

# **B. TECH. PROJECT REPORT**

On

## **Growth and Optimization of TiO<sub>2</sub> Nanostructures and study its application as a photodiode**

By  
Rohit Gupta



**DISCIPLINE OF ELECTRICAL ENGINEERING  
INDIAN INSTITUTE OF TECHNOLOGY INDORE**

**December 2017**

# **Growth and Optimization of TiO<sub>2</sub> Nanostructures and study its application as a photodiode**

**A PROJECT REPORT**

*Submitted in partial fulfillment of the  
requirements for the award of the degrees*

*of*  
**BACHELOR OF TECHNOLOGY**  
*in*  
**ELECTRICAL ENGINEERING**

*Submitted by:*  
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**(Associate Professor, IIT INDORE)**



**INDIAN INSTITUTE OF TECHNOLOGY INDORE**  
**December 2017**

## **CANDIDATE’S DECLARATION**

I hereby declare that the project entitled “**Growth and optimization of TiO<sub>2</sub> nanostructures and study its application as a photodiode**” submitted in partial fulfillment for the award of the degree of Bachelor of Technology in ‘Electrical Engineering’ completed under the supervision of **Dr. Vipul Singh, Associate Professor, Electrical Engineering, IIT Indore** is an authentic work.

Further, I declare that I have not submitted this work for the award of any other degree elsewhere.

**Rohit Gupta**

**(140002027)**

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## **CERTIFICATE by BTP Guide**

It is certified that the above statement made by the student is correct to the best of my knowledge.

**Dr. Vipul Singh,**  
**Associate Professor,**  
**Department of Electrical Engineering,**  
**IIT Indore**

## Preface

This report on "Growth and optimization of TiO<sub>2</sub> nanostructures and study its application as a photodiode" is prepared under the guidance of Dr. Vipul Singh.

Through this report, I have tried to give a detailed description of TiO<sub>2</sub> nanostructures and its application in fabrication of photodiode. I have grown hydrothermally TiO<sub>2</sub> nanorods on FTO coated glass substrate and performed SEM and XRD studies of TiO<sub>2</sub> nanostructures.

I have also studied the effect of parameter variation by changing concentration of precursor, reaction time and positioning of the substrate on the growth of TiO<sub>2</sub> nanorods. I also tried the nanostructures growth by using different substrates namely ITO coated glass, FTO coated glass and normal glass substrates.

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B. Tech, IV Year

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## Acknowledgements

The final outcome of this project required a lot of guidance and assistance from many people and I am very fortunate to have received those whenever and wherever I was in need.

I feel highly privileged to work under the supervision of Dr. Vipul Singh, who has been a constant source of strength and inspiration. He has always been approachable and has helped me overcome many difficulties that I faced during the project. I wish to thank him for his kind support and valuable guidance. Without his guidance the project would have not been completed.

I owe my profound gratitude to all the PhD scholars of MNRG lab who were there to help me with their valuable suggestions and moreover for their timely encouragement during the course of the project.

My special thanks to my parents for their support and understanding, and of course for bearing with me during the times when I was all busy with the project.

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## **Abstract**

There is a growing need for large area, user friendly, economical, integrated optoelectronic devices so that they can be integrated into many novel applications such as efficient light emitting diodes (LEDs), photodetectors, solar cells, wearable electronics and implantable biomedical devices etc. These demands are difficult to be achieved by existing rigid technology hence, oxide semiconductors gained increased scientific and industrial interest in the last decade as an alternative to traditional solid-state solutions.

Metal oxides have emerged as an important class of semiconducting materials and have potential to overcome above mentioned issues. Initially,  $\text{TiO}_2$  was commercially well-known material used in paints, protective coatings for metals, printing ink and sunscreens due its non-toxicity and biocompatibility. In the past decade,  $\text{TiO}_2$  thin films and nanostructures have become suitable candidates for emerging electronic devices like photodetectors, transistors and solar cells.  $\text{TiO}_2$  nanostructures have drawn considerable attention of scientific community because of their ease of preparation, improved optoelectronic properties, crystallinity, high specific area, chemical & thermal stability and bio-friendly nature. All in all,  $\text{TiO}_2$  is one of the most promising alternative to conventional semiconductors for optoelectronic applications like ultraviolet (UV) lasers, light emitting diodes, field-effect transistors, photodetectors, nano-generators and solar cells primarily due to its wide band gap (3.2 eV), high refractive index, excellent UV emission and absorption properties.

Oxide nanoparticles provide an increased photoresponse as high as two orders of magnitude compared to large particles used in the similar application. It is now possible to reproducibly make nanomaterials due to advancements in chemical synthesis and various characterization techniques.

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## Abbreviations

UV-VIS	Ultraviolet - Visible
SEM	Scanning Electron Microscopy
XRD	X-ray Diffraction
P3HT	Poly (3-Hexylthiophene – 2,5 - diyl)
FTO	Flourine doped Tin Oxide
ITO	Indium Tin Oxide
PEDOT	poly(3,4-ethylenedioxythiophene)
PSS	polystyrene sulfonate
FWHM	Full Width at Half Maximum





# Chapter 1 – Introduction

## 1.1 Nanotechnology

Nanomaterials are the materials that have one of their dimensions smaller than 100 nm. These can be polymeric, electronic, ceramic, metallic or composite. Based on their arrangement, they can be categorized as nanotubes, nanorods, nanolayers, nanoparticles. In nanotubes, two dimensions of the nanostructure are in nanometer scale. Nanorods are similar in structure to nanotubes but with rod like solid structure. Nanolayers have only one characteristic dimension in nanometer scale with a thickness of few nanometers and thousands nanometers long. Nanoparticles are the finest nanomaterials with a diameter of less than 100nm.

The most important factor that led to the development of nanotechnology is that they exhibit enhanced properties that can be tuned by controlling their size. This is termed as Quantum confinement effect that starts to dominate when the size of material gets down to few nanometers (or comparable to wavelength of an electron). As the size is reduced when in nanoscale, the energy bands gets discretized. Moreover, the band gap increases with further reduction in size leading to blue shift in the optical properties as shown in fig. 1.1. A quantum dot is confined in 3D, a quantum wire in 2D and a quantum well in 1D. These confinements are the potential wells bounding the particles leading to their increased randomness.

