A

Project Report

On

# "GROWTH OF $TiO_2$ NANOCOATINGS FOR BIOMEDICAL APPLICATIONS"

SUBMITTED TO

Department of Electronics,

Kavayitri Bahinabai Chaudhari

North Maharashtra University, Jalgaon.

Submitted By


**Miss. Ghate Ashwini Shantilal**

**Seat No: 385059**


For the degree of

**Master of Science**

**Under The Guidance of**


**Prof. A. M. Mahajan**

Senior professor and Head
Department of electronics
Kavayitri Bahinabai Chaudhari
North Maharashtra University, Jalgaon.
**425001**


In the Academic year

**2022-23**

# CERTIFICATE

This is to certify that the project report entitled

**"GROWTH OF $TiO_2$ NANOCOATINGS FOR BIOMEDICAL APPLICATIONS".**

Submitted By

**Miss. Ghate Ashwini Shantilal**

This is to certify that, this is the original independent work of the student herself, under my super vision during her stay in this University in the 2022-2023 for the partial fulfillment of project report. To the best of my knowledge all the references studied for the preparation in this work have been properly acknowledged.

Date: /05/2023
Place: Jalgaon

**Prof. A. M. Mahajan**
(Project Guide)
Senior Professor and Head,
Department of Electronics
KBCNMU, Jalgaon

**External Examiner**

# Acknowledgement

I sincerely thanks to my guide, **Prof. A. M. Mahajan Sir,** for his valuable suggestion during my project work and also to Kavayatri Bahinabai Chaudhari North Maharashtra University, Jalgaon for his cooperation encouragement. Gracious gratitude to all the faculty of the Department of Electronics & Friends for their valuable advice & encouragement.

I have a great pleasure to express my sincere feeling gratitude towards the **Prof. A. M. Mahajan Sir** for their very much grateful guidance given time to complete this project work.

My special gratitude to **Dr. Lalit Patil Sir , Dr. Jaspal bange sir & Mr. Vaibhav Borokar sir** for their inspiration cooperation, encouragement & invaluable guidance during the progress of project working all phases.

Special thanks to My Friend **Mr. Manish G. Patil** for helping hands in project.

Also, the project work impossible to complete without timely and valuable cooperation of the teaching & non-teaching staff of Electronics Department.

Last but not the least to express our highest gratitude to our parent for their energetic moral & economical friendly support that boosted our moral. It is because of them we have reached the place where we are today.

**Date: / 05 /2023** **(Miss. Ghate Ashwini Shantilal)**

`

# Abstract


Titanium dioxide ($TiO_2$) nanocoatings have garnered significant interest in the field of biomedical applications due to their unique properties and potential benefits. This study focuses on the growth of $TiO_2$ nanocoatings and their potential applications in the biomedical field. The growth of $TiO_2$ nanocoatings is explored through various deposition techniques, including physical vapor deposition (PVD), chemical vapor deposition (CVD), and sol-gel methods. The influence of deposition parameters, such as temperature, pressure, and precursor concentration, on the coating properties is examined.

The biomedical applications of $TiO_2$ nanocoatings are diverse and include areas such as implantable devices, drug delivery systems, biosensors, and tissue engineering. The antimicrobial properties of $TiO_2$ nanocoatings, especially under ultraviolet (UV) light irradiation, make them suitable for implant surfaces and wound dressings to reduce the risk of infections. $TiO_2$ nanocoatings also show promise as drug delivery vehicles, with their large surface area and controlled release capabilities.

Furthermore, $TiO_2$ nanocoatings can be utilized in biosensors for sensitive detection of disease markers or pathogens. In tissue engineering, $TiO_2$ nanocoatings can enhance cell attachment, proliferation, and differentiation on scaffold materials, promoting tissue regeneration.

This review provides an overview of the growth techniques for $TiO_2$ nanocoatings and highlights their potential applications in the biomedical field. The advantages, challenges, and future prospects of $TiO_2$ nanocoatings for biomedical applications are discussed. Understanding the growth processes and exploring the full potential of $TiO_2$ nanocoatings can lead to the development of innovative biomedical solutions with improved biocompatibility, antimicrobial properties, and drug delivery capabilities.

# CONTENTS

# Chapter 1

# *Introduction*

# Introduction

In recent years, there has been a growing interest in the development of advanced nanocoatings for biomedical applications. Among various nanocoating materials, titanium dioxide ($TiO_2$) has emerged as a promising candidate due to its unique properties and potential benefits. $TiO_2$ nanocoatings offer a wide range of applications in the biomedical field, including implantable devices, drug delivery systems, biosensors, and tissue engineering.

The growth of $TiO_2$ nanocoatings plays a crucial role in determining their properties and performance in biomedical applications. Several deposition techniques have been employed to fabricate $TiO_2$ nanocoatings, including physical vapor deposition (PVD), chemical vapor deposition (CVD), and sol-gel methods. These techniques allow for precise control over the coating thickness, morphology, and crystalline structure, enabling the tailoring of $TiO_2$ nanocoatings to specific biomedical requirements.

One of the key advantages of $TiO_2$ nanocoatings is their inherent biocompatibility. When implanted in the human body, $TiO_2$ forms a thin oxide layer on its surface, facilitating tissue integration and minimizing adverse reactions. This biocompatibility, combined with the ability to control surface properties, makes $TiO_2$ nanocoatings suitable for various biomedical applications, particularly in the context of implantable devices.

$TiO_2$ nanocoatings also possess unique photocatalytic properties. Under ultraviolet (UV) light irradiation, $TiO_2$ exhibits antimicrobial activity, which can be harnessed to reduce the risk of infections on implant surfaces and in wound dressings. Moreover, the large surface area of $TiO_2$ nanocoatings makes them ideal for drug delivery systems, as they can be functionalized to encapsulate and release therapeutic agents in a controlled manner.

In the field of biosensors, $TiO_2$ nanocoatings have shown great potential. They can be modified to selectively capture and detect specific molecules or analytes, enabling sensitive and rapid detection of disease markers or pathogens. This capability opens up possibilities for point-of-care diagnostics and early disease detection.

In tissue engineering, $TiO_2$ nanocoatings have been investigated for their ability to enhance cellular responses. They can promote cell attachment, proliferation, and differentiation when applied to scaffold materials, facilitating tissue regeneration and integration. This makes $TiO_2$ nanocoatings promising candidates for improving the performance of tissue-engineered constructs and enhancing patient outcomes.

Overall, the growth of $TiO_2$ nanocoatings holds great promise for advancing biomedical applications. By understanding the deposition techniques and tailoring the properties of $TiO_2$ nanocoatings, researchers can unlock their full potential for improving biocompatibility, antimicrobial properties, drug delivery capabilities, and tissue regeneration. This review aims to provide an overview of the growth techniques for $TiO_2$ nanocoatings and explore their wide-ranging applications in the biomedical field.

## 1.1 What is $TiO_2$?

$TiO_2$ stands for titanium dioxide, which is a naturally occurring oxide of titanium. It is a white, powdery substance that is widely used in a variety of industrial and consumer applications. $TiO_2$ is known for its high refractive index, which makes it an excellent material for use as a pigment in paints, coatings, plastics, and other products. It is also used as a photocatalyst, in sunscreen, and in the manufacture of ceramics, electronics, and other materials. $TiO_2$ is considered to be a safe and non-toxic material, and is approved for use in food, drugs, and cosmetics by regulatory agencies around the world.
Titanium dioxide ($TiO_2$) is a widely used inorganic compound that is renowned for its diverse range of applications. It occurs naturally in the form of minerals, such as rutile and anatase, but can also be synthesized in the laboratory.

Here are some key points about $TiO_2$:

**Chemical Composition:** Titanium dioxide is composed of titanium (Ti) and oxygen (O) atoms, with the chemical formula $TiO_2$.

**Physical Properties:** $TiO_2$ exists as a white, odorless, and tasteless powder. It is insoluble in water and most organic solvents but can dissolve in concentrated acids or alkalis under certain conditions.

**Photo catalytic Properties:** One of the most significant characteristics of $TiO_2$ is its photocatalytic activity. When exposed to ultraviolet (UV) light, $TiO_2$ can initiate a chemical reaction that breaks down organic compounds, pollutants, and bacteria. This property finds applications in air purification, self-cleaning surfaces, and wastewater treatment.

