SYNTHESIS OF NATURAL FIBER TEMPLATED HIGH SURFACE AREA NANO-STRUCTURED TiO_2 AND ITS APPLICATION IN PHOTOCATALYSIS

A Project Thesis Submitted in Partial Fulfillment of the

Requirements

for the Degree in

Bachelor of Technology in Chemical Engineering

By

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CERTIFICATE

This is to certify that project entitled "**SYNTHESIS OF NATURAL FIBER TEMPLATED HIGH SURFACE AREA NANO-STRUCTURED TiO_2 AND ITS APPLICATION IN PHOTOCATALYSIS**" submitted by **Rituraj Borah (Roll No. – 110CH0412)**, in partial fulfillment of the requirements for the award of Bachelor of Technology in Chemical Engineering at National Institute of Technology, Rourkela (Deemed University) is an authentic work carried out by him under my supervision and guidance.

To the best of my knowledge, the matter embodied in the project thesis has not been submitted to any other University/Institute for the award of any Degree or Diploma.

Date:

Place: Rourkela

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ACKNOWLEDGEMENT

I would like to thank NIT Rourkela for giving me the valuable opportunity to use their resources and work in such an inspiring environment. I would like to express my gratitude to my honorable supervisor Dr.Santanu Paria, Associate Professor, Department of Chemical Engineering. I am utterly thankful for his exemplary guidance and encouragement. I would also like to thank Ph.D. student Mr. Rahul Purbia for his help. I am thankful to Dr. Sushmita Mishra, Department of Chemical Engineering for allowing me to use the TGA and BET facility for my work. I would like to express my gratitude to Ceramic Engineering Department for allowing me to use the FESEM facility. I am thankful to Physics department for permitting me to use the X-ray Diffractometer for my research. I would like to thank IACS, Kolkata for providing me the opportunity to carry out the Raman Spectroscopy analysis. Last, but not the least I am very thankful to all my friends at NIT Rourkela who were great moral and practical support during my work.

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ABSTRACT

Photocatalytic degradation of various organic pollutants under irradiation of light is possible by using TiO_2 as a photocatalyst. Activity of TiO_2 mainly in the UV range makes it necessary to modify TiO_2 by doping in order to impart activity in the visible region. We report here a wet chemical synthesis of S doped TiO_2 and Pure TiO_2 hollow tube structures by depositing precursor on Kapok fiber and Banana Fiber used as sacrificial templates. The doping of elemental sulfur is done, so that the synthesized material exhibits photocatalysis under visible light. The most advantageous features of this process are cost effectiveness, less time consumption, eco-friendliness and simplicity. The use of Kapok fiber and Banana fiber as template for the synthesis provides the condition for facile crystallization and growth of TiO_2 nanostructures in a single step process. Although at a temperature more than 600 ^{0} C, rutile phase starts to form, in this synthesis even at 750 ^{0} C of calcination temperature purely anatase phase was present. Another important feature of this synthesis method is that the hollow tubular structures obtained ensures high specific surface area. This synthesis process of nanostructures of TiO_2 thus can be considered for industrial production. The prepared material was characterized using XRD (X-Ray Diffractometer), Raman Spectroscopy, FESEM (Field Emission Scanning Electron Microscopy), EDS (Energy Dispersive Spectrometer), UV-Spectroscopy, BET (Brunauer–Emmett–Teller), TGA (Thermogravimetric Analysis). Photocatalytic study of the synthesized material was done by degradation of Methylene Blue under the irradiation of visible light. High activity of S-doped TiO_2 under visible light was found.

Keywords: Synthesis, Kapok fiber, Banana Fiber, template, nanoparticles, photocatalysis

Chapter 1

INTRODUCTION

1.1 INTRODUCTION:

Synthesis and application of materials of nano-size has been a crucial field of research for the last decades. It is well known that materials of size in the nano-range (1-100 nm) exhibit different properties than their bulk counter parts. The enhanced properties of nano-ranged materials have found application in different fields like environmental science, electronics, green technology, biotechnology etc. A very useful such application is photocatalysis. Due to quantum confinement effect and enhanced surface to volume ratio the catalytic properties of nanomaterials are much higher than usual bulk materials. The researchers are working on to find more environment friendly, facile and economic methods for the synthesis of nanomaterials.

There are various methods for synthesis of nano-materials. Since the past two decades, considerable efforts have been made to develop synthetic strategies for nanomaterials with controlled shape, size, composition and latitudinal arrangement. Synthesis using templates is one of the most effective strategies for attaining high degree of synthetic control. A template is a pre-existing material of similar dimensions as the nano-materials which is used as base for synthesis. Template based synthesis has certain advantages over template free synthesis. Researchers have been trying to use different materials as templates. There are numerous reports on synthesis of nanomaterials based on different natural and artificial templates. Research is being carried out to find easily available and cost effective templates for efficient synthesis of nanomaterials.[1]

TiO_2 (Titanium Di-oxide) has been a material of significant research in the last decades due to its applications in different fields. Nanomaterials of TiO_2 are found to exhibit excellent activity as a catalyst in photochemical reactions. Due to low cost, non-toxicity and stability, TiO_2 has many advantages over other photocatalytic materials. [2]

Photocatalysis is basically a phenomenon where a reaction is catalyzed by UV or visible light. The mechanism of photocatalysis is shown in fig. 1. The whole process takes place through a sequence of a number of steps. There is a certain band gap or energy difference between the valence band and conduction band of TiO_2. Light of energy greater than this band gap excites the electron in the valence band to get promoted to the conduction band. The anatase phase of TiO_2 has a band gap of 3.2 eV while the band gap of rutile is 3.0. But Anatase is found to be more active as a photocatalyst as compared to rutile. This behavior is explained by different theories. Under the incidence of light when the electrons from the valence band get promoted to the conduction

band, holes get created in the valence band which are strongly oxidizing. These holes oxidize water molecules to form hydroxyl free radicals. Hydroxyl free radicals are strongly oxidizing in nature, which can oxidize organic matters present in the solution. The free electrons generated can again react with oxygen molecules adsorbed on the catalyst surface to form superoxide ion. Superoxide ions can oxidize organic matter or can combine with H^+ to form peroxide free radicals. Although TiO_2 is considered as an excellent photocatalyst, its activity is mainly limited in the UV range. UV light possesses the required amount of energy for excitation of the electron in the valance band. But UV light is not abundantly found like natural sunlight. The UV range constitutes only about 4% of the total spectrum of sunlight. So it becomes necessary to modify TiO_2 in order to obtain visible light activity. Extensive research efforts have been made on how to reduce the band gap of TiO_2. It is reported that visible light activity can be acquired by metal or non-metal doping, dye sensitization and coupling semiconductors.[3] Various studies have concluded that doping with metals and non-metals reduces the band gap of the material which in turn ensures photocatalytic activity in the visible range.

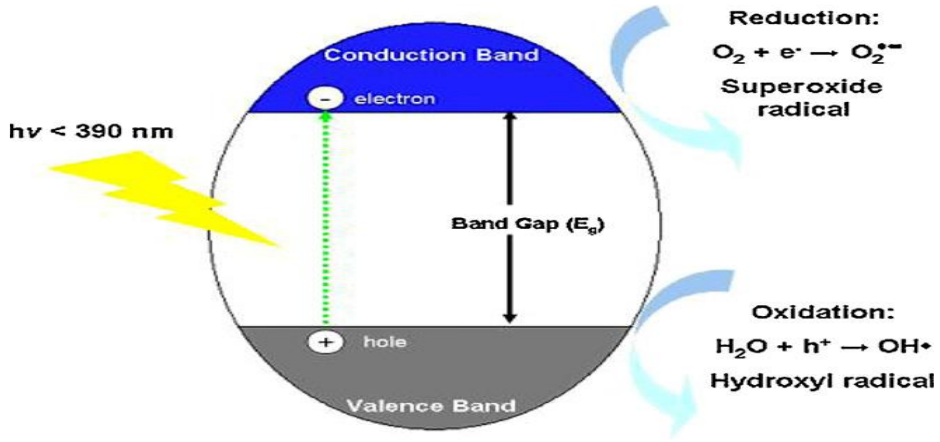


Fig. 1 Mechanism of photocatalysis

Kapok fiber: Kapok (*Ceiba Pentandra*) is seed-hair fiber obtained from the fruits of the Kapok tree. It is also known as Java Cotton or Java Kapok. It is common in tropical regions. The fibers obtained from the fruit is yellowish, light weighted and lustrous. The diameter of the fibers is around 20 micron. The fibers have smooth surface and uniform texture. Other properties of Kapok

fiber are moisture resistance, quick drying and resilience. It contains lignin, cellulose and a carbohydrate. The weight of kapok fiber is one eighth of that of normal cotton. The main uses of this fiber are stuffing of pillows and mattresses, as insulating material and substitution for absorbent cotton for surgery.