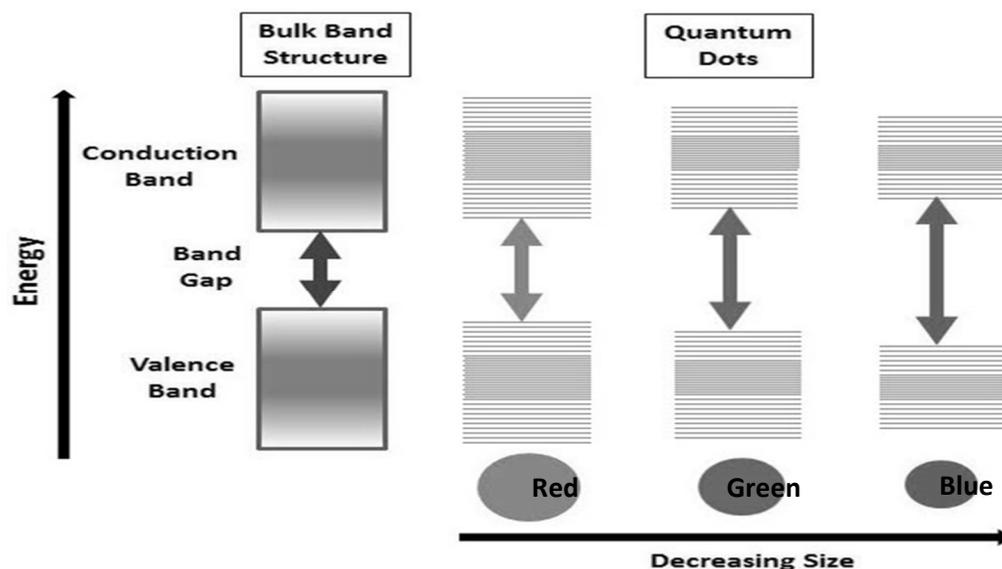


Fig. 1.1 Quantum confinement effect on band diagram

Another factor that makes nanoparticles behave differently compared to their bulk is that the surface-to-volume ratio is increased. This makes the atoms on the surface to dominate the controlling of properties compared to inside ones. Since the particles on surface are weakly bonded via dangling bonds, the properties of nanomaterial gets modified due to dominating influence of these particles. This also affects the interaction of individual particles with other materials in the surroundings. The relative increase in the surface area is an important factor for instance in efficient charge carrier generation at the junction of semiconductors in a photodetector.

## 1.2 Titanium dioxide and its applications

TiO<sub>2</sub> belongs to the family of transition metal oxides. TiO<sub>2</sub> exists commonly in three forms namely anatase, rutile and brookite. Anatase and rutile are tetragonal in structure and are physically, chemically and biologically stable in nature. Whereas, brookite form has an orthorhombic structure but is unstable in nature. Anatase TiO<sub>2</sub> gets converted into rutile form at higher temperature (>550<sup>0</sup>). The rutile phase becomes more stable than anatase for particle sizes greater than 14 nm. Once the rutile phase formed, it grew much faster than the anatase. TiO<sub>2</sub> is a wide bandgap semiconducting material with a bandgaps of 3.2 eV, 3.02 eV and 2.96 eV for anatase, rutile and brookite respectively. It is inherently an n-type semiconductor and exhibit good photovoltaic and photocatalytic properties.

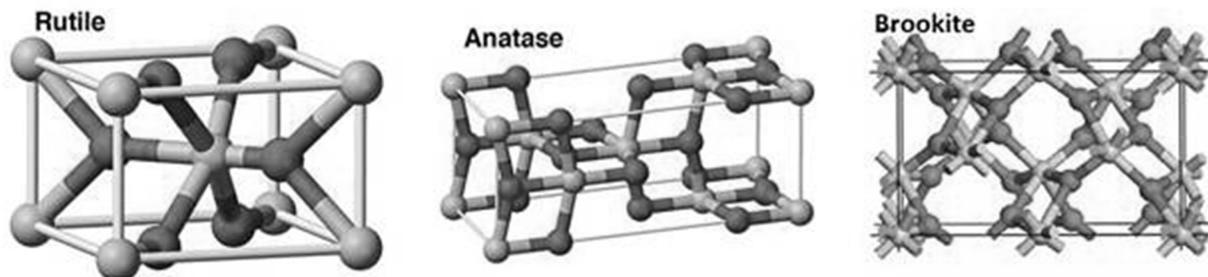


Fig. 1.2: Common forms of Titanium dioxide

The valence band of TiO<sub>2</sub> is composed of the 2p orbitals of oxygen hybridized with the 3d orbitals of titanium, while the conduction band is only the 3d orbitals of titanium. When TiO<sub>2</sub> is exposed to near-UV light, electrons in the valence band are excited to the conduction band leaving behind holes (h<sup>+</sup>). The excited electrons (e<sup>-</sup>) in the conduction band are now in a purely 3d state and because of dissimilar parity, the transition probability of e<sup>-</sup> to the valence band decreases, leading to a reduction in the probability of e<sup>-</sup>/h<sup>+</sup> recombination.

Following are some of the applications of Titanium dioxide in devices:

- Solar Cells
- Photodetector
- Gas Sensor
- Cladding of Fiber Optic cable
- Lithium Ion batteries
- Memristor

### **1.3 Overview of various synthesis methods**

Two approaches can be followed towards synthesis of nanomaterial. One is the “top-down” approach, in which bulk materials are broken into nano-sized particles. Another is the “bottom-up” approach, which involves clustering of atoms or molecules to form required nanostructures. Latter technique is more controlled and provides variety of nanostructures to be synthesized by controlling the reaction kinetics. Following are some basic bottom-up approach for the synthesis of TiO<sub>2</sub> nanostructures:

#### **1.3.1 Hydrothermal method**

Hydrothermal synthesis is bottom-up synthesis approach conducted in steel vessel called autoclaves which needs controlled temperature and pressure. The reaction is conducted in aqueous solution and temperature can be elevated above the boiling point of water, reaching the vapor pressure. This process is easiest and controlled process for making nanostructures. The growth can be controlled by changing temperature and amount of precursor solution.