**Pigment and Opacity:** $TiO_2$ is widely used as a white pigment in various industries, including paints, coatings, plastics, and cosmetics. It imparts excellent opacity, brightness, and whiteness to the materials it is incorporated into.

**UV Protection:** Due to its ability to absorb and scatter UV radiation, $TiO_2$ is utilized in sunscreens and other personal care products for providing protection against harmful UV rays.

**Catalysis:** $TiO_2$ is used as a catalyst in various chemical reactions. Its surface can facilitate the transformation of reactants, making it valuable in processes like oxidation, reduction, and hydrogenation.

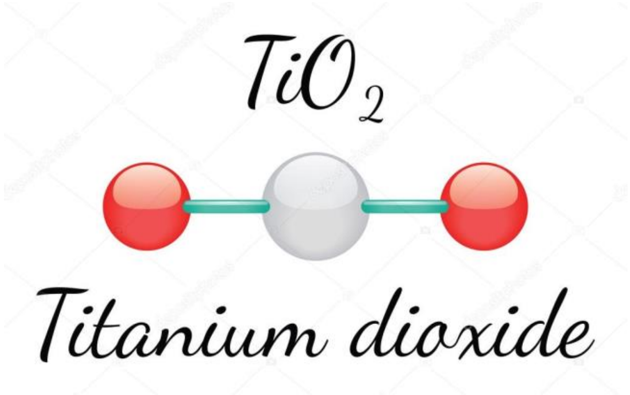
**Energy Applications:** $TiO_2$ plays a crucial role in the field of renewable energy. It is used as a component in solar cells, where it acts as a semiconductor and assists in converting sunlight into electricity.

**Biomedical Applications:** $TiO_2$ finds applications in medicine, including drug delivery systems, dental materials, and orthopedic implants, due to its biocompatibility and antimicrobial properties.

**Coatings and Films:** $TiO_2$ coatings and films offer enhanced durability, scratch resistance, and UV protection to various surfaces, including glass, metals, and plastics.

**Safety Considerations:** While $TiO_2$ is generally considered safe for most applications, there have been concerns raised regarding the inhalation of fine $TiO_2$ particles in certain occupational settings. Safety measures and regulations are in place to mitigate potential risks.

$TiO_2$'s versatility and wide-ranging properties make it an invaluable compound in numerous industries, contributing to advancements in technology, environmental protection, and everyday products.




**Here is a table of some properties of titanium dioxide ($TiO_2$):**

| Property | Value |
|---|---|
| Chemical formula | $TiO_2$ |
| Molecular weight | 79.87 g/mol |
| Density | 4.26 g/cm3 |
| Melting point | 1,843 °C |
| Boiling point | 2,972 °C |
| Color | White |
| Crystal structure | Tetragonal, anatase or rutile |
| Band gap energy | 3.0 eV (anatase) or 3.2 eV (rutile) |
| Refractive index | 2.49 (anatase) or 2.71 (rutile) |
| Thermal conductivity | 11.7 W/(m·K) (rutile) |
| Dielectric constant | 85 (anatase) or 121 (rutile) |
| Solubility | Insoluble in water and organic solvents |

## 1.2 Precursors for $TiO_2$:-

For the deposition of $TiO_2$ (titanium dioxide) by various techniques like Spin coating, TCVD (Thermal Chemical Vapor Deposition) system as a several precursors can be used. The choice of precursor depends on the specific requirements of the deposition process, such as film properties, deposition temperature, and equipment availability. Here are some commonly used precursors for $TiO_2$ deposition:

**Titanium tetrachloride ($TiCl_4$):** $TiCl_4$ is a widely used precursor for $TiO_2$ deposition. It is a volatile liquid that can be easily vaporized and transported to the substrate. $TiCl_4$ is known for its high reactivity and provides good control over film growth and composition.

**Titanium tetraisopropoxide (TTIP):** TTIP is another popular precursor for $TiO_2$ deposition. It is a liquid precursor that can be vaporized and transported to the substrate. TTIP offers better control over the deposition process, enabling the synthesis of high-quality $TiO_2$ films.

**Titanium acetylacetonate ($Ti(acac)_4$):** $Ti(acac)_4$ is a solid precursor that is commonly used in T-CVD processes. It is a thermally stable compound that can be vaporized at elevated temperatures. $Ti(acac)_4$ allows for the deposition of $TiO_2$ films with controlled crystallinity and desired properties.

**Titanium alkoxides:** Various titanium alkoxides, such as titanium isopropoxide (TIP) and titanium ethoxide (TEOT), can be used as precursors for $TiO_2$ deposition. These liquid precursors offer good film quality and control over the deposition process.

It's important to note that the specific choice of precursor depends on the deposition conditions, equipment compatibility, and desired film properties. The precursor selection should be based on the requirements and constraints of your specific $TiO_2$ deposition process.

## 1.4 Why titanium dioxide is good for biomaterial?

Titanium and titanium alloys are one of the most used implant materials for biomedical applications due to their outstanding properties, including high biocompatibility, resistance to body fluid effects, great tensile strength, flexibility and high corrosion resistance.

Titanium is a good biomaterial for several reasons:

1) **Biocompatibility**: The biocompatibility of titanium dioxide ($TiO_2$) is an important consideration when evaluating its potential use in biomedical applications, such as drug delivery, implants, and tissue engineering. Overall, $TiO_2$ is considered to be biocompatible, meaning it does not cause significant adverse reactions or toxic effects in biological systems under normal conditions. However, it's important to note that biocompatibility can depend on various factors, including the specific form of $TiO_2$, its surface characteristics, particle size, and the route of exposure.

   Here are some key points regarding the biocompatibility of $TiO_2$:

   - **Inert Nature:** $TiO_2$ is generally considered an inert material, meaning it does not chemically react or degrade in biological environments. This characteristic contributes to its biocompatibility.
   - **Low Toxicity:** Under normal conditions, $TiO_2$ nanoparticles are not highly toxic. However, some studies have suggested that high concentrations or prolonged exposure to $TiO_2$ nanoparticles may have cytotoxic effects on certain cell types. The toxicity of $TiO_2$ nanoparticles is influenced by factors such as particle size, surface charge, and surface coatings.
   - **Surface Modification:** The surface properties of $TiO_2$ can be modified to enhance its biocompatibility. Surface modifications, such as the addition of biocompatible coatings or functionalization with biomolecules, can improve cell adhesion, reduce immune responses, and promote better integration with biological systems.
   - **Clearance and Degradation:** $TiO_2$ nanoparticles are typically not biodegradable. They are often cleared from the body through various mechanisms, including phagocytosis by macrophages and clearance via the lymphatic system. The long-term accumulation of $TiO_2$ nanoparticles in certain organs, such as the liver or spleen, may require further investigation for specific applications.
   - **Regulatory Considerations:** Biocompatibility assessments of $TiO_2$, especially for medical devices and implants, are subject to regulatory requirements in different countries. These evaluations involve comprehensive testing, including in vitro studies, animal experiments, and clinical trials, to ensure the safety and compatibility of $TiO_2$-based materials for specific biomedical applications.

   It is important to note that the biocompatibility of $TiO_2$ can vary depending on its specific form, such as nanoparticles, thin films, or bulk materials. Additionally, individual variations in biological responses and specific application requirements should be considered when assessing the biocompatibility of $TiO_2$ for a particular use.

2) **Resistance to body fluid effects:** Resistance to body fluid effects refers to a material's ability to withstand the effects of bodily fluids, such as blood, saliva, and other biological fluids. When a material is implanted in the human body, it comes into contact with these fluids, which can cause degradation or corrosion of the material over time.

Materials with good resistance to body fluid effects are desirable for medical implant applications, as they can maintain their mechanical and surface properties over an extended period without breaking down or corroding. For example, implantable devices such as pacemakers, stents, and joint replacements must be able to resist the corrosive effects of bodily fluids to function effectively over the long term.

Some materials that are known for their good resistance to body fluid effects include titanium and its alloys, cobalt-chromium alloys, and certain ceramics and polymers. These materials have been extensively tested for their biocompatibility and ability to resist corrosion and degradation in the body, which makes them suitable for use in medical implant applications.