Banana fiber: Banana fiber is obtained from the stems of banana trees (*Musa Acuminata*). The composition of the fibers is basically cellulose and lignin. Banana fiber can be obtained after the harvesting of the banana trees. Although it is now a days used in textile industries, it is very cheap because it is a waste material of the banana cultivation. Using Banana fiber as a template can be advantageous considering its easy availability and low cost.

The main objectives of the project are as follows:

1. To synthesize high surface area nanostructured Sulfur-doped TiO_2 and pure TiO_2 material using Kapok Fiber and Banana Fiber as natural sacrificial templates.

2. To characterize the synthesized material in order to investigate its different physical, morphological and chemical properties.

3. To evaluate the photocatalytic property of the material under visible light for environmental application.

Chapter 2

Literature Review

2. LITERATURE REVIEW:

2.1 Titanium Dioxide (TiO_2):

TiO_2 (Titanium Dioxide) is basically an oxide of Ti (Titanium). It has three polymorphs: Anatase, Rutile and Brookite. TiO_2 has been a material of a wide range of application. Due to its low cost, non-toxicity and chemical stability it is used in various different commercial products like sunscreen, pigment, toothpaste, ointment etc. After Fujishima and Honda reported photocatalytic splitting of water molecules using TiO_2 electrodes in the presence of ultra-violet light in 1972, its application in energy and environmental science has attracted enormous attention from the researchers.[4] As the most promising photocatalyst, TiO_2 materials are sought as potential solution to many serious environmental and pollution related challenges of the modern world. TiO_2 is expected to play a big role in solving problems of energy crisis by utilization of solar energy based on water splitting devices and photovoltaics. [5] In the recent years there has been a tremendous advancement in preparation and application of TiO_2 nanomaterials. Preparation of TiO_2 nanomaterials in different forms like nanoparticles, nanorods, nanowires and nanotubes has been accomplished through various synthesis methods. These materials have been found effective to be used in various applications. [2]

2.2 Synthesis of TiO_2 nanoparticles:

TiO2 nanoparticles are synthesized by various methods such as sol gel, micelle and reverse micelle method, sol method, solvothermal method, templated synthesis method etc.[2] Although there are number of different methods to prepare TiO_2 nanomaterials, template directed synthesis has certain advantages due to its simplicity and versatility. There is a number of works on using various natural and synthetic materials as a template. Natural fibers with fine structures such as cotton wool, spider silk, dog hair, gills of mushroom, wood etc have already been reported to be used as templates for synthesis of nanomaterials. Natural fibers are gaining more and more research attention as they are cheap, easily available, pollution free and renewable. Fig. 2 (a) shows a classification of various templates. Fig. 2 (b) gives an over view of the synthetic strategy of template based synthesis. [1]

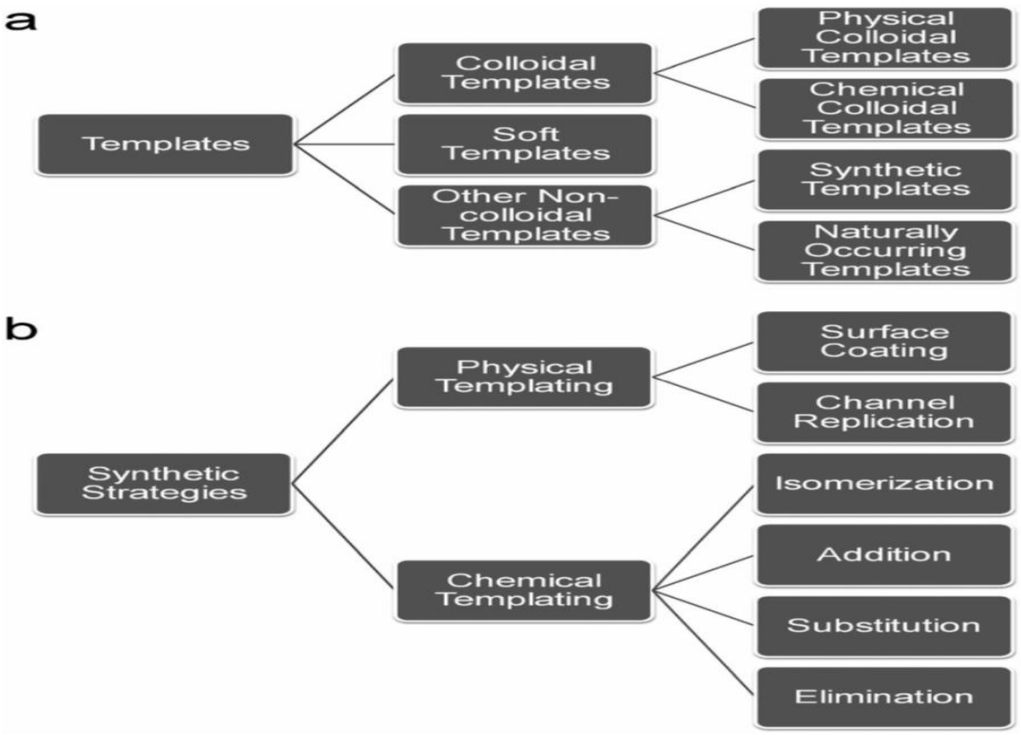


Fig. 2. Classification of various templates

2.3 Visible light active TiO_2:

Doping with metal and non-metal atoms imparts better activity of the TiO_2 material under visible light. Doping with various metal atoms such as Ag, Cr, V, Co, Fe etc has shown improved visible light activity in photocatalysis. Non-metals such as P, F, C, N are also used as dopants to dope TiO_2 material through different processes. It is reported that sulfur can also be used as a dopant to reduce the band-gap. Due to larger ionic size it is more difficult to dope with sulfur than doping with nitrogen. Doping of sulfur of oxidation state S^{6+} is more likely than S^{2-}. Although there are various methods for doping sulfur into TiO_2, sol gel method is more advantageous as compared to the others regarding simplicity and better control over size. [3]

2.4 Photocatalysis:

Photocatalysis means photon assisted reaction enhanced by a catalytically active material rather than light acting as a catalyst in reactions.[6-8] If the photo-excitation step takes place in an adsorbate molecule and then it reacts with the catalyst in the ground state, the process is called catalyzed photoreaction. If the initial photo-excitation step occurs in the catalyst material and the catalyst in the excited state reacts with the adsorbate molecule in the ground state, the process is referred to as sensitized reaction. Usually, heterogeneous photocatalysis refers to semiconductor-sensitized photocatalysis or simply semiconductor photocatalysis.[9-10] Photocatalytic activity makes TiO_2 an excellent material for various applications such as dye sensitized solar cells, water purification, anti-bacterial action etc. In purification of water by degradation of organic pollutants, a photocatalytic material simply catalyzes degradation of the pollutant in the presence of light in a photocatalytic reaction.

2.4. TGA (Thermogravimetric Analysis):

Thermogravimetric Analysis is a characterization method to investigate the physical and chemical properties of a material as a function of temperature in a controlled atmosphere. TGA gives the measurement of mass of the sample with variation of temperature. From the characteristics of the mass vs temperature plot, different physical and chemical changes occurring throughout the temperature variation can be known. This method of characterization is useful for a wide range of materials such as thermoplastics, elastomers, thermosets, metals, metal oxides, ceramics etc. A TGA combined with DSC (Differential Scanning Calorimetry) instrument even allows you to study thermal events without a mass change such as glass transition, melting or other solid-solid transitions.

2.5 XRD Analysis (X-Ray Diffraction):

Atomic scale structural correlations are investigated directly and nondestructively through X-ray diffraction experiments. Characteristic X-ray scattering pattern are easily obtained for any crystalline material. The patterns are highly sensitive to the variation of structural order of the

crystalline material. Large sample areas are covered efficiently by specially arranged X-ray topography methods. In the semiconductor industry, all these features are very useful because it is very important to control crystallinity of a material perfectly for fabrication of devices. The basic equation of X-ray diffraction is given by Bragg`s law. The crystallinity of a material is investigated by obtaining the X-ray diffraction pattern by varying the Bragg`s angle. A device called Goniometer rotates to vary the angle of incidence which vary the Bragg`s angle. Informations like atomic position in a crystal, chemical bonds, their disorder and various other information are also obtained from X-ray diffraction method.