#### **1.3.2 Solvothermal method**

This method is similar to hydrothermal method except that the solvent is nonaqueous. Due to this, the temperature can be increased much higher before vapor pressure saturation reaches, since many organic solvents have very high boiling points. The solvothermal method normally has better control than hydrothermal methods of the size and shape distributions and the crystallinity of the TiO<sub>2</sub> nanoparticles. The solvothermal method has been found to be a versatile method for the synthesis of a variety of nanoparticles with narrow size distribution and dispersity.

Synthesis of nanostructured TiO<sub>2</sub> using sol-gel involves acid-catalyzed hydrolysis of Titanium alkoxide followed by condensation.

### **1.3.3 Sol-Gel method**

This is also a well-known method for synthesis of TiO<sub>2</sub> nanostructures. In this process, sol (a colloidal suspension) is formed from the hydrolysis and polymerization reactions of the precursors. This leads to gradual transition of liquid sol into solid gel. Titanium alkoxide and Titanium tetrachloride are the common precursors used. Synthesis of nanostructured TiO<sub>2</sub> using sol-gel involves acid-catalyzed hydrolysis of Titanium alkoxide followed by condensation. Synthesis of Ti-O-Ti chains is favored by low content of water, low hydrolysis rates, and excess titanium alkoxide in the reaction mixture.

### **1.3.4 Direct Oxidation method**

Nanostructured TiO<sub>2</sub> can be synthesized by oxidizing the surface of Titanium metal using oxidants. Crystalline TiO<sub>2</sub> nanorods can be obtained by direct oxidation of titanium metal with hydrogen peroxide. The growth can be controlled by adding some inorganic salts of Sodium halides or sulphate. Fluoride and Sulphate favors pure anatase form whereas chloride helps in formation of rutile TiO<sub>2</sub>. Growth of TiO<sub>2</sub> nanotubes has also been reported in some papers.

### **1.3.5 Electrodeposition**

This method is used to make a metallic coating on the surface of any substrate via reduction at the cathode. The metallic substrate to be coated is made cathode and dipped into solution containing salt of the metal to be deposited. The basic idea behind the process is to reduce the metallic ions on the surface of substrate.

## **1.4 Characterization Techniques**

### **1.4.1 Scanning Electron Microscopy**

Scanning Electron Microscope (SEM) is a type of electron microscope that images a sample by scanning it with a beam of electrons in a raster scan pattern. The electrons interact with the atoms that make up the sample producing signals that contain information about external morphology (texture), chemical composition, and crystalline structure and orientation of the materials making up the sample.

The working principle is similar to that of optical microscope where a beam of electrons is used in place of light. This help in achieving much more resolution of images (as wavelength of an electron is 10<sup>5</sup> times shorter than that of light) and even nanostructures can be visualized with a good resolution.

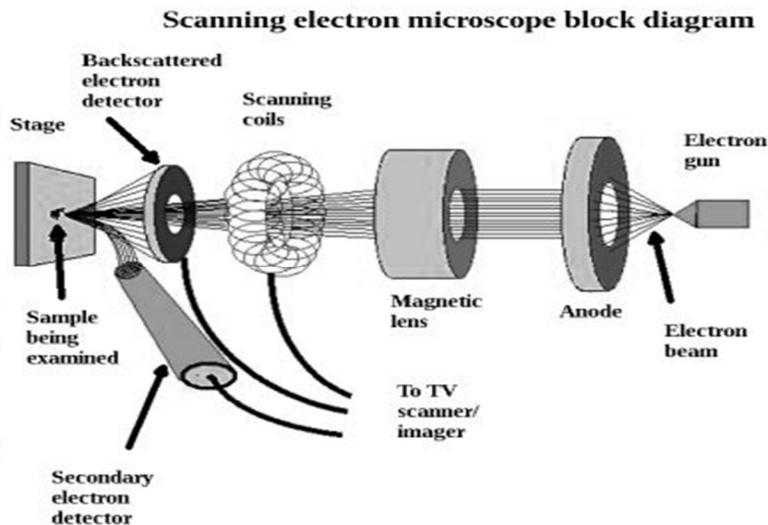


Fig 1.3: Scanning Electron Microscope block diagram

Back scattered electrons are the same incident electrons that are reflected off the specimen. This shows the surface arrangement of particles in specimen. Secondary electrons are the electrons that are emitted by specimen being knocked off by the incident electrons.

Back scattered electrons are the same incident electrons that are reflected off the specimen. This shows the surface arrangement of particles in specimen. Secondary electrons are the electrons that are emitted by specimen being knocked off by the incident electrons.

### 1.4.2 X-ray diffraction crystallography

X-rays are electromagnetic radiation of wavelength about the same size as an atom. X-ray diffraction has been in use in two main areas, for the fingerprint characterization of crystalline materials and the determination of their structure. Once the material has been identified, X-ray crystallography may be used to determine its structure, i.e. how the atoms pack together in the crystalline state and what the interatomic distance and their angles are.

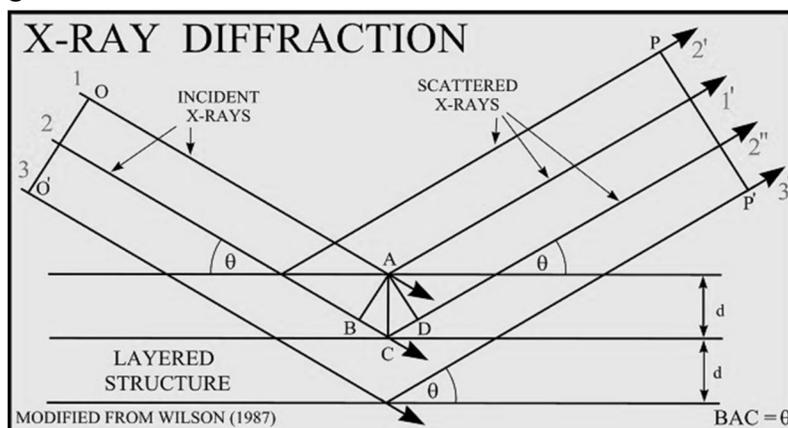


Fig. 1.4: X-ray diffraction Crystallography

Bragg's law is used to describe the condition on  $\theta$  for the constructive interference:  $2d\sin(\theta) = n\lambda$ ,

where,  $n$  is a positive integer and  $\lambda$  is the wavelength of incident x-rays.

