p/n-doped (I ₂ /Na)	-50 to 100	10^5	Historical reference (Nobel 2000)

I.4. Chemical Structure of Intrinsically Conductive Polymers (ICPs)

Polymers are electrical insulators because their molecular chains are made of covalently bonded atoms; specifically, in saturated carbon compounds, the valence electrons cannot delocalize, so there are no charge carriers or pathways for electrical conduction. In conjugated carbon-based molecules (especially Intrinsically Conductive Polymers, ICPs), electron delocalization happens through interactions between bound electrons, allowing electrical conductivity. The conductivity of these polymers can be adjusted across a very wide range, from insulating to semiconducting, by changing the dopant concentration. Based on their structure, conjugated ICPs can be divided into different families [18].

Table I.3: Chemical structures of these conductive polymer families.

ICP Family	Example	Chemical Structure
Polyenic Systems	Polyacetylene	
Aromatic Systems	Poly(p-phenylene)	
Heterocyclic Aromatic Systems	Polypyrrole, Polythiophene	
Mixed Aromatic-Vinylenic Systems	Poly(p-phenylene vinylene)	
Systems with heteroatoms in the main chain	Polyaniline	

I.5. Electronic Structure of Conductive Polymers

Conventional semiconductor theory explains conduction in conductive polymers through two conditions for intrinsic conductivity: (1) overlapping molecular orbitals forming delocalized wavefunctions, and (2) partial filling of these orbitals for free electron movement. In band theory, atomic orbitals overlap to create quasi-continuous valence and conduction bands; inorganic semiconductors conduct via thermal excitation across narrow bandgaps at room temperature, while wide bandgaps block this, and metals achieve high conductivity from partially filled bands. Understanding conductive polymers requires analyzing charge carriers and band structure: molecularly doped polymers transport charge via hopping between

dopant sites (two-center model), while intrinsically conducting polymers like polyacetylene (Figure I.2) demonstrate band formation as ethylene's π (HOMO) and π^* (LUMO) orbitals progressively overlap, narrowing the HOMO-LUMO gap until discrete levels merge into near-continuous valence and conduction bands [19, 20].

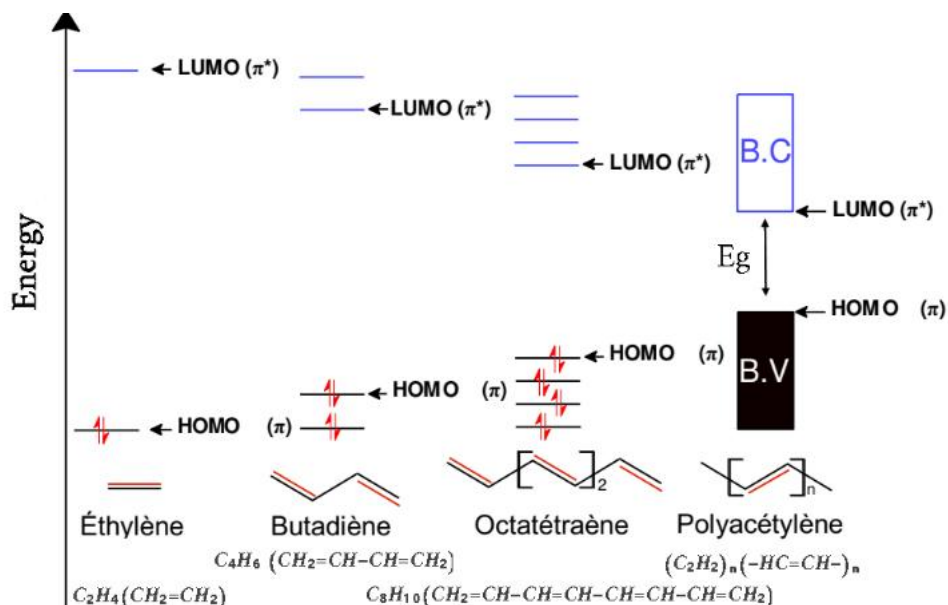


Figure I.2: Molecular orbital (π) diagram of polyacetylene and its model compounds (ethylene, butadiene, and octatetraene).

The valence band includes all energy states at or below the HOMO (Highest Occupied Molecular Orbital). At 0 K, this band is fully filled with electrons, making it the highest-energy band containing electrons in their ground state. The conduction band comprises all energy states above the LUMO (Lowest Unoccupied Molecular Orbital). The region between the HOMO and LUMO is called the "bandgap" (E_g) and is defined by its width, which contains no allowed energy levels. It can also be described as the difference between the ionization potential (IP: the energy needed to remove an electron from the HOMO) and the electron affinity (EA: the energy required to add an electron to the LUMO). Both the molecular orbital energies and the bandgap depend on the conjugation length of the polymer chain [21-23]. The width of their bandgap serves as the criterion to classify a material as either a conductor, semiconductor, or insulator (Figure I.3). Indeed, insulators possess a very large bandgap ($E_g > 3\text{eV}$) that entirely blocks electron transfer, semiconductors exhibit a small bandgap enabling electron transition from the valence band (VB) to the conduction band (CB) through simple thermal excitation, while metals lack a bandgap altogether, resulting in the overlap of the two bands. π -Conjugated polymers (CPs) are initially regarded as wide-bandgap semiconductors or insulators prior to doping. Their conductivity can be

enhanced to levels comparable to those of metals via chemical modification of their structure (doping), which reduces the bandgap by adding charge (Figure I.3).

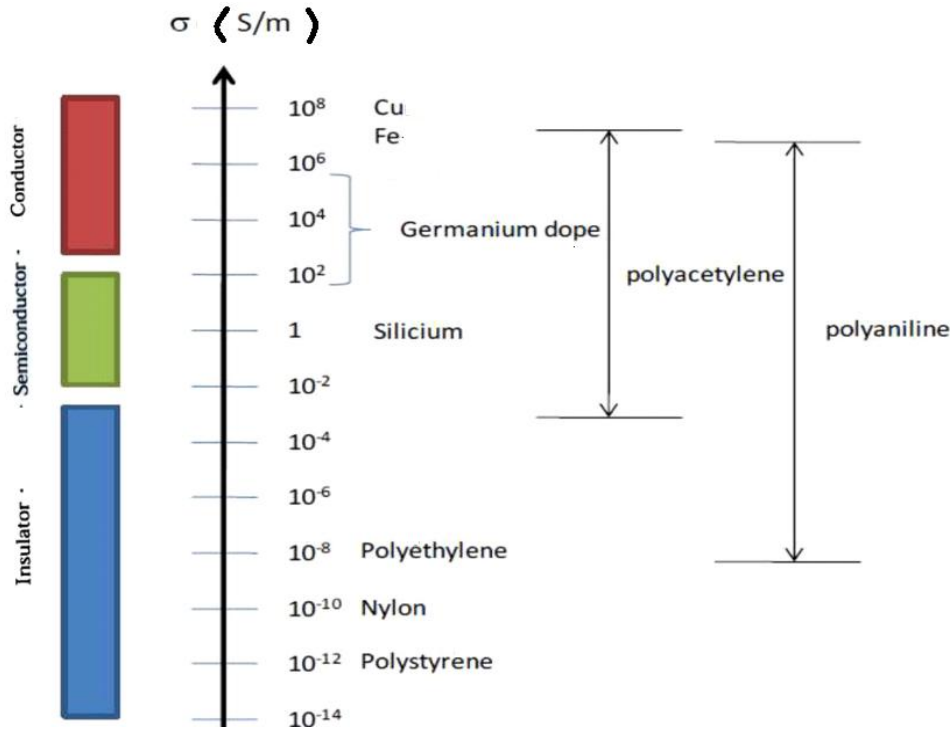


Figure I.3: Conductivity scale of different materials [24-26].

Conductive polymers are categorized into two groups based on their ground state symmetry:

- Polymers with Degenerate Ground States: These polymers can exist in multiple structurally different forms that have the same energy levels. For example, polyacetylene has two different configurations (A and B phases) that are energetically equivalent (Figure I.4).
- Polymers with Non-Degenerate Ground States: Most conductive polymers have two resonance forms with different energy levels. For example, polyaniline exhibits an energy difference between its aromatic and quinoid forms.

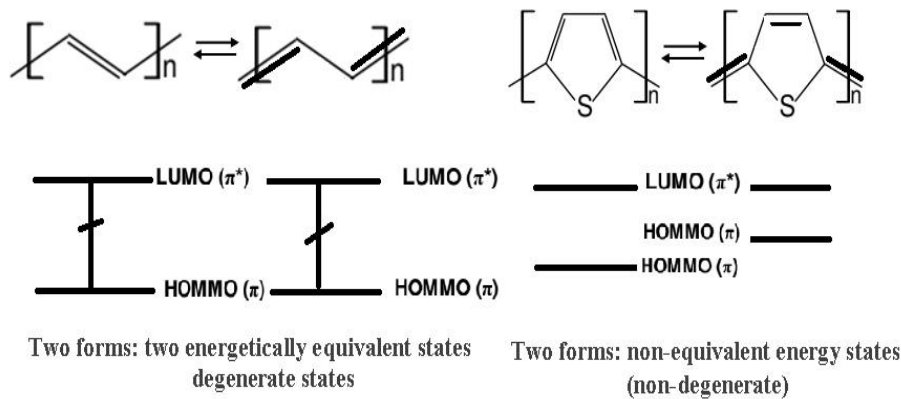
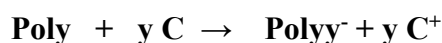
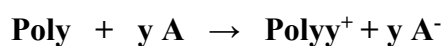


Figure I.4: Representation of degenerate and non-degenerate states [27].

I.6. Doping of Conductive Polymers

As previously mentioned in earlier sections, neutral conductive polymers are either insulators or can be regarded as wide-bandgap semiconductors. Increasing their conductivity involves a chemical process called doping. Doping is a chemical process that decreases the bandgap of these polymers by adding mobile charge carriers. The nature of doping in semiconducting polymers fundamentally differs from that in inorganic materials semiconductors. There are two main doping mechanisms for semiconducting polymers: redox doping and acid-base doping. Redox doping can be either p-type or n-type. P-type doping involves oxidation of the π -conjugated system, resulting in electron withdrawal and transforming the polymer chains into polycations (+). Electrical neutrality is then maintained by adding an appropriate number of counter-anions into the polymer matrix. Conversely, n-type doping reduces the π -conjugated polymer, converting it into polyanions (−) by inserting dopant cations. P-type and n-type dopants can be explained as follows:



The chemical reactants (cations C and anions A) that dope the polymer. It is well established that p-doped polymers demonstrate significantly greater stability compared to n-doped polymers. The latter tend to degrade when exposed to even trace amounts of water or other proton sources. Generally, n-doping has several disadvantages relative to p-doping (Figure I.5). n-doped polymers react rapidly with atmospheric oxygen, losing their excess electrons and reverting to a neutral state. As a result, these materials require storage in inert environments. During doping, the insertion of charge carriers into the polymer chain causes local structural distortions and creates localized states within the bandgap.

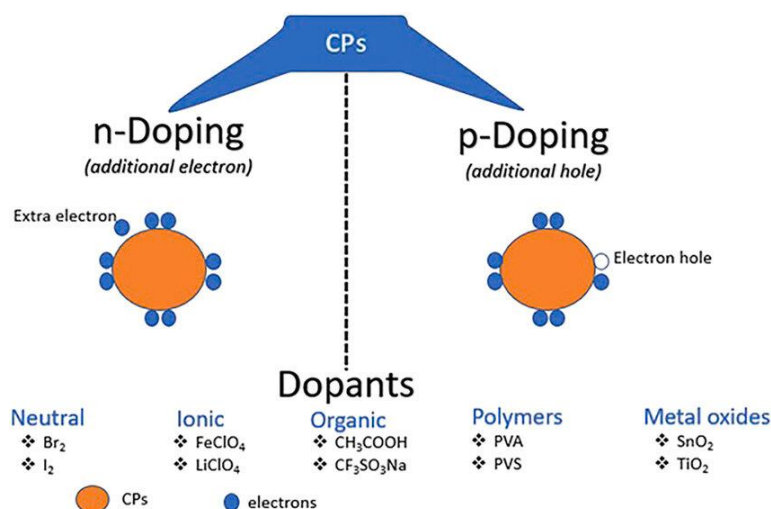


Figure I.5: Types of Dopants for Conductive Polymers.

These combined charge-structure defects are called quasiparticles. Depending on the polymer's resonance structure, two types of quasiparticles exist: in polymers with a non-degenerate ground state, the charge carriers are polarons or bipolarons, while in those with a degenerate ground state, the charge carriers are solitons [29-31]. There is a direct relationship between the mobility of charge carriers and the polymer's conductivity. The movement of charge carriers is influenced by the degree of polymer conjugation, its crystallinity (packing density), the proximity of the polymer chains, and temperature, which also has a direct, proportional effect. The conductivity of conductive polymers depends on the nature, concentration, and size of the dopants, as well as the doping time. Based on molecular weight, dopants can be classified as large or small. Large dopants are difficult to filter out from the polymer chain because they are strongly bound to it. In contrast, small dopants can more quickly dope the polymer and are easier to remove.

I.7. The charge carriers

Polymer oxidation generates positive charge carriers (p-type), while reduction produces negative charge carriers (n-type). The resulting structure in both cases is called a polaron. When two electrons are removed or added, it is called a bipolaron.

A polaron is a single positive or negative charge ($\pm e$), coupled to a local deformation of the macromolecular chain (Figure I.6), and is localized over a finite number of rings. Electronic transport in the material occurs through the movement of polarons along the polymer chain.

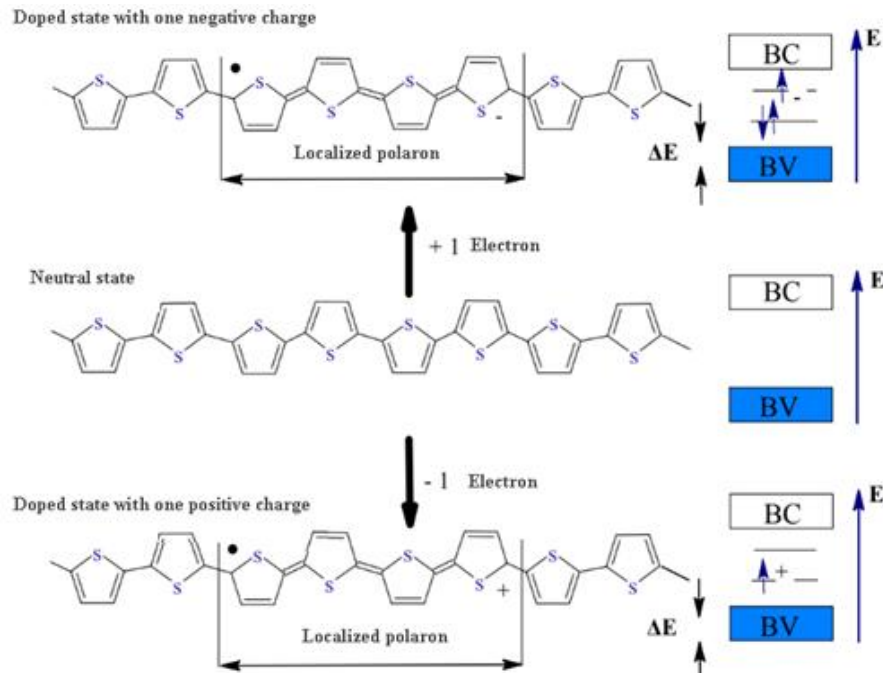


Figure I.6: Mechanism of polaron formation in polythiophene

In this band representation, the polaron-induced deformation reveals two energy levels within the gap: one near the VB (Valence Band) and the other, a 'symmetric' level, near the BC (Conduction Band). In the case of a positive polaron (with an electron removed), the level near the VB is occupied by a single electron, and the level near the BC is unoccupied.

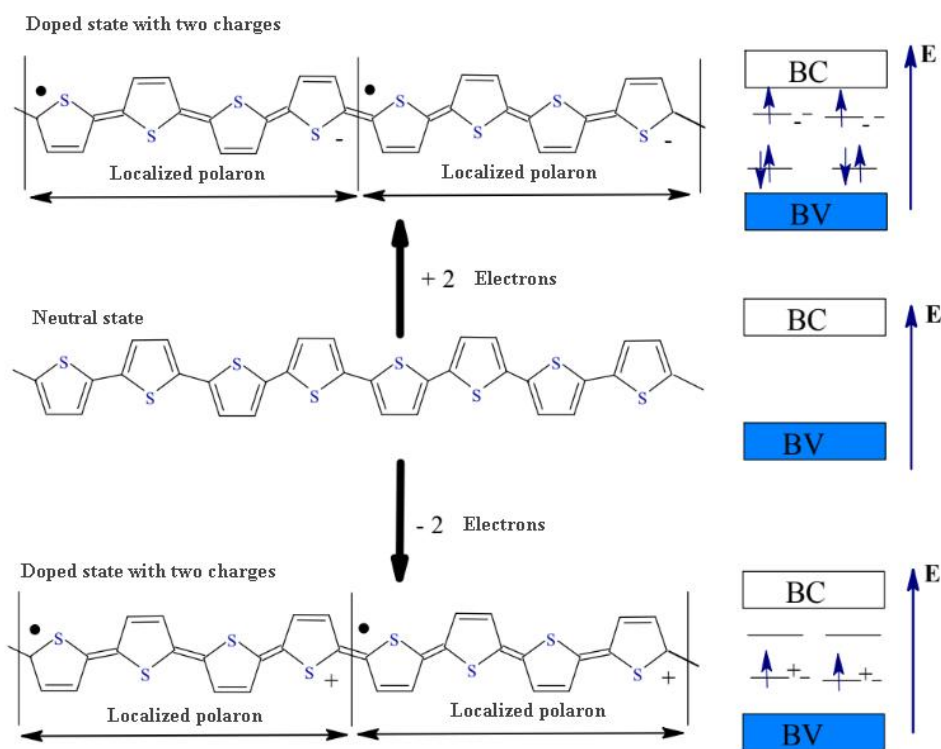


Figure I.7: Doping mechanism with two polarons on the polythiophene chain.

Conversely, in the case where an electron is added—the case of a negative polaron—two electrons now occupy the level near the VB, and one electron occupies the level near the BC. Suppose a polaron has been created and a second electron is removed (or added), thus creating a second polaron of the same sign. Two scenarios are possible (Figure I.7) [29,30].

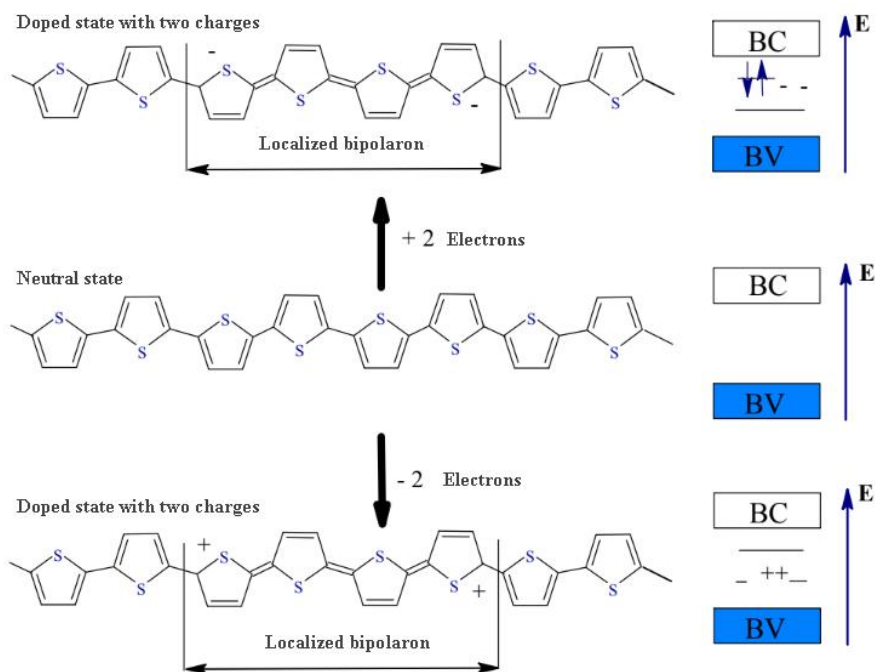


Figure I.8: Doping mechanism with a bipolaron on the polythiophene chain.

The bipolaron, represented in (Figure I.8), carries a charge ($\pm 2e$), which is coupled to a local deformation of the macromolecular chain and is localized over a finite number of rings. In this case, electronic transport in the material occurs through the movement of bipolarons along the polymer chain [29,32].

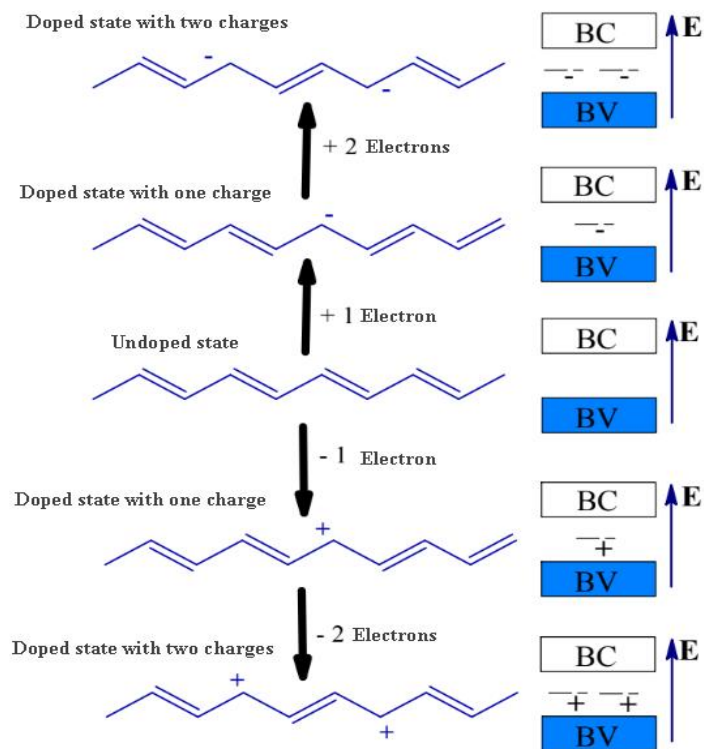


Figure I.9: Doping mechanism with solitons for *trans*-polyacetylene.

The soliton is a defect created by inserting positive or negative charges. The charged soliton has no fixed size and is therefore spread out along the entire conjugated chain. Doping polyacetylene can be described as follows: Removing two electrons successively creates the first radical, then a second; when they recombine, they form spinless charge carriers, and this process continues. n-Type doping can also occur by adding electrons, which generate negatively charged solitons. The structural change linked to the formation of charged solitons is shown in (Figure I.9). The energy level of the soliton is located within the bandgap [36].

I.8. Polyaniline

Conventional semiconductor theory explains conduction in conductive polymers through two conditions for intrinsic conductivity: (1) overlapping molecular orbitals forming delocalized wavefunctions, and (2) partial filling of these orbitals for free electron movement [34-36]. In band theory, atomic orbitals overlap across neighboring atoms to form quasi-continuous energy bands; traditional inorganic semiconductors conduct when thermal excitation bridges narrow bandgaps between the valence and conduction bands at room temperature, while wide bandgaps prevent sufficient electron promotion under ambient conditions; and metals exhibit high conductivity via partially filled bands [35-36]. Charge transport in molecularly doped polymers occurs via hopping between dopant molecules acting as charge-transfer sites, best described by the two-center model of carrier movement between discrete molecular locations. The electronic structure of intrinsically conducting polymers follows a band model, exemplified by polyacetylene (Figure I.2), where successive ethylene units progressively overlap π bonding (HOMO) and π^* antibonding (LUMO) orbitals, reducing the HOMO-LUMO energy gap [37-38]. As chain length increases dramatically, these discrete energy levels merge into two broad, nearly continuous bands—the valence band and conduction band—enabling metallic-like conductivity [39-40].

I.8.1. Different Forms of Polyaniline Based on Its Oxidation State

Polyaniline consists of a succession of benzenoid-type aromatic rings bridged by a nitrogen heteroatom. The Polyaniline structure synthesized by chemical or electrochemical methods, depending on its oxidation state, can be described by the following formula (Figure I.10):

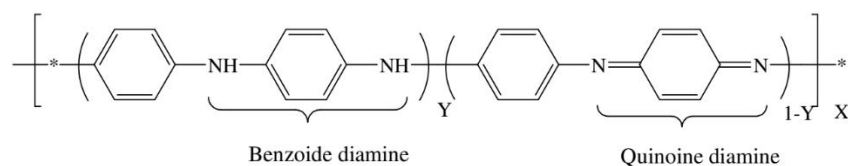


Figure I.10: General structure of Polyaniline.

Depending on its oxidation state, PANi exists in different forms, distinguished by the amine/imine ratio. The three essential forms are leucoemeraldine, emeraldine, and pernigraniline (Figure I.11) [44].

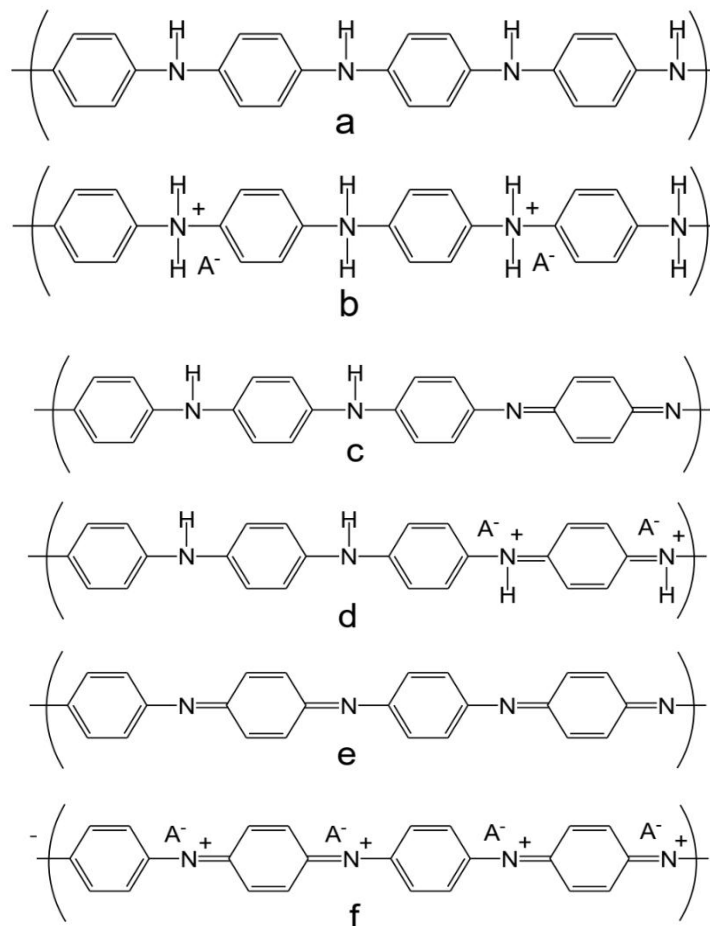


Figure I.11. PANi structures according to the oxidation state. a) Leucoemeraldine base, b) Leucoemeraldine salt, c) Emeraldine base, d) Emeraldine salt, e) Pernigraniline base, f) Pernigraniline salt.