2.6 RAMAN SPECTROSCOPY:

Raman spectroscopy is a spectroscopic method to gain information about molecular vibrations which can be useful for identification and quantitation of a sample. This technique involves incidence of monochromatic light (i.e. laser) on the sample and detection of the scattered light. A major portion of the light scattered have the same frequency as the source of excitation, which is known as Rayleigh or elastic scattering. The energy of a very small portion of the scattered light (ca. 10-5% of the incident light intensity) is altered from the frequency of incident laser due to interactions between the vibrational energy levels of the molecules of the sample and the incident electromagnetic waves. The plot of intensity of the "shifted" light against the frequency is called the Raman spectrum of the sample. In general, a Raman spectrum is plotted with respect to the laser frequency such that the Rayleigh band lies at 0 cm^{-1}. On this scale, the band positions will lie at frequencies that correspond to the energy levels of vibration of different functional groups. The Raman spectrum can thus be interpreted similar to the infrared absorption spectrum.

2.7 FESEM (Field Emission Scanning Electron Microscopy):

Electron Microscopy is a very important characterization tool in nanotechnology. In electron microscopy the imaging is done using electron beams. The electrons are mostly generated by heating a tungsten filament. This type of emission is called thermionic emission. Crystal of LaB6 is also used for the generation of electron beams. The use of LaB6 results in a higher electron density in the beam which provides better resolution than that with the conventional device. In a

field emission (FE) electron microscopy, the electron beam generation is not accomplished by thermionic emission. In field emission, electrons are emitted from the surface of a conductor under the influence of a strong electric field. The cathode here is an extremely thin and sharp needle of tungsten with a tip diameter of 10-100 nm. The acceleration voltage between cathode and anode is commonly in the order of magnitude of 0.5 to 30 kV, and extreme vacuum (10^{-6} Pa) is required in the column of the microscope. The resolution of images produced by FESEM is better than images of normal SEM with thermionic electron emission because the electron beam produced by field emission is 1000 smaller than the beam produced by thermal electron gun. In FESEM the penetration of low kinetic energy electrons close to the immediate material surface is reduced. Also need for placing a conducting coating on the insulating material is eliminated. High quality images are produced with almost negligible electrical charging of the samples. The major application of FESEM includes analysis of cross section of semiconductor devices for gate width, oxide film thickness and construction details, determination of thickness of advanced coating, study of biological structures, study of contaminants etc.

2.8 EDX (Energy Dispersive X-ray Spectroscopy):

EDX (Energy Dispersive X-ray Spectroscopy) is basically a technique for identification of the elemental composition of materials. The main applications of this technique include material research, troubleshooting, deformulation etc. An EDX spectroscopy system is attached to electron microscopy instruments (SEM or TEM). The EDX spectroscopy generates data in the form of a spectra where elemental analysis of the sample can be done from the peaks corresponding to different elements. A quantitative analysis of the elemental composition of the material is obtained from the plot generated. It is also possible to carry out elemental mapping and image analysis of a sample. In an approach involving multiple techniques, EDX is a very powerful tool in analysis of contamination and in investigations related to industrial forensic science. This technique can be quantitative, semi-quantitative or qualitative. It also delivers latitudinal distribution of the elements by mapping. EDX spectroscopy is a non-destructive technique. The samples can be analyzed without much preparation in this technique. Complementary techniques are also available for situations where combined data acquired from Microscopy and EDX spectroscopy is insufficient for identification of a specimen. Fourier Transform Infra-red (FTIR) Microscopy, Nuclear

Magnetic Resonance Spectroscopy (NMR), RAMAN Microscopy, X-ray photoelectron spectroscopy (XPS) or Time-of-Flight Secondary Ion Mass Spectrometry (SIMS) are the techniques available for further analysis in such situations. Typical Industries using SEM/EDX are aerospace, materials, minerals, automotive, glass, ceramics, refractories, healthcare, medical devices, semiconductors, electronics.

2.9 BET (Brunauer-Emmett-Teller) Analysis:

BET analysis is a technique to compute specific surface area of a material by using the phenomenon of physical adsorption of gas on the material surface. The computation is based on the amount of adsorbed gas used corresponding to a single layer of molecule on the material surface. Physical adsorption is governed by relatively weak intermolecular forces called Van Der Waals forces acting between the gas molecules and the exposed surface of the material under analysis. The analysis is generally done at liquid nitrogen temperature. Measurement of amount of adsorbed gas can be carried out through a continuous flow or volumetric procedure. The measurement is based on the BET equation as follows:

$$\frac{1}{\left[V_a\left(\frac{P_0}{P}-1\right)\right]}=\frac{C-1}{V_m C}\times\frac{P}{P_0}+\frac{1}{V_m C}$$

For the volumetric method the adsorbate gas usually recommended is nitrogen. Preparation of the sample before analysis is very crucial before BET analysis. For preparation for the analysis, the sample is first outgassed. Outgassing is a process where all the gases and vapors trapped in the material is removed. This is very important because, due to the presence of gases and vapors trapped in the sample the result may vary from the original values. The gas is admitted into a space above the prepared outgassed powder sample to obtain a defined equilibrium gas pressure P. Use of diluent gases, such as helium, is not necessary, although helium can be used for other reasons

(for example to measure the dead volume). In this process only pure gases are used. Gas mixtures are not employed to avoid interfering effects of thermal diffusion.

2.10 UV-Visible Spectroscopy:

Ultraviolet-Visible spectroscopy is a spectroscopy technique based on absorption of electromagnetic radiation. Light in the visible and adjacent (near-UV and near-infrared (NIR)) range is utilized in this technique. Due to absorption of certain wavelength of light for excitation of electrons from ground state to excited state, compounds have characteristic electromagnetic spectra. Thus, a compound may be determined observing the electromagnetic spectrum. Moreover quantitative investigation such as computation of concentration can also be done from this technique as absorption of certain wavelength is proportional to the concentration of the compound.

Chapter 3

Materials and Methods

3. MATERIALS AND METHODS:

3.1 MATERIALS:

3.1.1 Materials of synthesis:

The precursor chosen was TBOT (Tetra-butyl-ortho-titanate). Precursor is the compound that contains the metal element whose oxide is to be synthesized. Sigma Aldrich reagent grade TBOT (97%) was used for the synthesis. The medium in which the TBOT solution is prepared is ethanol (Merck). For Sulfur doping, Thiourea (Merck) was used a source of elemental sulfur. The template materials Kapok fiber and Banana fiber were obtained from the market. Kapok fiber is an easily available cotton like fiber used to stuff pillows, cushions etc. Banana fiber is procured from the stems of banana trees.

3.1.2 Instruments for synthesis:

For the synthesis, the sonicator used for uniform mixing of the solutions was obtained from Elmasonic. A furnace with digital temperature control system was used for the calcination of the samples.

3.1.3 Instruments for characterization:

For characterization the TGA apparatus used was STA 409C, NETZSCH Technologies. The X-ray Diffractometer used was a Rigaku Ultima-IV (Japan). The FESEM used was a NOVA NANO SEM 450 from FEI. The EDX spectroscopy apparatus attached to the FESEM apparatus was obtained from Bruker. The UV-Visible Spectrometer used is Shimadzu-3600. The BET surface area analyzer was obtained from Quantachrome. The Raman spectroscopy apparatus was obtained from Spex. For the photocatalytic study a simple experimental set up was made using a metal halide lamp from Havells and a magnetic stirrer obtained from IKA.

3.2 EXPERIMENTAL PROCEDURE:

The method of synthesis is very simple, time saving and efficient. The templates used here are sacrificial templates, which means that the templates are removed to obtain the target material. The synthesis method can be divided in to four steps. The first step is preparation of template. The second step is preparation of the precursor solution which is TBOT in ethanol. In the third step precursor molecules adsorb on the template surface. Since the template material taken is natural there is no need for modification of the surface groups of the template. When the precursor molecules adsorb on the surface of the fibers the precursor material replicates the structure of the template. After drying of the precursor coated template, the template is removed by calcination in the fourth step. During calcination along with the removal of the template, the precursor compound is converted into the target material in a reaction taking place in high temperature. After removal of the template, the structure is retained in the target material. Thus, this synthesis process has very good control over shape and size of the target material.

3.2.1 Template preparation:

The template to be used for synthesis has to be free from contaminants. The Kapok fiber and Banana fiber obtained from the market were washed in flowing water to remove dust particles and contaminants. After drying in oven, the fibers were then washed again in ethanol. The fibers were prepared to be used as templates after drying in oven completely.