$2d\sin(\theta)$  is the total path difference between two rays.

$$\text{Crystallite size, } D = \frac{0.9\lambda}{\beta \cos(\theta)}$$

Where  $\beta$  is termed as FWHM

## 1.5 Organic-Inorganic heterojunction

Organic-inorganic hybrid photoelectric devices draw considerable attention because of their unique features by combining the relatively low ionization potential of the organic molecules and the high electron affinity of inorganic semiconductors. Hybrid design exhibits a greatly enhanced photocurrent, a fast response, and a shorter recovery time. Compared with other types of photodetectors, organic-inorganic hybrid photodetectors have unique features, taking advantage of both the superior intrinsic carrier mobilities and the broad-band absorption of inorganic based devices, as well as easy-formation properties, excellent mechanical flexibility, and tunable functionality through modification of the structures of the molecules or the monomers, of the polymers of the organic based devices.

## Chapter 2 – Theory and Design

### 2.1 TiO<sub>2</sub> nanostructures growth

TiO<sub>2</sub> can be used to make a variety of nanostructures and with ease. Due to oxygen defects present in TiO<sub>2</sub> lattice, it is intrinsically an n-type semiconductor.

The various nanostructures of TiO<sub>2</sub> are shown in fig. 2.1

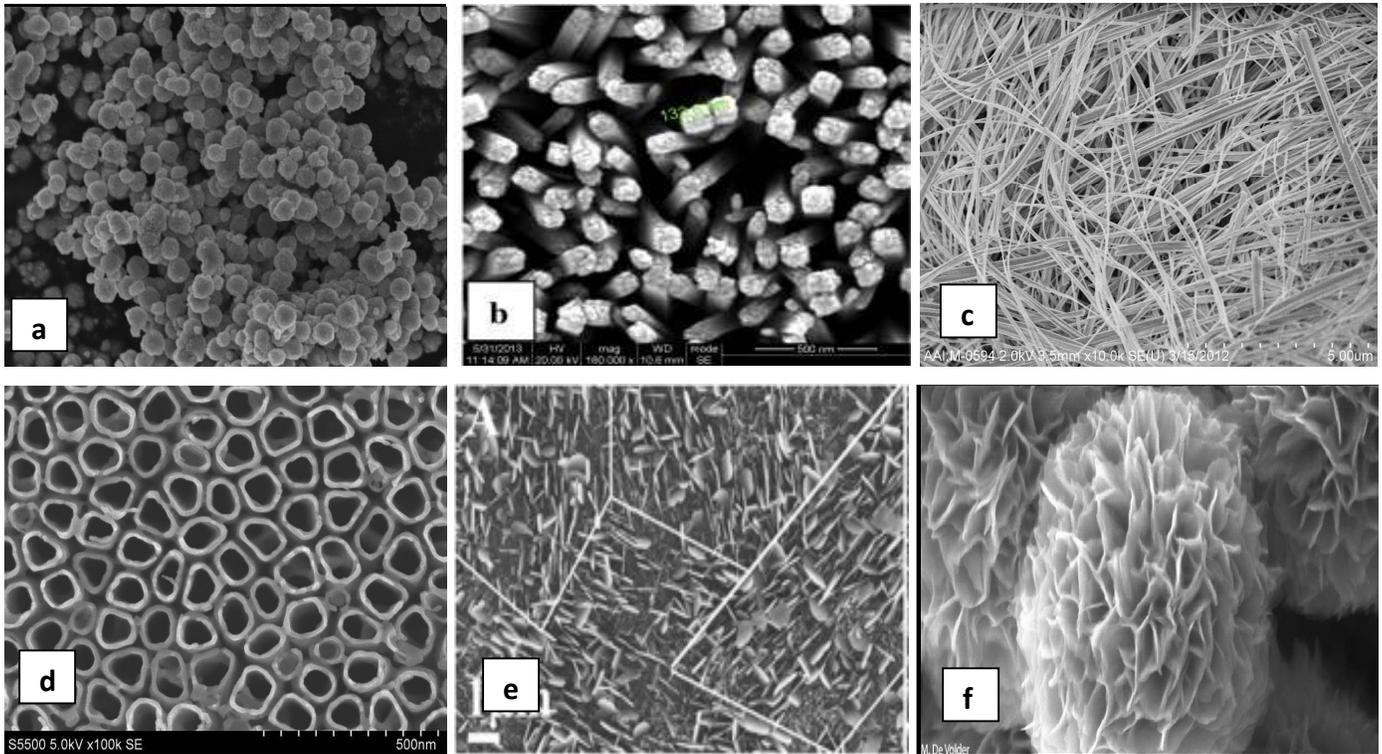


Fig. 2.1: Various TiO<sub>2</sub> nanostructures: (a) Nanoparticles (b) Nanorods (c) Nanowires  
(d) Nanotubes (e) Nanosheets (f) Nanoflowers

Single crystal nanorods or nanowires offer direct electrical pathways for photogenerated electrons and could increase the electron transport rate, which in turn may improve the performance of photovoltaic devices.

FTO and ITO coating: Fluorine doped tin oxide (FTO) and Indium tin oxide (ITO) are very important materials that are electrically conductive as well as optically transparent. Thus used for conductive coating over glass as a transparent electrode for optoelectronic applications and thin film photovoltaics. Moreover these can be easily fabricated and handled, cut, insulated and tempered using standard techniques. FTO is very important for growth of TiO<sub>2</sub> without the need for any seed layer for nanostructures growth.

The lattice structure of FTO is tetragonal which matches with that of anatase and rutile forms of  $\text{TiO}_2$ . Actually there is just 2% lattice mismatch between FTO and rutile  $\text{TiO}_2$ .