Leucoemeraldine is composed of 100% reduced benzene diamine units, which are easily oxidized in air. Emeraldine is composed of 50% reduced benzene diamine and 50% oxidized quinone di-imine units. The conductive form of PANi, emeraldine salt, is obtained by acid doping of the emeraldine base form. This doping is reversible and corresponds to the protonation of the nitrogen atoms on the imine sites. Finally, pernigraniline is composed entirely of chains of oxidized quinone diimine units. This solid is easily hydrolyzable in an acidic medium [42]. PANi in its leucoemeraldine form is an insulator that cannot be modified by an acid-base reaction. Acid doping of the emeraldine base form yields the emeraldine salt

form, leading to a significant increase in conductivity. This conductivity is due to the formation of a perfectly alternating network throughout the polymer chain. Further oxidation to obtain pernigraniline is followed by a significant decrease in conductivity, returning to an insulating material; it is therefore an insulator-conductor-insulator system. Thus, PANi's conductivity varies not only with its oxidation state but also with its degree of protonation. At pH values above 4, PANi is primarily in its emeraldine base form (Figure I.12) [43].

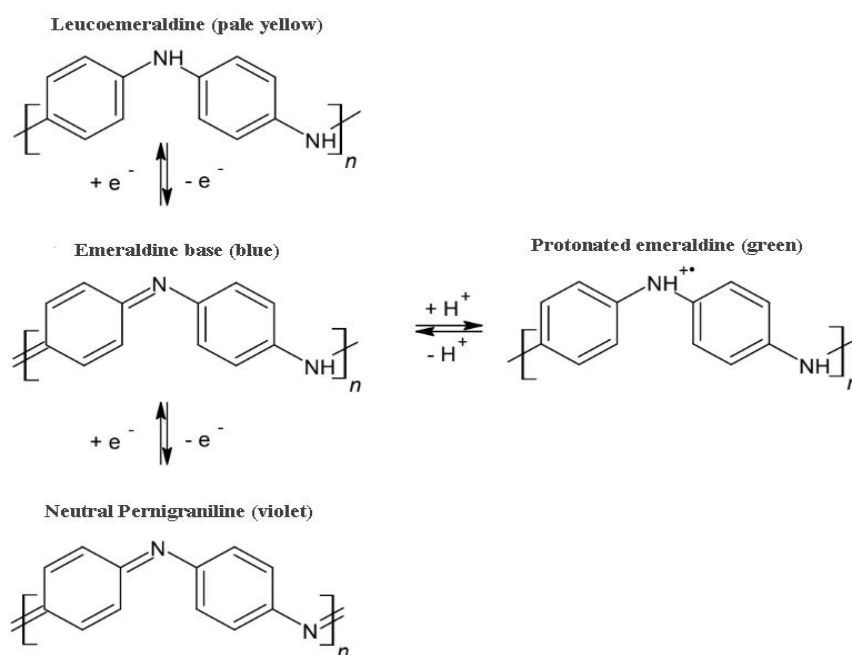


Figure I.12: polyaniline color associated with different degrees of oxidation and protonation.

When the latter is subjected to an acidic solution, the number of quinoid units decreases, and the number of radical cations increases, leading to the emergence of the emeraldine salt form. At very low pH, it is generally found in its conductive form. Still, PANi exhibits very interesting electrochromic properties that depend on its degree of oxidation (Figure I.12) [43].

I.8.2. Polymerization Mechanism of PANI

The mechanisms of the chemical and electrochemical polymerization of aniline, as studied by various authors [44-45], are very similar. Polymerization occurs in steps; it is a polycondensation. The first step of polymerization is the oxidation of the monomer into a resonance-stabilized radical cation (Figure I.13).

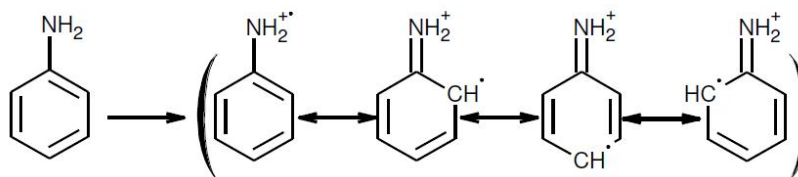


Figure I.13: Formation of the radical cation of aniline.

➤ For the second step, two mechanisms are proposed:

1- Either the coupling of a radical cation with a molecule of the aniline (Figure I.14).

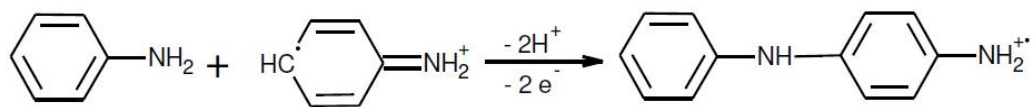


Figure I.14: Propagation of the polymer chain by cation-radical/aniline coupling.

2 - Or the coupling of two cation-radicals in two resonance forms (Figure I.15).

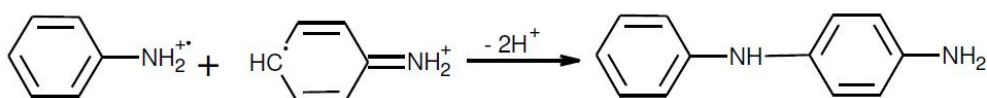


Figure I.15: Coupling of two cation-radicals

The second mechanism is more widely accepted by the scientific community. The next step involves chain propagation: the dimer is oxidized to form a cation radical, which can couple either with the oxidized monomer or with the oxidized dimer radical cation (Figure I.16).

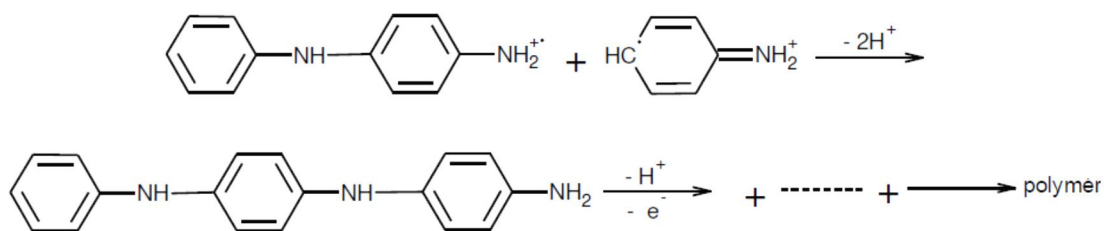


Figure I.16: Propagation of the polyaniline chain.

According to (Figure I.17), the polyaniline obtained is in its fully reduced form (leucoemeraldine). However, in reality, during propagation, it oxidizes to yield the pernigraniline form (Figure I.17).

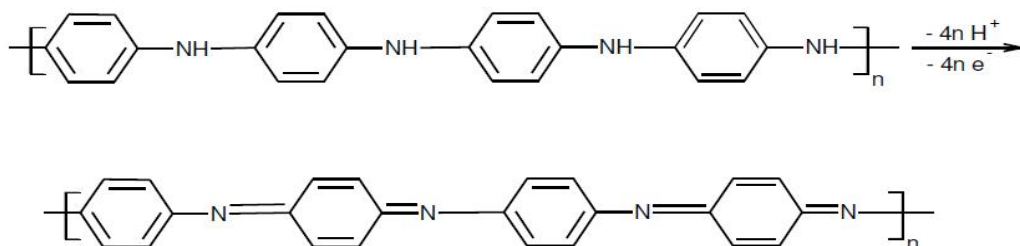


Figure I.17: Oxidation of the leucoemeraldine form to pernigraniline.

In the following step, the fully oxidized polymer is reduced to its semi-oxidized state (emeraldine) by reaction with the monomer (Figure I.18).

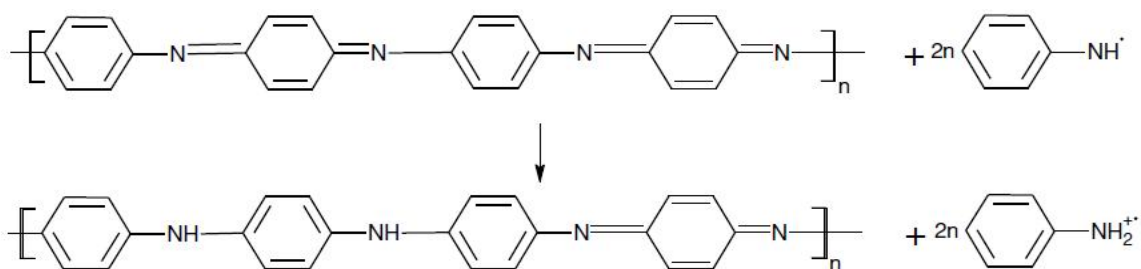


Figure I.18: Transformation from the fully oxidized state to the semi-oxidized state .

I.8.4. Synthesis of Polyaniline

PANI can also be produced by chemical or electrochemical methods. These two synthesis routes are the most widely used by researchers in this field. The chemical method involves the oxidation of aniline, while the electrochemical method involves anodic oxidation.

I.8.4.1. Chemical Synthesis of PANI

The most commonly used method for the chemical synthesis of PANI is the oxidation of aniline with an oxidizing agent, with ammonium persulfate $((\text{NH}_4)_2\text{S}_2\text{O}_8)$ being the most widely used [49]. This operation is typically carried out in an acidic medium. This process directly yields the conductive form of PANI (emeraldine salt), as shown in (Figure I.19). The advantage of chemical synthesis is its high production yield. However, the main drawback of this synthesis route is the lack of control over the final oxidation state of the resulting polymer material.

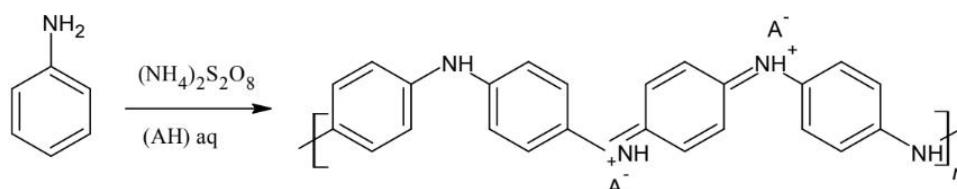


Figure I.19: Synthesis of polyaniline by chemical oxidation of aniline in an acidic aqueous medium [47,48].

I.8.4.2. Electrochemical Synthesis of PANI

PANI can be produced electrochemically by electro-oxidizing aniline at an inert electrode using various electrochemical methods, including galvanostatic, potentiostatic, or sweep techniques. Sweep methods such as cyclic voltammetry are the most common. Thick and uniform PANi films form and are subsequently delaminated from the electrode surface. This method involves cycling between -0.25 and 1 V and stopping at a potential corresponding to the desired final oxidation state of PANi. In the presence of a dopant, protons are absorbed, and anions are expelled to maintain charge neutrality in the system when cathodic potentials are applied; the reverse occurs at anodic potentials [49].

Genies et al. studied the mechanism of electrochemical PANI formation in an acidic solution. They proposed that the formation of the aniline radical cation is the rate-limiting step in an acidic system and is therefore crucial for the formation of short-chain polymer units (dimers and tetramers). (Figure I.20) shows the electropolymerization mechanism of aniline in an acidic solution proposed by these researchers.

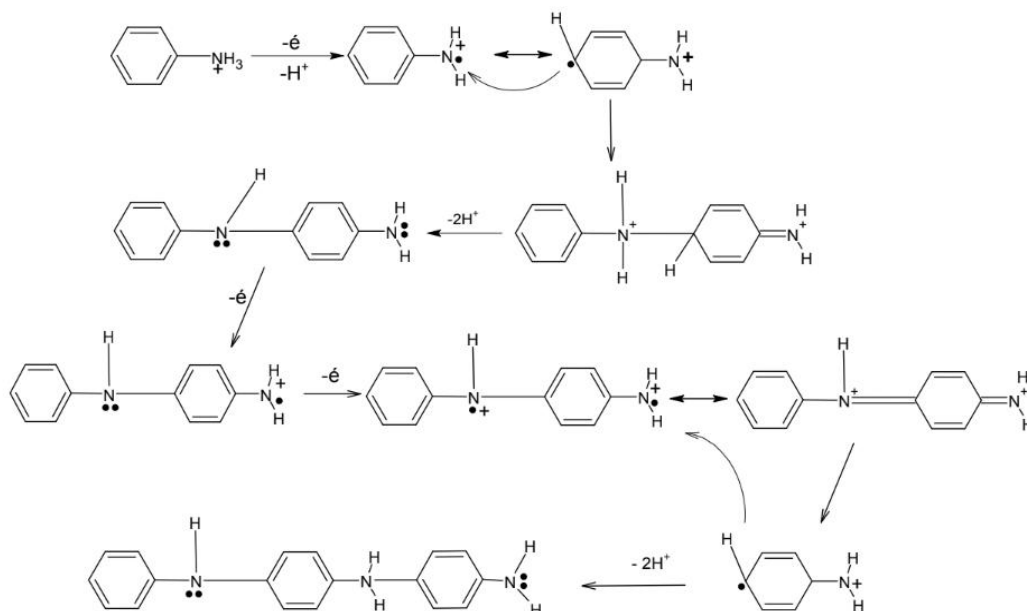


Figure I.20: Mechanism of the electrochemical polymerization of aniline.

The main drawbacks of electrochemical methods for producing PANi are that only small-scale production is feasible. Furthermore, extracting these minute amounts of the material from the electrode surface for external applications without damaging it is nearly impossible. However, in electrochemical synthesis, the oxidation state of the polymer can be controlled by adjusting the final electrochemical potential, enabling the production of a more homogeneous material with well-defined properties. Additionally, the material in this form can be processed and cast as free-standing films on external devices [50,51].

I.8.5. Doping Mechanism of Polyaniline

The electrical conductivity of conjugated polymers can be significantly increased through doping. Chemical doping, which is reversible [35], involves: extracting electrons by oxidizing the polymer chain to create an electron deficiency (p-type doping) or injecting electrons by reducing the polymer chain to produce an excess of electrons (n-type doping). PANI doping can be achieved by treating emeraldine base with a strong acid such as HCl, H₂SO₄, or H₃PO₄ to produce the doped form (emeraldine salt) [53]. During the synthesis of polyaniline, the reaction medium is acidic, meaning polymerization and doping happen simultaneously. Most researchers agree that doping occurs through protonation of nitrogen

atoms at the imine sites (quinoid rings). Also, increased delocalization—through resonance, charge distribution, and spin—along the chain enhances conductivity in PANi doped with strong acids. (Figure I.21) illustrates the proposed mechanism for PANi doping [52].

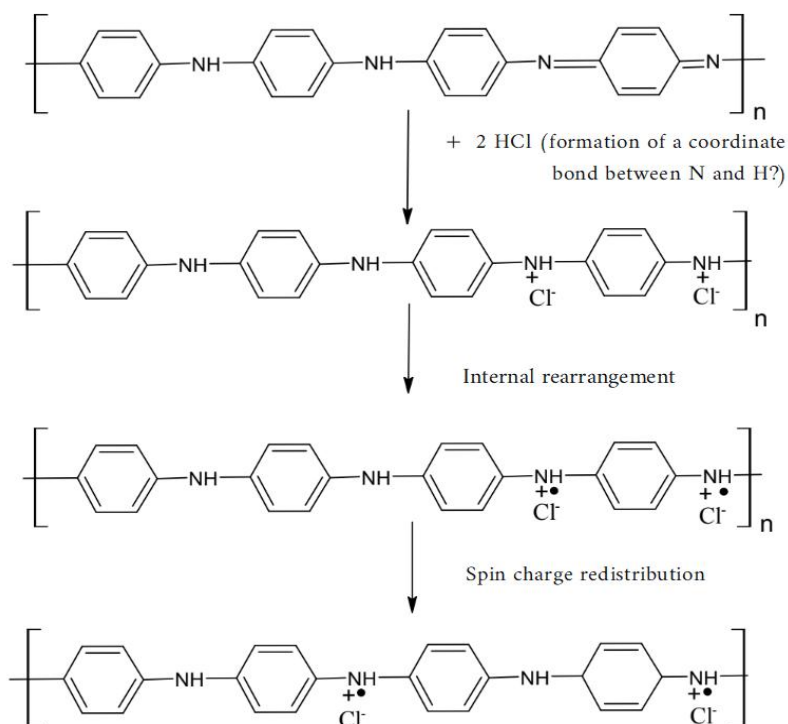


Figure I.21: Doping mechanism of PANi with hydrochloric acid.

I.8.5. Physico-chemical Properties of Polyaniline

Whether in its neutral or conductive state, polyaniline is a simple and inexpensive polymer to produce. For industrial use, it must possess excellent stability in air and be easy to process. The chemical and thermal stability of PANi-EB (emeraldine base) and PANi-ES (emeraldine salt) have been repeatedly demonstrated in the literature. However, processing this polymer remains challenging due to issues of instability and insolubility [54].

Like most other conductive polymers, PANi features an aromatic π -conjugated system that renders its structure highly rigid. Furthermore, strong interchain interactions increase the system's rigidity, rendering PANi insoluble in most organic solvents. Only a few solvents can dissolve the polymer, and even then, only in very small quantities. These include N-methylpyrrolidinone (NMP), certain amine solvents, and concentrated sulfuric acid [55-57].

In the first two cases, the polymer can only be dissolved in its emeraldine base form because the polyaniline emeraldine salt undergoes deprotonation in these relatively basic solvents. The solubility of PANi-EB in NMP enabled the polymer to be produced as films and fibers [58], which could be doped after solvent evaporation. However, the formation of gelatinous

aggregates was observed when the polyaniline concentration exceeded 4-6% in this solvent [60]. Only in concentrated sulfuric acid can polyaniline be dissolved in its emeraldine salt form. It remains very difficult to dissolve the protonated polyaniline in any other solvent. One reason for this phenomenon is the polymer's very high degree of crystallinity when doped. X-ray diffraction studies confirmed a very high crystallinity percentage of 50% for PANI-ES, compared to an almost negligible level for PANi-EB. It is well known that dissolving crystalline polymers is more challenging than dissolving amorphous polymers.

I.8.5.2. Conjugation Length Effect

In addition to the effect of oxidation state, the effect of polymer chain length must also be considered. For a constant oxidation state, the λ_{max} position of the HOMO-LUMO transition of the quinoid ring in the EB form shifts toward the blue for short chains, and toward the red for long chains. When PANi-EB is treated with an acid capable of protonating the imine sites, positive polarons form on the structure following an electronic rearrangement within the material. This electronic transformation is accompanied by a characteristic change in the UV-visible spectrum. The UV-Visible spectrum of PANi in its salt form dissolved in NMP shows bands at 360 nm, 440 nm, and 807 nm. These bands are characteristic of protonated polyaniline [61]. They correspond to the electronic transitions: π - π^* (band at 360 nm), π -polaron (band at 440 nm), and polaron- π^* (broad band at 807 nm).

I.8.6. Influence of Synthesis Parameters on Properties

According to the literature, several influences of synthesis parameters on the properties have been reported [62, 63].

I.8.6.1. Influence of Reaction Temperature

During the synthesis of PANi-ES at room temperature, we observed an increase in the reaction temperature. This exothermic nature is not without consequence for conductivity, as we found that the resulting samples exhibited very low electrical conductivity. Indeed, previous work shows that a low synthesis temperature increases the crystallinity of polyaniline and, consequently, its conductivity [64]. We also observed that temperature significantly influences other product properties, particularly the reaction yield, which decreases exponentially with increasing reaction temperature [65].

I.8.6.2. Influence of Reaction Time

The reaction time required for polymerization is 1.5 hours. Indeed, according to Erdem et al. [66], the yield increases rapidly over the first hour. Beyond 5 hours, no further variations are observed.

I.8.6.3. Influence of Acid Solution Concentration

Hydrochloric acid solution is the most commonly used for protonating PANi and its derivatives. It promotes the solubilization of the monomer in water and limits side reactions. The concentration of the HCl solution is a very important parameter that determines the electrical conductivity of the synthesized samples. Using a strong acid such as HCl yields a product with high electrical conductivity. However, higher acid concentrations (2M) have the opposite effect on this parameter [67]. Stejskal related the conductivity to the degree of crystallinity, which increases with the concentration of the HCl solution used [68]. In addition to the oxidation state, the polymer's conductivity also depends on its degree of protonation. At pH values above 4, polyaniline is primarily present in its emeraldine base form. When this form is treated with an acid solution, the number of quinoid units decreases, and the number of radical cations increases, yielding the emeraldine-salt form [69,70].

I.8.7. Factors Influencing the Electrical Conductivity of Polyaniline

Several factors can influence the electrical conductivity of PANI, including oxidation state, dopant type, structure, molecular weight, degree of crystallinity, and interchain distance [71]. At high molecular weights, macromolecular chain deformation can occur, leading to decreased electrical conductivity [72]. The intramolecular mobility of charged species along the chain and the intermolecular hopping of charge carriers increase with crystallinity, resulting in enhanced electrical conductivity.

I.9. Applications of Conductive Polymers (π -Conjugated)

π -Conjugated polymers are considered the class of conductive polymers that, in their neutral or doped state, either alone or blended with other conventional polymers, provide access to a full range of electronic properties, from insulating to conductive. They offer the advantage of easy processing and low cost, combined with great flexibility. Recently, the applications of conductive polymers, particularly in plastic electronics, have become increasingly prevalent [73-74]. This is true whether they are used as semiconductors in their undoped state, as conductors when doped, or specifically for their ability to alter properties based on their oxidation state. In their undoped form, they serve as organic analogues of inorganic semiconductors. At this stage, they can replace inorganic semiconductors in conventional electronic and optoelectronic devices, such as photovoltaic cells [75], field-effect transistors [76-77], and OLEDs [78], particularly for creating flexible displays [79].

In their doped state, conductive polymers can be applied in plastic electronics as components of circuits and various electrodes (transparent anodes in OLEDs and cathodes in electrolytic capacitors) [80-82]. Thus, they are used in the formulation of paints, inks, and conductive

adhesives for various applications, such as conductive coatings, anti-corrosion treatment, and electromagnetic shielding or antistatic protection [83-84]. We will present some applications that are potentially interesting for conductive polymers and hybrid materials. More specifically, these applications include anti-corrosive coatings and optoelectronics.

I.9.1. Anti-Corrosion Coatings

Metal corrosion involves oxidation of the metal by a reducing agent. Steel struggles in aggressive conditions, such as atmospheric pollution or corrosive substances. Conductive polymers, such as undoped PANI, provide anti-corrosive protection while preserving steel conductivity via a barrier layer between the metal and the environment. Undoped PANI coatings drastically reduce steel corrosion rates in acidic media [83]. Upon contact, steel iron oxidizes to stable Fe_2O_3 , forming a passivation layer that halts further oxidation, while PANI-EB reduces to leucoemeraldine base. Atmospheric oxygen re-oxidizes PANI to emeraldine base, maintaining the protective oxide [84] (Figure I.22).

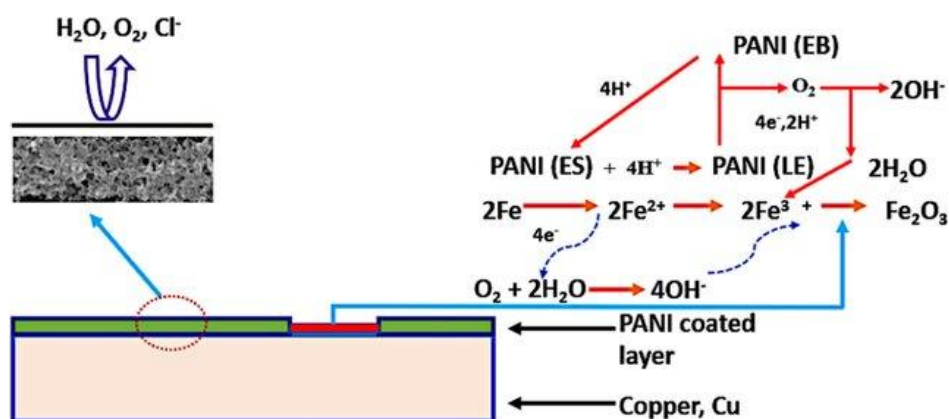


Figure I.22: Anti-corrosion layer of PANI-coated on a metallic surface.

I.9.2. Light-Emitting Diodes (LEDs)

The principle of light-emitting diodes is to convert electrical energy into light energy. Certain conjugated polymers have been used in the fabrication of LEDs [85,86] (e.g., PPV, polythiophene [87], or polyfluorene [88]) by leveraging the electrical properties of polymers to emit light upon electrical excitation. The simplest case of a diode (a single-layer diode) consists of a layer of semiconducting organic material sandwiched between two electrodes, typically a metal (cathode) and ITO (anode) (Figure I.23). Due to the energy barriers that must be overcome to inject charges (carriers) and the low charge carrier mobility, multilayer devices have been developed [89]. These include additional electron- and hole-transport layers that separate the emissive layer from the cathode and anode.

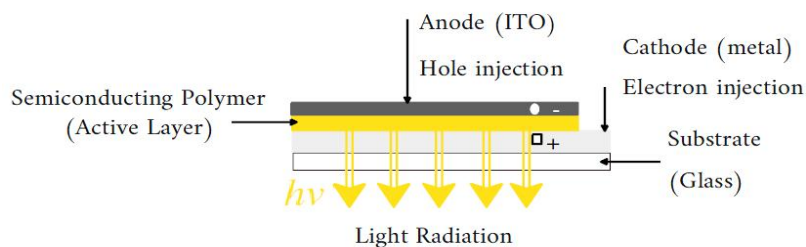


Figure I.23: Diagram of a "single-layer" light-emitting diode structure.

I.9.3. Photovoltaic Cells

Unlike light-emitting diodes that generate light from electricity, photovoltaic cells convert solar energy (photons) into electrical energy through a series of key operational steps: reception and absorption of radiation, creation of an exciton followed by its diffusion and dissociation, separation of charge carriers with transport to electrodes, and collection of charges in the external circuit as electrical current. In semiconducting polymers, this process is more complex due to the involvement of distinct molecular orbitals, where photons excite electrons from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO), analogous to transitions from the valence band (VB) to the conduction band (CB) in inorganic semiconductors (Figure. I.24). For optimal performance in organic photovoltaic cells, the semiconductor must exhibit a broad absorption spectrum to capture maximum sunlight energy, minimize recombination of photo-induced charges to preserve efficiency, and ensure high charge carrier mobility for swift transport to electrodes, thereby enhancing overall electrical output and device efficacy [90].

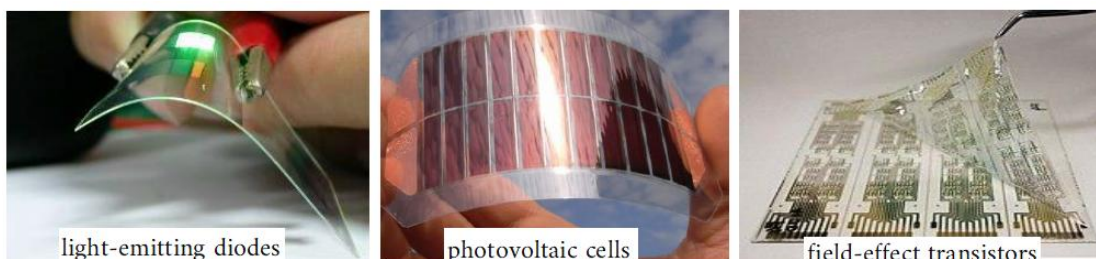
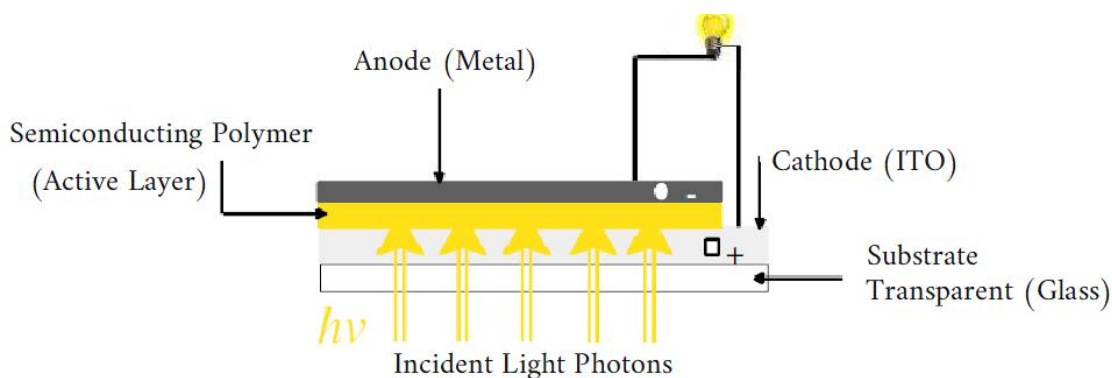


Figure I.24: Photovoltaic Cells based on Conductive Polymers.