3.2.2 Preparation of Precursor Solution:

A stock solution was prepared by adding 8.5 ml of TBOT to 41.5 ml of anhydrous Ethanol. The solution was put in sonicator for 5 minutes for uniform mixing. Two 100 millimolar solutions of 40 ml volume were prepared from the stock solution. The two solutions were labelled solution A and solution B. To Solution A, 0.608 gm of Thiourea was added. The solution was then put in the sonicator for 5 minutes for dissolution of Thiourea.

3.2.3 Coating of Template with Precursor:

0.4 gm of Kapok fiber was then dipped in solution A. 0.4 gm of Banana fiber was dipped in the solution B. Both the solutions were then put in the sonicator for 10 minutes. Precursor molecules were successfully adsorbed on the surface of the template fibers. The fibers were then taken out to dry in oven for 1 hour.

3.2.4 Template Removal: After drying, both the fibers were calcined at 4 different temperatures 450, 550, 650, 750 ^{0} C dividing each fibers into 4 parts. The duration of calcination was 2 hours. It has to be noted that the rise in temperature inside the furnace should not be rapid. During calcination the conversion $Ti^{4+} \rightarrow TiO_2$ takes place and the template burns out. S-doped TiO_2 hollow tubular nanostructures were obtained after calcination of the Kapok fiber template. Pure TiO_2 hollow tubular nanostructures were obtained after calcination of Banana fiber template.

After taking out the fibers for drying the both the remaining solutions were calcined at 500 ^{0} C to study the TiO_2 structure obtained without template.

Chapter 4
Results and Discussion

4. RESULTS AND DISCUSSION:

4.1 TGA (Thermogravimetric analysis):

Fig. 3 shows the plots of thermogravimetric analysis of the template materials and precursor coated templates. In the first plot for kapok fiber, the first weight loss is due to moisture loss. In the second loss the fiber burns out showing a steep decrease in weight. Complete removal takes place at about 450^0 C. In the plot for precursor coated Kapok fiber, the first loss is due to the loss of moisture and volatile compounds. The steep decrease in weight after that is due to the conversion $Ti^{+4} \longrightarrow TiO_2$ and burning of the fiber. Finally the template burns out and TiO_2 is left. In the fig. 4. TGA plots of Banana fiber and precursor coated Banana fiber are shown. The phases of weight loss are attributed to the same processes as Kapok fiber. Banana fiber burn out completely at a temperature of 500 ^{0}C.

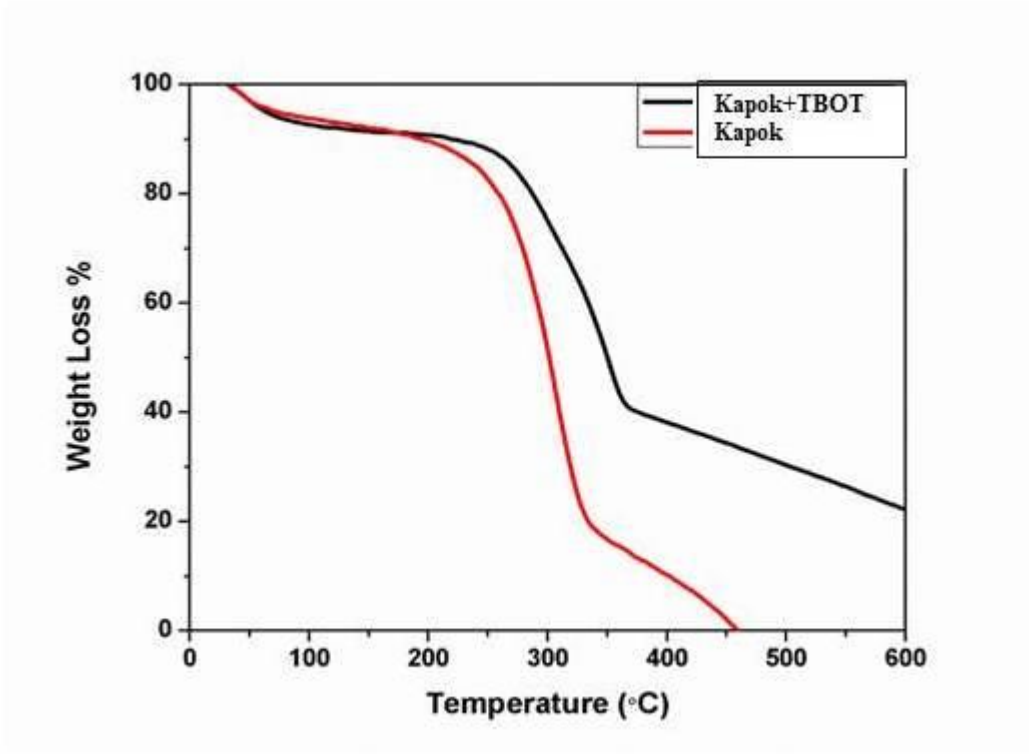


Fig. 3 TGA analysis of Kapok fiber and precursor coated Kapok fiber

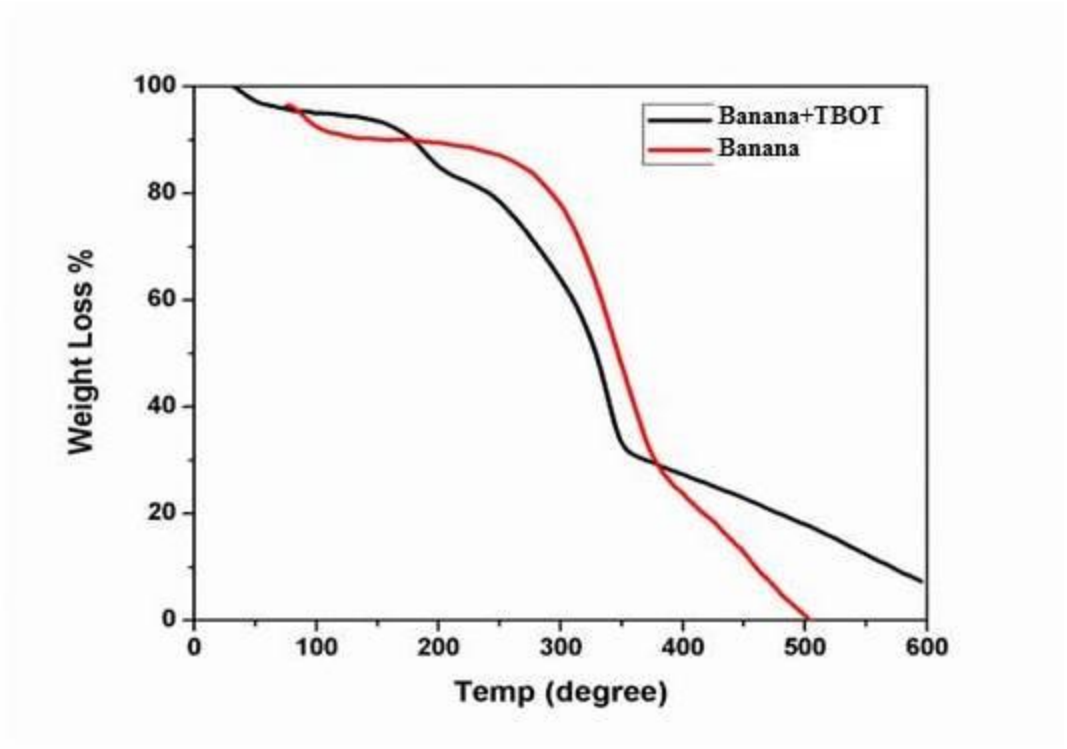


Fig. 4 TGA analysis of Banana fiber and precursor coated Banana Fiber

4.2 Physical Properties of the material synthesized:

The material synthesized using both the templates was very light in weight which is because of the hollow structure. The materials were white in color. White color is very important for its application in pigments, paints etc.