## 2.2 Photodiode Device Architecture

Photodetectors are devices that sense the presence of light and give a response as a change in current. Typical photodetectors are photodetector based on p-n junctions, p-i-n photodiodes, Schottky barrier, metal-semiconductor-metal, and metal-insulator-semiconductor. Conventional photodetectors generally require an external reverse biasing to sweep apart the photogenerated electron-hole pairs and collect the excitons at the electrodes. Thus in many cases, energy supply is a major challenge when huge number of sensors are needed. Recent studies of nanoscale devices have opened up the window for self-powered photodetectors that can be easily fabricated using nanowires or nanorods which can be synthesized easily, directly from their solution phases. These devices have a very low dark current and a great photoresponse even without any external biasing.

A photodetector can be used in various applications such as biosensors, in solar astronomy, in water sterilization, in pollution monitoring, and in smoke and fire alarms.

The typical architecture of a hybrid Organic-Inorganic heterojunction photodiode comprises a layer of  $\text{TiO}_2$  nanostructure which is grown hydrothermally over a flexible substrate coated with transparent conductive coating of FTO. Subsequently a layer of organic semiconductor P3HT (acting as p-layer) is spin coated on the top of it. Electrodes can be deposited using thermal evaporation or sputtering. The schematic diagram of the hybrid photodiode is shown below:

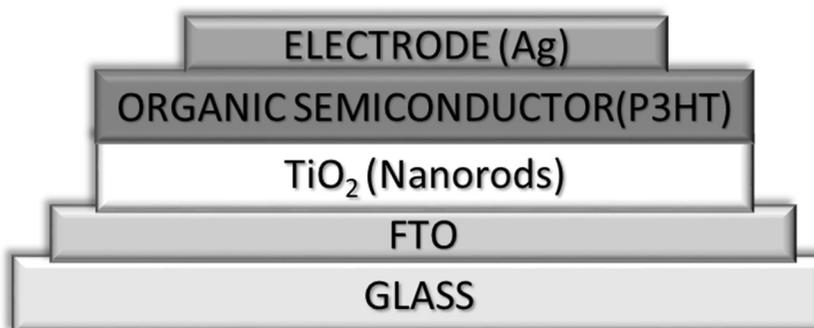


Fig. 2.2: Architecture of hybrid photodiode

The active semiconductor layer comprises a heterojunction of  $\text{TiO}_2/\text{P3HT}$  which act as acceptor/donor system that provides interfaces for exciton dissociation (sandwiched between electrodes with different work function) for efficient charge extraction. The charge carriers generated upon the light absorption are collected at the reverse biased electrodes.

Fabricating p-type  $\text{TiO}_2$  has remained a challenge and as a consequence, it is hard to fabricate low cost and efficient  $\text{TiO}_2$  p-n homojunction based photo detectors. Hence in order to fabricate a cost effective and high performance photo detector p-type  $\text{TiO}_2$  has been replaced by solution processed and stable p-type organic semiconductor, namely Poly(3-Hexylthiophene) (P3HT). In particular P3HT, due to its low cost of fabrication techniques, high mobility and ease of processability is considered as complementary alternative for the p-type inorganic semiconductors.

The performance of organic photo detectors relies on the high charge carrier mobility, strong absorption, and energy level alignment of donor and acceptor organic semiconductors. Previous reports have shown that in the case of organic semiconductors, photo detection requires the efficient dissociation of optically generated excitons. This dissociation occurs at the interface between electron donating and accepting materials at a low applied bias.

The band diagram for the above structure at the various interfaces is shown below:

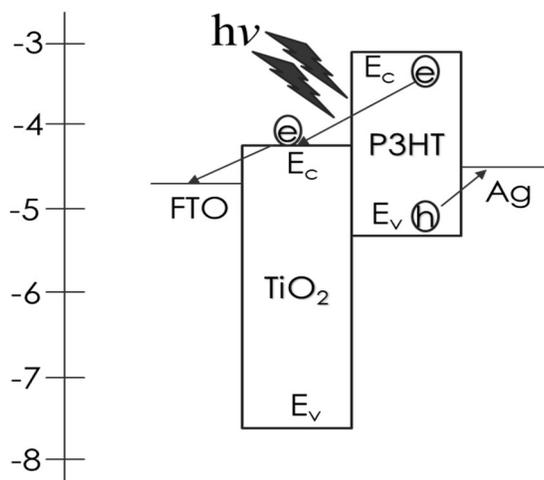


Fig. 2.3: Band diagram for interfaces of photodiode

The work functions for FTO and Silver are approximately -4.5 eV and -4.7 eV respectively. The conduction band and valence band for TiO<sub>2</sub> are at -4.2 eV and -7.4 eV respectively and that for P3HT are at -3.2 eV and -5.2 eV respectively. It is evident from the band diagram that the excitons generated upon incident of light gets dissociated even without any external biasing.

The schematic for exciton generation and dissociation is shown in fig. 2.4.