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Chapter 2: *Thin-film deposition techniques*

II.1. Introduction

Polyaniline (PANI), an intrinsically conductive polymer, garners significant interest due to its electroactive properties, excellent thermal stability, and remarkably low synthesis cost. Thin PANI layers, typically under 1 μm thick, play a crucial role in advanced electrochemical applications, including sensors, supercapacitors, and anti-corrosion coatings. Unlike bulk powders, these thin films offer a precisely controlled interface with the substrate, enabling anisotropic conductivity, superior adhesion, and optimized charge transport. Synthesis protocols for PANI thin films are tailored to desired morphologies—such as nanofibers or dense films—and targeted properties, such as conductivity and doping levels. The predominant in situ chemical polymerization oxidizes aniline in an acidic medium using oxidants like ammonium persulfate directly on substrates (e.g., glass, ITO, steel). This simple approach yields uniform deposits but demands rigorous pH and temperature control to minimize aggregate formation. Electrochemical techniques, including galvanostatic and potentiostatic modes, excel in controlled layer-by-layer growth, allowing precise doping and thickness modulation. Physical methods such as spin-coating or the Langmuir-Blodgett deposition process can be used to pre-synthesize PANi solutions, ideal for ultra-thin films. Emerging advanced strategies, such as plasma polymerization and layer-by-layer (LbL) self-assembly, facilitate integration into hybrid nanocomposites to enhance performance. This chapter provides a comprehensive overview of these methods, their key operating parameters, relative advantages/disadvantages, and essential optimization approaches [1].

II.2. Thin Films

A thin film of a given material is a layer of that material deposited onto a solid support called a substrate, where one of its dimensions (the thickness) has been significantly reduced (Figure II.1). This small measurement constitutes the primary characteristic of a thin film. The effect of the interfaces will play a non-negligible role on the physical properties of the deposited material. A thin film of the same material deposited on a substrate can have substantially different physical properties [2].

The essential difference between a material in its bulk state and in a thin film state is related to the fact that in the bulk state, the role of the boundaries (the surfaces) in the properties is negligible, while in a thin film, the effects related to the boundary surfaces become predominant [3]. It is evident that the thinner the film, the more significant this two-dimensional effect will be. When the thickness of a thin film exceeds a certain threshold, the

thickness effect becomes minimal, and the material regains the properties of a bulk material [4].

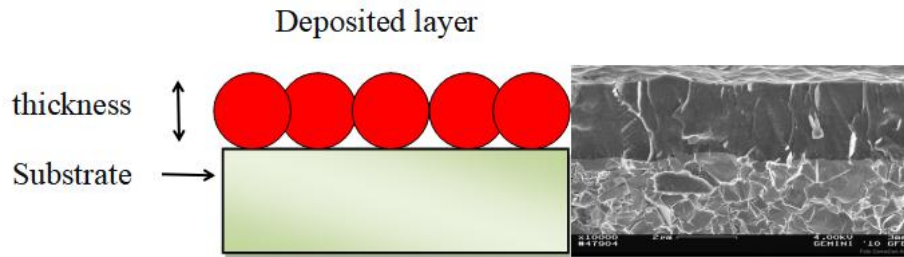


Figure.II.1: A thin film of a material is a layer deposited on a solid support.

II.3. Historical Overview of Thin Films

The development of thin-film technology advanced considerably in the late 19th and early 20th centuries, with key contributions from August Kundt's studies on optical properties, John Stone's electrical characterizations, and further improvements in deposition techniques such as vacuum evaporation and sputtering. These developments paved the way for modern uses in optics, electronics, and semiconductor devices [5]. A thin film is a precisely layered material with a significantly reduced thickness (usually from nanometers to micrometers) that is deposited on a substrate material, such as glass, quartz, silicon, or aluminum, selected based on the deposition requirements. Its importance lies in the unique physicochemical properties conferred by this specific structure, especially its thinness. The main difference between bulk materials and thin films is that boundary effects on properties are typically neglected in bulk materials, whereas surface boundary effects dominate in thin films. Thin films have been used for many decades across various applications. The oldest and still most common uses are in optical devices. Although metallurgy and photography have historically used thin films, modern applications now extend to fields such as chemistry, biochemistry, and medicine—especially in sensors like gas detectors and DNA biochips.

II.4. Interest and Characteristics of Thin Films

The interest in thin films stems primarily from the economical use of materials relative to their physicochemical properties, the simplicity, and the cost of the technologies implemented for their fabrication. A wide variety of materials are used to create these thin films: metals, metalloids, alloys (binary, ternary, quaternary), refractory compounds (oxides, nitrides, carbides), organometallic compounds, and polymers [6].

The procedure used to fabricate a thin film is always linked to a support on which it is constructed. Consequently, it is imperative to consider this major factor in the design, namely that the support strongly influences the structural properties of the layer deposited on it. Thus, a thin film of the same material and same thickness can have significantly different physical properties depending on whether it is deposited on an amorphous substrate or a monocrystalline silicon substrate. As a result, a thin film is anisotropic by construction [7].

Modifying the surface of a substrate makes it possible to couple the properties of the core material (or substrate) and the surface material: the latter can either come directly from the substrate in the case of surface treatment, or be an additional material for a surface coating. Modifying the surface of a substrate imparts one or more additional physicochemical properties to it (corrosion resistance, electrical insulation). Using a substrate with low added value helps reduce manufacturing costs while achieving the required surface physicochemical properties. Early surface modifications had an aesthetic purpose (painting, gold plating, enameling), while more technical applications concerned metallurgy [4,8].

II.5. Thin Film Deposition Principle

To create a thin film on a solid surface (substrate), coating material particles must, in some processes, travel through a conductive medium to make close contact with the substrate, while in others, a neutral medium is sufficient. When they reach the substrate, some of the coating particles adhere (via van der Waals forces) or chemically react with it.

These particles may be atoms, molecules, ions, or ionized molecular fragments. The transport medium can be a solid, liquid, gas, or vacuum.

- **Solid Medium:** In this scenario, the substrate directly contacts the solid, with only diffusing particles from the solid forming the layer. Achieving thin films by solid contact is often difficult—for example, when oxygen diffuses from silica to form a thin SiO₂ layer on a silicon substrate.
- **Liquid Medium:** This approach is more practical than solid-phase methods, as materials are more adaptable in this state (including liquid-phase epitaxy, electrochemical deposition, and sol-gel techniques).
- **Gas or Vacuum Medium:** In CVD (Chemical Vapor Deposition), the main difference between gas-phase and vacuum deposition is the particles' mean free path.

Thin film formation and growth proceed through distinct sequential stages that determine film quality, uniformity, and properties. These stages apply to methods like SILAR and CBD used for polymer films such as polyaniline (PANI).

- **Preparation Stage:** Prepare deposition precursors—ions, molecules, or atoms—in solution or vapor form, precisely controlling concentration, pH, temperature, and purity to ensure controlled nucleation and reaction kinetics. For CBD of PANI, this involves mixing aniline monomer, acid (e.g., HCl), and oxidant (e.g., APS) at optimal ratios (e.g., 0.1 M each) to promote oxidative polymerization without aggregation.
- **Transport Stage:** Transport precursors to the substrate via the deposition medium—liquid bath for CBD/SILAR, vapor or gas for others—governed by diffusion, convection, or flow dynamics. Stirring in CBD enhances ion diffusion and homogeneity, while rinsing steps in SILAR remove loosely bound species, preventing defects.
- **Condensation and Deposition Stage:** Precursors condense on the substrate via physical adsorption or chemical reactions, yielding solid deposits whose mechanisms dictate microstructure and functionality. This stage encompasses:
 - a. **Nucleation:** Initial attachment and clustering of particles on the substrate, influenced by surface energy and precursor concentration.
 - b. **Coalescence:** Merging of nuclei into islands, promoting continuity and reducing pinholes.
 - c. **Growth:** Lateral and vertical thickening via layer-by-layer or island growth, controlled by deposition time and cycles to achieve desired thickness (e.g., 100–500 nm for PANI films).

Precise parameter tuning across stages yields uniform, adherent films with tailored electrical and morphological properties.

II.6. Classification of thin film growth modes

The growth morphology of thin films is primarily determined by the relative interaction energies between substrate atoms and deposited film atoms, leading to three fundamental growth modes (Figure II.2):

II.6.1. Layer-by-Layer Growth (Frank-van der Merwe Mode):

This growth mode occurs when the material-substrate interaction is exceptionally strong, leading to two-dimensional (layer-by-layer) deposition where adsorbed species condense to form complete monolayers sequentially [9].

II.6.2. Island Growth (Volmer-Weber Mode):

This three-dimensional growth mechanism occurs when deposited atoms preferentially bond with each other, leading to the direct nucleation of nanoscale islands on the substrate surface without initial monolayer formation [10].

II.6.3. Mixed Growth Mode (Stranski-Krastanov):

This transitional growth mechanism begins with 2D layer formation due to strong substrate interactions, then shifts to 3D island growth as strain accumulation and reduced interfacial energy drive nanostructural reorganization, enabling the precise fabrication of quantum dots and strained-layer devices [11].

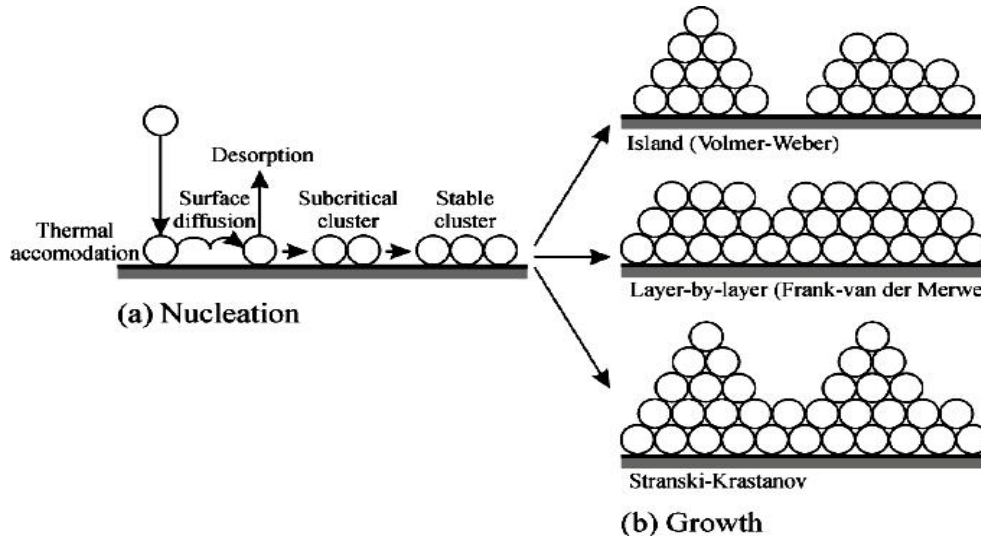


Figure II.2: Thin Film Formation and Growth Stages.

Achieving optimal thin film properties requires precise control of deposition parameters, including substrate quality, temperature, lattice matching, technique, chemical composition, and growth rate, to engineer a dense, defect-free microstructure with tailored functional characteristics.

II.7. Thin-film deposition techniques

The broad applications of thin films have driven researchers to develop various methods for preparing these layers. This diversity stems from the wide range of thin-film applications. In general, preparation methods are divided into two main categories: physical methods and chemical methods [12].

II.8. Physical Methods for Thin-Film Deposition

II.8.1. Physical Vapor Deposition(PVD):

Physical Vapor Deposition (PVD) encompasses vacuum-based techniques in which materials transition from the condensed phase to the vapor phase and subsequently condense on substrates to form thin films. These processes occur through physical mechanisms rather than chemical reactions [13].

II.8.2. Cathode sputtering:

Cathode sputtering is a technique used to deposit various materials such as refractory metals, insulators, and ceramics by placing the substrate in a low-pressure argon gas container, where an electric discharge ionizes the gas, and the resulting ions are accelerated by a voltage to collide with the cathode (made of the material to be deposited), causing atoms to dislodge and deposit onto the substrate. In some cases, reactive gases are added to argon, chemically reacting with the ejected atoms to form desired compounds. Among its key advantages are ease of implementation and strong adhesion to the layer. However, drawbacks include slow deposition rates, non-uniform thickness across the surface, and high costs [14].

II.8.3. Laser Ablation Deposition (PLD):

This technique involves directing a high-intensity laser beam onto a target made of the material to be deposited on a substrate placed a few centimeters away and parallel to the target. The target partially absorbs the laser beam, ejecting a large amount of material in the form of a dense, luminous vapor (plasma). The plasma's energy density depends on the target material's composition, shape, and laser properties such as wavelength and pulse duration.

A neutral or reactive gas may be introduced into the chamber to control layer growth and modify film surface properties. Additionally, substrate heating can be applied during deposition to provide supplemental energy to the deposited materials, thereby enhancing thin film crystallization [15].

II.8.4. Vacuum thermal evaporation (VTE):

This method relies on evaporating or sublimating the materials to be deposited as thin films under low-pressure, high-temperature conditions, in which the materials are placed in an evacuated crucible and heated using either a focused high-energy electron beam or Joule heating, causing them to condense on the substrate surface [16].

II.9. Chemical Methods for Thin-Film Deposition:

II.9.1. Sol-Gel Technique

The sol-gel technique is one of the oldest discovered methods, but its practical application began in the **1960s** due to its unique advantages over other deposition techniques. The process involves preparing a stable solution (sol) typically composed of chemical compounds dissolved in an alcoholic medium [17]. Through chemical reactions between the solvent and solute, this solution evolves into a gel phase. This technique can be performed using two primary methods:

➤ Dip-Coating Method

This method relies on immersing the substrate into the sol-gel solution, forming a thin film on its surface. The film thickness depends on: withdrawal speed (vertical pulling rate of the substrate), solution viscosity, Surface tension and its gradient, gravitational forces and drag forces [18]. This technique is implemented through three sequential steps:

1. Substrate immersion in the solution.
2. Controlled withdrawal at a constant speed.
3. Evaporation of volatile compounds, leaving a solid thin film.

➤ Spin-Coating Method

The spin-coating technique involves depositing a fluid onto a substrate and then evaporating the solvent through centrifugation. However, in low-viscosity fluids, the resulting surface tends to be very uneven. To address this issue, the polymer can be mixed with a viscosifying material; however. Usually, this method entails dropping the solution onto a rapidly rotating substrate, where centrifugal force spreads the material evenly. Excess solution is expelled, and the remaining solvent evaporates, leaving a thin film [19]. This technique follows four essential steps (Figure II.3):

1. Dispensing – The sol-gel solution is dropped onto the substrate.
2. Spreading – High-speed rotation distributes the solution evenly.
3. Spin-off – Excess solution is ejected, stabilizing film thickness.
4. Drying and thermal treatment – Removes residual solvents, forming a solid film.

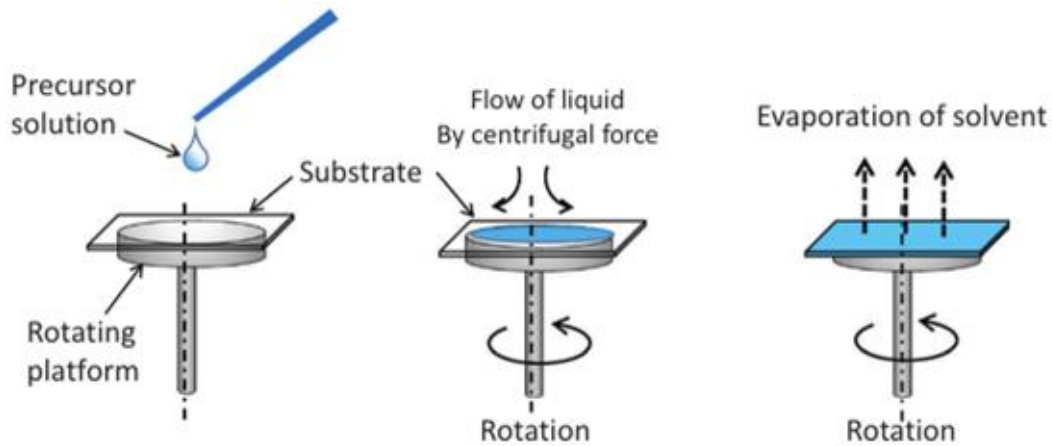


Figure II.3: Chemical deposition method using spin coating.

II.9.2. Atomic Layer Deposition (ALD)

Atomic layer deposition (ALD) is a technique used to produce ultra-thin atomic layers. The principle of this technique consists of successively exposing the surface of the substrate to

different chemical precursors in order to obtain ultra-thin films; the deposition of an atomic layer is carried out in four stages (Figure II.4) [20]:

1. Injection of the first precursor in gaseous form onto the substrate surface to form a monolayer consisting of chemisorbed and physisorbed species.
2. Purging of the reaction chamber with ultra-pure nitrogen to remove any unreacted species and by-products of the first reaction.
3. Injection of the second gaseous precursor onto the surface and formation of the desired material layer.
4. Purging of reaction by-products.

In addition, this technique enables the production of very thin, high-purity layers of a wide range of materials.

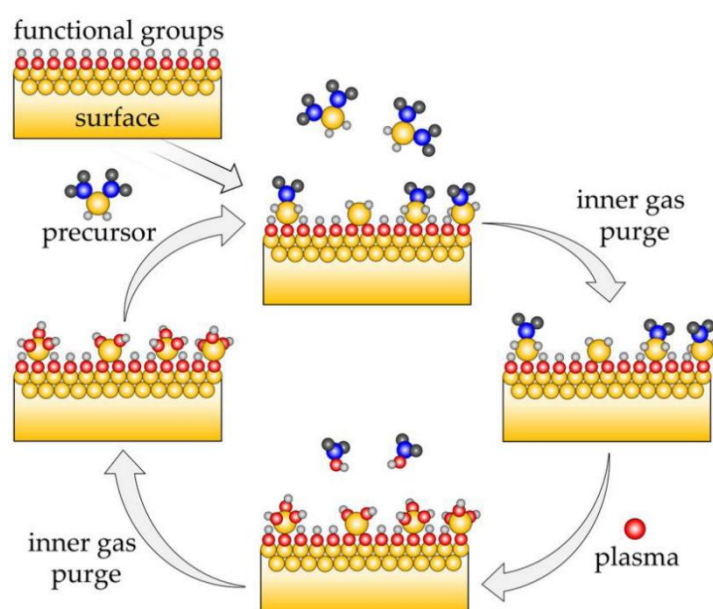


Figure II.4. Schematic diagram of atomic Layer Deposition (ALD)

II.9.3. Molecular self-assembly

A self-assembled monolayer is a molecular assembly formed spontaneously by immersing a suitable substrate in a solution composed of two active surfactants in an organic solvent. The two most common surfactants for forming self-assembled monolayers are thiols on gold and silanes on glass or quartz substrates. The spontaneous self-assembly of hybrid materials is a key advantage of this method. By simply dipping a hydroxylated substrate into a solution of deposited materials, the molecules spontaneously adsorb onto the surface to form a molecular coating [21,22]. The first step in the self-assembly of a monolayer must be carried out in an anhydrous environment. The presence of water in the system would cause the molecules in

solution to polymerize before they could even anchor to the surface. When the system is anhydrous, the hydroxyl groups of the source react with the alkoxy (or chloro) groups of the silane to form strong Si-O-Si covalent bonds (Figure II.5) [21,22].

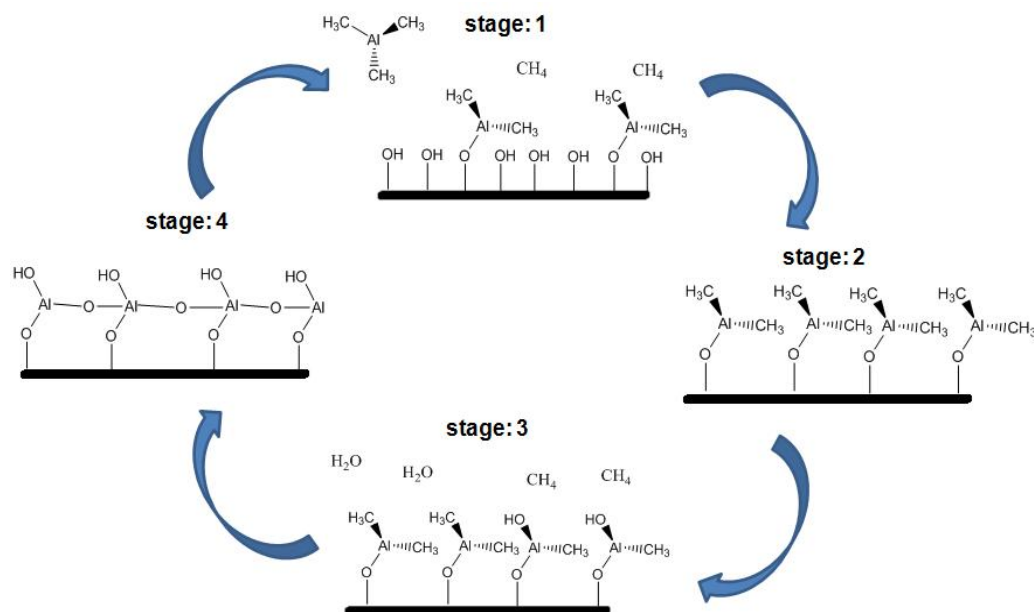


Figure.II.5: Schematic diagram of molecular self-assembly [22].

II.9.4. Langmuir–Blodgett (LB) technique

Langmuir Blodgett monolayers are formed at the aqueous interface and transferred onto a substrate (Figure II.6). After solvent evaporation, this material forms a monolayer on the water surface. A mobile barrier compresses this film, leaving no free space on the surface [23-24].

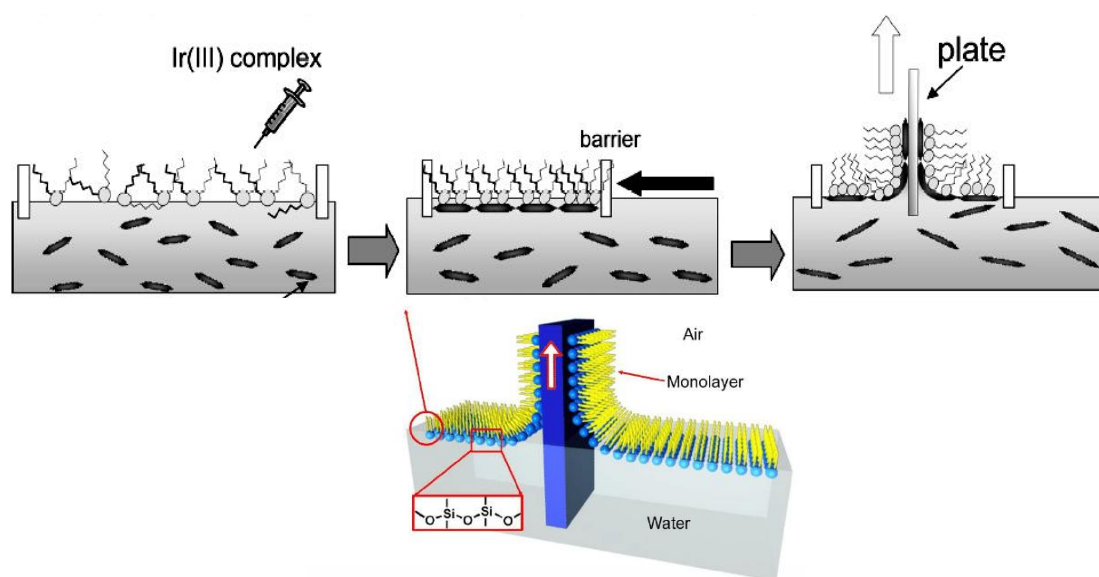


Figure.II.6: Deposition of Langmuir Blodgett monolayers.

All the polymers are arranged parallel to each other and, schematically, perpendicular to the plane of the liquid surface, with the hydrophilic end in contact with the water. The substrate is immersed perpendicularly, then gently withdrawn [23-24].

II.9.5. Chemical Vapor Deposition (CVD) :

This method vaporizes materials and reacts their vapors with other liquids, gases, and vapors to produce thin, transparent films free from metals, insulators, and semiconductors. The process requires substrate heating through induction, thermal radiation, laser, or Joule heating (Figure II.7) [25].

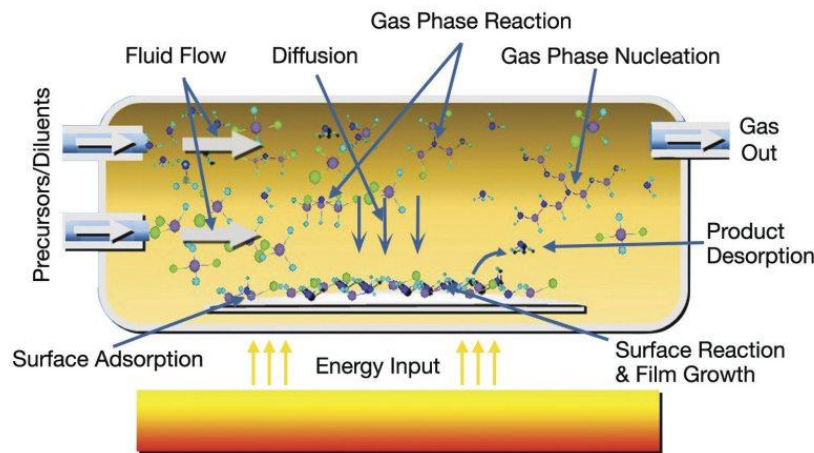


Figure II.7: Schematic diagram of chemical Vapor Deposition

➤ Low-Pressure Chemical Vapor Deposition (LPCVD)

This operates under low pressure with two reaction types [26]:

- **Cold-Wall Reactor:** The substrate is heated while deposition occurs at atmospheric pressure, with limited reaction efficiency at the substrate level.
- **Hot-Wall Reactor:** Deposition occurs at low pressure (~ 9.99 Pa) since the entire chamber is heated, resulting in superior substrate deposition.

➤ Plasma-Assisted Chemical Vapor Deposition (PACVD)

This method activates chemical deposition reactions at relatively low temperatures ($< 300^\circ\text{C}$). A drawback is potential plasma-substrate interactions, which may introduce impurities into the layer. To improve quality, slight substrate heating is necessary [27].

➤ Laser Chemical Vapor Deposition (LCVD)

The laser beam either heats the substrate to enhance surface reactions or activates gaseous precursors, offering advantages like homogeneous composition, excellent adhesion, and ultrathin coherent layers with rapid deposition, though it requires high reaction temperatures and may cause gas-phase contamination [28].

II.9.6. Chemical Bath Deposition Method (CBD):

Chemical deposition, also known as solution growth deposition, is an established technique. Thin films produced via chemical bath deposition result from chemical reactions occurring within a solution. This technique deposits thin films on substrates partially immersed in a dilute solution containing metal ions and a chalcogen source (Figure II.8) [29]. This technique can be used to synthesize thin films of polymers, especially conducting polymers like polyaniline (PANI) and polypyrrole (PPy). This simple, room-temperature method involves oxidative polymerization in an aqueous bath, making it cost-effective for large-area deposition on glass or other substrates. Films show semiconducting behavior with tunable properties for sensors and optoelectronics.