3) **Tensile strength:** Tensile strength is the maximum stress that a material can withstand before it fails or breaks under tension. The term "great tensile strength" usually refers to a material that can withstand a high amount of tensile stress without breaking or deforming. In other words, a material with great tensile strength can withstand a high pulling force without breaking or snapping.

   The tensile strength of a material is an important property for many engineering applications, especially those involving load-bearing structures or components. Materials with high tensile strength are desirable for applications where the material is subjected to high loads or stresses, such as in the aerospace, automotive, and construction industries.

   For example, some high-strength materials like carbon fiber composites or high-strength steel alloys can have tensile strengths that are several times higher than conventional materials like aluminum or mild steel. This allows for the design of lighter and stronger structures that can withstand greater stresses and loads, which can be beneficial for reducing weight and improving performance in many applications.

4) **Flexibility:** Flexibility is the ability of a material to bend or deform under an applied force without breaking or cracking. Materials with high flexibility can bend, twist, or stretch without suffering permanent deformation or damage.

5) **Corrosion resistance:** Titanium dioxide ($TiO_2$) is known for its high corrosion resistance, especially in harsh environments. $TiO_2$ is a stable oxide, which means it does not readily react with other chemicals or corrode under normal conditions. This makes it an excellent material for use in corrosive environments, such as in the chemical or petrochemical industries.

6) **Mechanical properties:** Titanium has excellent mechanical properties, such as high strength, low density, and good fatigue resistance, which makes it suitable for load-bearing applications in the body.

7) **Osseointegration:** Titanium has the ability to integrate with bone tissue through a process called osseointegration. This means that when a titanium implant is placed in the body, it can form a strong bond with the surrounding bone tissue, which improves the stability and longevity of the implant.

8) **Surface properties:** The surface properties of titanium can be modified to improve its performance in specific applications. For example, titanium can be coated with biocompatible materials to enhance its ability to integrate with bone tissue, or it can be coated with antibacterial agents to prevent infections.

# Chapter 2

# *Study of PMMA*

## 2.1 What is PMMA?

Poly(methyl methacrylate), or PMMA, is known by many different names, including Plexiglas and acrylic. The biocompatibility of PMMA material has gained it the medical moniker of “bone cement.”

PMMA stands for poly(methyl methacrylate), which is a synthetic polymer made from methyl methacrylate monomer. PMMA is a transparent thermoplastic that is widely used in various applications, such as optical lenses, automotive parts, medical devices, and even as a substitute for glass in some applications. PMMA is lightweight, shatter-resistant, and has excellent optical properties, including high transparency and low haze. It is also biocompatible, which makes it suitable for use in medical applications, such as dental implants and contact lenses. PMMA can be processed using various techniques, including injection molding, extrusion, and machining, which makes it a versatile material for different industries.

**Fig:- Poly (methyl methacrylate)PMMA Substrate**

Poly (methyl methacrylate) (PMMA) is a transparent thermoplastic synthesized by emulsion polymerization, solution polymerization, and bulk polymerization from the MMA monomer. This acrylate has high resistance to sunlight exposure and good optical properties, widely used to substitute and enhance the glass performance. This polymeric compound is attractive; hence is stable, affordable, has been explored in multiple structural and forms—like sheets, films, and tubular, even spherical composites— from nanotechnology to upper metrics/scales with variety being applied in all kinds of industries. One of the main advantages of PMMA is that it contains less potentially harmful subunits from the synthesis, like bisphenol-A, commonly found in other types of polymers such as polycarbonates, polysulfones, and epoxy resins. It is a superior polymeric material for analytical separation, sensing, biomedical and medical applications due to biocompatibility, and is used for electrolysis, polymer conductivity, viscosity measurements, solar nano/micro concentrator lens for solar cells. In practice, the PMMA surface properties can be tailored by surface modification through graft copolymerization or by the incorporation of a surfactant into the polymer matrix.

## 2.2 Uses of PMMA

Acrylic plastic or PMMA finds its application in a variety of industries due to its properties, easy processing and cost-effectiveness. PMMA is processed by injection molding, compression molding, extrusion or casting.

The extensive polymethyl methacrylate uses are a result of its advantageous properties and adaptability. This transparent plastic is used in a lot of markets. Some of the most common applications of PMMA are discussed below:

- **Glass Substitute**

  Acrylic glass is used as a shatterproof alternative for windows and skylights. It is also commonly used in aquariums and aircraft canopies. A lot of hockey rinks also use PMMA. Illuminated sign boards that display advertisements or directions are also usually made up of PMMA.

- **Construction and Design**

  Windows, doors, panels, canopies etc., all use polymethyl methacrylate due to its excellent properties such as heat insulation and light transmission. The polymer may also be used in the construction of sinks, baths, knobs or tap tops.

- **Automobile Industry**

  One of the most important industries that require PMMA is the transportation and automobile industries. From car windows to windshields, acrylic sheets can be found in a lot of spaces. It is used in the manufacturing of various automotive parts. The aviation and marine industry also require this polymer. Car indicator covers and panels are also made using plexiglass.

- **Healthcare Industry**

  PMMA polymer is also known as bone cement in the healthcare industry. It is used by orthopaedic surgeons for procedures like joint replacement or treating bone damages. It can also be used to fill in the gaps between bones. Optical fibres used for endoscopy also consist of PMMA.

- **Cosmetic Usage**

  PMMA has also found its usage in various beauty products and injectables. It is used in cosmetic procedures that treat ace, facial lines, wrinkles etc.

- **Lamps and Lighting**

  The light-emitting potential, transparency and other such properties allow PMMA to be used in LED lights and lamps. You can find PMMA being used in street and traffic lights. It is manufactured in various colour options, which adds to its usability in lamps and other lighting devices.

- **Electronic Devices**

  Acrylic glass can be used in the display of various electronic equipment, including tv screens, laptops and smartphones. This is due to its properties, such as transmittance and high optical clarity.
  Solar Devices

  The application of polymethyl methacrylate PMMA in solar panels is a result of its UV stability and light transmission ability. It can also be used in the construction of greenhouses, aquariums and marine centres. Other products where this polymer finds its application include paint, furniture and optical fibres used for telecommunication.

## Advantages of PMMA

PMMA has several advantages over other polymers like polycarbonate (PC) and polystyrene etc. It doesn't scratch easily or yellow over time. PMMA is used as an alternative to other transparent polymers in situations where extreme strength is not required.

Some of the advantages of PMMA include:

- Economical
- Resistance to weathering
- Various colorings options
- Tensile strength
- Easy to process and handle
- Versatility
- Biocompatibility
- UV Stability
- Durability
- Transmittance and better optical clarity
- Recyclable
- Non-toxic

## 2.3 Characteristics of PMMA:-

PMMA, which stands for polymethyl methacrylate, is a transparent thermoplastic polymer known for its unique characteristics.

Here are some key characteristics of PMMA:

- **Transparency:** PMMA exhibits exceptional optical clarity, allowing over 92% of visible light to pass through. It has a high refractive index, making it a popular alternative to glass in applications where transparency is essential, such as optical lenses and display screens.

- **Lightweight:** PMMA is lightweight, weighing about half as much as glass. This property makes it suitable for applications where weight reduction is desired, such as aircraft windows, automotive components, and lightweight structures.

- **High Impact Strength:** PMMA has good impact resistance compared to other transparent polymers. It can withstand moderate impacts without shattering, making it a safer alternative to glass in applications where impact resistance is crucial, such as protective barriers or safety glazing.

- **Chemical Resistance:** PMMA exhibits excellent resistance to many chemicals, including acids, alkalis, and most organic solvents. This property makes it suitable for use in chemical processing equipment, protective coatings, and laboratory applications.

- **UV Resistance:** PMMA has good resistance to ultraviolet (UV) radiation. It does not yellow or degrade significantly when exposed to sunlight or other UV sources, making it suitable for outdoor applications such as signage, architectural glazing, and outdoor displays.

- **Easy Processing:** PMMA is a thermoplastic that can be easily molded and shaped using various processes, including injection molding, extrusion, and thermoforming. It has a wide processing temperature range and can be fabricated into complex shapes, making it versatile for different manufacturing methods.