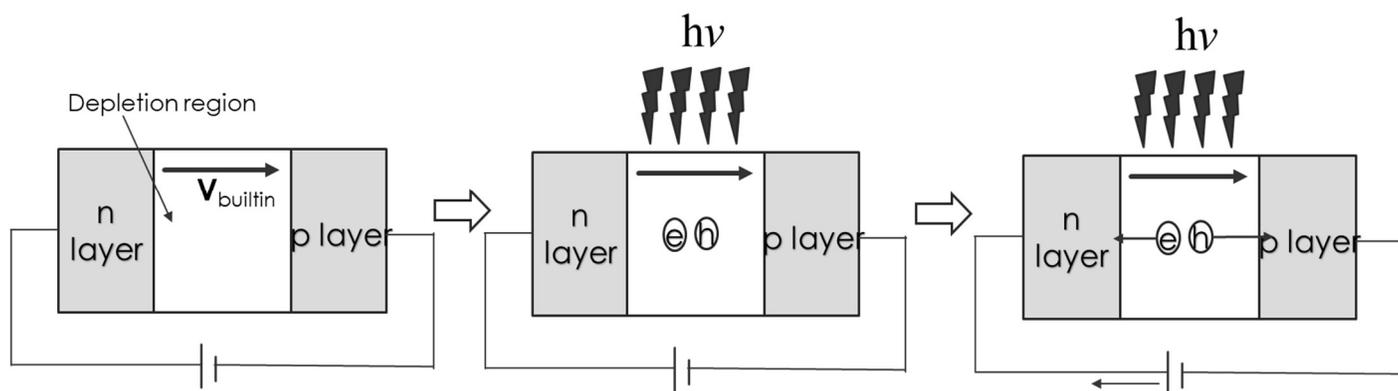


Fig. 2.4: Schematic for exciton generation and dissociation

## Chapter 3 – Experimental Procedure

This chapter presents the various experimental procedures used for the growth of TiO<sub>2</sub> nanorods via hydrothermal method. The general steps involved in the experiment has been given in the form of a flow diagram is shown below. A brief description of various methods through which nanostructures of TiO<sub>2</sub> are synthesized is given in section 1.3.

The factors that were changed to achieve best growth:

- 1.) Initial concentration of precursor
- 2.) Growth time
- 3.) Growth on different substrates
- 4.) Angle of placing the substrate

(Caution: Some of the materials used in the lab can be corrosive or harmful to our body. We must ensure that we use safety goggles, rubber gloves, and masks whenever necessary to ensure our safety.)

The following steps were taken for the growth:

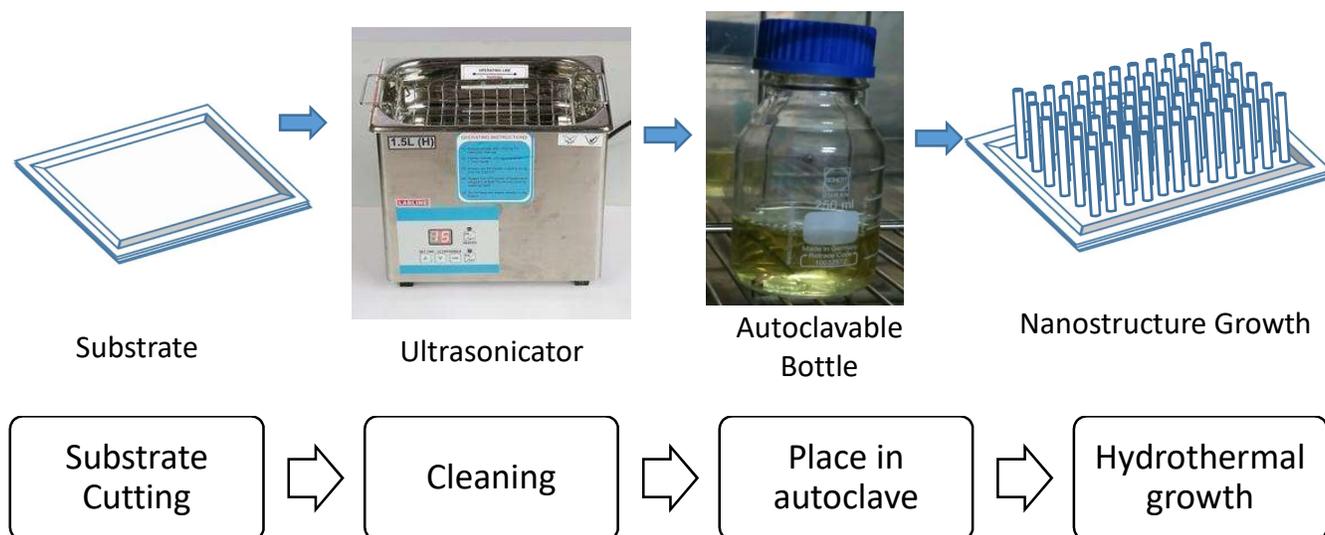


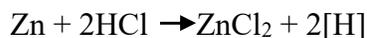
Fig 3.1 Flow diagram showing steps involved in nanostructure growth

### 3.1 Substrate cutting

The glass substrates of required dimensions were cut with the help of diamond cutter. Three different substrates namely ITO coated glass, FTO coated glass and normal glass were used. The dimension of substrates were different for different characterization. Substrates that were placed horizontally had a dimension of 1.2 cm × 1.2 cm glass substrate were required whereas for inclined substrates it was taken to be 1.2 cm × 3 cm.

### 3.2 Etching of ITO and FTO coated glass

Etching was done in case of ITO and FTO coated glass substrates. The substrates were covered with Scotch tape, and it is the region defined by the scotch tape that decided the dimensions of the ITO and FTO electrodes later. It must be noted that region of the substrate not covered by Scotch tape is etched away. Etching was done using a dilute HCl solution in a petridish. While Zn turning are gradually added. It is known that Zn and HCl react with each other as



It is the nascent Hydrogen that evolves almost immediately and leads to the etching of ITO and FTO electrodes, leaving behind the electrodes covered with scotch tape. Besides this there exists another method of etching samples using aquaregia solution. However, this method is more severe and many times leads to damage of the scotch tape itself.

### 3.3 Cleaning procedure

The next stage involves cleaning the substrates. The substrates were cleaned for inorganic impurities clinging to the surface of these substrates by using the ultrasonic bath. First, substrates were ultrasonicated for 10 minutes in acetone and then taken out and dried. In second step, substrates were ultrasonicated in Isopropyl alcohol for 10 minutes and then dried. In third step, substrates were ultrasonicated in DI water for 5 minutes. All these steps should be sequential followed by hydrophilic treatment.

### 3.4 Hydrothermal synthesis

The final stage of experiment involved the growth of TiO<sub>2</sub> nanorods via hydrothermal process. The reagents used for preparing the solution were deionized water, concentrated HCl and Titanium butoxide as the precursor. This was done by first preparing 1:1 solution of deionized water and concentrated HCl (50 mL each) in an autoclavable bottle and stirred for 5 minutes. Then 1.6 mL of precursor was added drop wise into the solution under constant stirring for another 5 minutes.