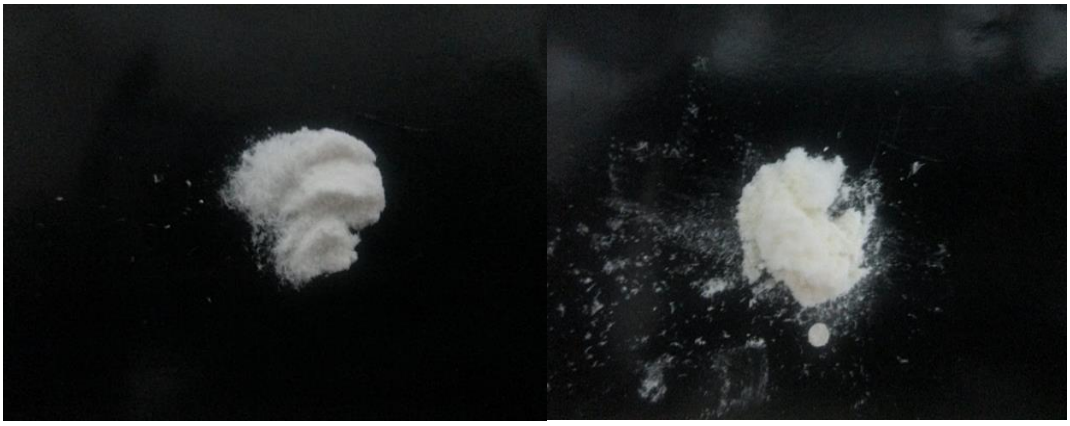


Fig. 5 Pictures of the S-doped TiO_2 and pure TiO_2 material synthesized

4.3. FESEM observation:

Fig. 6 shows the FESEM images of raw kapok fiber. The average diameter of kapok fiber is around 20 micron. Fig. 7 shows FESEM images of Raw Banana fibers. The micrograph shows how smaller fibers of 2-3 micron are forming a single fiber which is not visible with naked eyes.

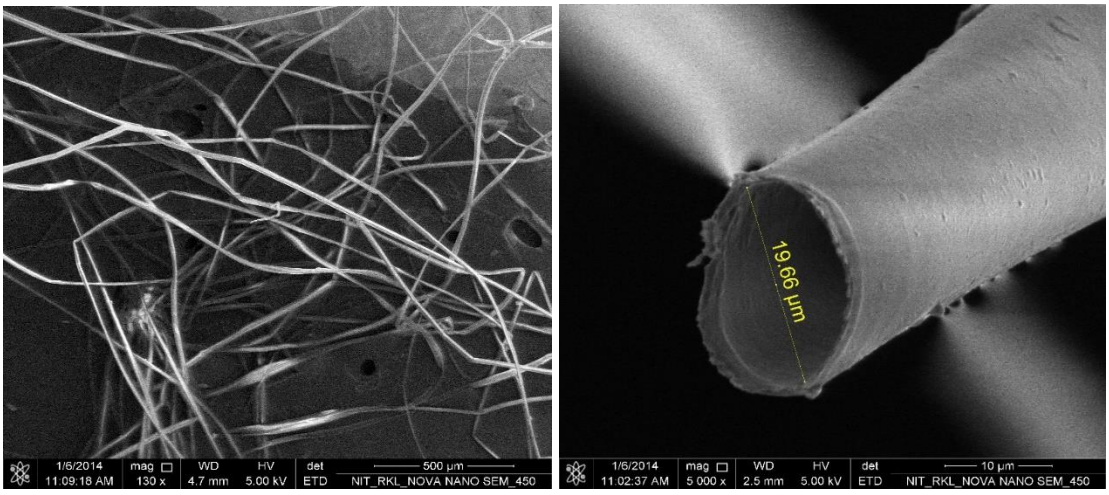


Fig. 6 FESEM micro graphs of Kapok Fiber

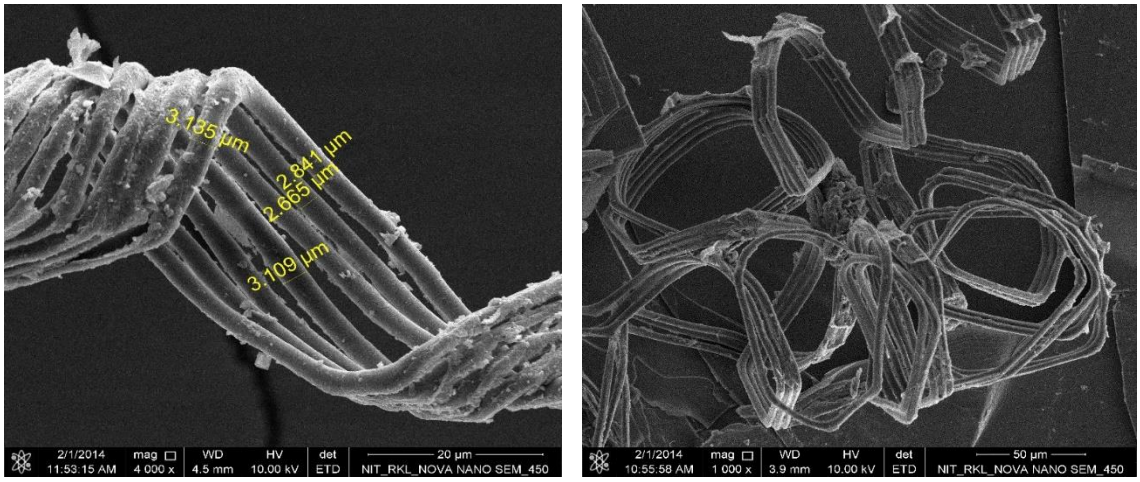


Fig. 7 FESEM micrographs of Banana Fiber

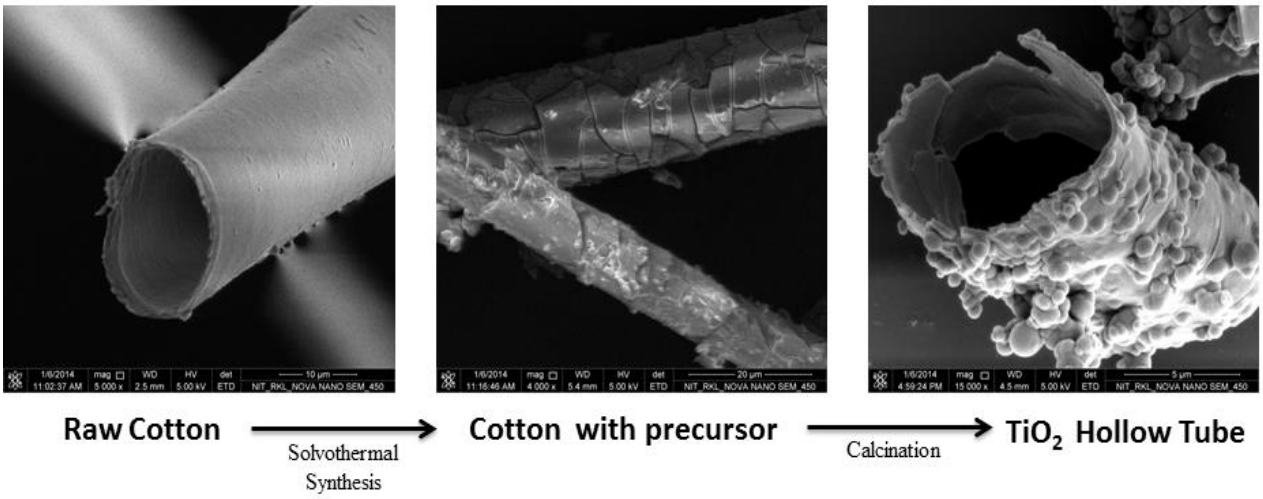


Fig. 8 FESEM images of raw cotton, cotton coated with precursor and TiO_2 particles after calcination

Fig. 8 shows the FESEM images of raw Kapok fiber without coating, fiber after coating and TiO_2 tubular particles after removal of the fiber by calcination. The first image shows the smooth, almost