- **Weather ability:** PMMA is highly resistant to weathering and retains its mechanical and optical properties over time. It does not become brittle or degrade significantly when exposed to outdoor environments, making it a popular choice for outdoor applications.

- **Electrical Insulation:** PMMA is an excellent electrical insulator, offering high dielectric strength and low electrical conductivity. It is used in electrical components, light guides, and optical fibers where electrical insulation is required.

These characteristics make PMMA a versatile material used in a wide range of applications, including automotive parts, architectural glazing, lighting fixtures, medical devices, displays, and signage.

## 2.4 Why we use $TiO_2$ coated PMMA substrate for biomedical application.

$TiO_2$ (titanium dioxide) coated PMMA (polymethyl methacrylate) substrates find applications in biomedical fields due to the following reasons:

**Enhanced Biocompatibility:** The $TiO_2$ coating on the PMMA substrate can improve the biocompatibility of the material. $TiO_2$ has been shown to promote cell adhesion and proliferation, making it suitable for applications involving cell culture, tissue engineering, and implantable devices. The coating can create a favorable surface for cell attachment and growth.

**Antibacterial Properties:** $TiO_2$ coatings possess antibacterial properties, particularly under UV light exposure. When UV light interacts with $TiO_2$, photocatalytic reactions occur, leading to the generation of reactive oxygen species (ROS) that can destroy bacteria and inhibit their growth. This antibacterial effect is beneficial for applications where preventing bacterial contamination or infection is crucial, such as medical implants and wound dressings.

**Biocompatible Coating Stability:** $TiO_2$ coatings on PMMA substrates can provide a stable and durable biocompatible surface. The coating acts as a barrier, protecting the underlying PMMA material from degradation and potential leaching of harmful substances. This stability ensures the long-term performance and safety of the biomedical device or substrate.

**Optimal Optical Properties:** PMMA is already known for its excellent optical transparency, and the $TiO_2$ coating does not significantly affect this property. Therefore, $TiO_2$-coated PMMA substrates can maintain their optical clarity, making them suitable for applications involving optical components, such as lenses, waveguides, and biomedical imaging devices.

# Chapter 3

# *Synthesis methods*

## 3.1 Types of synthesis methods

In this chapter, an overview was carried out on the different methods that are used or have been used to prepare titanium dioxide nanoparticles. There are various methods that can be used to synthesize $TiO_2$ and the most commonly used methods include sol-gel process, chemical vapor deposition (CVD) and hydrothermal method among others.

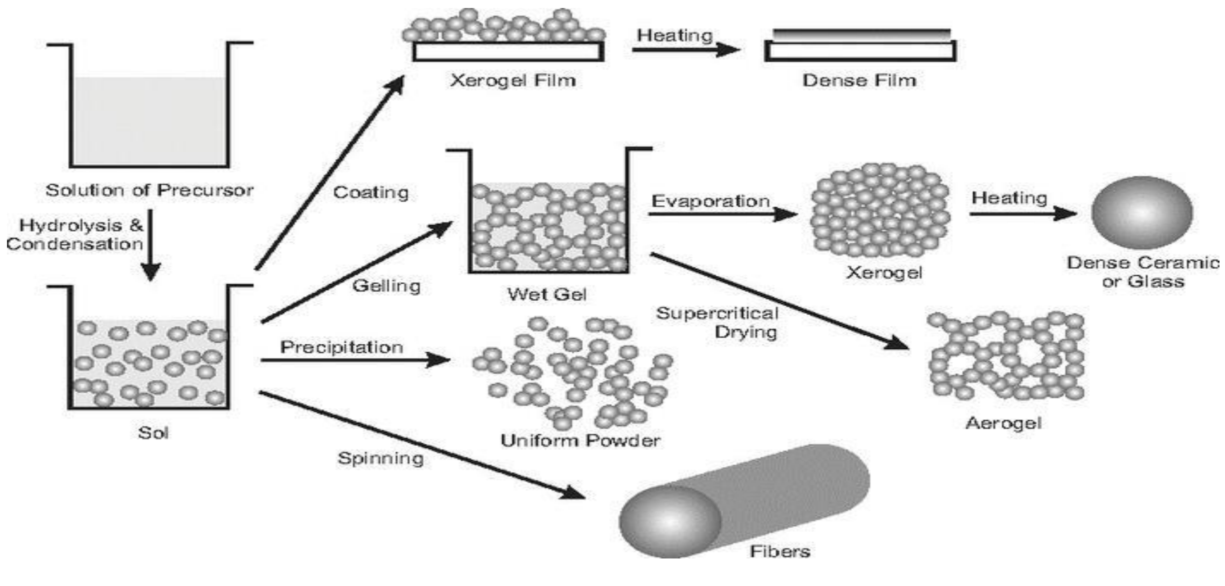
**Certainly! Here is a list of various synthesis methods for titanium dioxide (TiO2):**

1. **Sol-Gel Method**
2. **Hydrothermal/Solvothermal Method**
3. **Solvothermal Decomposition**
4. **Chemical Vapor Deposition (CVD), etc.**

### 1) Sol-gel method:-

Sol-gel process is a wet-chemical technique that is mostly used in the field of materials science and ceramic engineering. The sol-gel method is a versatile and widely used technique for the synthesis of titanium dioxide ($TiO_2$) nanoparticles or thin films. It involves the formation of a sol, a colloidal suspension of nanoparticles in a liquid, followed by gelation and subsequent heat treatment to obtain the desired $TiO_2$ material.

**Figure: Different sol-gel process steps to control the final morphology of the product**



**Here is a brief overview of the sol-gel method for $TiO_2$ synthesis:**

1) **Sol Preparation:** Titanium alkoxides, such as titanium isopropoxide or titanium tetraisopropoxide, are typically used as precursors. These alkoxides are mixed with a suitable solvent, such as alcohol or water, to form a clear solution known as the sol. The solvent choice depends on the desired properties and applications of the TiO2 material.

2) **Hydrolysis:** The titanium alkoxide undergoes hydrolysis when exposed to moisture, resulting in the formation of titanium hydroxide. Water or acid is usually added to the sol to induce hydrolysis, which can be controlled by adjusting the pH of the solution. Hydrolysis converts the titanium alkoxide into a more stable form that can subsequently polymerize.

3) **Gelation:** After hydrolysis, the sol undergoes a gelation process, where the particles aggregate and form a three-dimensional network structure called a gel. Gelation can occur spontaneously through the self-assembly of particles or be induced by adding a cross-linking agent.

4) **Aging and Drying:** The gel is allowed to age for a certain period to promote further particle growth and structural stability. The aging time can vary from hours to days. Subsequently, the gel is dried through evaporation or controlled heating to remove the solvent and water, leaving behind a solid material.

5) **Calcination:** The dried gel is subjected to a heat treatment process called calcination. This step involves heating the material at high temperatures (typically 400-800°C) in an oxygen-rich atmosphere. Calcination serves multiple purposes, including the removal of organic residues, densification of the material, and transformation of the amorphous gel into crystalline TiO2.