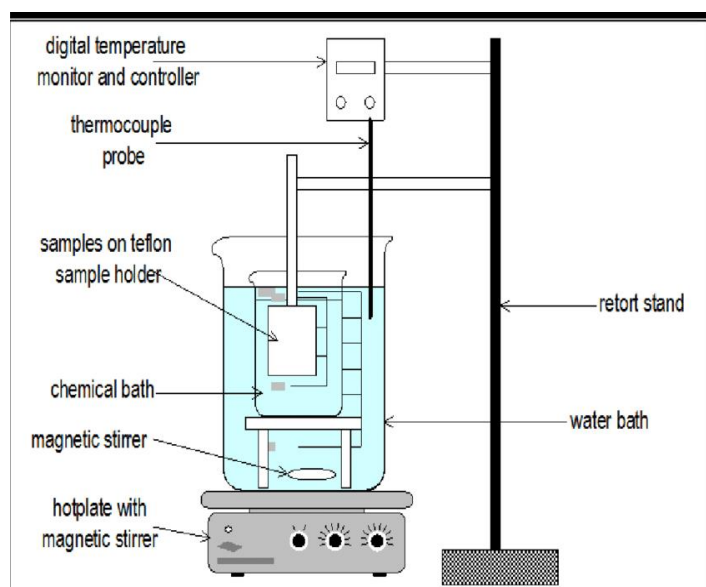


Figure II.8. Schematic diagram of chemical bath deposition (CBD)

II.9.6.1. CBD Process Overview

Prepare a bath with monomer (e.g., aniline or pyrrole), acid (HCl or H_2SO_4), and oxidant (ammonium persulfate, APS); stir at room temperature while immersing cleaned substrates vertically. Polymerization occurs spontaneously, forming films via controlled precipitation; deposition time (e.g., until color change from blue to green for PANI), and stirring control,

thickness, and uniformity. Rinse the films with distilled water after deposition and dry at room temperature.

For example, Polyaniline Thin Films can be prepared by mixing aniline monomer with HCl and APS oxidant in a bath, immersing glass substrates, and stirring magnetically until PANI forms via oxidative polymerization. The resulting films exhibit resistivity of $28.82 \times 10^4 \Omega \cdot \text{m}$, a negative TCR ($-0.00576/^{\circ}\text{C}$), and activation energies of 0.1207 eV (low T) and 0.3123 eV (high T), confirming their semiconducting nature. They show photosensitivity, with photocurrent increasing with light intensity and decreasing with source distance.

CBD offers a low-cost, no-vacuum setup, scalability, and room-temperature processing, making it ideal for flexible electronics and composites like WO_3 -PANI. Unlike inorganic chalcogenides, polymer films can be grown by solution-based oxidative methods, yielding porous structures for electrochemical applications. This complements techniques such as SILAR in thin-film research on advanced materials.

The primary factor affecting the deposition of polymer thin films

Several key factors influence the synthesis and quality of polyaniline (PANI) thin films prepared by Chemical Bath Deposition (CBD), including precursor concentrations, pH, temperature, deposition time, and stirring conditions. These parameters affect polymerization kinetics, film uniformity, thickness, morphology (e.g., porous vs. compact), adhesion, and electrical properties like conductivity and bandgap.

Precursor Concentrations: Monomer (aniline), oxidant (e.g., APS), and acid (e.g., HCl or H_2SO_4) concentrations control nucleation and growth rates; higher levels accelerate deposition but risk aggregation or uneven films. Optimal ratios (e.g., 0.1 M aniline and 0.1 M APS in 1 M HCl) yield uniform, semiconducting films with resistivities of 10^4 – $10^5 \Omega \cdot \text{m}$.

pH and Temperature: Acidic pH (1–3) protonates aniline for emeraldine salt formation, enhancing conductivity; neutral pH reduces yield and doping. Room temperature (20–30°C) suits CBD, but higher temperatures (up to 31°C) boost kinetics and oxidation degree (higher IQ/IB FTIR ratio), while excess heat (>40°C) causes hydrolysis or poor adhesion.

Deposition Time and Stirring: Longer immersion (15–60 min, until color shift to green) increases thickness but may lead to cracking; stirring ensures homogeneity by aiding ion diffusion and preventing precipitation. Substrate type (glass or ITO) and cleaning also affect nucleation sites for improved adhesion.

Resulting Film Quality: Optimized conditions yield amorphous, photosensitive films with a granular morphology, a tunable bandgap (~2–3 eV), and a negative TCR, ideal for sensors.

Poor control yields low conductivity or peeling, underscoring the need for precise parameter tuning akin to your prior SILAR work on polymers.

II.9.7. Successive Ionic Layer Adsorption and Reaction (SILAR):

Successive Ionic Layer Adsorption and Reaction (SILAR) is a solution-based thin-film deposition technique used to grow nanostructured materials, particularly semiconductor thin films, quantum dots, and core-shell structures. It is a simple, cost-effective, and versatile method that allows precise control over film thickness and composition at the nanoscale. The SILAR method involves sequentially immersing a substrate into cationic and anionic precursor solutions, separated by rinsing steps to remove loosely adsorbed ions. The process relies on electrostatic adsorption and chemical reaction at the substrate surface, leading to layer-by-layer growth (Figure II.9) [30]. The SILAR method can be used to synthesize thin films of polymers, particularly conducting polymers such as polypyrrole (PPy) and polyaniline (PANI). This technique enables room-temperature deposition on various substrates, producing uniform, adherent films suitable for applications in sensors, supercapacitors, and electrochemical devices.

II.9.7.1. SILAR Process Overview

SILAR involves sequential immersion of a substrate into cationic and anionic precursor solutions, followed by rinsing to remove excess ions, with cycles repeated to control thickness. For polymers, oxidative polymerization occurs: the substrate adsorbs monomer cations (e.g., pyrrole in acid), then reacts with an oxidant precursor to form the polymer layer. Factors like precursor concentration, pH, immersion time (typically 10 s per step), and cycle number (e.g., 20 cycles for ~250 nm thickness) influence growth rate and film quality.

For example, polypyrrole thin films can be prepared as follows: Prepare 0.1 M pyrrole in 0.1 M H₂SO₄ (cationic bath) and 0.1 M ammonium persulfate (APS) in 0.1 M H₂SO₄ (anionic bath). Dip the substrate (glass or stainless steel) into a cationic bath for 10 seconds (adsorption), rinse with water, then dip into an anionic bath for 10 seconds (reaction), rinse again, and repeat the cycles. Finish with a final rinse to remove any remaining monomer. The films are amorphous and hydrophilic (contact angle 30–48°), with FTIR peaks confirming pyrrole ring vibrations (e.g., 1535 cm⁻¹ C=C, 1047 cm⁻¹ N-H). Therefore, SILAR-deposited polymer films like PPy and PANi exhibit porous nanostructures ideal for electrochemical sensors and energy storage, with high specific capacitance (e.g., 776 F/g for PANI-TiO₂ composites). Advantages include low cost, no need for vacuum equipment, substrate flexibility, and precise thickness control at low temperatures. This aligns well with thin film characterization in inorganic and materials chemistry research.

II.9.7.2. Steps in SILAR Deposition:

1. Cationic Adsorption:

- The substrate is immersed in a solution containing positively charged metal ions (e.g., Cd^{2+} , Zn^{2+} , Pb^{2+}).
- These ions adsorb onto the negatively charged surface of the substrate.

2. First Rinsing:

- The substrate is rinsed with deionized water to remove unadsorbed ions.

3. Anionic Reaction:

- The substrate is immersed in a solution containing chalcogenide anions (e.g., S^{2-} , Se^{2-} , Te^{2-}).
- The anions react with the adsorbed cations to form a compound (e.g., CdS , ZnSe , PbTe).

4. Second Rinsing:

- Another rinsing step removes excess anions and byproducts.

This cycle is repeated multiple times to achieve the desired film thickness.

Advantages of SILAR include its low-cost and simple setup (no vacuum or high-temperature requirements), precise thickness control (adjustable via cycle numbers), room-temperature operation (ideal for sensitive substrates), versatility (compatible with metal chalcogenides, oxides, and core-shell structures), and ability to form uniform coatings on complex and porous substrates.

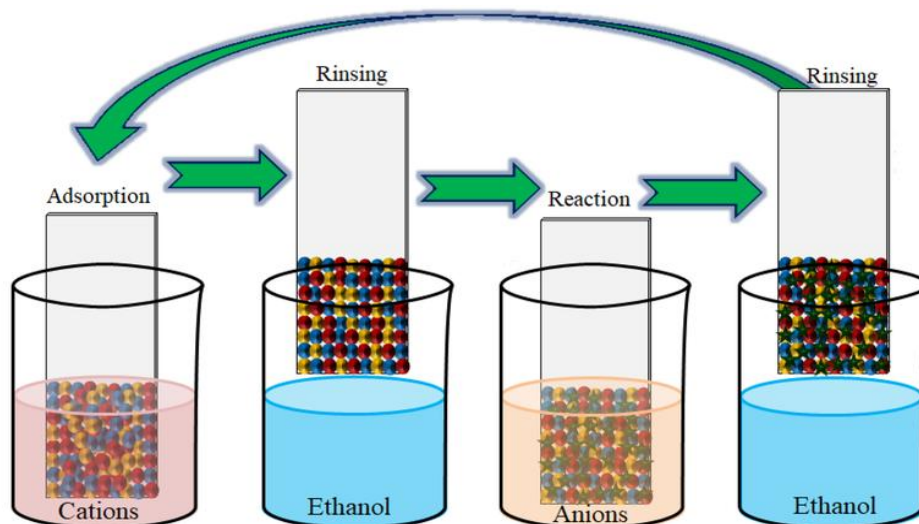


Figure II.9: Principle of SILAR Thin Film Deposition Technique.

II.9.8. Thermal Chemical Spray Method:

The Thermal Chemical Spray Method is an additive manufacturing process that utilizes high-temperature chemical reactions to deposit functional coatings (Figure II.10). This technique involves:

- **Precursor decomposition:** Chemical precursors are thermally activated in a high-energy environment (typically 1500-3500°C)
- **Particle acceleration:** Resulting particles are propelled toward the substrate at supersonic velocities (300-800 m/s)
- **Impact consolidation :** Molten or semi-molten particles flatten and solidify upon impact, forming lamellar microstructures

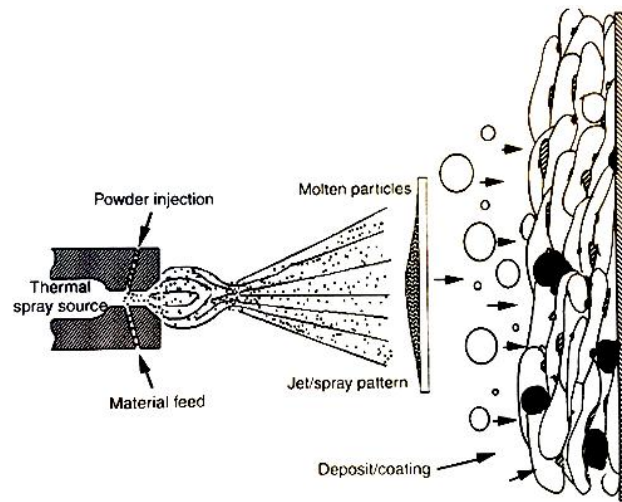


Figure II.10: Thermal Chemical Spray Method [31].

II.10. Advantages and Disadvantages of Deposition Methods:

Table II.1: Presents the advantages and disadvantages of physical and chemical deposition methods [32].

Method Type	Advantages	Disadvantages
Physical Methods	- Wide range of depositible materials, including insulators. - High layer density. - Lower contamination. - Easy process control.	- Low deposition rate. - Difficult processing.

Chemical Methods	- Selective deposition. - High-quality layers.	- Low density. - Radiative contamination.
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II.11. Criteria for Selecting the Appropriate Deposition Technique:

The electrical and optical properties of thin films are highly dependent on their **structure**, morphology, and the nature of impurities present. Consequently, depositing the same material using two different techniques will yield different results. Therefore, it is essential to establish a correlation between thin-film characteristics and deposition techniques.

II.11.1. Applications of Thin Films

Thin films are an extremely important technology due to their widespread applications in various fields, particularly:

Table II.2: Illustrating thin film applications by usage field [33].

Category	Applications of Thin Films
Microelectronics	- Semiconductor devices, integrated circuits, transistors, resistors, LEDs, wireless communications.
Chemistry , Coatings	- Anti-corrosion coatings (water-resistant layers). - Optical coatings (anti-reflective, protective layers).
Sensors , Detectors	- Used on metallic, silicon-based, and ceramic substrates. - Infrared detectors, magnetic memory, audio/video systems, optical lenses.
Energy , Solar Cells	- Multilayer photovoltaic cells (light to electrical energy). - Thin-film solar panels (lightweight, flexible).
Displays , Optoelectronics	- LED/LCD screens. - Optical discs (CDs, DVDs). - Multilayer capacitors.

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Chapter 3: *Experimental Materials and Methods*

III.1. Introduction

The properties of thin films depend fundamentally on both the precursor materials and the deposition techniques; accordingly, this section describes the preparation of polyaniline thin films via chemical bath deposition (CBD). It represents one of the simplest and most economical chemical methods based on dip-coating principles. Chemical Bath Deposition (CBD) is a solution-based thin-film deposition technique that relies on controlled chemical reactions to form solid-phase materials on immersed substrates.

The process occurs through homogeneous and heterogeneous nucleation, driven by precipitation reactions in an aqueous or non-aqueous medium. We systematically examine the key parameters governing film formation, thickness measurement techniques, and comprehensive characterization of structural and optical properties. The principal analytical tools utilized in this applied work include: UV-Vis spectroscopy, Fourier-transform infrared (FTIR) spectroscopy, and optical microscopy. This study provides critical insights into the process-structure-property relationships essential for optimizing thin-film performance in functional applications.

III.2. Chemicals

All chemical reagents and compounds were of the highest purity, and the solutions were prepared using freshly distilled water. The raw materials include Aniline (C_6H_7N) (Aldrich, 97%), Ammonium persulfate (*APS*) ($(NH_4)_2S_2O_8$) (Aldrich, 97%), and Hydrochloric acid (Fluka, 99.8%), which were utilized to synthesize the **PANI** thin films. For thin film deposition, we utilized the following solutions and apparatus:

III.3. Preparation of Chemical Solutions

To initiate the deposition process, the necessary solutions for polyaniline synthesis must be prepared. In our experimental work, we employed three distinct solutions: (1) hydrochloric acid (HCl) solution, (2) ammonium persulfate ($(NH_4)_2S_2O_8$) solutions, and (3) aniline (C_6H_7N) solutions:

- a. Hydrochloric Acid (HCl) Solution, 16 mL of hydrochloric acid (HCl, 37%) was mixed with distilled water in a 2 L volumetric flask and diluted to the calibration mark using a magnetic stirrer.
- b. Ammonium Persulfate ($2NH_4^+$, $S_2O_8^{2-}$) Solutions Three concentrations were prepared (0.1 M, 0.01 M, 0.055 M):
 1. 0.1 M Solution: 5.7 g $(NH_4)_2S_2O_8$ + 250 mL prepared HCl solution

2. 0.01 M Solution: 0.57 g $(\text{NH}_4)_2\text{S}_2\text{O}_8$ + 250 mL prepared HCl solution
 3. 0.055 M Solution: 2.85 g $(\text{NH}_4)_2\text{S}_2\text{O}_8$ + 250 mL prepared HCl solution
- c. Aniline ($\text{C}_6\text{H}_5\text{NH}_2$): Three Solutions were prepared (0.1, 0.01, and 0.055 M):
1. 0.1 M Solution: 4.7 mL aniline ($d=1.02 \text{ g/cm}^3$, $\text{MW}=93 \text{ g/mol}$) + HCl solution to 250 mL final volume
 2. 0.055 M Solution: 2.35 mL aniline + HCl solution to 250 mL final volume
 3. 0.01 M Solution: 0.235 mL aniline + HCl solution to 250 mL final volume

Table III.1 The different chemicals were prepared with concentration values in the protocol

Solutions	Concentration	Quantity Used	Diluent Volume
Hydrochloric Acid (HCl)	~0.1 M	16 mL(37%)	984 mL Water
Ammonium Persulfate (NH_4) ₂ S ₂ O ₈	0.1 M	5.7 g	250 mL HCl(0.1 M)
	0.01 M	0.57 g	250 mL HCl(0.1 M)
	0.055 M	2.85 g	250 mL HCl(0.1 M)
Aniline $\text{C}_6\text{H}_5\text{NH}_2$	0.1 M	4.7 mL	245.3 mL HCl(0.1 M)
	0.01 M	0.235 mL	249.76 mL HCl(0.1 M)
	0.055 M	2.35 mL	247.65 mL HCl(0.1 M)

III.4. Protocol of glass substrate cleaning

When preparing thin films on glass substrates, it is crucial to emphasize the importance of cleaning the substrates and working in a sterile environment. In this study, 27 glass substrates (each with an area of $18 \times 18 \text{ mm}$) were selected due to their availability, low cost, and ability to preserve most optical properties—thanks to their high transparency in the visible spectrum and chemical stability, however, these substrates must be thoroughly cleaned to remove impurities and surface contaminants, as such residues can compromise the quality of the deposited material and lead to undesirable results.

The cleaning procedure for substrates prior to polyaniline thin-film deposition by CBD involves a systematic sequence of steps to ensure pristine surfaces free of contaminants, defects, and residues. It begins with a visual inspection to examine substrates for scratches or imperfections, followed by ultrasonic cleaning in a beaker with distilled water and detergent for 5 minutes, and then in acetone to dislodge particulates.

Substrates are then thoroughly rinsed with distilled water to remove all detergent traces, immersed in methanol for effective degreasing, dried vertically to prevent particle adhesion, and baked in an oven at 100 ± 5 °C for 30 minutes to achieve complete dryness. Finally, a post-cleaning protocol involves weighing each substrate individually, labeling them, and sealing them in clean packaging for storage, thereby optimizing adhesion and uniformity of the subsequent polyaniline layers [1-3].

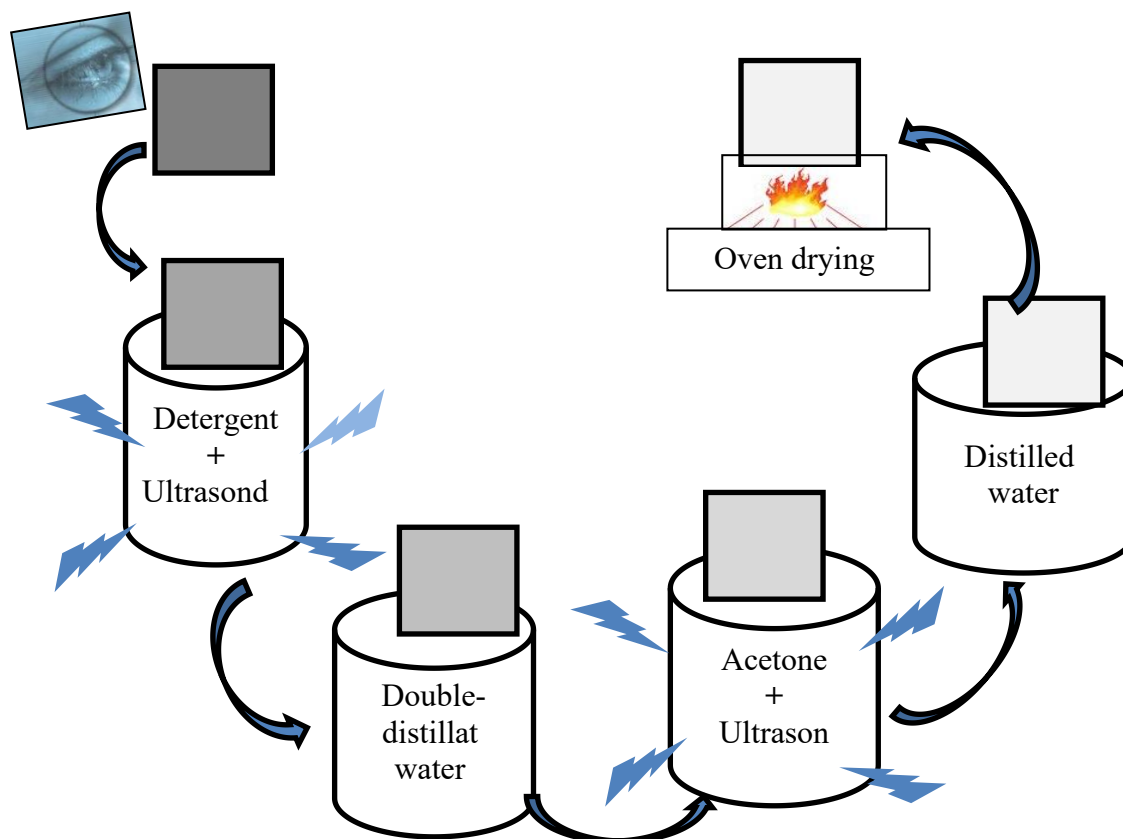


Figure III.1: Flowchart illustrating the substrate cleaning process steps.

III.5. Protocol of polyaniline thin films formation via the *CBD* method

To deposit *PANi* films using chemical bath deposition (CBD), begin by thoroughly cleaning the micro-glass substrate in an ultrasonic bath containing acetone, ethanol, and deionized water. Prepare the deposition solution by dissolving the aniline monomer in 1 mol/L HCl to ensure protonation. Then, gradually add ammonium persulfate (*APS*) as an oxidizing agent while stirring continuously. Once the solution has stabilized, immerse the substrate in it at room temperature for the chosen reaction time, based on the desired thickness.

After deposition, rinse the substrate with deionised water and let it air dry. Optional post-treatments, such as mild thermal annealing or acid doping, can enhance conductivity and surface morphology, yielding uniform films with controlled thickness and superior electrochemical properties. The chemical bath deposition method is an effective method for depositing high-quality polyaniline thin films. The protocol involves repeated cycles of successive dipping of the cleaned glass substrate into three beakers containing specific percolator solutions. Firstly, the substrate was immersed in a beaker containing an acidic HCl solution (C_{An} , 0.010–0.100 mol/L) with dissolved aniline for 15 minutes to absorb a layer of aniline molecules onto the substrate surface. Then, a solution of ammonium persulfate ($C_{S_2O_8^{2-}}$; 0.010–0.100 mol/L) is slowly added to the initial mixture to promote the polymerisation of the adsorbed aniline (C_{An} ; 0.010–0.100 mol/L), forming a polyaniline layer. The reaction is then maintained for a fixed time (10–60 minutes) at different temperatures (25–55°C) to obtain the desired layer thickness, as shown in (Figure III.2).

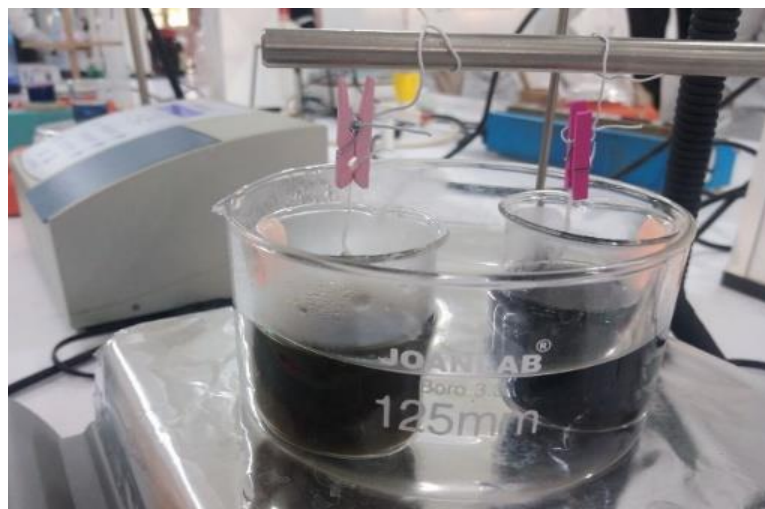
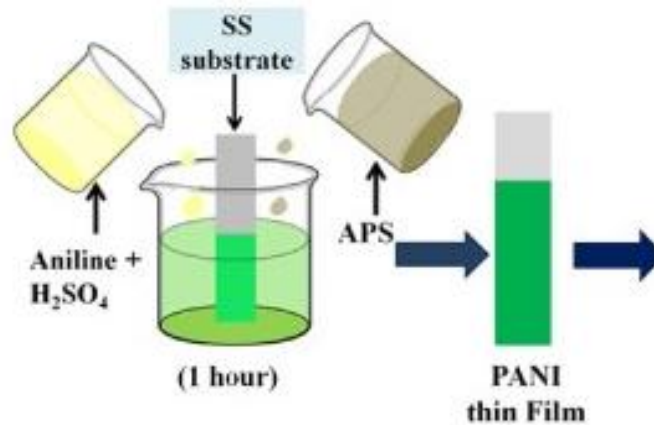


Figure III.2: Deposition method for PANi thin films deposited on a glass substrate via CBD technique under the optimal conditions: $C_{S_2O_8^{2-}} = (0.01-0.1 \text{ mol/L})$, $C_{An} = (0.01-0.1 \text{ mol/L})$, $T^\circ = (25 - 55^\circ\text{C})$, and $t = (10 - 60 \text{ min})$

The temperature, solution concentration, and number of cycles directly influence the layer's morphology and properties [4]. The *CBD* method offers precise control of thin-film growth while requiring only simple equipment. The temperature, solution concentration, and number of cycles directly influence the morphology and properties of the layer. The *CBD* method offers precise control of thin-film growth while requiring only simple equipment. The mechanism for the creation of *PANi* Films on the chosen glass surface can be depicted in the (Figure.III.3) and through the subsequent reactions:

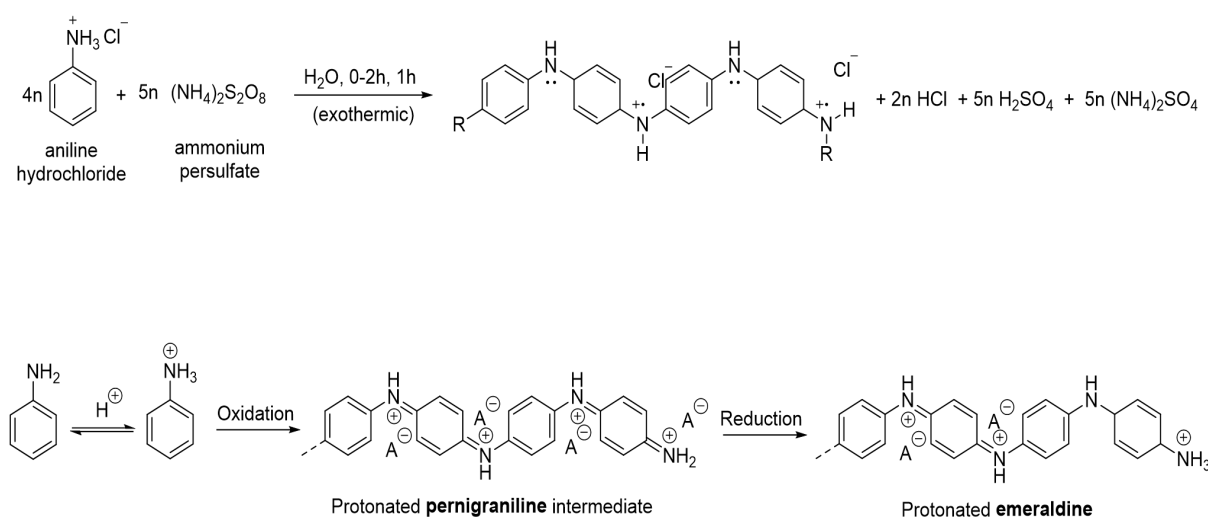


Figure III.3. Detailed mechanism for the polymerisation of aniline to *PANi* using ammonium persulfate and hydrochloric acid.