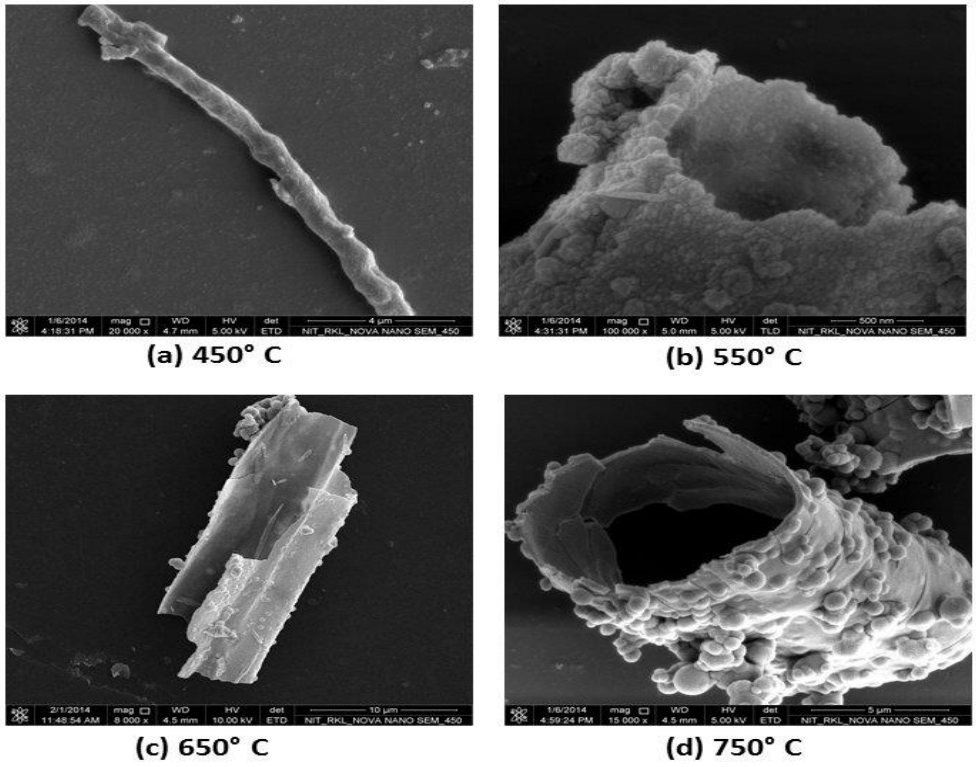


Fig. 9. FESEM images of nanostructures obtained after calcination of Kapok fiber template

perfect tubular structure of this template material. The replication of the shape of the fiber is clearly visible which indicates a high surface to volume ratio of the synthesized material. The tubular shape of the particles after calcination is apparent in the third image.

Fig. 9 shows FESEM images of Nanostructures obtained after removal of Kapok fiber template. Replication of the tubular structure is apparent from the images.

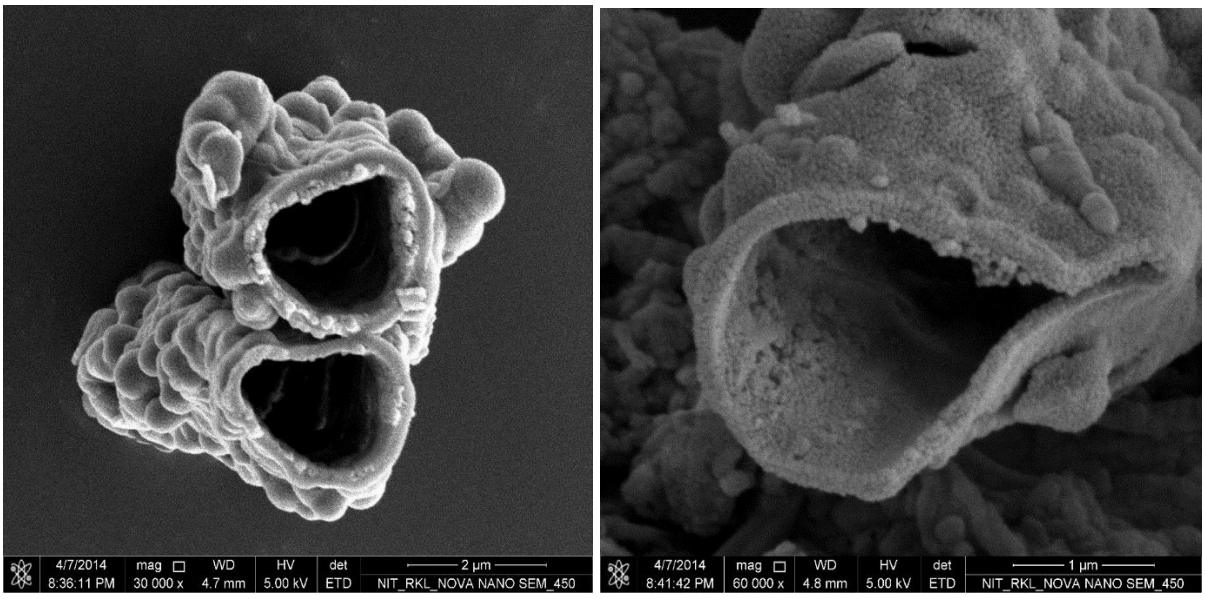


Fig. 10. Nanostructures obtained after calcination on Banana fiber Template

Fig. 10 shows FESEM images of the nanostructures obtained by synthesis using Banana fiber as the template material. Around 2 micrometer diameter of the hollow particles is apparent on the image. Due to formation of a single Banana fiber by smaller fibers close to each other, tubular structures obtained were attached to one another. In Fig. 11 a closer image of a tubular nanostructure is shown. The thickness measured on the basis of the scale given is found to be 82.07 nanometer and 91.38 nanometer. It shows that TiO_2 nanostructures formation is taking place.

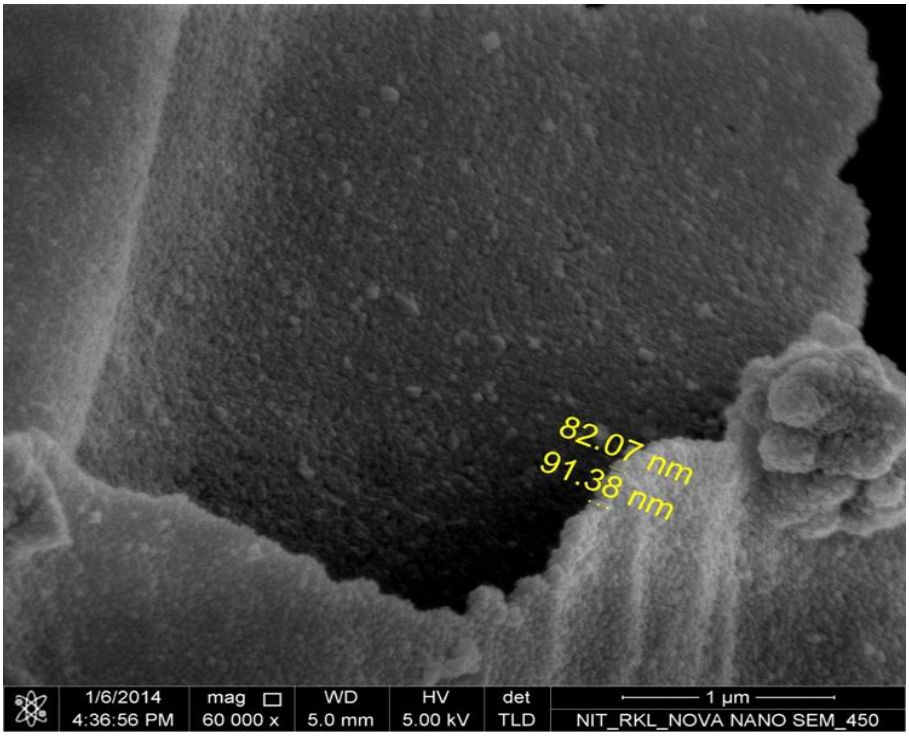


Fig. 11. Thickness of the tubular nanostructures:

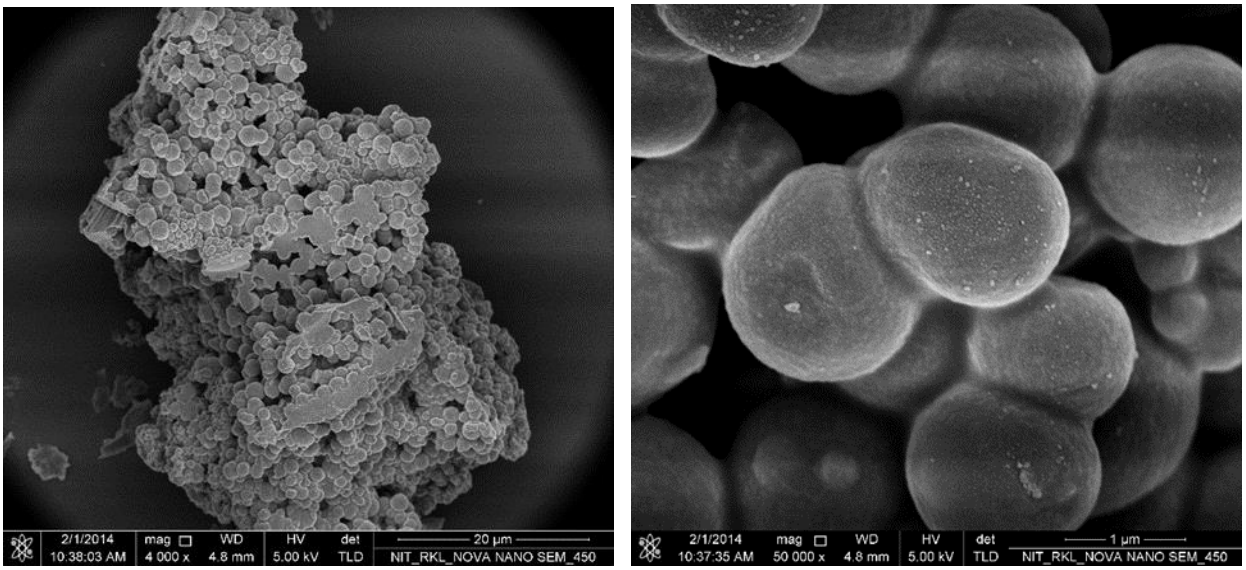


Fig. 12. Particles obtained after calcination of the precursor solution

Fig. 12 shows the FESEM micrographs of the particles produced by calcination of the precursor solution. The images show how the particles of spherical shape are agglomerating.