Then one set of ITO coated, FTO coated and normal glass were placed horizontally facing upwards and one set were placed at some inclination facing downwards. It was ensured that there is sufficient amount of solution below the substrates for growth to take place, in case of inclined placement.

The bottles were then kept in an oven at 130<sup>0</sup> C for 6 hours. Autoclavable bottles were used to ensure that sufficient vapor pressure is present inside the bottle at the reaction temperature and there is no leakage of any gases. After the synthesis time, the bottles were cooled and made to reach the ambient temperature. The substrates were then taken out, rinsed extensively with deionized water and allowed to dry in ambient air.

Above experiment is repeated by changing the concentration of precursor and reaction time.

## Chapter 4 – Analysis, Discussion and Results

### 4.1 Scanning Electron Microscopy

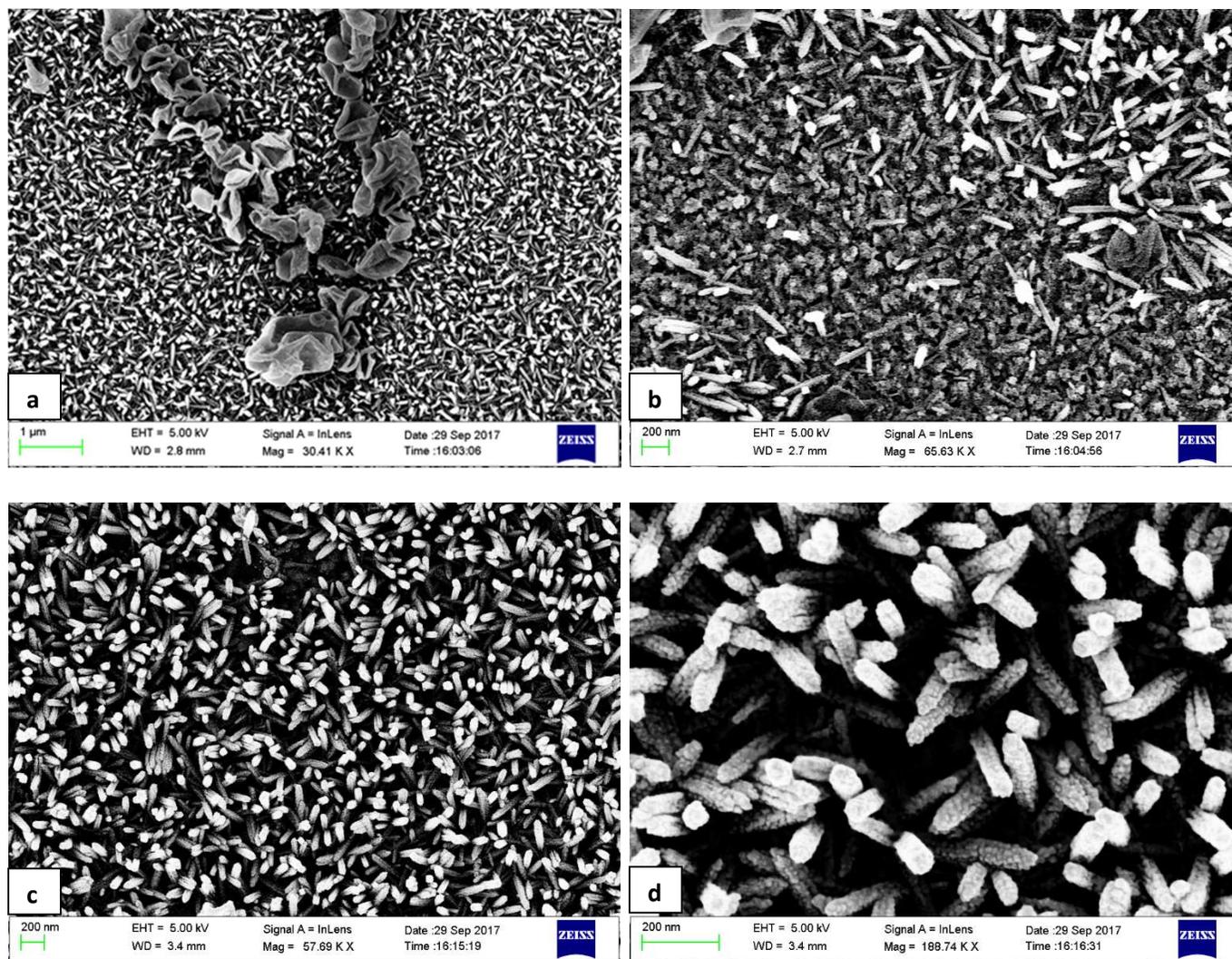


Fig.4.1: SEM images of TiO<sub>2</sub> nanostructures on : (a) and (b) FTO substrate placed horizontally; (c) and (d) FTO substrate placed inclined

The SEM images verifies that the nanostructures formed are of nanorods with an average diameter of 55 nm and length of 450 nm approximately on the FTO coated glass substrate.