This reaction mechanism illustrates the process of oxidative polymerisation of protonated aniline in highly acidic environments, catalysed by ammonium persulfate. The reaction proceeds via the formation of a highly oxidized, protonated polymer chain (protonated Pernigraniline) as an intermediate. This protonated Pernigraniline is then reduced to the more stable and electrically conductive form, protonated Emeraldine, which is the form of interest for many *PANi* applications [5,6].

The chemical bath deposition (CBD) method represents a simple, cost-effective, and environmentally friendly alternative for thin-film fabrication. This technique enables convenient control of film thickness, is compatible with large-area substrates, and operates at relatively low temperatures while generating minimal chemical waste [9]. Owing to these advantages, CBD has emerged as a promising strategy for the large-scale fabrication of polyaniline (*PANi*) thin films.

The structural, optical, and electrical properties of PANi thin films synthesized by CBD are highly sensitive to several operational parameters, including aniline concentration, oxidant concentration, solution acidity, deposition temperature, and the number of immersion cycles. Conventionally, process optimization has been performed using the “one factor at a time” (OFAT) approach, in which each parameter is adjusted independently. Although straightforward, this method is time-consuming and costly, and it cannot identify interactions between variables [7,8]. Additionally, Design of Experiments (DoE) optimization is often impractical due to the large number of experiments required [8,9]. In contrast, chemometric optimization techniques enable simultaneous evaluation of multiple parameters, thereby improving predictive accuracy while significantly reducing experimental effort and cost. Experimental design methodologies are widely applied to optimize synthesis conditions and systematically investigate factor interactions [7-12].

These approaches substantially reduce the number of required experiments while ensuring statistically robust and reliable results. In the present study, a multivariable chemometric optimization strategy based on the Box–Behnken design was employed to efficiently synthesize PANi thin films on glass substrates using the CBD technique.

III.6. Design of Experiments (DoE) optimization

Design of Experiments (DoE) optimization is a systematic, statistical approach for identifying the best combination of input factors to maximize or minimize outcomes more efficiently than traditional "one-Factor-at-a-time" (OFAT) methods. It reduces the number of experiments needed, helps map the design space to understand factor interactions, and is crucial for enhancing process quality, decreasing variability, and supporting Quality by Design (QbD). Although experimental design is not a recent innovation, the timeline below (Figure III.4) highlights its long history. Early scientists addressing experimental organization were agricultural engineers, constrained by multiple factors, limited experiment duplication, and lengthy trial durations—prompting Fisher's 1925 breakthrough method for simultaneous multi-factor study, later refined by statisticians through experiment tables that drastically reduced trials without compromising results; adopted by major corporations post-Taguchi's quality work, these 18th-20th century statistical methods enabled process optimization without full physicochemical knowledge, revealing that product quality depends fundamentally on process design understanding rather than the final product itself, with experimental design emerging as the essential tool for resolving all process-related questions [13-16].

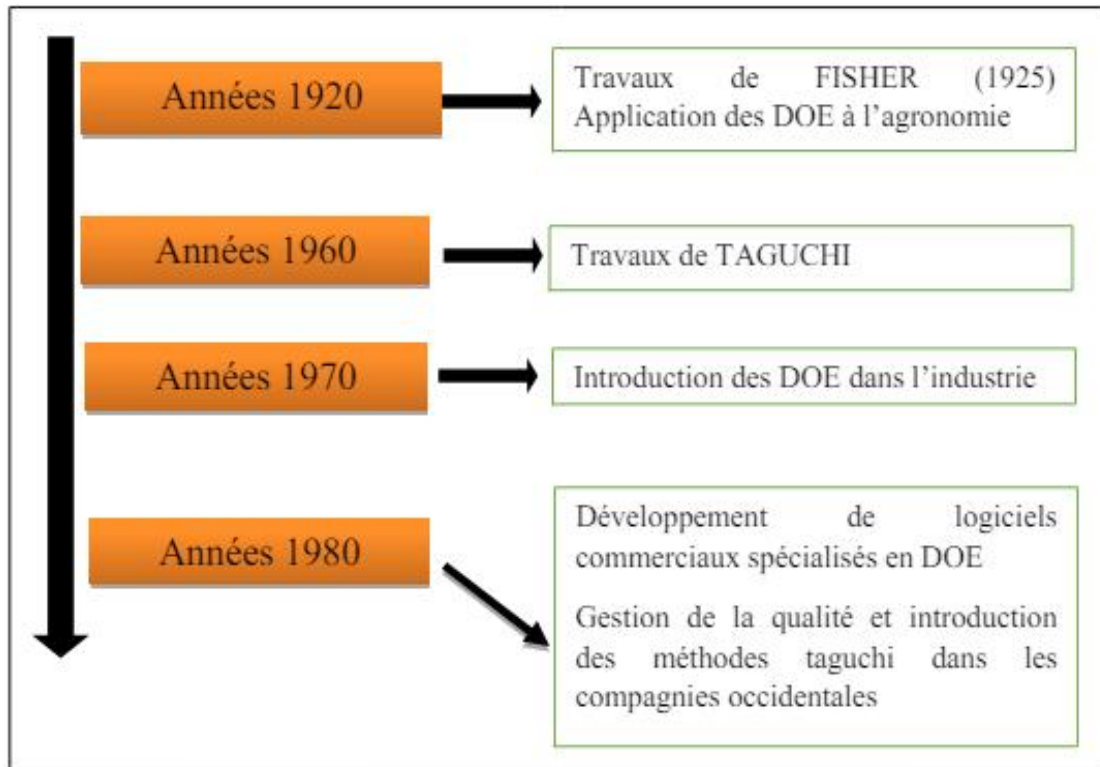


Figure III.4: Historical Overview of Experimental Design [13]

Experimental design optimizes experimental study organization by simultaneously and methodically varying levels of input factors to measure their effects on system outputs, maximizing research output with minimal experiments while ensuring optimal response quality/accuracy when investigating relationships between response (Y) and factors (X_i), which take the form:

$$Y = f(X_i)$$

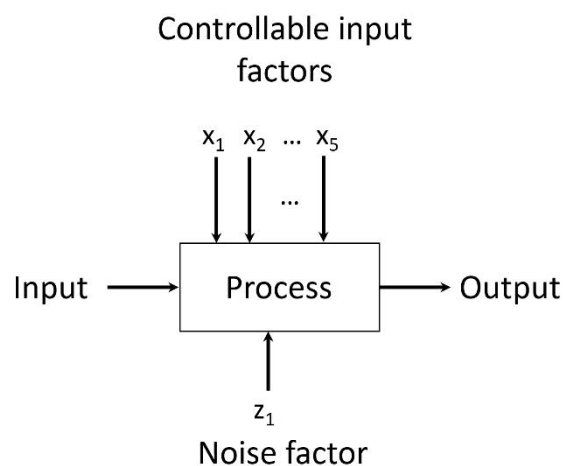


Figure III.5: Schematic diagram of this process.

Factor ($X_1, X_2, X_3, \dots$): A quantifiable physical quantity (continuous or discrete), measured or recorded at the system input, expected to affect the system output [14-18].

Response ($Y_1, Y_2, Y_3, \dots$): A measurable physical quantity (continuous or discrete), evaluated at the system output, representing the effect of factors on the system objective [14-18].

Factor Study Domain: The set of values a quantitative factor can take between a minimum (called *low level*) and maximum (called *high level*), where factors are transformed into coded variables $X_1, X_2, \dots$, ranging between (-1) and (+1) [13-16].

Experimental Space: The geometric domain where each factor is represented by an axis, and combinations of factor levels define experimental points. [14-18]

Variable coordinates: Variable coordinates necessitate factor transformation to simplify problem solving through two key modifications, changing measurement units and shifting the measurement origin, resulting in low-level substitution with coordinate (-1) and high-level with (+1), where original variables (A) and transformed variables (X) relate as follows:

$$X = \frac{A - A(-1)}{A(+1) - A(-1)} \quad (\text{Eq III.1})$$

Where:

A: the factor value at the specified level. The advantage of coded coordinates is that they enable experimental designs to be presented identically regardless of the chosen study domains, factor magnitudes, or units [14,17].

III.6.1. Experimental matrix

The experimental matrix is a two-dimensional table where the first column contains the experiment number, followed by a column for each factor, then the response column, with rows representing experimental runs. The total number of experiments dictated by the experimental design is: Number of experiments = N^p , where N is the number of factor levels and p is the number of factors. Thus, the two-level three-factor design consists of $2^3 = 8$ experiments (see Table III.3:), and the three-level three-factor design consists of $3^3 = 27$ experiments [17-22].

Table III.3: Example of a Two-Level Three-Factor Experimental Design

Experiments	Factor 1	Factor 2	Factor 3	Response
1	-1	-1	-1	Y_1
2	+1	-1	-1	Y_2
3	-1	+1	-1	Y_3
.	.	.	.	.
.	.	.	.	.
.	.	.	.	.
.	.	.	.	.
.	.	.	.	.

III.6.2. Selecting the Appropriate Experimental Design

Different experimental designs can be classified into two categories based on the desired objective:

Factor Screening Designs: These enable the identification of factors affecting the observed response. In this type of design, many factors can be studied with a few experiments. The mathematical models are 1st-order polynomials that can account for interactions between two factors [20-21].

Model without interaction:

$$y = a_0 + \sum_{i=1}^N a_i x_i + e \quad (\text{Eq III. 2})$$

Model with interactions:

$$y = a_0 + \sum_{i=1}^N a_i x_i + \sum_{i=1, j>i}^{k-1} a_{ij} x_i x_j + e \quad (\text{Eq III. 3})$$

2. Optimization Designs: These are used to develop a predictive mathematical model of the system. The goal is to accurately model the behaviour of the studied response. They are used in the optimization phase [20-22]. The mathematical models are generally 2nd-order polynomials that account for interactions between every pair of factors:

Where:

Y: is the response

X_i: is the level of the factor.

III.6.3. Types of Experimental Designs

Experimental designs can be classified into three types based on their objectives:

- a. **Factor Screening Designs:** Designed to identify the most influential **factors** on a specific response using the minimum number of tests.
- b. **Full Factorial Design:** The simplicity or complexity of implementing this design depends on the relevant factors and hypotheses to be formulated. This method studies all possible combinations of factors considered in the experiment, denoted as $\mathbf{X}^K$ (indicating K factors at X levels). The design measures factor effects by simultaneously changing factor levels in each test, reducing the number of experiments while increasing the number of factors studied.
- c. **Fractional Factorial Design:** These designs are primarily used to identify the factors with the greatest influence on a response variable from a large number of potential factors, particularly in situations where little is known about the cause-and-effect relationships.
- d. **Plackett-Burman Design:** Plackett-Burman matrices are essentially Hadamard matrices, where the two scientists simplified and systematized their design. These designs do not consider interactions between main factors and can thus be classified as Resolution fractional factorial designs.
- e. **The Box-Behnken design:** Introduced by Box and Behnken in 1960, the Box-Behnken design is an experimental methodology for second-order models that estimates specific interactions using three-level factors (-1, 0, +1), requires fewer experimental points than central composite designs for equivalent factors (reducing costs), and is geometrically constructed via cube-based configurations for 3-4 factors [13,17, 22].

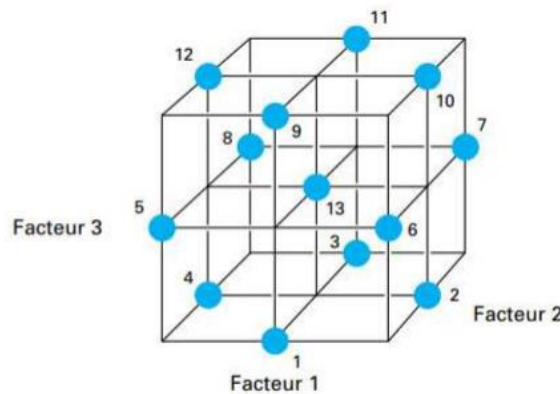


Figure III.6: Box-Behnken design for three factors.

The Box-Behnken design is a type of response surface design that does not include a fractional factorial or full factorial design. Therefore, a three-factor design contains 15 tests (12 edge points and 3 center points), as shown in the figure. Their objective aligns with optimization designs, but the factors are not independent. When constructing such designs, it is essential to account for the constraint that their sum equals a constant.

III.6.4. Desirability Function

The Desirability function (DF) is a widely used technique for discovering global optimal conditions. It distinguishes and creates a function for each individual response (D). Thus, the desirability function defines the global function (D) to be maximized after selecting the comprehensive values of the influential factors, while accounting for their interactions. The primary advantage of this function is its ability to handle both qualitative and quantitative responses through a simple, rapid transformation of different types of measurable responses. We must first transform the response (U) into a specific desirability function over the $[0, 1]$ interval, where a threshold value of 1 indicates complete desirability. When the desirability value is (0), the response is undesirable, representing the minimum applicability threshold for this function [18-22].

The desirability function enables response optimization and is formally defined by:

$$D = \begin{cases} 0 & y_i \leq y_{min} \\ \left| \frac{y_i - y_{min}}{y_{max} - y_{min}} \right| & y_{min} < y_i < y_{max} \\ 1, & y_i \geq y_{max} \end{cases} \quad (\text{Eq III. 4})$$

The values of this function range between 0 and 1. A value of 0 is assigned when the factors produce an unacceptable response, and a value of 1 represents the maximum achievable performance for the factors under study.

III.6.5. Design of Experiments Software

DOE software includes libraries for classical designs and allows the creation of custom designs. While we *could* calculate experimental coefficients using spreadsheets (with programming effort and time), it's far better to use specialized software. These tools not only compute coefficients but also perform statistical calculations to evaluate model quality, predict responses across the study domain, plot response surfaces, and identify optima. Key

software includes: JMP, Minitab, Statistica, Statgraphics, Unscrambler, Pirouette, and Modde. In this study, the Minitab Software was used to analyze our data. This software is specialized commercial statistical software developed by Minitab LLC for Windows. It is widely used for teaching statistics and explicitly targets businesses by focusing on Six Sigma methodology to enhance efficiency [20-21].

III.7. Optimization Model Selection

In this study, we chose to use a Box-Behnken Design (BBD), which involves varying all factors across experiments to estimate their effects. In other words, we examine the effect of one factor while holding the others constant. The main advantages of these designs are their low cost, fewer experiments needed, and the ability to explore potential interactions between factors. A Box-Behnken design (BBD) consists of 2^k experiments, where k is the number of factors, and 2 levels for each factor. It is especially useful for preliminary studies or optimization. In this study, a full factorial design with 27 experiments was used to assess the significance of physicochemical factors, such as reaction time $t = (10 - 60 \text{ min})$, medium temperature $T^\circ = (25 - 55^\circ\text{C})$, aniline concentration $C_{An} = (0.01-0.1\text{mol/L})$, and persulfate concentration $C_{S_2O_8^{2-}} = (0.01-0.1 \text{ mol/L})$ —in improving the optical properties of the deposited layers.

Table 3 shows the input factors and their levels in the experiment. To study the different interactions between physicochemical factors affecting the reaction, we employed an experimental design method with four independent factors at varying levels: Temperature (T), time (t), aniline concentration C_{An} and $C_{S_2O_8^{2-}}$ concentration, with three replicates at the center point.

Table III.4: Factor levels tested in the study of optical properties of deposited layers:

Factor	Unit	Symbol	Low level (-1)	Center (0)	High level (+1)
Aniline Concentration	mol/L	C_{An}	0.01	0.055	0.1
Persulfate Concentration	mol/L	$C_{S_2O_8^{2-}}$	0.01	0.055	0.1
Time	min	t	10	35	60
Temperature	$^\circ\text{C}$	T°	25	40	55

In this study, band gap energy (Eg) was selected as the response (Y) to determine optimal factor conditions. Data were analyzed using Minitab 18 to determine individual main effects and interaction effects among the studied factors. The total number of experiments was calculated by:

$$N_{\text{exp}}^{\text{br}} = 2\varepsilon + P \quad (\text{Eq III. 5})$$

Where:

ε : Number of studied factors

P: Center points added to test quadratic curvature between low/high levels.

Center points are used to estimate the clarity and curvature of the model being applied. Thus, 27 experiments were conducted in this study, including a combination of the studied factor levels as shown in Table II.4. The results of the mentioned design can be applied in terms of the regression model and theoretical response through the following equation [20-24].:

$$(y) = a_0 + \sum_{i=1}^k a_i x_i + \sum_{i=1}^{k-1} \sum_{j=i+1}^k a_{ij} x_i x_j + \varepsilon \quad (\text{Eq III. 6})$$

Where:

ε :is the residual term,

a_0 : is the response value at the center of the domain,

a_i : are the linear coefficients,

a_{ij} : and a_{ijk} denote the interaction coefficients between the tested factors.

x_i, x_j, x_k : are the independent variables [20-24].

Minitab 18 statistical software for Windows was used to create the experimental design (DoE) and analyze the data obtained from the experiments. The F-value and p-value tests were used to analyze the coefficients. A second-order mathematical equation was used to calculate the regression coefficients. The lack-of-fit test was used to assess the adequacy of the mathematical models. The model's statistical significance was verified using the F-test. Response surface plots were applied to illustrate the effects of the independent variables on the selected responses. The best model was chosen based on the highest R^2 value, and the p-values of the model terms should be less than 0.05 [20-24].

Table III.5: Experimental parameters and visual observations of deposited layers

Sample	T° (°C)	t (min)	[An]	[S ₂ O ₈ ²⁻]	Observed Color
1	25	10	0.055	0.055	Light olive green
2	55	10	0.055	0.055	Light olive green
3	25	60	0.055	0.055	Slightly dark olive green
4	55	60	0.055	0.055	Green precipitate with crusty layer
5	40	35	0.01	0.01	Transparent color
6	40	35	0.1	0.01	[No data]
7	40	35	0.01	0.1	Dark purple
8	40	35	0.1	0.1	Dark green with purple layer
9	25	35	0.055	0.01	Yellowish brown
10	55	35	0.055	0.01	Brown
11	25	35	0.055	0.1	Green clumps
12	55	35	0.055	0.1	Blue-green precipitate
13	40	10	0.01	0.055	Light pink
14	40	60	0.01	0.055	[No data]
15	40	10	0.1	0.055	Dark blue
16	40	60	0.1	0.055	[No data]
17	25	35	0.01	0.055	Deep purple
18	55	35	0.01	0.055	Transparent purple
19	25	35	0.1	0.055	Greenish blue
20	55	35	0.1	0.055	Ink-like waves
21	40	10	0.055	0.01	[No data]
22	40	60	0.055	0.01	Light olive green
23	40	10	0.055	0.1	Blue
24	40	60	0.055	0.1	Dark greenish blue
25	40	35	0.055	0.055	Dark greenish
26	40	35	0.055	0.055	Dark greenish blue
27	40	35	0.055	0.055	Dark greenish blue

III.8. Thin films characterization

The morphological, optical, and electrical properties of Polyaniline thin films prepared under optimal conditions by chemical bath deposition were characterized using techniques such as FTIR spectroscopy, UV-Vis spectroscopy, optical microscopy, X-ray diffraction, and scanning electron microscopy.

III.8.1. Analysis by UV-Vis spectrophotometry

Spectroscopic methods are simple. Absorbance measurements allow us to study changes in the thickness of thin layers using their spectra. To carry out our work, we used an Edinburgh UV-Vis spectrophotometer (DS5 Dual Beam UV-Vis) recording spectrophotometer. Controlled by a computer, it can scan between 200 and 900 nm. This spectrometer is equipped with a double-beam system that allows the influence of the substrate to be subtracted instantly, leaving only the absorbance of the layer being analyzed to be measured (Figure III.7) [25].

The absorbance of the thin layers of the deposited complexes is measured in relation to a blank glass slide (reference beam). To carry out this study, a blank glass slide is inserted into the optical path of the reference beam, while the layer deposited on the substrate is inserted into the optical path of the second beam. These measurements made it possible to obtain the absorbance ($A=f(\lambda)$) and transmittance ($T=f(\lambda)$) spectra.

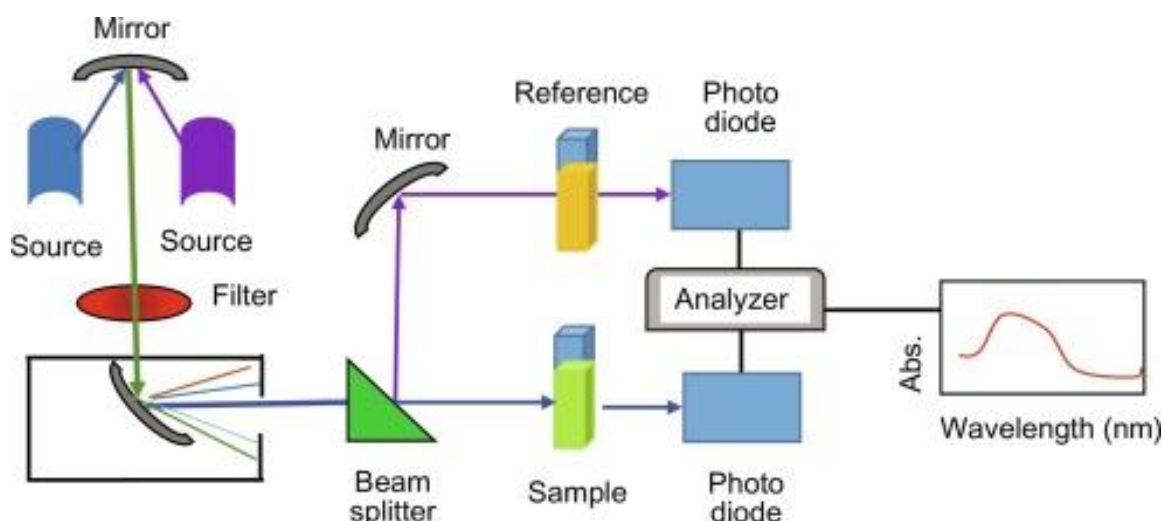


Figure III.7: Principle of characterization using a UV-Vis spectrophotometer.

III.8.2. Characterization by infrared spectrometry (FTIR)

Infrared technology uses the electromagnetic radiation range between 1 and 50 μm to identify compounds by measuring the sample's light absorption (Figure III.8). The FTIR spectra were recorded in the wavelength range (400 - 4000 cm^{-1}) via a PerkinElmer 1000 FTIR spectrometer. The mid-infrared range provides more information about the structures being analyzed. As a result, it is widely used as a non-destructive method for identifying organic and inorganic molecular compounds, providing a fingerprint. Fourier transform infrared spectrometry, which complements the initial dispersive method, offers numerous options for spectral processing and enables the analysis of microstructures (thin layers, crystals, or powders) [25].

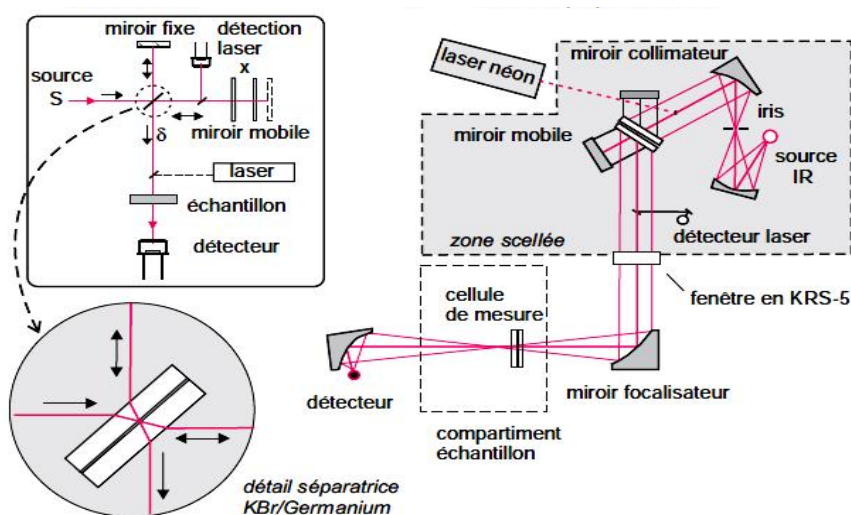


Figure III.8: Optical diagram of an infrared spectrophotometer.

III.8.3. Characterization of surface morphology

Scanning electron microscopy (FEI-Quanta 200 SEM) was used to evaluate the morphology of polyaniline thin films. It employs a concentrated electron beam to scan the surface and generate high-quality images of various samples. The resolution of the FEI-Quanta 200 SEM is 3.0 nm, and it can magnify up to 300,000x. This microscope belongs to a series that features a super-conical objective lens. This lens design ensures high resolution at typical analytical working distances (e.g., 10 mm). The hyper-conical shape of the lens also allows for extensive specimen tilt at these working distances.

For microscopic characterization of the surface condition of the deposited thin layers, we used a Nikon 200 optical microscope at 1500 $\times$ magnification. We also used a scanning

electron microscope equipped with a field emission gun to achieve submicron resolution. The images obtained were analyzed using the ANALYSIS 833 image analysis system.

This software enables thresholding and particle detection to quantify particles by size and determine their average size.

The thin layers were characterized using a scanning electron microscope with a very fine beam of monokinetic electrons, which scans the sample surface where interactions occur. These interactions are detected by a sensor that controls the brightness of a cathode ray oscilloscope, whose scanning is synchronized with the electron beam [26] (Figure III.9).

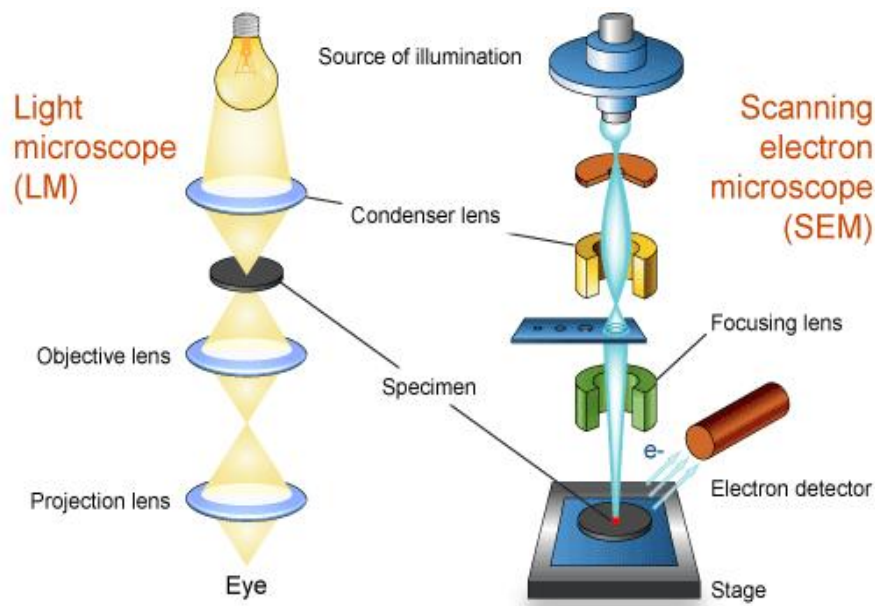


Figure III.9: Characterization of thin films using optical and electron microscopes.

III.8.4. Structural characterization by X-ray diffraction

For thin films, grazing-incidence X-ray diffraction is more appropriate than the Bragg-Brentano configuration. This is because the irradiated volume is larger than in a $\theta/2\theta$ configuration. The smaller the angle of incidence, the shallower the penetration depth. As a result, the information obtained from the diffractograms relates more to the sample than to its substrate [27]. In our case, the structure of PANi thin films was analyzed using X-ray diffraction (Analytical X-Pert PROMPD), with XRD patterns recorded in the $20\text{-}100^\circ$ 2θ range at 0.05° increments using $\lambda = 1.5406 \text{ \AA}$ (CuK α source) at ambient temperature. The phase identification of thin films was performed using a grazing-incidence diffractometer (Figure III.10).