4.4 XRD analysis:

The X-ray diffraction technique was used to study the crystallinity and crystallite size of the samples. . Fig. 13. shows the XRD patterns of the nanostructures synthesized on Kapok fiber Template. The sharp intense peak at the Bragg angle of 25.3 is representative for anatase phase reflections in all the samples. The patterns demonstrate clearly that all of the samples are well crystallized, and the widened peaks indicate the nano-size and some defects of the samples. Variation of crystallite size with the calcination temperatures is apparent in the result. The average crystallite size decreases with increase in calcination temperature. The phase composition of all the samples is anatase.

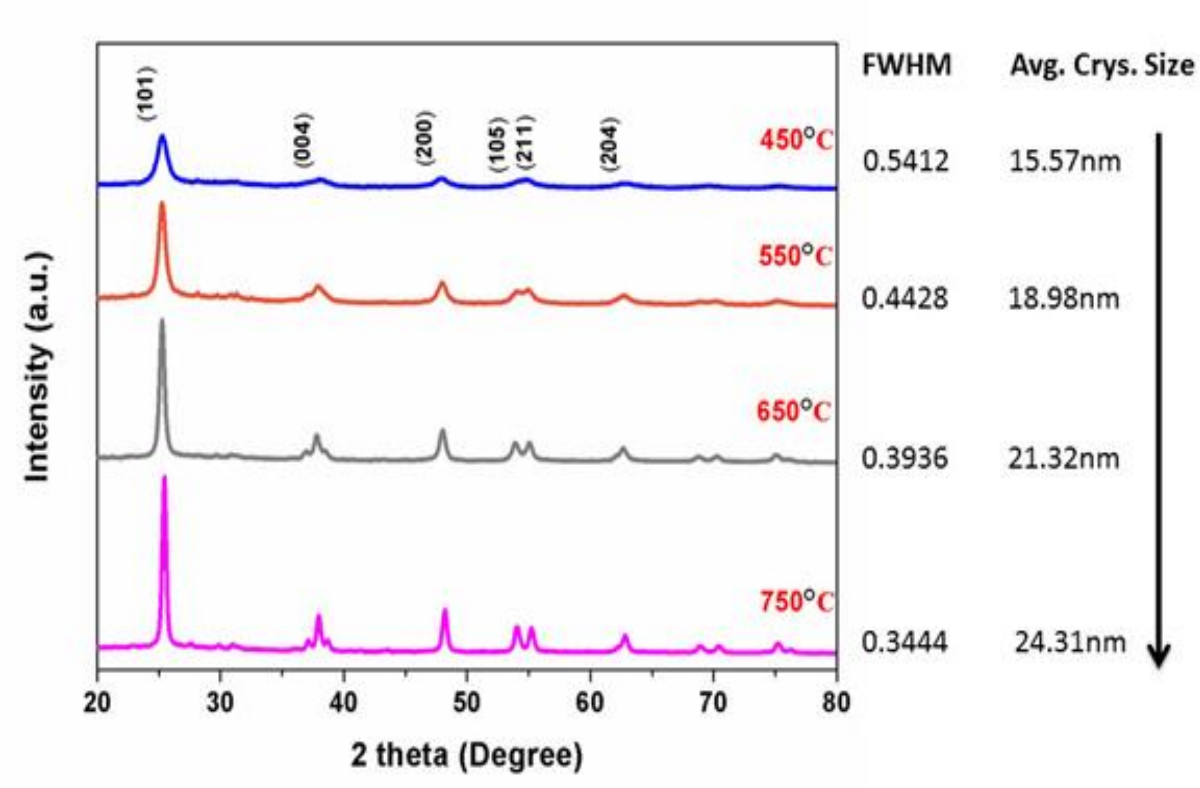


Fig. 13. XRD results of the S-doped TiO_2 synthesized on kapok fiber template

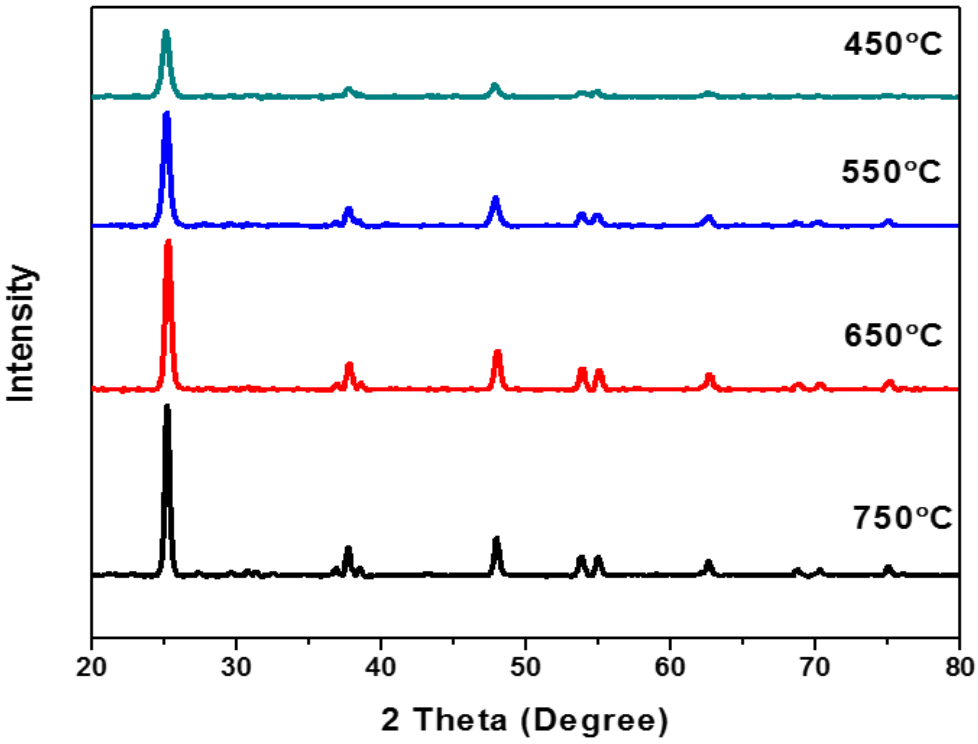


Fig. 14. XRD results of pure TiO_2 synthesized on banana fiber template

Fig. 14 shows the XRD results of the nanostructures synthesized using Banana fiber template. The peaks at 25.3 degree Braggs angle signifies anatase phase. There is no peak for rutile. The particles synthesized at four different temperatures have no rutile phase. The peaks indicate well crystallized materials.

4.5 Raman Spectroscopy Analysis:

In the XRD results of the S-doped TiO_2 it is found that even at 750 ^{0} C purely anatase phase is present. Usually above temperature 600 ^{0} C rutile phase starts to form. So Raman spectroscopy was done to confirm the anatase phase of the material. The anatase and rutile phases of TiO_2 can be sensitively identified by Raman spectroscopy Based on the Raman spectra, anatase and rutile phase of TiO_2 can be determined. The peaks for anatase phase on the Raman spectra are at 144,

197, 399, 515, 519 (superimposed with the 515 cm-1 band), and 639 cm^{-1}. The typical Raman bands for the rutile phase appear at 143 (superimposed with the 144 cm-1 band due to anatase phase), 235, 447, and 612 cm^{-1}. Additionally, the band at 144 cm-1 is the strongest one for the anatase phase and the band at 143 cm-1 is the weakest one for the rutile phase. The Raman spectroscopy result in Fig. 15 shows the material is purely anatase.