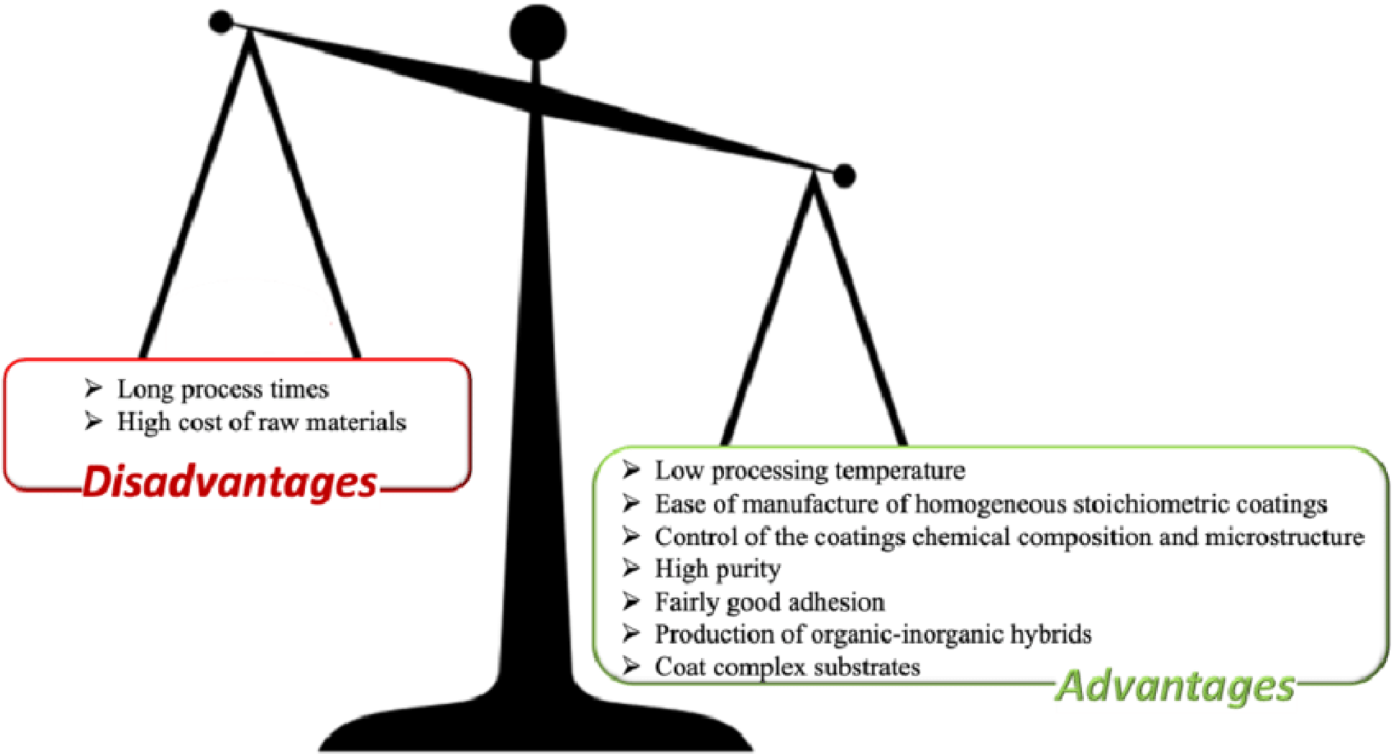
6) **Post-treatment:** Depending on the desired properties, the calcined TiO2 material may undergo additional post-treatment steps, such as surface modification, doping with other elements, or coating onto substrates, to enhance its performance for specific applications.

The sol-gel method offers several advantages, including precise control over particle size, homogeneity, and morphology of TiO2 materials. It also allows the incorporation of various dopants and the production of thin films on different substrates. These properties make it a valuable technique for a wide range of applications, including photocatalysis, solar cells, sensors, and coatings.

## ❖ Sol-gel process parameters affecting properties of $TiO_2$:-

There are various parameters that influence the size and properties of the $TiO_2$ particles produced via the sol-gel process. To get $TiO_2$ particles with desirable properties, the parameters that influence hydrolysis and condensation reactions of the sol-gel process should be controlled. It has been established that some parameters are more important than others. The parameters include pH, nature and concentration of the catalyst, water/precursor molar ratio, reaction temperature, precursor concentration, type of solvent and type of precursor.

## ❖ Advantages & Disadvantages of Sol-gel:-



## 2) Hydrothermal methods:-

These are two processes, solvothermal and hydrothermal which are almost similar.

The hydrothermal method is a process of crystallizing a substance at a high temperature and high vapor pressure using an aqueous solution of the material. It is commonly depicted as crystal synthesis or crystal growth from substances which are insoluble in customary temperature (100°C) and pressure (<1 atm). The process is carried out in autoclaves under controlled temperature and pressure. It allows the use of temperatures above the boiling point of water/organic solution. Hydrothermal synthesis is characterized as a concoction response occurring in a dissolvable at temperatures over the dissolvable breaking point and at pressures above bar.