## 4.2 X-ray Diffraction Crystallography

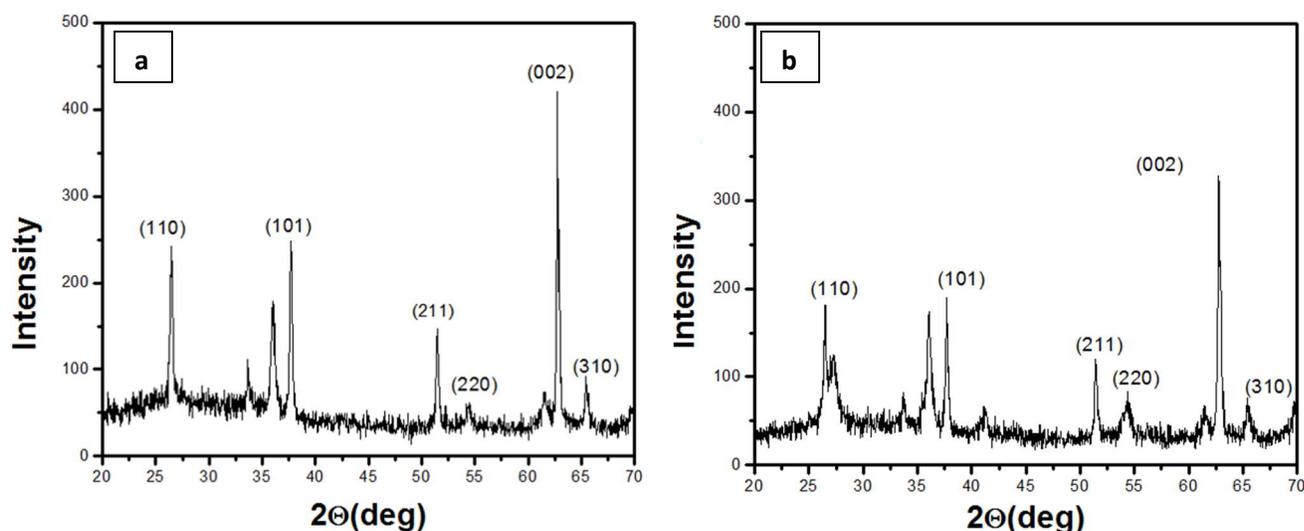


Fig. 4.2: XRD results of the samples: (a) FTO placed inclined (b) FTO placed horizontally

The calculation for the XRD is given in the appendix. It has been verified that the XRD results corresponds to that of rutile  $\text{TiO}_2$  with  $a=b= 0.43$  nm and  $c= 0.29$  nm

## 4.3 Absorption Spectroscopy

The nature of excited state and the processes of absorption and emission of light are central ideas in the modern spectroscopy. Absorption spectroscopy refers to the interaction (absorption) of electromagnetic radiation (160 - 780nm) by matter. In common cases most chemical species molecules or compounds are made up of electrons. The electrons in turn located in different orbitals which are associated with different energies. When light of sufficient energy falls on an electron in the ground state, the electron absorbs some of the energy and gets excited to the higher energy level. These energy levels are typically known as HOMO and LUMO respectively.

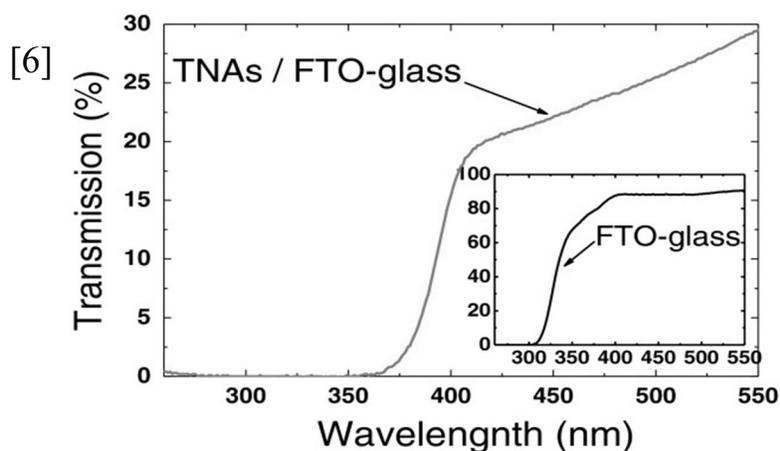


Fig. 4.3: UV-Vis absorption spectra of  $\text{TiO}_2$  nanorods array and FTO glass substrate (inset)

This is a typical absorption spectra of TiO<sub>2</sub> nanorods and FTO glass substrate [6]. It can be observed that there is a sharp edge at 420 nm which corresponds to energy bandgap of rutile TiO<sub>2</sub> nanorods. An absorption edge for the FTO glass substrate is about 310 nm, as shown in the inset of Figure 3. From these two transmittance spectra, we can conclude that only light with the wavelength between 310 and 420 nm can reach the TNAs and contribute to the UV photoresponsivity.

#### **4.4 Effect of parameter variations on result:**

The following results were observed when certain reaction parameters were varied:

1. Effect of substrate: The growth of vertically aligned TiO<sub>2</sub> nanorods were observed on the FTO coated glass. In case of ITO coated glass the SEM images didn't show any clear nanorods, the images were mostly of ITO. In normal glass there was nothing at all. This can be due to the good lattice matching between FTO and that of rutile TiO<sub>2</sub> (just 2% lattice mismatch). That's why FTO acted as nucleation site for the growth. The growth on ITO or glass would be possible if proper seed layer is coated over them that would provide the necessary nucleation site for the growth.
2. Effect of Initial precursor concentration: The density of the nanorods could be varied by changing the initial titanium precursor concentration in the growth solution. Increasing the concentration of precursor led to an increase in density of nanorods. Moreover, this also led to more porous nanorods.
3. Effect of reaction time: Changing the reaction time has a great impact on the growth of nanorods. Increasing the time gave nanorods of larger diameter and were longer in length. But subsequently, white precipitates were observed in the solution which mean that the grown structures started to peel off the FTO surface.
4. Effect of inclination: This didn't have much effect on the growth of nanorods. SEM images of horizontally placed substrate showed presence of some precipitates and less aligned nanorods around them. This may be because either the growth got hindered or the precipitates acted as the new nucleation site for the further growth of nanorods.

## **Chapter 5 – Conclusion and Future work**

We may conclude that well aligned TiO<sub>2</sub> nanorods were observed on the FTO coated glass substrate. Results obtained from SEM clearly shows that the structures obtained are nanorods and XRD result verifies the presence of rutile Titanium dioxide. Thus we have successfully grown the nanorods of rutile TiO<sub>2</sub> over FTO substrate which can be subsequently coated with organic semiconductors such as P3HT that will act as p-layer for the photodetector.

In future we may proceed to photodiode fabrication using the grown TiO<sub>2</sub> nanorods and work on its performance improvement. We may also attempt the fabrication of device on flexible substrate for high performance photodiode. Investigation on band bending and interface analysis of P3HT/TiO<sub>2</sub> organic – inorganic heterojunction can also be performed. We may also incorporate a hole transport layer like PEDOT:PSS and study its effect on the device performance. Finally, we may also employ the photodetector for numerous applications that are mentioned in above sections.

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