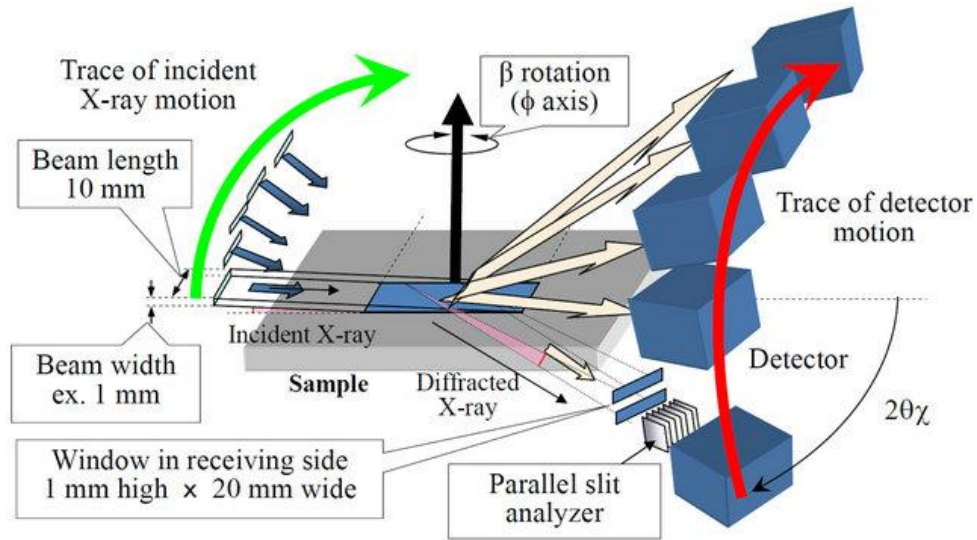


Figure III.10: Principle of thin film characterization by XRD.

Detection is performed by a Peltier-cooled detector. The high energy resolution of this detector ($\Delta E < 0.3$ keV) allows elimination of unwanted diffraction lines (such as $K\beta$) and a large part of the fluorescence. The beam-sample angle remains constant and its value is set at $\alpha=1^\circ$ [27].

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Chapter VI:
Results and discussion

VI.1. Introduction

This chapter presents and analyzes experimental results on the deposition and properties of thin polyaniline layers produced by chemical bath deposition (CBD). The deposition parameters were optimized using the Box-Behnken methodology, which enabled an effective assessment of how key variables such as bath temperature, deposition time, and precursor concentration influence the quality of the films.

The results highlight the structural, morphological, optical, and electrical characteristics of the films, linked to the optimal conditions identified. An in-depth discussion compares these findings with the underlying physicochemical mechanisms and existing literature on intrinsically conductive polymers.

This multivariate Box-Behnken approach facilitated modeling of the responses and improved performance, potentially for use in electrochemical sensors and energy applications. FTIR, XRD, SEM, and conductivity measurements illustrate how parameters affect the films' crystallinity, conductivity, and stability. This chapter aims to emphasize the observed trends and their practical significance. The following sections detail the raw data, optimization models, and comparative analyses. Finally, prospects for further improvement and applications are discussed.

VI.2. Box-Behnken optimisation

A multivariable optimization study employing the efficient Box-Behnken design (BBD) was selected to systematically investigate the synthesis of polyaniline (PANi) thin films, utilizing a 27-run experimental matrix that captures key operational parameters and their levels as detailed in [Table VI.1](#). The resulting band gap energy (E_g) ranged widely from 2.263 to 5.952 eV across trials, underscoring the strong influence of synthesis conditions and enabling the precise identification of optimal combinations for high-quality films tailored for optoelectronic applications such as sensors or solar cells. BBD's advantages—requiring fewer experiments than full factorial designs while supporting quadratic response surface methodology (RSM) for contour plotting and optimization—avoid axial instabilities, and subsequent ANOVA and diagnostics confirm model adequacy and provide actionable insights for scalable PANi production.

Table VI.1: Experimental matrix of twenty-seven (27) trials with uncoded values of the operational factors studied (T° , t , C_{An} , and $C_{S_2O_8^{2-}}$), the experimental ($E_{g\ exp}$) and predicted ($E_{g\ pred}$) Band gap values, managed with a Box-Behnken design

Experiments	Operating factors				Band gap values	
	T (°C)	t (min)	C_{An} (mol/L)	$C_{S_2O_8^{2-}}$ (mol/L)	$E_{g\ exp}$ (eV)	$E_{g\ pred}$ (eV)
1	25	10	0.055	0.055	3.956	4.039
2	55	10	0.055	0.055	4.078	4.182
3	25	60	0.055	0.055	3.952	3.974
4	55	60	0.055	0.055	2.492	2.534
5	40	35	0.01	0.01	2.656	2.661
6	40	35	0.1	0.01	2.485	2.554
7	40	35	0.01	0.1	5.587	5.642
8	40	35	0.1	0.1	3.669	3.790
9	25	35	0.055	0.01	2.678	2.683
10	55	35	0.055	0.01	2.449	2.474
11	25	35	0.055	0.1	5.173	5.231
12	55	35	0.055	0.1	4.065	4.143
13	40	10	0.01	0.055	4.438	4.502
14	40	60	0.01	0.055	3.939	3.899
15	40	10	0.1	0.055	3.654	3.777
16	40	60	0.1	0.055	2.647	2.666
17	25	35	0.01	0.055	3.726	3.704
18	55	35	0.01	0.055	3.730	3.668
19	25	35	0.1	0.055	3.484	3.338
20	55	35	0.1	0.055	2.263	2.076
21	40	10	0.055	0.01	3.576	3.440
22	40	60	0.055	0.01	2.715	2.746
23	40	10	0.055	0.1	5.952	5.712
24	40	60	0.055	0.1	4.765	4.692
25	40	35	0.055	0.055	2.851	2.851
26	40	35	0.055	0.055	2.848	2.851
27	40	35	0.055	0.055	2.854	2.851

(Figure VI. 1) illustrates the correlation between the predicted and experimentally determined bandgap energies. Analysis of the graph reveals the effectiveness and robustness of the predictive model for band-gap energy, derived from a Box–Behnken design optimisation of thin polyaniline films. The excellent agreement between the experimental results and the predictions confirms the model's ability to elucidate the influence of synthesis conditions on the band gap energy, enabling reliable optimisation of fabrication processes.

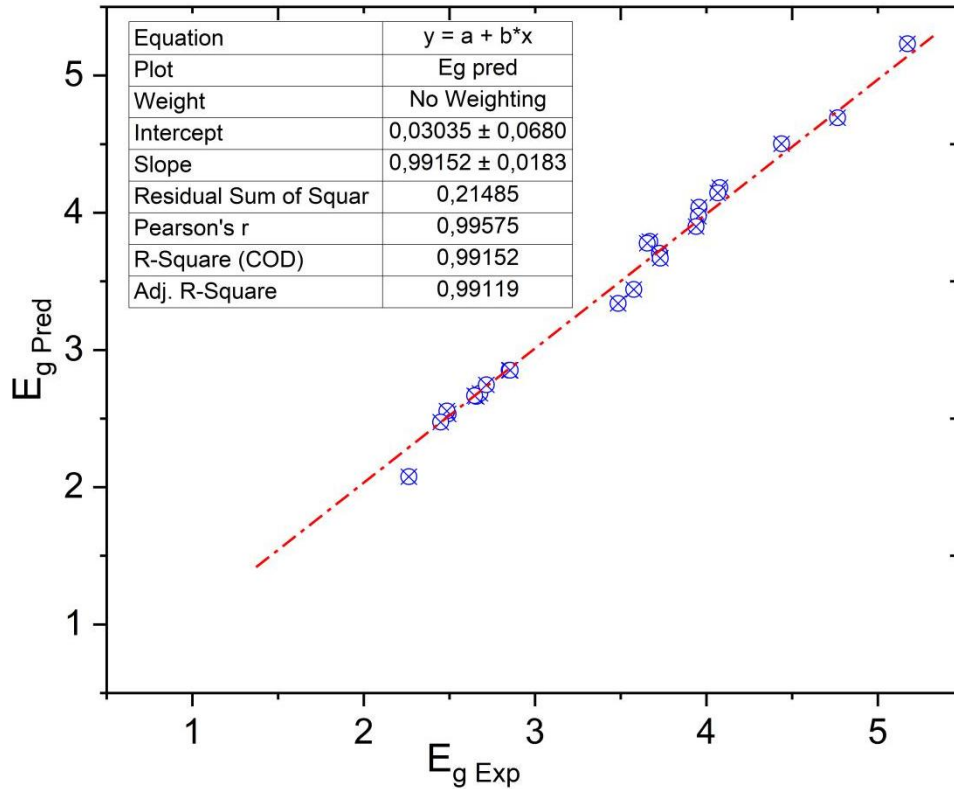


Figure VI.1: Correlation plot illustrating the agreement between the experimental band gap energy ($E_{g \text{ Exp}}$) and the predicted band gap energy ($E_{g \text{ pred}}$) for the synthesized polyaniline thin films.

VI.2.1. Significant effects and coefficients of the adopted model

The obtained results demonstrated a strong correlation between the expected ($E_{g \text{ pred}}$) and experimental ($E_{g \text{ Exp}}$) energy gap values, indicating that the projected model response is closely aligned with the experimental data. This study investigated the impact of four independent operational parameters on the chosen response (E_g) using a *BBD* method to establish the optimal conditions. To ascertain the best settings for the minimal value possible of the gap energy ($E_{g \text{ min}}$). A quadratic polynomial equation can elucidate the mathematical

link among three significant variables, as evidenced by the response and analysis of variance offered in Table VI.2. According to the statistical parameters, two parameters C_{An} and $C_{S_2O_8^{-2}}$ are highly significant. with p-values less than 0.05. The interactions among the components. specifically the squares $C_{S_2O_8^{-2}} * C_{S_2O_8^{-2}}$, $t * t$, $T^\circ * T^\circ$, and $C_{An} * C_{An}$ are highly significant with a p-value of 0.

Table VI.2: ANOVA was used to analyze the data for the deposition of polyaniline using the CBD technique under various operating conditions (T° , t , C_{An} , and $C_{S_2O_8^{-2}}$).

Source	DF	Adj SS	Adj MS	F-Value	P-Value
Model	14	17.6032	1.2573	100.27	0.000
Linear	4	13.6677	3.4169	272.49	0.000
T°	1	0.8764	0.8764	69.89	0.000
T	1	1.5308	1.5308	122.08	0.000
C_{An}	1	1.9976	1.9975	159.30	0.000
$C_{S_2O_8^{-2}}$	1	9.2629	9.2629	738.70	0.000
Square	4	2.5130	0.6282	50.10	0.000
$T^\circ * T^\circ$	1	0.0927	0.0926	7.39	0.019
$t * t$	1	1.6768	1.6767	133.72	0.000
$C_{An} * C_{An}$	1	0.1297	0.1297	10.35	0.007
$C_{S_2O_8^{-2}} * C_{S_2O_8^{-2}}$	1	1.4398	1.4398	114.82	0.000
2-Way Interaction	6	1.4225	0.2370	18.91	0.000
$T^\circ * t$	1	0.4349	0.4349	34.69	0.000
$T^\circ * C_{An}$	1	0.2611	0.2611	20.82	0.001
$T^\circ * C_{S_2O_8^{-2}}$	1	0.1340	0.1339	10.68	0.007
$t * C_{An}$	1	0.0447	0.0447	3.57	0.083
$t * C_{S_2O_8^{-2}}$	1	0.0185	0.0185	1.48	0.248
$C_{An} * C_{S_2O_8^{-2}}$	1	0.5293	0.5292	42.21	0.000
Error	12	0.1505	0.0125		
Lack-of-Fit	10	0.1505	0.0150	2375.70	0.000
Pure Error	2	0.0000	0.0000		
Total	26	17.7537			
Model Summary					
S	R-sq	R-sq(adj)	R-sq(pred)		
0.111980	99.15%	98.16%	95.12%		

The interaction between the studied operating parameters: $T^\circ * t$, $T^\circ * C_{An}$, $C_{An} * C_{S_2O_8^{2-}}$ and $T^\circ * C_{S_2O_8^{2-}}$ were highly significant, as revealed in the Pareto graph (Figure 3) and Table 2, with p -values of $p \ll 0.05$. By combining the other operating factors, we discovered that the interaction between persulphate ions and aniline concentrations has a greater impact on the polyaniline deposition process than other interactions ($C_{An} * C_{S_2O_8^{2-}} > T^\circ * t > T^\circ * C_{An} > T^\circ * C_{S_2O_8^{2-}}$). However, two interactions $t * C_{S_2O_8^{2-}}$ and $t * C_{An}$ present a non-significant effect with p -values > 0.05 . With a confidence interval greater than 95%, the statistical results showed that the operational factors and their interactions were statistically significant.

The significance of each parameter is shown by its adjusted sum of squares (Adj SS). The following quadratic polynomial equation can be used to determine the mathematical link between the response (E_g) and the four primary operational parameters (T° , t , C_{An} , and $C_{S_2O_8^{2-}}$):

$$E_g = 2.567 + 0.0016 T^\circ - 0.03342 t + 10.77 C_{An} + 14.14 C_{S_2O_8^{2-}} + 0.000586 T^\circ * T^\circ + 0.000897 t * t + 77.0 C_{An} * C_{An} + 256.6 C_{S_2O_8^{2-}} * C_{S_2O_8^{2-}} - 0.000879 T^\circ * t - 0.3785 T^\circ * C_{An} - 0.2711 T^\circ * C_{S_2O_8^{2-}} - 0.0940 t * C_{An} - 0.0604 t * C_{S_2O_8^{2-}} - 179.6 C_{An} * C_{S_2O_8^{2-}} \quad (\text{Eq.VI.1})$$

The proposed model is highly significant and fits the data well, with a very low p -value (0.000) and an F -value of 100.27 for the calculated model. The obtained R^2 value of 99.15% indicates that this model explains over 99% of the variance. The high R^2 value (95.12%) indicates a good agreement between the predicted ($E_{g \text{ pred}}$) and experimental ($E_{g \text{ exp}}$) values. The reliability of our model was also verified by calculating the Stone–Geisser coefficient using the following formula [36]:

$$Q^2 = 1 - SSE/SSO = 0.999 \quad (\text{Eq.VI.2})$$

where the sum of squared errors is denoted by SSE . The SSO displays the sum of squares of the observed values. According to *Tenenhaus* [36], if the sum of squares of observed values (SSO) is greater than the sum of squared errors (SSE), then $SSE/(SSO < 1)$ for $Q^2 > 0$. When Q^2 is negative, the model is considered to have predictive validity. The model under study is considered unsatisfactory [36–38]. The *Stone-Geisser* coefficient Q^2 in our situation is 0.999, which suggests that the model in use has extremely good predictive validity. An F -value of 100.72 and $p=0.000$ were obtained in the test of fit for missingness. This suggests that our

model follows the quadratic regression hypothesis rather than the linear regression hypothesis. It can forecast the deposition process by estimating the gap energy [36-40].

VI.2.2. Pareto chart

The Pareto chart is the first stage in the ongoing process of optimising the factors that influence the process through responsiveness (see Figure VI.2). It enables the identification of key influences and their interactions, indicating progress in resolving the issue for each corrective action. The Pareto chart leads to quality improvement. Parameter-by-parameter graphs of the main effects were created to represent the regression analysis results.

These graphs show the significant factors within a 95% confidence interval, along with the main effects, which represent the deviations between high and low levels for each factor. When the impact of a factor is positive, i.e., when the factor moves from a low level to a high level, the gap energy value (E_g) increases. Conversely, if the effects are adverse, there is a decrease in E_g at the high level for the same factor. Each effect was plotted horizontally on a Pareto chart at the 95% confidence level, with a T -value of 36.76. A t -test was then performed to determine whether they were significantly different from zero.

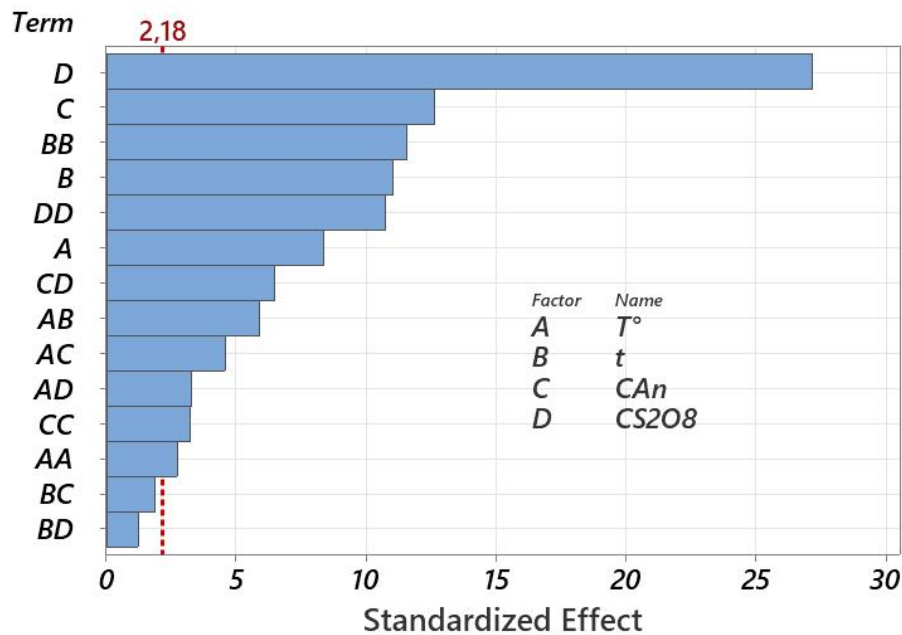


Figure VI. 2. Pareto chart showing the influence of individual and overlapping underlying factors.

The Pareto plot shows that the factor bars of the four main parameters, in terms of T° , t , C_{An} , and CS_{2O_8} , and some of their interactions term $T^\circ * t$, $T^\circ * C_{An}$, $C_{An} * C_{S_2O_8^{-2}}$ and $T^\circ * C_{S_2O_8^{-2}}$

cross the reference point at 2.18, suggesting that these terms have a significant impact on PANi thin film deposition at p -values less than 0.05, whereas the other interaction terms ($t * C_{S_2O_8^{2-}}$ and $t * C_{An}$) are not statistically significant at p -values greater than 0.05 (see Figure VI.2 and Table VI. 2). It cannot be determined whether the effect of the factor increases or decreases the gap energy value. This number signifies the absolute influence value, ranging from the most significant E_g value to the slightest impact.

VI.2.3. Effect of the main factors

The influence of key operating factors on PANi thin film deposition, including mean C_{An} , $C_{S_2O_8^{2-}}$, T° , and t , and their interactions were studied. The results obtained are shown in (Figure VI.3) According to the graphs of the main effects of ammonium persulfate concentration ($C_{S_2O_8^{2-}}$), aniline dose (C_{An}), bath temperature (T°), and reaction time (t) are related to the highest significant effects, reaching 0.8786, -0.4080, -0.3572, and -0.2703, respectively. Thus, as illustrated by the deviation of their curves from the low level (-1) to the high level (+1), the two factors illustrate a positive effect on the PANi Thin film deposition, and strongly statistically significant p -values were found, well below 0.05. Therefore, the concentration of aniline (C_{An}) significantly influences the band gap energy, as higher monomer concentrations promote longer polymer chains and increased π - π conjugation, leading to a lower band gap. Similarly, the dose of the oxidant ($C_{S_2O_8^{2-}}$) affects the oxidation level of polyaniline; an optimal oxidant concentration improves polymerisation and conductivity, while excessive oxidant may cause over-oxidation, resulting in structural defects and changes in band gap energy. Overall, the observed trends confirm that the band gap energy of polyaniline is highly sensitive to synthesis conditions, which govern its molecular structure and electronic properties. An increase in reaction temperature (T°) generally decreases the band gap energy, attributable to enhanced chain growth, longer conjugation, and improved molecular ordering at higher temperatures.

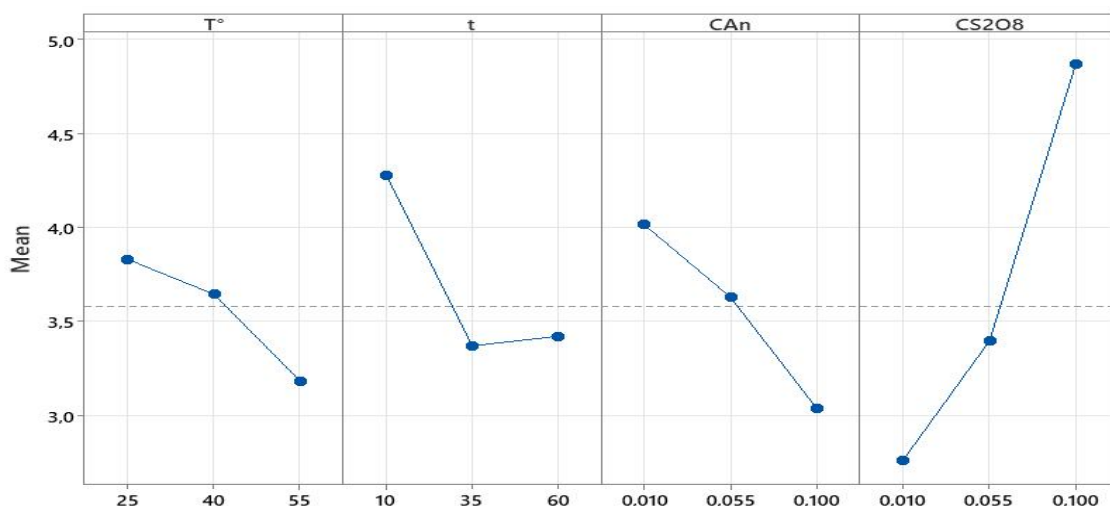


Figure VI.3: Individual effects of the main factors (T° , t , C_{An} , and $C_{S_2O_8^{2-}}$) on the band gap energy of polyaniline.

The slight rise in the mean value as the reaction time increases from 35 to 60 minutes is due to the reaction continuing at a slower rate after the initial polymerisation stage. Most rapid reaction occurs within 35 minutes, but some chain growth continues. Extended reaction time allows for better molecular ordering and structural stabilisation. Secondary processes, such as chain rearrangement, may also take place. The system gradually approaches equilibrium, so changes become less noticeable over time, resulting in only a small increase in the average value.

a. Effect of the initial concentration of persulfate ions

The concentration of persulfate ions plays a key role in the deposition of polyaniline thin films ($PANi$), as it directly influences the polymerization rate and film structure. At high persulfate ion concentrations, polymerization is faster, resulting in less homogeneous films with irregular morphology. Additionally, an excess of persulfate ions can promote the formation of porous films, thereby reducing film density and mechanical properties. On the other hand, too low a concentration can slow polymerization, resulting in films of low thickness and poor quality. It is therefore essential to optimize the persulfate ion concentration to ensure high-quality deposition, balancing polymerization rate and film homogeneity [41].

b. Effect of aniline initial concentration

Polyaniline films were deposited using initial aniline concentrations ranging from 0.01 to 0.10 mol/L. (Figure VI.3) illustrates that aniline concentration significantly affects the deposition

and quality of polyaniline thin films. At higher concentrations, polymerisation is accelerated, resulting in faster film formation but a less homogeneous structure and reduced density. Conversely, lower concentrations enable more precise control of film thickness, albeit at the cost of slower deposition, which can result in less conductive films. Aniline concentrations that are too low can restrict film growth. Excessive concentrations promote the formation of porous structures and poor-quality films. Therefore, the optimum aniline concentration must be carefully controlled to produce polyaniline films with good electrochemical and mechanical properties [42].

c. Effect of medium temperature

The effect of medium temperature on the deposition of *PANi* thin films was also investigated, and the results are revealed in (Figure VI.3). The energy gap (E_g) The values of the gaps decrease gradually with increasing medium temperature. In contrast, the deposition of *PANi* thin films decreased with increasing temperature. This phenomenon can be explicated by the negative effect of temperature on the deposition of polyaniline (*PANi*) thin films, which is influenced by polymerisation kinetics, chemical stability, and film morphology. Excessively high temperatures accelerate polymerisation, leading to irregular, poor-quality films. Additionally, excessive temperatures can degrade polyaniline, thereby affecting its electrochemical and mechanical properties. Rapid solvent evaporation at high temperatures can also alter the film's structure, making it porous. Therefore, the temperature must be carefully controlled to obtain high-quality, high-performance films [43].

d. Effect of reaction time

Reaction time plays a crucial role in the deposition of polymer thin films, as it influences the polymer's solubility and the substrate surface, and controls the evolution of film thickness. In this case, the energy gap values (E_g) progressively decline with increasing contact time, indicating that reaction time negatively affects the quality of polyaniline (*PANi*) thin films, primarily by influencing polymerisation and film formation. Prolonged contact time can result in excessive polymerization, leading to irregular film growth and surface defects, which reduce the uniformity and quality of the deposited films. Prolonged contact time also promotes the accumulation of by-products and impurities, which can affect the chemical stability and electrochemical properties of polyaniline. Excessive contact time can also upset the balance between polymerization rate and film formation, resulting in more porous, less

coherent films. Ultimately, excessive contact time can degrade polyaniline's properties, affecting its conductivity and stability in practical applications [44].

VI.2.4. Interactions effects

As shown in Figure 4, it appears that there is a notable interaction between the reaction temperature and the other factors: contact time ($T^\circ * t$), aniline concentration ($T^\circ * C_{An}$) and persulfate ions dose ($T^\circ * C_{S2O8}$), also the square's interactions $C_{S2O8} * C_{S2O8}$, $t * t$, $T^\circ * T^\circ$, and $C_{An} * C_{An}$ are more significant due to the non-parallelism of the action limits, as illustrated in Figure 5, which depicts the interactions among the four values. The Pareto chart confirms this, indicating a p -value below 0.05. Conversely, the interactions ($t * C_{S2O8}$ and $t * C_{An}$) exhibited negligible impacts, as can be seen from the almost parallel boundaries and p -values beyond 0.05 in the ANOVA table and Pareto chart, which both surpassed the baseline of 2.18.

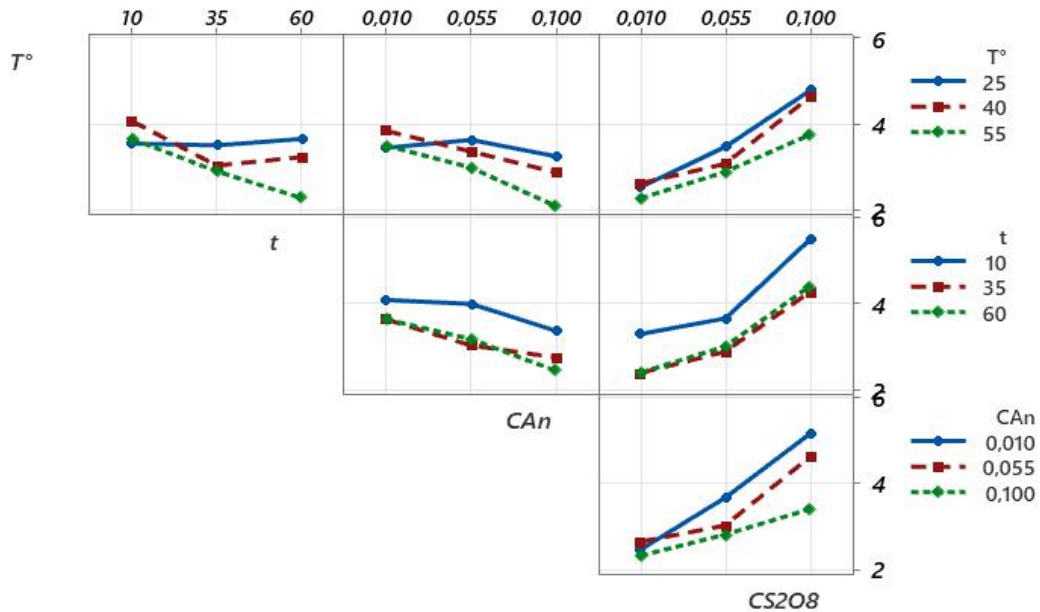


Figure VI.4: Interaction effects of the main factors (T° , t , C_{An} , and $C_{S_2O_8}$) on the band gap energy of polyaniline thin films.