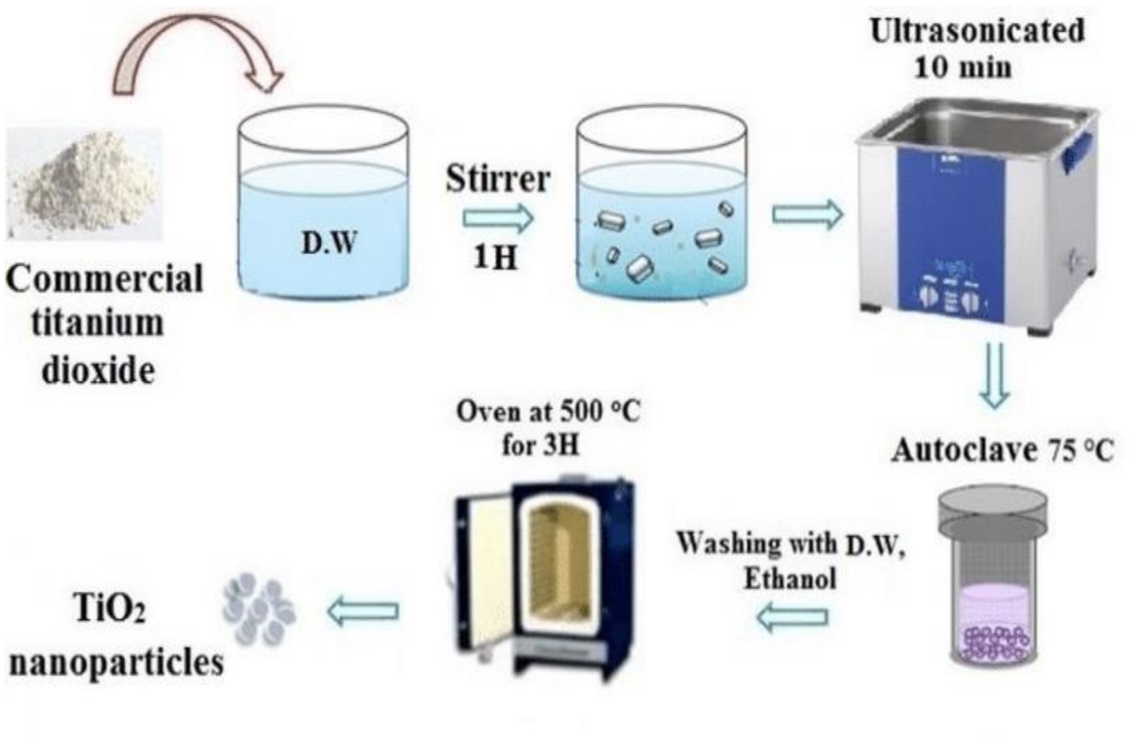



**Fig:- Synthesize of $TiO_2$ nanoparticals using the hydrothermal method**

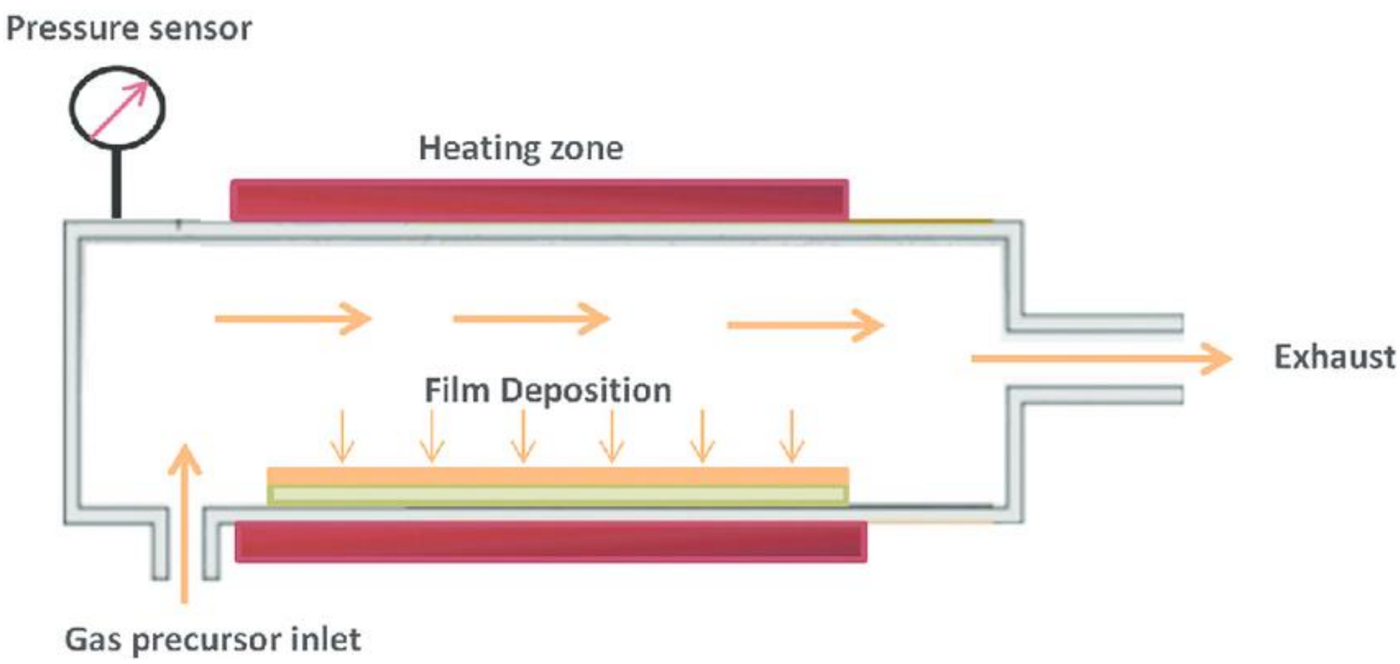
## 3) Solvothermal methods:-

Compared to hydrothermal method, the solvothermal method uses a non-aqueous solvent, has better control of the properties of $TiO_2$ and the temperature can be increased much higher meaning high boiling point solvents can be used. The hydrothermal strategy exploits that by expanding temperature and pressure the essential properties of water and consequently its capacities as a solvent changes. Important characteristics such as the ionic product density, thermal conductivity, viscosity, heat capacity and the dielectric constant are all highly pressure and temperature dependent and by tuning the synthesis parameters, specific solvent properties can be obtained. Feng et al. produced $TiO_2$ nanorods by treating titanium tetrachloride solution saturated with sodium chloride at 160°C for 2 h. Kim et al. used the solvothermal method to prepare $TiO_2$ of good quality without the use of surfactants.

# 4) Chemical Vapor Deposition (CVD):-

**The process steps involved in Chemical Vapor Deposition (CVD) for the deposition of titanium dioxide ($TiO_2$) are as follows:**

1)Substrate Preparation
2)Reactor Setup
3)Precursor Introduction
4)Heating
5)Reaction and Deposition
6)Film Growth and Control
7)Cooling and Purging
8)Film Characterization



# Chapter 4

# *Spin-Coating*

## 4.1 What is Spin-Coating?

Spin-coating is a commonly used technique for depositing thin films onto flat substrates. It involves applying a liquid solution or suspension (called the coating material) onto a substrate and rapidly spinning the substrate, causing the liquid to spread out uniformly due to centrifugal force. The excess liquid is then removed, leaving behind a thin, smooth, and uniform film.

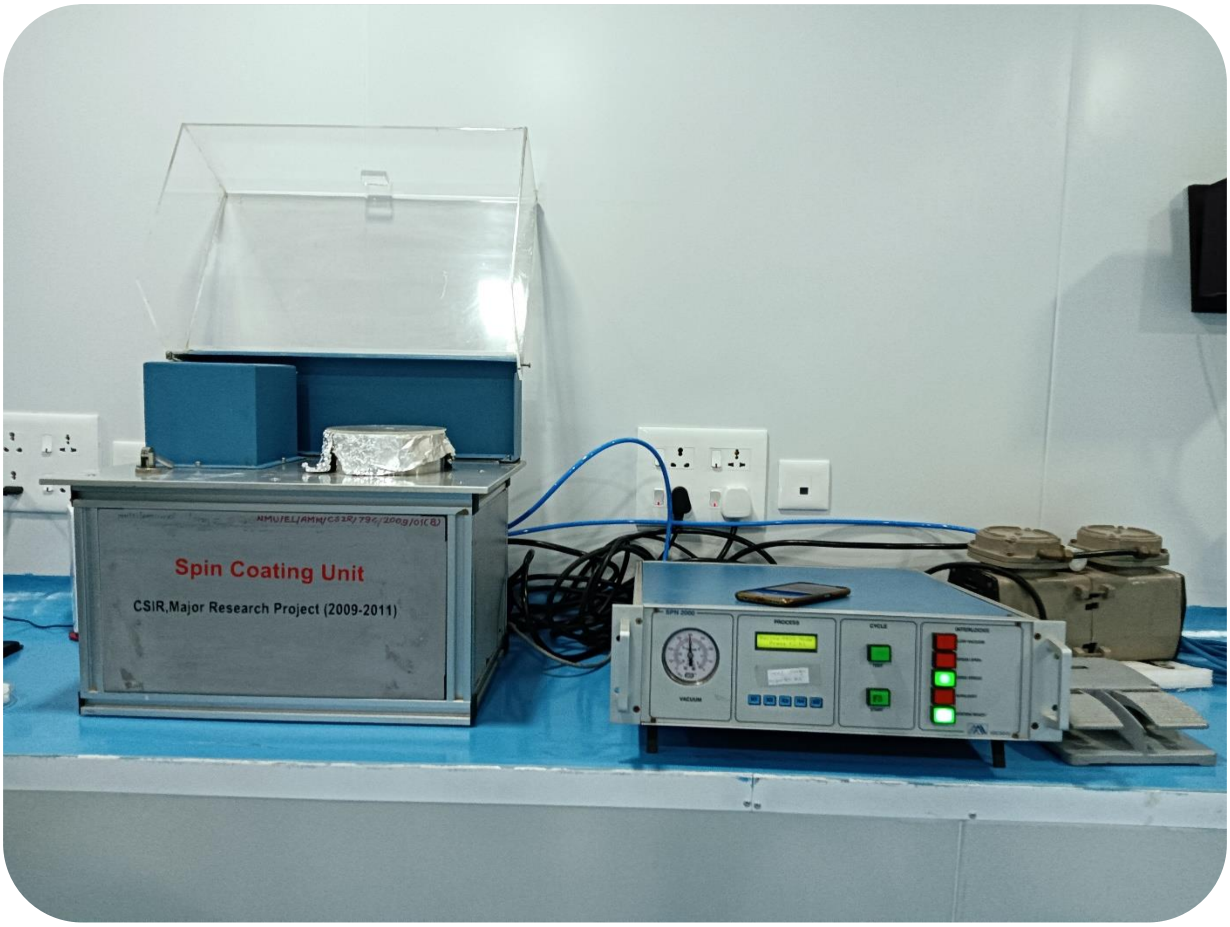



**Fig:- Spin-Coating Unit**

### Here's a brief overview of the spin-coating process:

Coating Material Preparation: The coating material, which can be a solution or suspension, is prepared by dissolving or dispersing the desired material (e.g., polymers, nanoparticles, or organic compounds) in a suitable solvent. The concentration and viscosity of the coating material are optimized for spin-coating.

1) **Substrate Preparation:** The substrate on which the thin film will be deposited is thoroughly cleaned to ensure a clean and defect-free surface. It is typically a flat and rigid material, such as a glass slide or silicon wafer.

2) **Dispensing the Coating Material:** A small volume of the coating material is dispensed onto the center of the substrate. The volume is chosen to ensure complete coverage of the substrate during the spinning process.

3) **Spinning:** The substrate is placed on a spin-coating machine, typically consisting of a spinning chuck or platform. The spinning process is initiated, and the substrate rapidly accelerates to a predetermined rotational speed. As the substrate spins, centrifugal force causes the coating material to spread out radially, forming a thin liquid layer.

4) **Film Formation:** The spinning action continues for a predetermined duration, allowing the liquid to uniformly cover the entire surface of the substrate. During this time, solvent evaporation occurs, leading to the formation of a solid thin film. The spinning speed, spinning time, and temperature (if required) are carefully controlled to optimize film thickness and properties.

5) **Film Drying:** After the desired spinning time, the spinning is stopped, and the substrate is left to dry in ambient conditions or in a controlled environment, depending on the nature of the coating material. The drying process allows the solvent to evaporate completely, leaving behind a solid thin film.

### ➢ Spin-coating offers several advantages:

- **Simple and Cost-Effective:** Spin-coating is a relatively simple and cost-effective technique, requiring minimal equipment and expertise.

- **Uniformity**: The spinning action ensures uniform spreading of the coating material, resulting in a thin film with excellent uniformity across the substrate surface.

- **Controllable Film Thickness**: By adjusting parameters such as spinning speed and time, the film thickness can be precisely controlled, making spin-coating suitable for applications requiring specific thicknesses.

- **Versatility:** Spin-coating can be used with a wide range of materials, including polymers, organic compounds, nanoparticles, and hybrid materials.

Spin-coating finds applications in various fields, including microelectronics, optoelectronics, photovoltaic, displays, sensors, and coatings. It enables the fabrication of thin films with controlled thickness, smoothness, and uniformity, making it a valuable technique in research, development, and production processes.

# Chapter 5

# ***Experimental Methods***

## 5.1 Experiment for First process:-

The synthesis were performed as follows: first, solution A was prepared by mixing 3 ml titanium tetra-isopropoxide (97 % Aldrich) and 10.6 ml of anhydrous ethanol (99.8 % Aldrich) while solution B contained 0.3 ml anhydrous ethanol, 0.15 ml distilled water, and 11.1 ml of acetic acid (99.7 % Aldrich). Solution B was then added drop by drop into solution A to obtain a clear transparent sol. After a few hours, the sol becomes milky and after several hours a gel is obtained. Subsequently, a drying step at room temperature is performed during 25 days to remove volatile solvents and then a dry crystals is obtained. The resulting crystal or substance is calcined at 150 °C during 2 h and milled in an agate mortar.

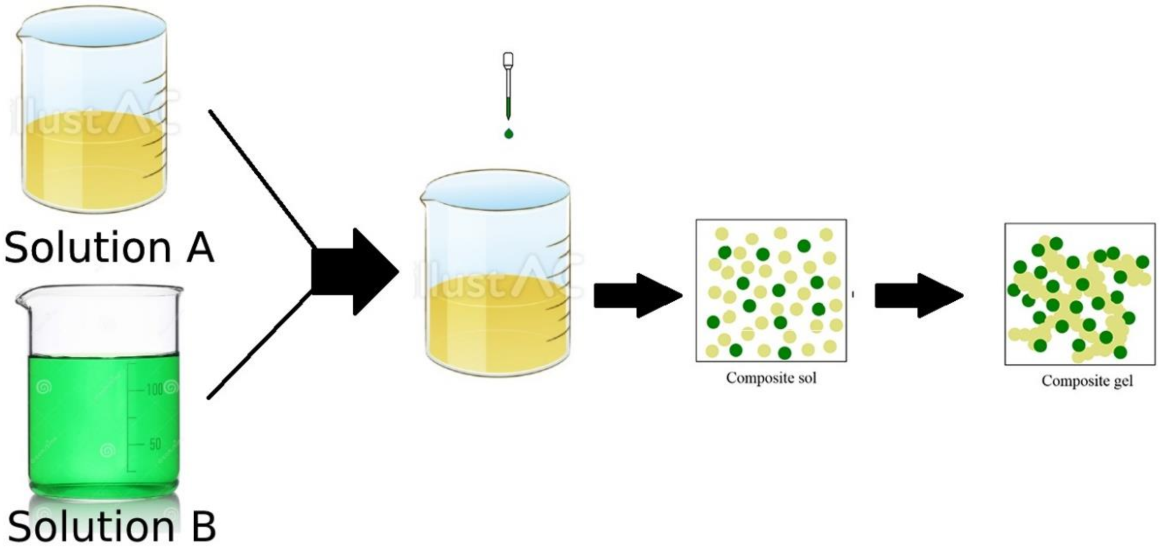



**Fig: Process flow diagram to represent the sol-gel process for synthesis of $TiO_2$ Nano coating.**

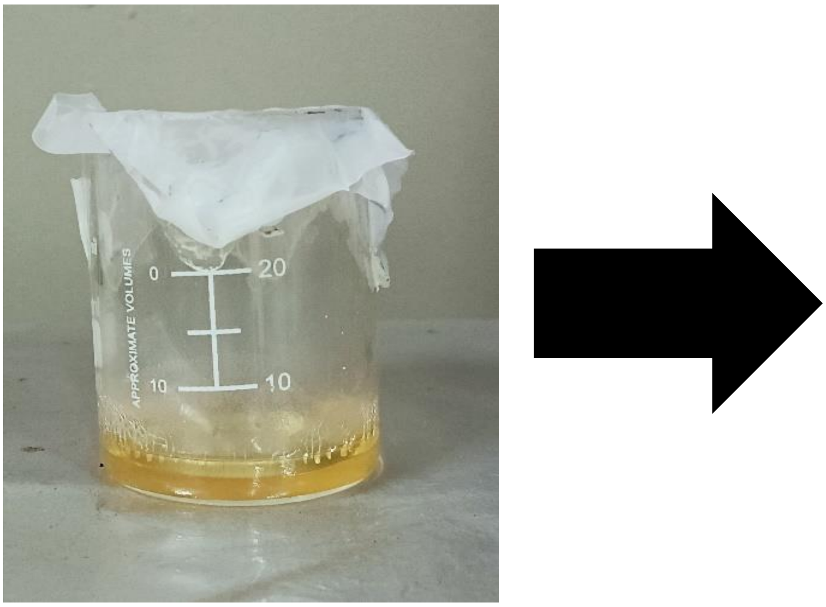


**Fig: - After 13 days**

**Fig: - After 16 days**


**Fig:- The resulting crystal or substance is calcined at 150 °C during 2 h**

**Fig: - After the calcination**

**Fig:- Milled in an agate mortar**

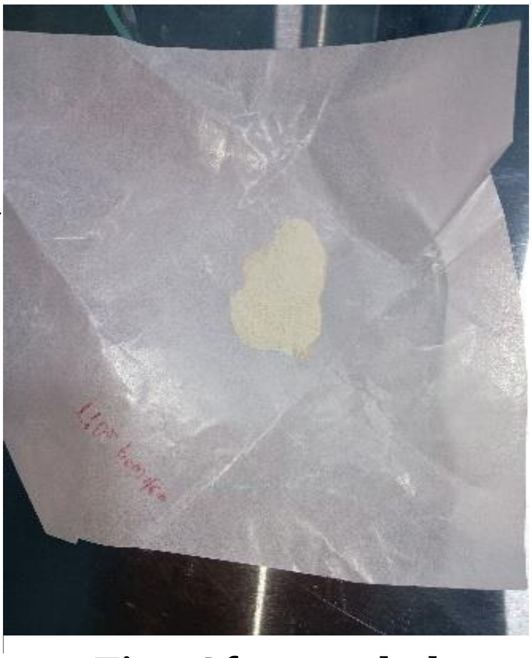
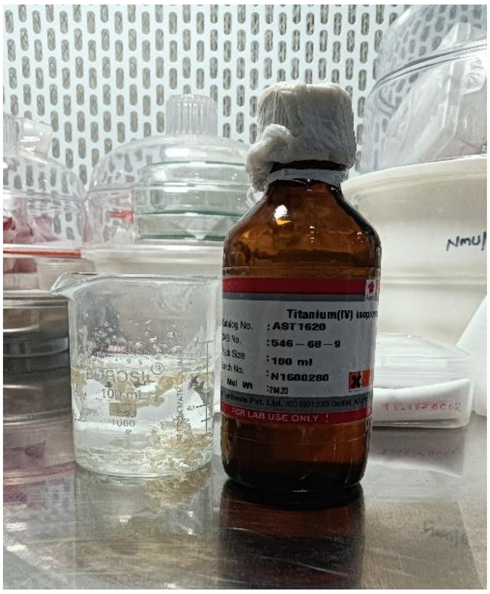