Three-dimensional surface plots, which describe the relationship between the influencers and the selected answer, can help understand the main and interactive effects of the evaluated factors. The Three dimensional surface plots in this study reveal that the reported E_g values were primarily connected with four (4) main factors: T° , t , C_{An} and $C_{S_2O_8}^{-2}$ (see Figure VI.5). As range efficiency levels approach 96.86%, the interplay of these elements results in the greatest adjusted mean power. The lowest E_g values were obtained when the studied factors were

applied at the maximum levels of medium temperature (T°) and contact time (t), combined with moderate C_{An} and $C_{S_2O_8^{-2}}$ yield the lowest E_g values (~ 1.9 – 2.4 eV), promoting a more conductive, emeraldine salt form of PANi suitable for electrochemical applications. The $T^\circ * t$ interaction shows a synergistic decrease in E_g at elevated levels, attributable to enhanced chain propagation and doping during oxidative polymerization, reducing conjugation defects. Similarly, lower C_{An} mitigates aggregation, while moderated $C_{S_2O_8^{-2}}$ prevents over-oxidation to less conductive forms ($p < 0.05$ for interactions). These trends align with prior studies on PANi thin films, in which bandgap narrowing enhances the optoelectronic performance of sensors or energy devices.

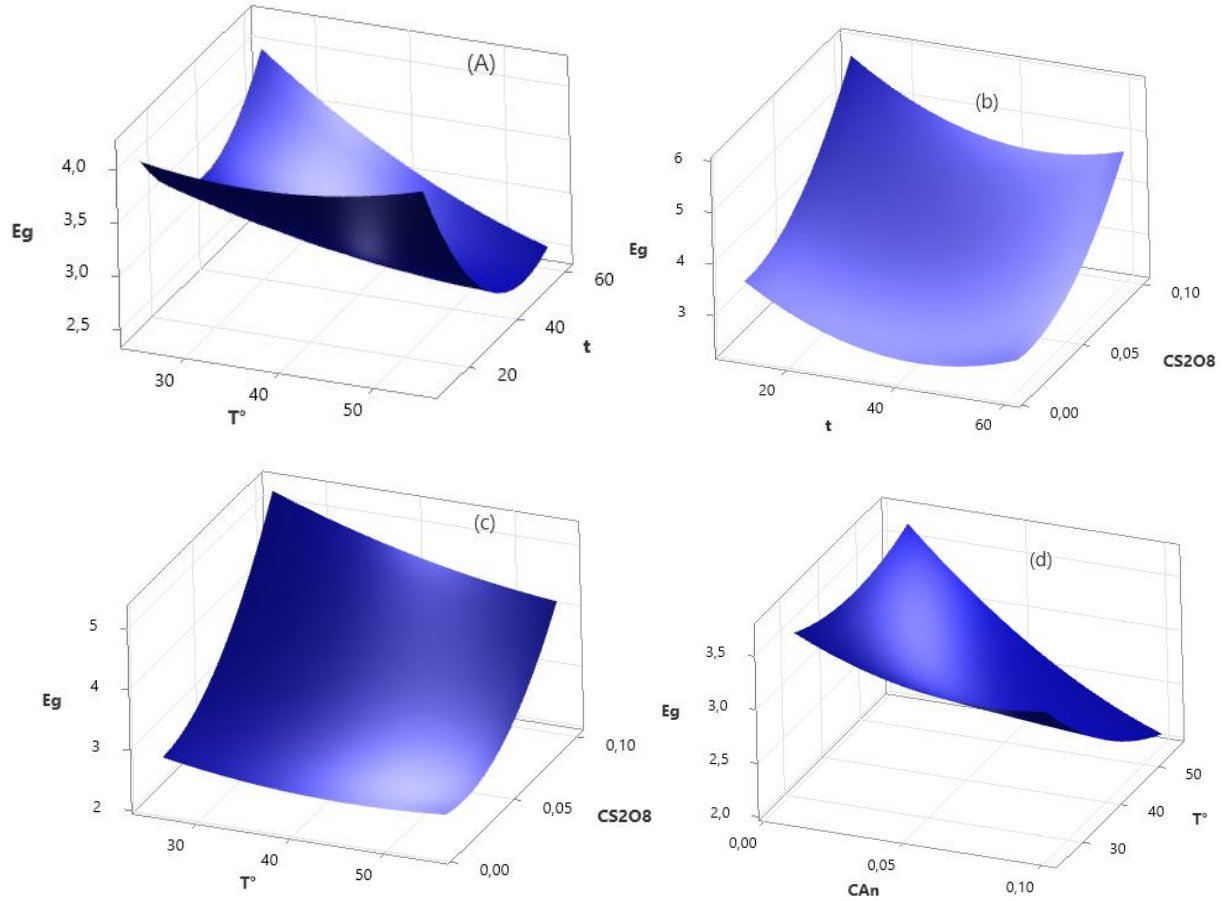


Figure VI. 5: Three diamentionals surfase plots for the effects of the main factors (T° , t , C_{An} , and $C_{S_2O_8^{-2}}$) on the band gap energy of polyaniline films: (a) T° vs t , (b) t vs $C_{S_2O_8^{-2}}$, (c) T° vs $C_{S_2O_8^{-2}}$, and C_{An} vs T° ($p < 0.05$).

VI.2.5. Validity of the model

The normal probability plot in (Figure VI.6) displays a straight line; the residuals as functions of fitted values, residuals vs observation order, and residual frequency histogram plots all reveal a random distribution. Based on these findings, the model was deemed appropriate for use and can be used to optimize the band gap energy of polyaniline films. The normal probability plot approximates a straight line, indicating a normal distribution of the residues. The symmetry of the residual histogram also confirms the normal distribution of the results. The residual-versus-fit and residual-versus-order plots demonstrate that the residuals are independent: they are randomly distributed on both sides of 0 and show no pattern. The presence of a pattern in the residual distribution may indicate that the model's assumptions are not met. According to these results, the model equation might be simplified by removing those factors non-statistically significant:

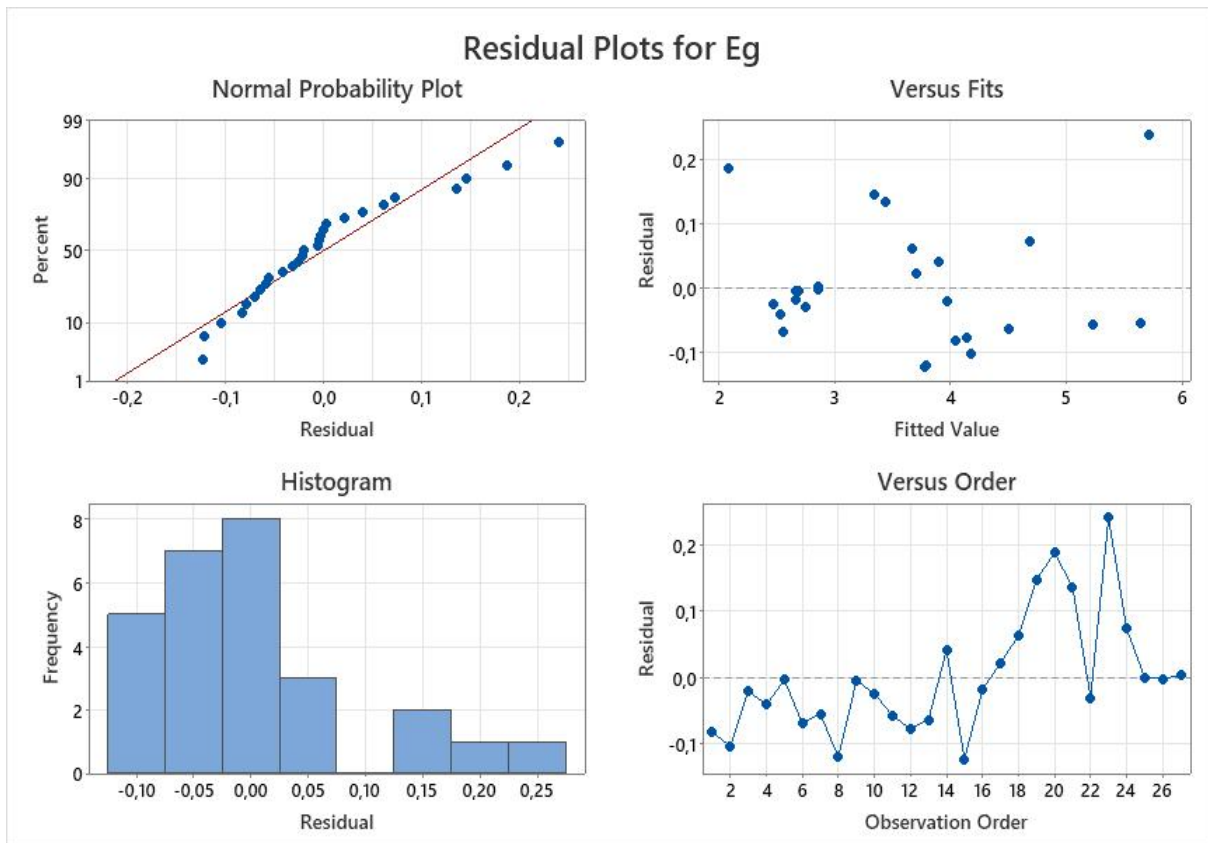


Figure VI.6. The normal probability plot and residual frequency histogram for the effects of the main factors (T° , t , C_{An} , and $C_{S_2O_8^{2-}}$) on the band gap energy of polyaniline films (response y is the band gap energy (E_g); $p < 0.05$).

The normal probability plot shows points that closely approximate a straight line, confirming that the residuals follow a normal distribution—a key assumption for valid inference in regression models. Deviations from linearity, such as systematic curves or heavy tails, would suggest non-normality (e.g., outliers or skewness), potentially invalidating p-values and confidence intervals; here, any minor departures are negligible, as supported by the symmetric, bell-shaped residual histogram centered at zero. This plot displays residuals randomly scattered around the zero line with no funnel shape or trend, indicating constant variance (homoscedasticity). A pattern of widening would signal heteroscedasticity, violating model assumptions and suggesting transformations such as $\log(E_g)$. Residuals appear structureless and balanced above/below zero across observation order, evidencing independence—no autocorrelation from experimental sequence or omitted time effects. Patterns like cycles would imply dependency, requiring model adjustments such as including order as a covariate. These diagnostics collectively validate the quadratic response surface model's assumptions (normality, independence, homoscedasticity), indicating that it is suitable for the optimization of E_g in polyaniline films. Non-significant terms ($p > 0.05$) can be removed to simplify the equation, enhancing parsimony without loss of fit—e.g., via stepwise regression or ANOVA.

VI.2.6. Responses optimization

Based on the statistical analysis, the main objective of the optimization process was to minimize the optical energy gap (E_g) of polyaniline thin films in order to enhance their electrical and optical properties for advanced functional applications. A lower band gap is directly associated with increased electrical conductivity, which is a key requirement for electronic and optoelectronic devices. In addition, reduced E_g values improve charge transport and light absorption efficiency, making such materials highly attractive for applications in solar cells, light-emitting diodes (LEDs), chemical sensors, and energy-storage devices such as supercapacitors.

Low-bandgap conducting polymers exhibit higher sensitivity to external stimuli, including light, temperature, and chemical species, due to enhanced charge carrier mobility. This property is particularly advantageous in sensing applications, where improved signal response and detection sensitivity are required. Moreover, narrowing the energy gap promotes better overlap between valence and conduction bands, facilitating electron excitation and improving electrochemical performance.

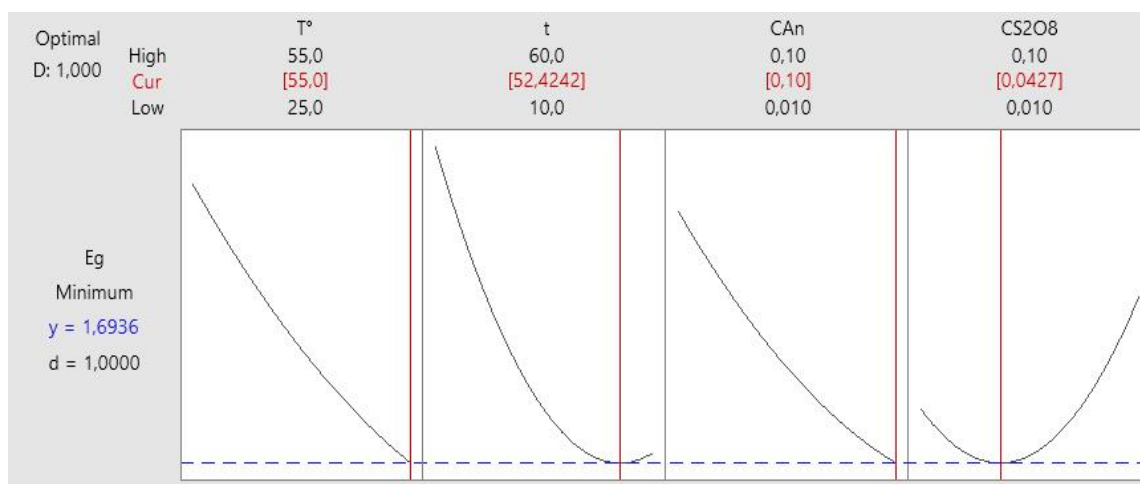


Figure VI.7: Optimization parameter profiles for achieving a minimum band gap energy (E_g) of polyaniline thin films.

(Figure VI.7) presents the optimization parameter profiles obtained from the Box–Behnken model, illustrating the combined effect of synthesis parameters on the minimization of the band gap energy of PANi thin films. The desirability-based optimization approach indicates excellent model adequacy, with an overall desirability function (DF) value of 1.000, confirming the reliability of the proposed model for predicting optimal conditions.

Under the optimized synthesis conditions—temperature of 55 °C, aniline concentration of 0.10 mol L⁻¹, ammonium persulfate concentration of 0.0427 mol L⁻¹, and optimized deposition time—the minimum predicted band gap energy was 1.411 eV. This low E_g value demonstrates the effectiveness of the chemical bath deposition method combined with chemometric optimization in tailoring the electronic structure of PANi thin films. The close agreement between experimental trends and model predictions further validates the robustness of the optimization strategy.

The obtained energy gap value is comparable to, and in some cases lower than, those reported in similar studies on polyaniline thin films prepared using chemical and electrochemical methods. Several authors have reported E_g values of 1.5–2.0 eV for PANi thin films, depending on synthesis conditions, dopant type, and film morphology. The slightly reduced band gap observed in this study can be attributed to optimized oxidant concentration and temperature, which favor improved polymer chain ordering and enhanced conjugation length. These structural improvements facilitate charge delocalization along the polymer backbone, thereby narrowing the energy gap.

Furthermore, the influence of oxidant and monomer concentrations is crucial in controlling nucleation and growth mechanisms during film formation. At optimal concentrations, uniform film morphology and reduced structural defects are achieved, thereby enhancing electronic

properties. Similar observations have been reported in previous studies, where controlled synthesis conditions resulted in improved conductivity and reduced optical band gaps. Overall, the response optimization confirms that the synergistic control of synthesis parameters is essential for achieving high-quality PANi thin films with superior optoelectronic properties. The optimized conditions identified in this work provide a reliable pathway for producing low-bandgap PANi thin films suitable for practical applications in electronics, sensing, and energy-storage technologies.

Table VI.3. Optimal factors for reaching a minimum E_g of polyaniline thin films.

Factor	Symbol	Level	Optimal Value	Desirability function (DF)
Time	t	+0.697	52.42min	d=1
Temperature	T°	+1	55°C	
Persulfate conc	C _{S208}	-0.272	0.0427 mol/L	
Aniline conc	C _{An}	+1	0.1 mol/L	
Optimal Eg	E _{g op}	/	1.411eV	
Predicted Eg	E _{g Pred}	/	1.693 eV	

VI.3. Characterization of PANi thin films

The *structure of PANi thin films* was analyzed using X-ray diffraction (Analytical X-Pert PROMPD), with *XRD* patterns recorded in the 20-100° 2θ range at 0.05° increments using $\lambda = 1.5406 \text{ \AA}$ (CuKα source) at ambient temperature. Scanning electron microscopy (*FEI-Quanta 200 SEM*) was used to assess the material's morphology. The *FTIR* spectra were recorded in the wavelength range (400 - 4000 cm⁻¹) via a PerkinElmer 1000 *FTIR* spectrometer. The *UV-vis* absorbance and reflectance spectra were recorded in the 200-900 nm region using an Edinburgh UV-Vis spectrophotometer (DS5 Dual Beam UV-Vis). The bandgap energy of these polymer films was determined using the reflectance spectrum :

$$\alpha = \frac{(1-R)^2}{2R} \quad (\text{Equ. VI.3})$$

$$(\alpha h\nu)^2 = A(h\nu - E_g) \quad (\text{Equ. VI.4})$$

where “α” signifies the absorption coefficient measured in units of cm⁻¹, “R” indicates the reflectance expressed as a percentage, and the factor "A" is contingent upon the presumed constant transition probability within the optical frequency spectrum.

VI.3.1. FTIR analysis

The FTIR spectra of conducting polymers are most significantly influenced by the characteristic vibration bands of the conjugated backbone, particularly the C=C stretching vibration ($\nu_{C=C}$) in the region (1500–1650 cm^{-1}), which reflects the degree of conjugation and doping level. Additional key features include $\nu_{C=N}$ or ν_{C-N} stretching in heteroaromatic systems, and the presence of quinoid and benzenoid bands in polymers like polyaniline, indicating oxidation states. The entrance investigation of $\nu_{C=C}$ was made using a Shimadzu FTIR-8700 spectrometer.

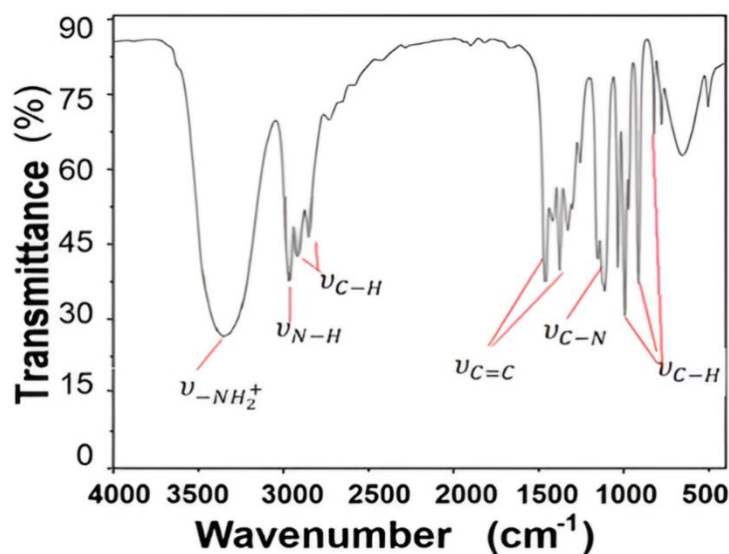


Figure VI 8: FTIR spectrum of polyaniline thin layers deposited on a glass substrate via the CBD technique under the optimal conditions ($C_{S_2O_8^{2-}} = 0.0427 \text{ mol/L}$, $C_{An} = 0.10 \text{ mol/L}$, $T^\circ = 55^\circ\text{C}$, and $t = 52.42 \text{ min}$)

The FTIR spectra of the deposited PANi layers grown under optimal conditions ($C_{S_2O_8^{2-}} = 0.0427 \text{ mol/L}$, $C_{An} = 0.10 \text{ mol/L}$, $T^\circ = 55^\circ\text{C}$, and $t = 52.42 \text{ min}$) are given in (Figure VI.8). The spectra of the analysed sample revealed many IR absorption peaks. The peaks observed between 1570 and 1480 cm^{-1} are attributed to the $\nu_{C=C}$ stretching vibration modes of the quinoid and benzenoid rings, respectively.

The stretching vibration of ν_{C-N} with the aromatic ring is represented by the peak at 1300 cm^{-1} . The peaks at 1110, 990, 975, and 909 cm^{-1} are associated with vibrations ν_{C-H} . Therefore, the peaks at 800, 606, and 511 cm^{-1} are associated with an increase in PANi porosity, as reported in a study. Conversely, the protonation of polyaniline induces stretching modes in the $-NH_2^+$ group ($\nu_{-NH_2^+}$), represented by a peak at 3440 cm^{-1} . The peak at 2930 cm^{-1} is associated with the ν_{N-H} stretching mode.

VI.3.2. XRD analysis

XRD diffractogram of the thin polyaniline film deposited on a glass substrate reveals three broad maxima located at approximately 15°, 19°, and 22° (2θ) as shown in (Figure VI.9). These are indexed to the (011), (022), and (200) planes, respectively, corresponding to JCPDS Card No. 53-1717. The peak at 16.3° is attributed to interchain periodicity, while the peak at 19.11° corresponds to lateral organisation reinforced by hydrogen bonds. The intense maximum at 22.34° is associated with π–π stacking of aromatic rings (plane (200), $d \approx 4.0$ Å).

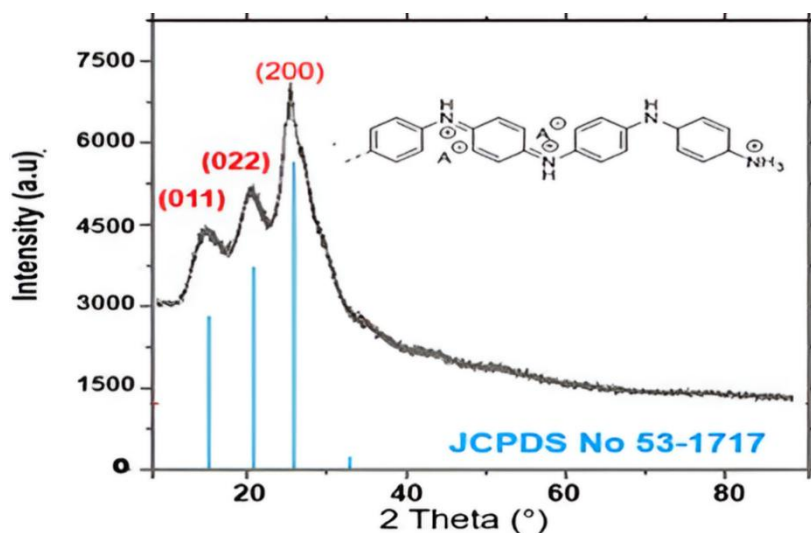


Figure VI.9: XRD spectrum of polyaniline thin layer deposited on a glass substrate using the CBD technique under the optimal conditions ($C_{S_2O_8^{2-}} = 0.0427$ mol/L, $C_{An} = 0.10$ mol/L, $T^\circ = 55^\circ\text{C}$, and $t = 52.42$ min).

The width and asymmetry of these peaks confirm that the material is semi-crystalline, with small ordered domains coexisting alongside a predominant amorphous phase. Superposition with the diffuse halo of the glass substrate explains the high background noise observed in the same angular region. This behaviour is consistently observed in polyaniline in the emeraldine state, which exhibits only short-range order, as reported in the literature [45, 46]. More recent works [10, 13] confirm that acid doping can improve chain alignment to a small extent, but does not lead to true three-dimensional crystallinity. The mean crystallite size (D) of the PANi thin films is determined via Scherrer's formula [47]:

$$D = \frac{k\lambda}{\beta \cos \theta_\beta} \quad (\text{Equ. VI.5})$$

Where β is the observed angular width at half maximum intensity (FWHM) of the peak, k is a dimensionless constant equal to 0.9, λ is the X-ray wavelength (0.1548 nm for $\text{CuK}\alpha$), and θ_β symbolizes the Bragg's law angle [47].

VI.3.3. Optical Microscopy (OM)

The microstructure of thin films constitutes one of the most critical physicochemical properties to control during deposition. Equally essential are the physical deposition parameters at each processing stage. Furthermore, thin-film properties are highly sensitive to the nature of the underlying substrate. This explains, for instance, why identical materials deposited at identical thicknesses can display divergent physical characteristics when formed on substrates of differing composition. Layer thickness is fundamentally governed by material properties, deposition rate, substrate temperature, and interfacial adhesion strength.

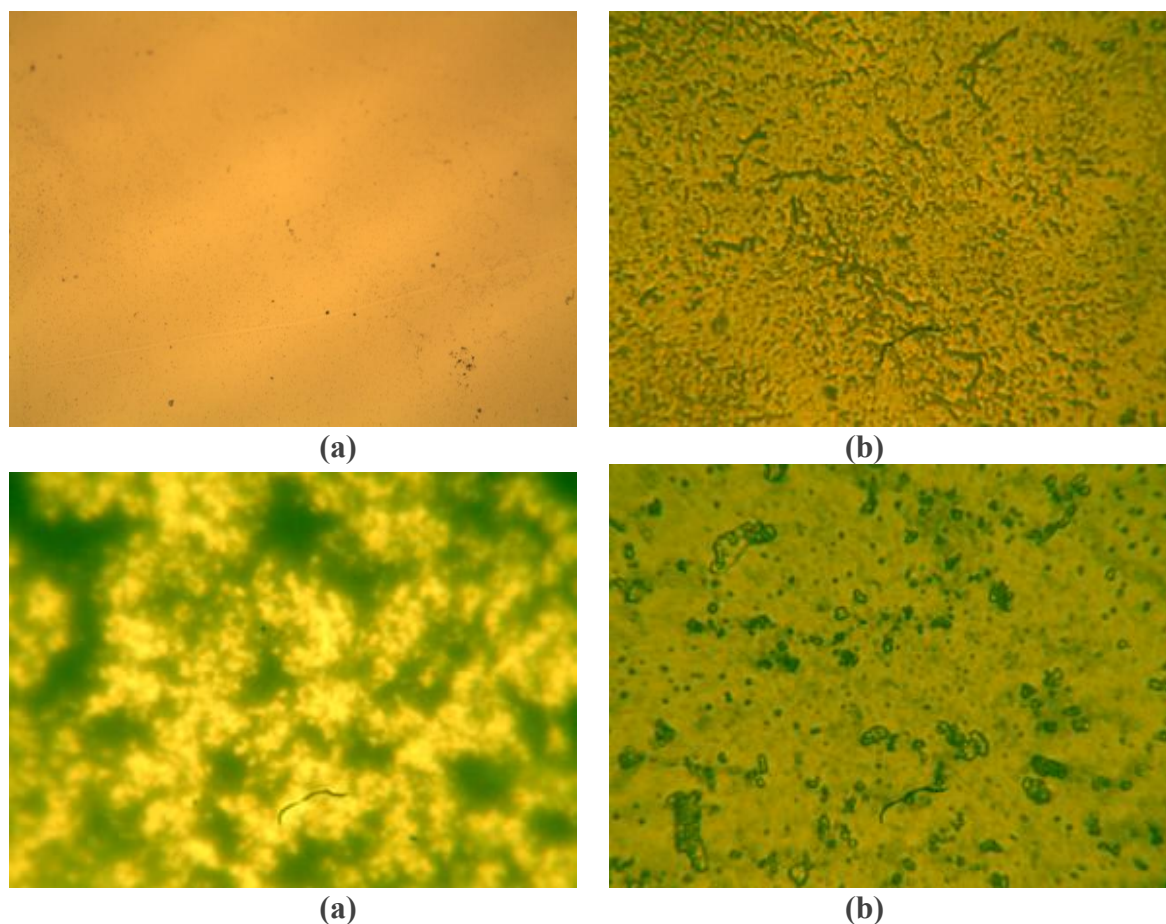


Figure VI.10: Optical Micrographs of Substrates: (a) before, and (b-d) After the deposition of Polyaniline (PANI) thin Layers at diverse magnifications: deposited under the optimal conditions ($C_{S_2O_8^{2-}} = 0.0427$ mol/L, $C_{An} = 0.10$ mol/L, $T^\circ = 55^\circ\text{C}$, and $t = 52.42$ min)

Optical micrographs of the deposited polyaniline (PANi) thin layers reveal a heterogeneous microscale morphology with an overall uniform coverage of the substrate surface, as shown in (Figure VI.10). Prior to deposition (Figure VI.10a), the substrate exhibits a relatively smooth and featureless surface, whereas after PANI deposition (Figure 10b–d), noticeable morphological changes are observed at different magnifications. The PANi layer exhibits an

amorphous structure, characterized by irregularly distributed domains and slight contrast variations, indicating non-uniform local thickness and surface roughness at the microscale. Despite this heterogeneity, the coating remains continuous and well-adhered, suggesting effective nucleation and growth of PANI under the optimized synthesis conditions ($C = 0.0427 \text{ mol L}^{-1}$, oxidant concentration = 0.10 mol L^{-1} , temperature and deposition time). These features confirm the successful formation of a homogeneous PANI thin film suitable for further structural and functional analyses.

VI.3.4. Surface morphological studies

The surface morphology of the synthesised polyaniline thin layers was investigated using SEM microscopy. (Figure VI.11,a,b,c,d) show micrographs of PANi films deposited under optimal conditions at different magnifications.

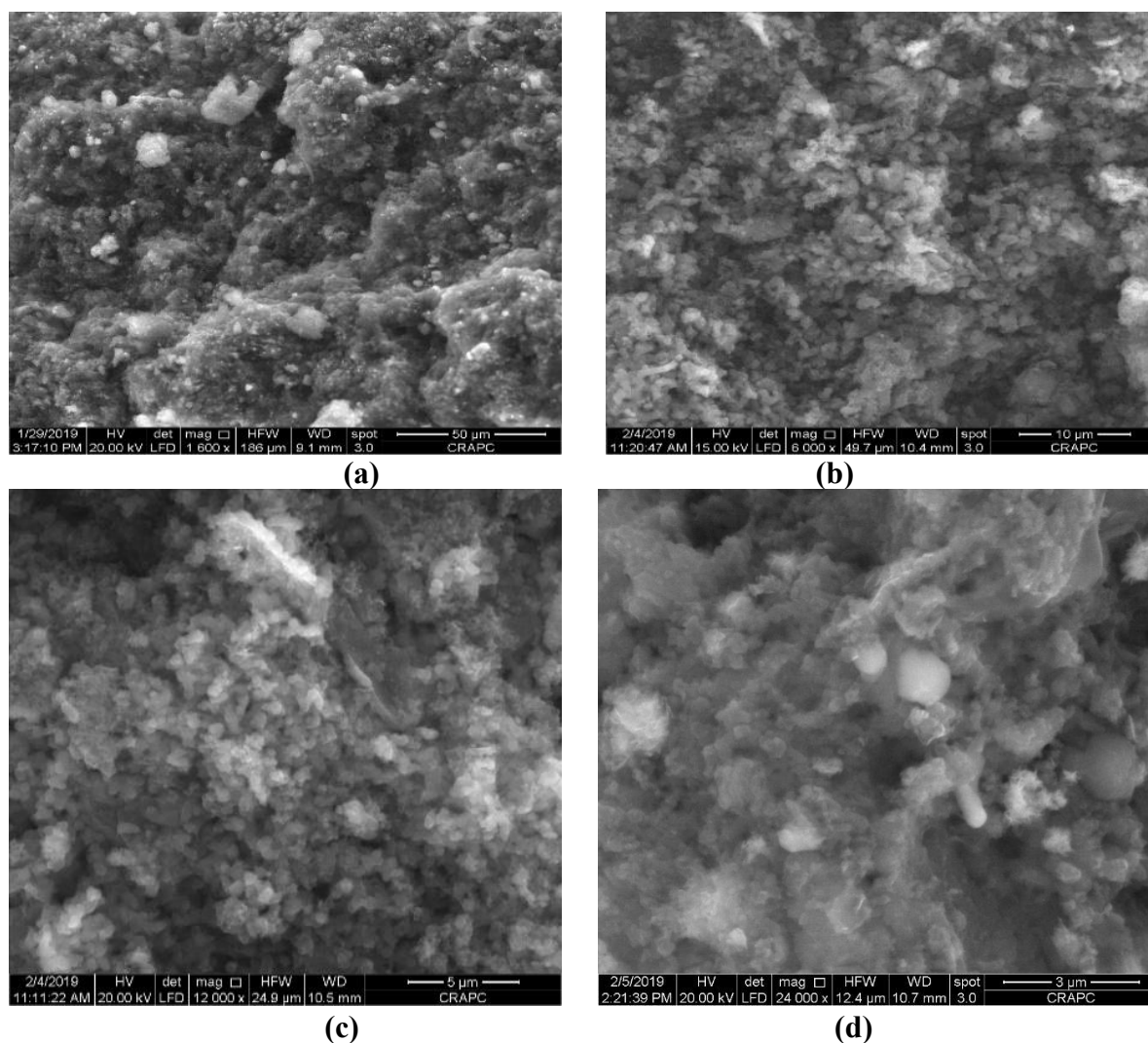


Figure VI.11: SEM images of polyaniline thin layer at diverse magnifications: (a) 1200x, (b) 6000 $\times$ magnification, (c) and (d) High-magnification SEM micrograph (12000 $\times$, and

24000x); deposited on a glass substrate via CBD technique under the optimal conditions ($C_{S_2O_8^{2-}} = 0.0427$ mol/L, $C_{An} = 0.10$ mol/L, $T^\circ = 55^\circ\text{C}$, and $t = 52.42$ min)

(Figure VI.11a) (1600× magnification) and (Figure VI.11b) (1600× magnification) show a broader view of the PANi thin films; their surfaces display a heterogeneous microstructure with noticeable grain agglomerates. Therefore, at high-magnification SEM micrograph (12000×), (Figure VI.11c) shows that the average particle size is approximately 0.5–2 μm, with a mean of about 1.25 μm. The cavities between particle agglomerates have diameters of 0.3–0.7 μm, indicating a porous structure. This morphology is advantageous for increasing the effective surface area of the thin film and can be beneficial by boosting surface area and improving ion diffusion in electrochemical applications.

(Figure VI.11d) provides a closer look at the granular structure at the submicron scale; the particle boundaries are more clearly resolved, and the grains appear more uniformly packed, with an estimated particle diameter of ~100–300 nm. The presence of nano-cavities and intergranular voids can also be observed, indicating a porous nanoscale structure [48]. This porosity could be critical in enhancing the electroactive surface area, facilitating dopant diffusion, and improving interaction with electrolytes in energy storage or sensing applications. Across both images, the film exhibits a highly textured and porous surface, which is favourable for many functional applications, such as in supercapacitors, sensors, and catalytic supports [49]. The observed roughness and voids may also positively impact adhesion properties when the film is deposited on substrates.

VI.4. Optical properties

UV-Vis analysis was employed to investigate the optical properties of polyaniline thin films, including light absorption, energy band gaps, electronic transitions, and absorption coefficient. The UV-Vis absorption spectra of the deposited thin layers obtained under optimal conditions (see Figure VI.12) display that all the polyaniline thin films exhibit a large, intense absorption band between 200 and 300 nm. The strong absorption bands observed in this region are primarily attributed to the predominant electronic state transitions ($\sigma \rightarrow \sigma^*$, $\sigma \rightarrow \pi^*$, $\pi \rightarrow \pi^*$, and $n \rightarrow \pi^*$), which are common in the energy band gap of conducting polymers, as documented by Yang et al. [50].

Electronic transitions in conducting polymers originate from their conjugated π -system and include $\pi \rightarrow \pi^*$ transitions in the UV region, which indicate backbone conjugation. Upon doping, new energy states such as polarons and bipolarons appear within the band gap,

leading to transitions such as $\pi \rightarrow \text{polaron}$, $\text{polaron} \rightarrow \pi^*$, and $\text{polaron} \rightarrow \text{bipolaron}$, which are responsible for absorption in the visible and near-IR regions. These transitions govern the optical properties and colour changes of conducting polymers.

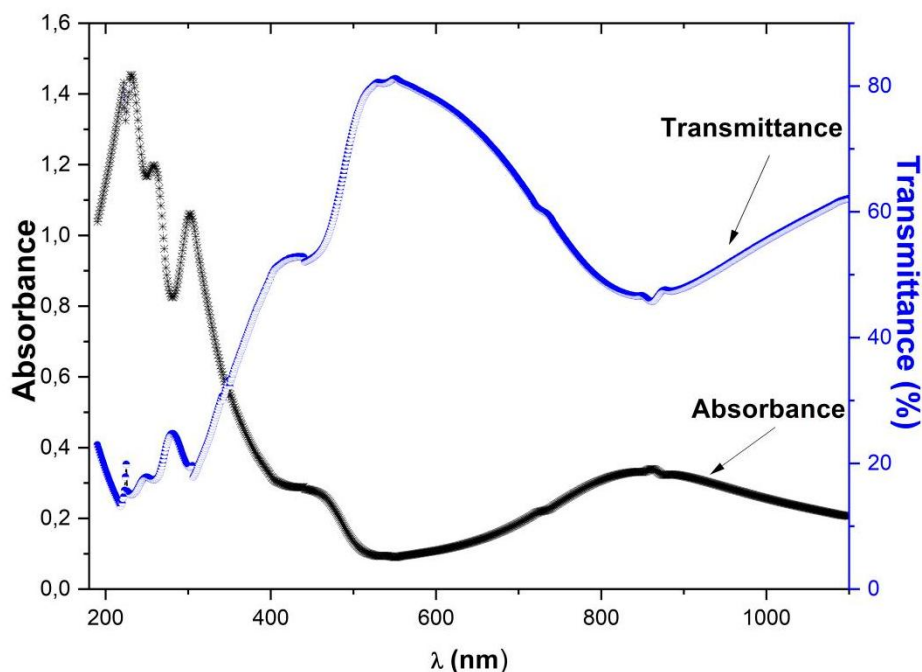


Figure VI.12: Transmittance and absorbance spectra of polyaniline thin layers deposited on a glass substrate via the *CBD* technique under the optimal conditions ($C_{S_2O_8^{2-}} = 0.0427$ mol/L, $C_{An} = 0.10$ mol/L, $T^\circ = 55^\circ\text{C}$, and $t = 52.42$ min).

In the $\pi \rightarrow \pi^*$ and/or $n \rightarrow \pi^*$ states, however, electronic transitions occur between the orbitals of the aromatic ring system. These transitions result from the promotion of an electron from a π -bonding or non-bonding orbital to the lowest unoccupied molecular orbital (π^*) [50–52]. All examined *PANi* thin films exhibit a peak absorbance between 235 nm and 245 nm, indicating a $\pi \rightarrow \pi^*$ or $n \rightarrow \pi^*$ electronic transition between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) [50–53]. The absorption coefficient and the gap's energy were calculated using the UV-Vis absorbance spectra of as-deposited thin layers produced under ideal conditions. ($C_{S_2O_8^{2-}} = 0.0427$ mol/L, $C_{An} = 0.10$ mol/L, $T^\circ = 55^\circ\text{C}$, and $t = 52.42$ min).

The information on direct transitions was obtained by analysing the spectral dependence of absorption near the fundamental absorption edges using one-electron theory. The following equation relates the absorption coefficient α to the energy gap [34–36]:

$$(\alpha h\nu) = A (h\nu - E_g)^{1/2} \quad (\text{Equ. VI.6})$$

Where " α " (cm^{-1}) is the absorption coefficient, and the factor (A) depends on the transition probability assumed to be constant within the optical frequency range. and E_g is the energy band gap value (eV) of the indicated transition ($\pi \rightarrow \pi^*$ or $n \rightarrow \pi^*$). For direct-band-gap materials, the Tauc plot is a plot of $(\alpha h\nu)^2$ versus photon energy.

The energy band gap E_g is determined by extending the linear section of this plot to the x-axis, where the absorption coefficient α reaches zero, indicating the minimum photon energy ($h\nu$) needed to initiate electronic transitions. In this context, the power value (1/2) in the Tauc relation indicates a direct allowed electronic transition and influences the adjustment of the absorption coefficient, enabling a precise evaluation of the energy band gap in direct-band-gap materials. The extrapolation of the straight-line graphs $[(\alpha h\nu)^2 = f(h\nu)]$ to zero absorption ($\alpha = 0$) provides the E_g value.

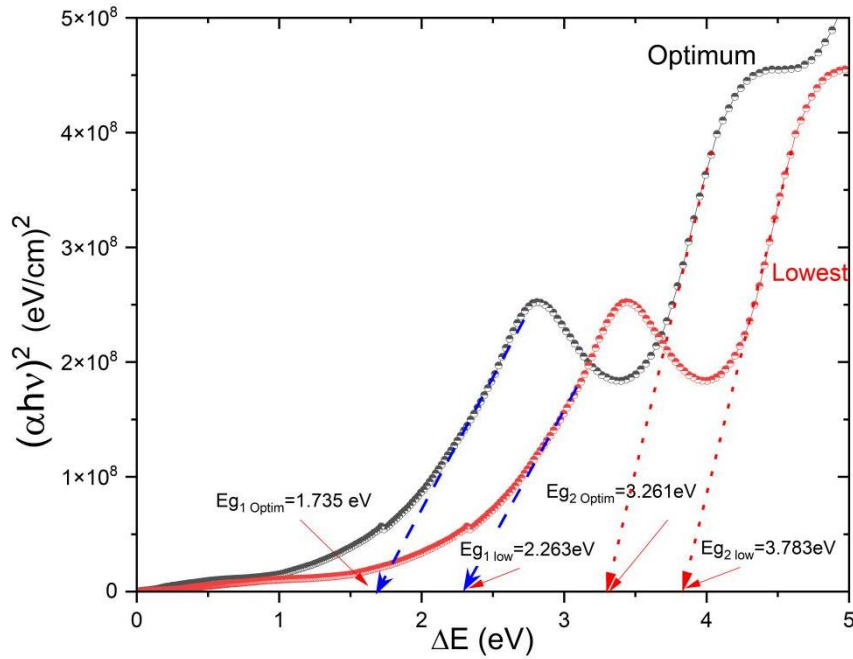


Figure VI.13: Evolution of $(\alpha h\nu)^2$ versus photon energy ($h\nu$) of the deposited polyaniline thin layers via the CBD technique under the lowest and optimal conditions.

(Figure VI.13) displays plots of $(\alpha h\nu)^2$ versus photon energy ($h\nu$) for the deposited polyaniline thin films under the lowest and optimal conditions. The band gap was estimated by extrapolating the linear region of the $(\alpha h\nu)^2$ versus $h\nu$ plot to the horizontal axis and taking the intercept. The as-deposited PANi films exhibit two distinct energy band gaps, corresponding to different types of electronic transitions. This dual-band-gap behavior occurs because the

material's band structure allows for two separate direct transitions at different energies, often due to band splitting or multiple band extrema. As a result, each transition appears as a distinct direct band gap. On the other hand, the lowest and optimal (E_g) values are 2.263 eV and 1.735 eV, respectively. As expected, the optimisation approach reduced the band gap in *PANi* films, thereby enhancing their optical and electrical conductivity by enabling electrons to move more easily between the valence and conduction bands. This improvement makes polyaniline more effective in applications such as sensors, batteries, supercapacitors, and flexible electronics. Additionally, a smaller band gap enables better absorption of lower-energy light, which is useful in optoelectronic devices such as photodetectors and solar cells. The tunability of polyaniline's band gap through doping or chemical modification also enables it to be tailored for specific applications, providing versatility and energy efficiency across a range of advanced technologies.

VI.5. Electrical Properties

The electrical conductivity of the polyaniline (*PANi*) thin films obtained was systematically measured using a *DC* four-probe technique. The temperature dependence of conductivity was measured in the dark between 150 and 450 K at a rate of 0.5 W/min using a calibrated two-probe technique to minimise contact resistance. The temperature dependence of conductivity (σ) exhibits Arrhenius-type behaviour, which is characteristic of semiconducting materials and can be described by the following equation [55-57]:

$$\sigma = \sigma_0 \cdot \exp\left(-\frac{E_a}{K_B T}\right) \quad (\text{Equ. VI.7})$$

where σ_0 is the pre-exponential factor related to intrinsic material characteristics, E_a is the activation energy for conduction. K_B is the Boltzmann constant (8.617×10^{-5} eV/K), and T is the absolute temperature [56,57]. By linearising this equation via the natural logarithm, one obtains :

$$\ln(\sigma) = -\frac{E_a}{K_B} \cdot \left(\frac{1}{T}\right) + \ln(\sigma_0) \quad (\text{Equ. VI.8})$$

Plotting $\ln \sigma$ against $\left(\frac{1000}{T}\right)$ yields a straight line whose slope corresponds to $\left(-\frac{E_a}{K_B}\right)$, enabling the extraction of the activation energy [56].

(Figure VI.14) illustrates the linear behaviour of the plots obtained in this study, confirming the validity of the Arrhenius model for the *PANi* films studied.

The calculated activation energies, pre-exponential factors (σ_0), and room temperature conductivities (σ_{298}) are summarised in Table 3. These values provide a quantitative insight into the energetic barriers encountered by charge carriers. The as-deposited films exhibited electrical conductivity at room temperature (σ_{298}) ranging from 0.057 S/cm to 4.30 S/cm across different HCl concentrations, demonstrating the significant impact of deposition parameters and film morphology on charge-transport properties [60, 61]. The observed increase in electrical conductivity with increasing temperature indicates thermally activated conduction, a characteristic of organic semiconductors, in which charge transport is likely to be governed by hopping between localised states or by thermal excitation of carriers. This temperature-dependent conductivity behaviour confirms the semiconducting nature of *PANi* thin films and provides essential data for optimising their structural and electronic properties for applications in organic electronic devices [60, 61].

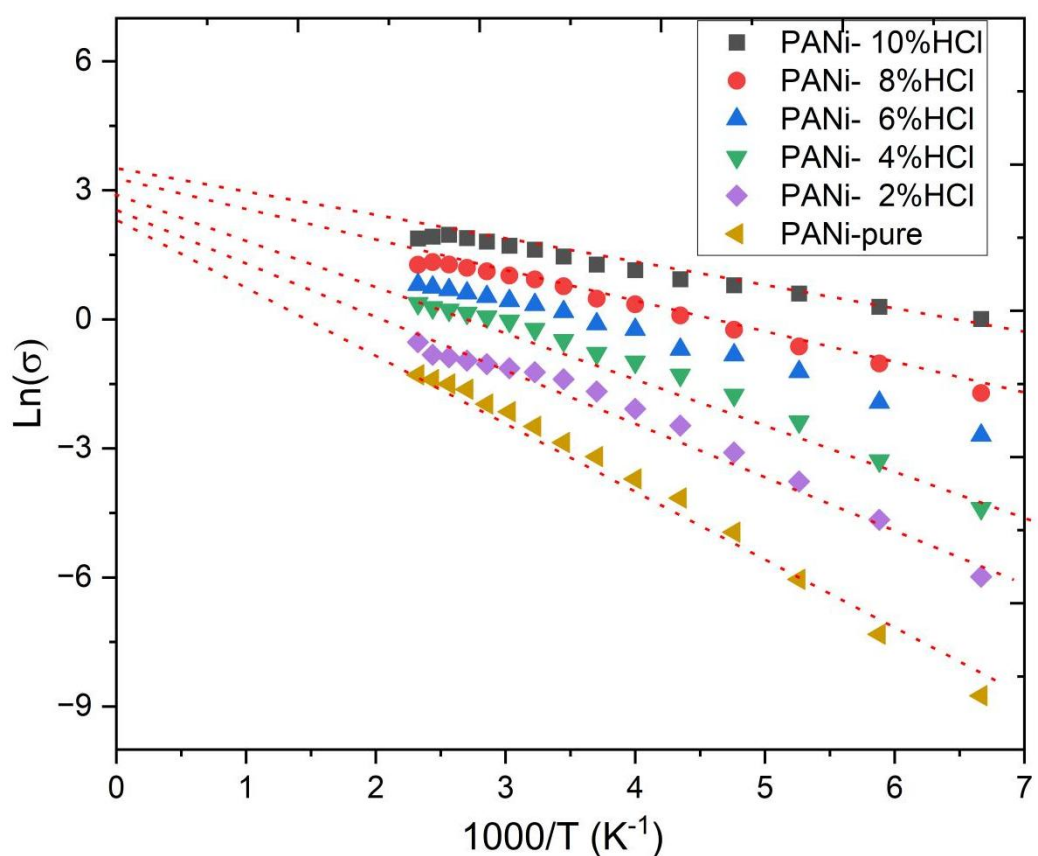


Figure VI.14: Effect of HCl amount on electrical properties of polyaniline thin layers deposited on a glass substrate via *CBD* technique under the optimal conditions ($C_{S_2O_8^{2-}} = 0.0427$ mol/L, $C_{An} = 0.10$ mol/L, $T^\circ = 55^\circ\text{C}$, and $t = 52.42$ min)

The obtained results indicate that the electrical properties of polyaniline (*PANi*) thin films are strongly influenced by the amount of hydrochloric acid (HCl) used as a dopant. These findings demonstrated that conductivity was greatly enhanced as the HCl content increased; for pure *PANi*, the pre-exponential factor (σ_0) increased from 2.2×10^{-3} S/cm to 4.3×10^{-2} S/cm for *PANi* doped with 10% HCl. On the other hand, the activation energy (E_a) dropped significantly from 0.52 eV (undoped) to 0.15 eV (10% HCl), suggesting that highly doped films facilitate charge-carrier mobility. This behaviour is due to the progressive protonation of the imine nitrogen atoms along the *PANi* backbone, which increases the density of polarons and bipolarons, enhancing delocalisation through $\pi \rightarrow \pi^*$ interactions. Additionally, acid doping promotes a more compact morphology and improved chain connectivity, reducing interfacial diffusion and creating more efficient conductive pathways. Consequently, films doped with 8–10% HCl exhibit the best balance between low activation energy and high intrinsic conductivity. These findings confirm that HCl doping simultaneously affects both the chemistry (protonation of the chains) and the microstructure (percolation and stacking), resulting in superior electrical performance. Therefore, optimising the HCl content is critical in tailoring the electrical behaviour of *PANi* thin films for potential applications in sensors, antistatic coatings, and electronic devices.

Table VI.4: Evolution of electrical factors (electrical conductivity and Activation Energies) of polyaniline thin films under the effect of the HCl amount.

Sample	σ_{298} (S/cm)	σ_0 (S/cm)	E_a (eV)
<i>PANi</i> -pure	4.301	2.2×10^{-3}	0.52
<i>PANi</i> -2% HCl	2.154	4.6×10^{-3}	0.47
<i>PANi</i> -4% HCl	1.197	8.1×10^{-3}	0.36
<i>PANi</i> -6% HCl	0.612	1.6×10^{-2}	0.28
<i>PANi</i> -8% HCl	0.249	2.9×10^{-2}	0.21
<i>PANi</i> -10% HCl	0.057	4.3×10^{-2}	0.15

VI.6. Comparative study

A systematic comparison was conducted with the results reported in the literature to assess the performance and quality of the thin polyaniline (*PANi*) layers obtained in this study. The

parameters examined included deposition conditions, optimisation methods, substrate type, and optical properties such as the band gap (E_g) and activation energy (E_a). Table VI.5 summarizes the methods used to produce and study the properties of PANi films over the past few years, along with the corresponding test conditions. By comparing our experimental results with those of other researchers, we can evaluate the effectiveness of our synthesis protocol, identify areas for improvement, and spot discrepancies caused by differences in experimental conditions or substrate characteristics. This comparative approach allows us to validate our experimental choices and pave the way for possible future optimisations.

Table VI.5: Comparison of the deposition method, optimisation approach, optimal conditions, and optical and electrical parameters of the as-obtained PANi layers with those published elsewhere.

Synthesis Method	Optimization Method	Optimal Conditions	Substrate	E_g (eV)	E_a (eV)	Refs
Chemical oxidative polymerization	OFAT	APS:HCl (1:1). 0–5°C. 4h reaction	Glass slide	~2.8	Not reported	[60]
Electrochemical deposition	DOE (Taguchi)	0.5 M aniline in H ₂ SO ₄ . 1.2 V vs Ag/AgCl. 10 min	ITO-coated glass	2.6–2.9	~0.47	[61]
Spin coating + thermal treatment	OFAT	1% wt aniline in NMP. 2000 rpm. 120°C annealing	Si wafer	2.45	0.62	[62]
In-situ polymerization	ANN	Neural network: monomer %. acid. time. temp	PET	2.3–2.7	0.35–0.55	[63]
Drop casting	OFAT	0.2 M aniline in 1 M HCl. dry at 60°C. 24h	FTO glass	2.6	0.41	[64]
Electrochemical polymerization	DoE (Full factorial)	pH 1.5. 1.0 V. 20 min. RT	ITO	2.5–2.65	0.38–0.49	[65]
CBD	DoE (Box-Behnken)	$C_{S_2O_8^{2-}} = 0.0427$ mol/L. $C_{An} = 0.10$ mol/L. $T^\circ = 55^\circ\text{C}$. and $t = 52.42$ min	Glass	1.69–1.73	4.31–0.057	This paper

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Conclusion

Polyaniline-based thin films were manually deposited onto a transparent glass substrate using the chemical bath deposition method. The primary operating parameters ($C_{S_2O_8^{2-}}$, C_{An} , T , and t) were optimized with a chemometric approach based on the Box–Behnken method. The optimization study showed that the best deposition results were achieved under these optimal conditions: $C_{S_2O_8^{2-}} = 0.0427$ mol/L, $C_{An} = 0.10$ mol/L, $T^\circ = 55^\circ\text{C}$, and $t = 52.42$ min.

Scanning electron microscopy revealed that the as-deposited polyaniline (PANi) thin films exhibited a crystalline microstructure with grain sizes ranging from 0.5 μm to 2 μm , as well as cavities and voids with diameters of 0.3–0.7 μm . Additionally, XRD analysis revealed that the deposited PANi thin layers exhibit a polycrystalline structure.

The UV-Vis absorption analysis shows that all the studied PANi samples exhibit strong absorption in the Ultraviolet region between 235 and 245 nm, conforming to $\sigma \rightarrow \sigma^*$, $\sigma \rightarrow \pi^*$, $\pi \rightarrow \pi^*$, and/or $n \rightarrow \pi^*$ electronic transitions between the lowest unoccupied molecular orbital (LUMO) and the highest occupied molecular orbital (HOMO). The abrupt change in the trajectory of the $(\alpha h\nu)^2 = f(h\nu)$ curve indicates that the deposited PANi layers are semiconducting, with an energy gap of 1.735–2.263 eV.

The electrical investigation also demonstrated that conductivity increased with rising HCl content. For pure PANi, the pre-exponential factor (σ_0) increased from 2.2×10^{-3} S/cm to 4.3×10^{-2} S/cm with 10% HCl doping. Conversely, the activation energy (E_a) decreased significantly, from 0.52 eV for the undoped sample to 0.15 eV for the 10% HCl sample, indicating that highly doped films facilitate charge carrier movement.

The gap energies fall within the range of highly efficient values, and the complexes studied can be considered potential materials for optical applications (solar cells, optical filters, etc.). The results obtained are certainly encouraging, but should not lead us to believe that the transition to a functional thin-film solar cell based on the complexes studied is a foregone conclusion. Improvements can be made by adding promoting agents and increasing the lateral size and thickness of the thin-film crystallites. A higher crystal growth rate due to impurity addition has been observed in many systems and is generally attributed to the formation of three-dimensional islands, which act as nucleation centers for further growth. Further research and more sophisticated experimentation will enable better results in the future.