**Fig:- After crush the powder form of $TiO_2$**

## 5.2 Experiment for Second process deposition on reference Si Substrate:-

TiO$_2$ solutions were prepared by sol–gel method. Titanium (IV) isopropoxide (TTIP) (Sigma–Aldrich Co.), hydrochloric acid (37% HCl) and deionized water (DI) are used as titanium precursor, catalyst and hydrolysis medium respectively. In general, TiO$_2$ solutions were prepared by dissolving TTIP to DI water under constant stirring for 30 min at 25 °C followed by 0.4 ml of HCl. The solutions were keep on continuous stirring for 2 h before they kept in room condition for 48 h ageing process.

| Sols | Volume (ml) | | |
|---|---|---|---|
| | DI | TTiP | HCl |
| 1s | 64 | 4 | 0.4 |




**Dissolving TTIP to DI water**


**Under constant stirring for 30 min at 25 °C followed by 0.4 ml of HCl**

**The solutions were keep on continuous stirring for 2 h before they kept in room condition for 48 h ageing process**

**After gel point deposition by the spin coating**


**Deposited samples**

# Chapter 6

# *Result*

## 6.1 FTIR Result for first process:-

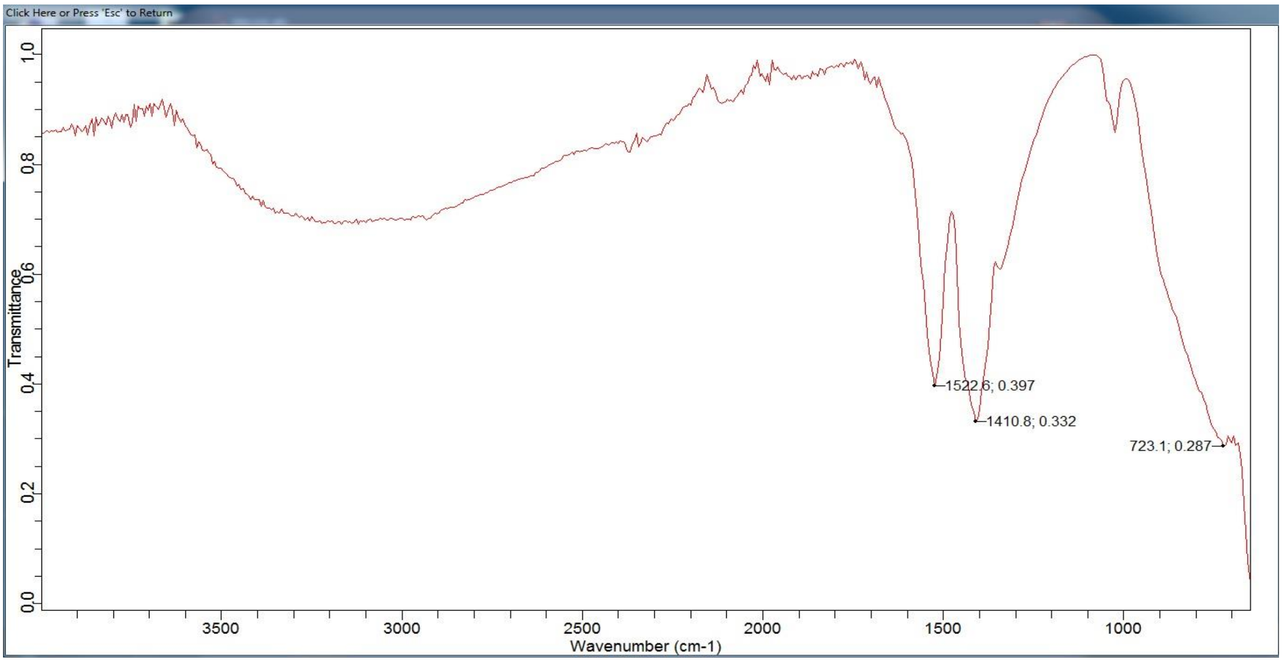



**Fig 1:- FTIR spectrum of $TiO_2$ nanoparticles**

## 6.2 Ellipsometry result of second process:-

| Process | Stages | RPM | Time | R.I | Thickness(nm) |
|---|---|---|---|---|---|
| K1 | 1 | 4000 | 30sec | - | - |
| K2 | 2 | 4000 | 30sec + 30sec | 1.5167 | 99.738 |
| K3 | 2 | 3001 | 30sec + 30sec | 1.5060 | 100.2 |
| K4 | 2 | 550 + k1 | 30sec + 30sec | 1.6121 | 103 |
| K5 | 2 | 4000 | 30sec + 2sec | 1.4888 | 83.955 |

# Future Scope $TiO_2$ nanocoating on PMMA

The future scope of $TiO_2$ nanocoatings on PMMA (polymethyl methacrylate) substrates holds great potential for various biomedical applications. Here are some key areas that could be explored:

Improved Biocompatibility: Future research can focus on enhancing the biocompatibility of $TiO_2$ nanocoatings on PMMA substrates

**Enhanced Mechanical Properties:** Future studies could investigate techniques to enhance the mechanical properties of $TiO_2$ nanocoatings on PMMA, such as increasing the coating thickness or introducing nanocomposite structures, to improve the overall strength and durability of biomedical devices.

**Advanced Drug Delivery Systems:** Future research could focus on developing innovative strategies to load and release therapeutic agents from the nanocoatings, enabling precise and localized drug delivery for various biomedical applications.

**Surface Modification for Specific Applications:** Future studies could explore surface modification techniques to impart specific properties, such as antibacterial activity, cell adhesion promotion, or protein immobilization, to the $TiO_2$ nanocoatings on PMMA substrates.

**Integration with Advanced Technologies**: $TiO_2$ nanocoatings on PMMA can be integrated with other emerging technologies to create advanced biomedical systems.

**Long-term Stability and Durability**: Understanding the long-term stability and durability of $TiO_2$ nanocoatings on PMMA substrates is essential for their successful implementation in biomedical applications. Future studies could investigate the aging mechanisms, biodegradation rates, and long-term performance of these nanocoatings under relevant physiological conditions to ensure their efficacy and safety over extended periods.

# Conclusion

Titanium dioxide thin films have been deposited onto silicon substrates by the spin coating technique. The refractive index and thickness of $TiO_2$ films were investigated by Ellipsometry. In conclusion, $TiO_2$ nanocoatings have demonstrated tremendous potential for biomedical applications. The growth of $TiO_2$ nano-laminates for biomedical applications offers exciting opportunities in tissue engineering, drug delivery systems, and biosensors. The ability to control the material's properties enables customization for specific applications, enhancing biocompatibility, functionality and performance. Further research and development in this field are likely to uncover even more potential applications and advance the use of $TiO_2$ nano-laminates in the biomedical field.

The future scope of $TiO_2$ nanocoatings on PMMA substrates in the biomedical field is promising. Further research and development efforts can lead to the design of innovative biomedical solutions with improved biocompatibility, advanced drug delivery capabilities, and integration with other cutting-edge technologies, ultimately enhancing patient care and treatment outcomes.

# References


1. Cédric B. D. Marien, Clément Marchal, AlainKoch, Didier Robert & Patrick Drogui. Sol-gel synthesis of $TiO_2$ nanoparticles: effect of Pluronic P123 on particle's morphology and photocatalytic degradation of paraquat. Environmental Science and Pollution Research 2016, DOI: 10.1007/s11356-016-7681-2.

**2.** Shuhadah. Yazid, Zulkifli Mohd Rosli, Jariah Mohamad Juoi. Effect of titanium (IV) isopropoxide molarity on the crystallinity and photocatalytic activity of titanium dioxide thin film deposited via green sol–gel route**.** Journal of Materials Research and Technology. 2 0 1 9;8(1):1434–1439, https://doi.org/10.1016/j.jmrt.2018.10.009.

3. Pallabi Paul, Kristin Pfeiffer, and Adrina Szeghalmi. Antireflection Coating on PMMA Substrates by Atomic Layer Deposition. Coatings 2020, 10(1), 64; https://doi.org/10.3390/coatings10010064.

4. Denis Nazarov, Ilya Ezhov, Natalia Yudintceva, Ilya Mitrofanov, Maxim Shevtsov, Aida Rudakova, Maxim Maximov. MG-63 and FetMSC Cell Response on Atomic Layer Deposited $TiO_2$ Nanolayers Prepared Using Titanium Tetrachloride and Tetraisopropoxide. Coatings 2022, 12(5), 668; https://doi.org/10.3390/coatings12050668.