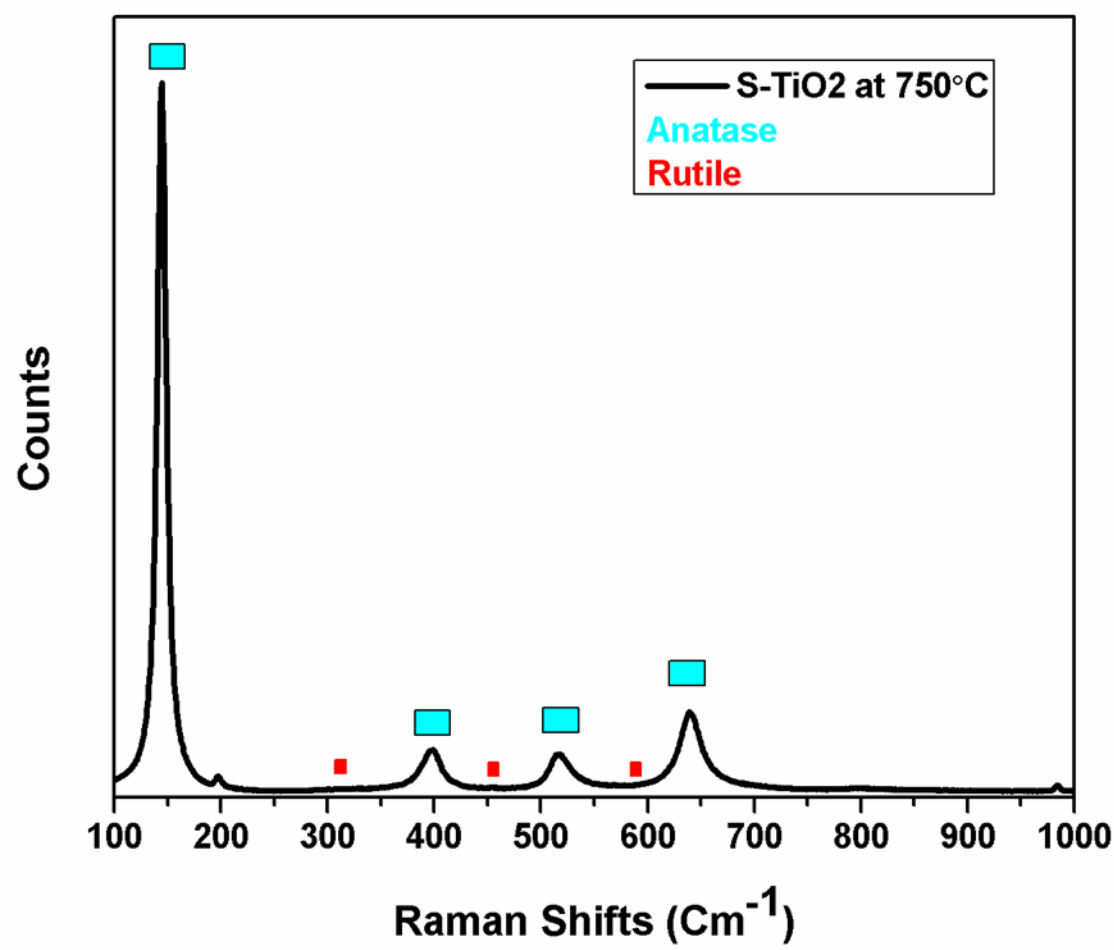
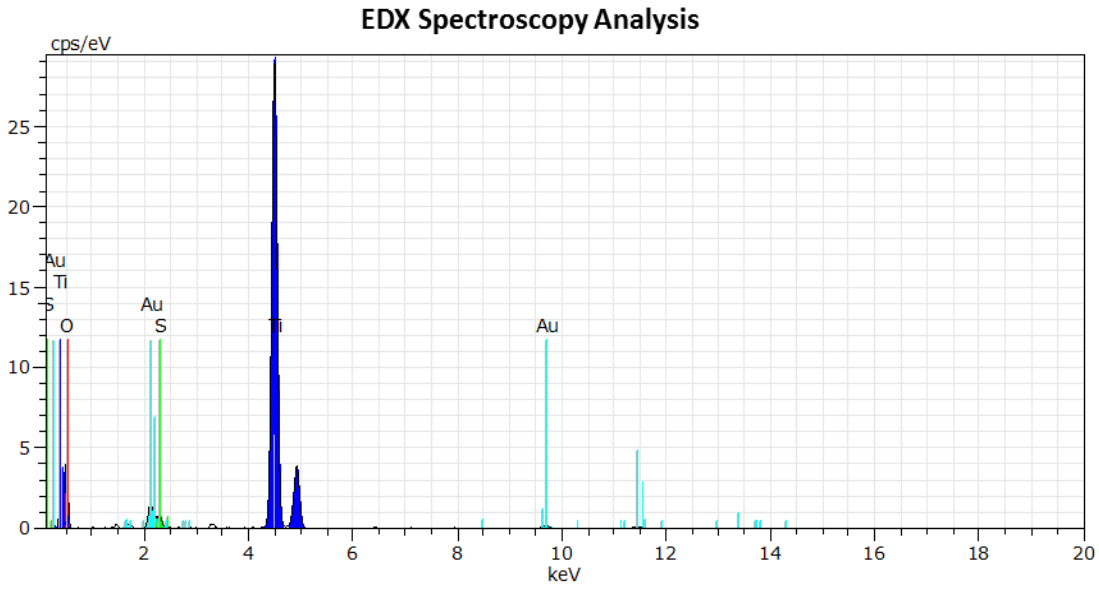


Fig. 15. Result of Raman Spectroscopy

4.6. EDX spectroscopy analysis: Fig. 16 of EDX spectroscopy result shows the elemental analysis of the synthesized materials.



Spectrum: spectrum 1.spx

El	AN	Series	Net unn. C [wt.%]	norm. C [wt.%]	Atom. C [at.%]	Error (1 Sigma) [wt.%]
Ti	22	K-series	122775	59.08	60.52	34.09	1.67
O	8	K-series	8410	37.80	38.71	65.26	5.45
S	16	K-series	2648	0.75	0.77	0.65	0.06
Au	79	L-series	1525	0.00	0.00	0.00	0.00
		Total:		97.63	100.00	100.00	

Fig. 16. EDX spectroscopy result of S-doped TiO_2 synthesized on Kapok fiber template

The table shows presence of S apart from Ti and O. The atomic percentage of O is clearly double that of Ti. Doping of elemental sulfur by .65% is confirmed in this result.

4.7 BET (Brunauer-Emmett-Teller) analysis:

BET analysis was carried out to calculate the specific surface area of the material. The table 1 shows the specific surface area values of nanostructures synthesized on Kapok fiber template. The variation of surface area with calcination temperature is observed. Specific surface area is the highest for the sample calcined at 450^0 C while it is lowest for the sample calcined at 750^0 C. The specific surface area was found to be decreasing with increase in calcination temperature. The

specific surface area of pure TiO_2 synthesized on Banana fiber template calcined at 450 ^{0} C was found to be 99.89 m^2/gm.

Calcination Temperature ^{0}C	Specific Surface area Kapok fiber Template m^2/gm
450	189.9
550	168.2
650	133.1
750	86.62

Table 1. BET specific surface area values

4.8 Photocatalytic study:

The photocatalytic activity of the samples was studied in a simple reactor set up fabricated as a part of this project. As a source of visible light a metal-halide lamp was used. A spacious wooden chamber was constructed using tough plywood material. To avoid too much heating inside the chamber, the design was made keeping the metal halide lamp outside the chamber. The light was irradiated from outside through a rectangular opening on top. The average temperature inside the chamber in three hours with the metal halide lamp on was found to be 38^0 C. No significant rise in temperature was noticed. Inside the chamber a magnetic stirrer was kept for continuous stirring. Fig. 17 shows the reactor set up used in the photocatalytic study. The photocatalytic study of the materials synthesized was done by degradation of Methylene Blue under the irradiation of simulated sunlight. 0.01 gm of the synthesized sample was taken to be mixed in a 50 ml solution of Methylene Blue in water of concentration .006 millimole. The solution with the S-doped TiO_2

Fig. 17. Set up for Photocatalytic study

was then put inside the chamber with the light on and stirring was started. In every 50 minutes 2 ml of the solution was taken out till the color faded to almost colorless. The samples collected were then analyzed in the UV spectrometer to determine the absorption spectrum. Same procedure was followed for the TiO_2 sample synthesized on Banana fiber template calcined at 450 ^{0} C.

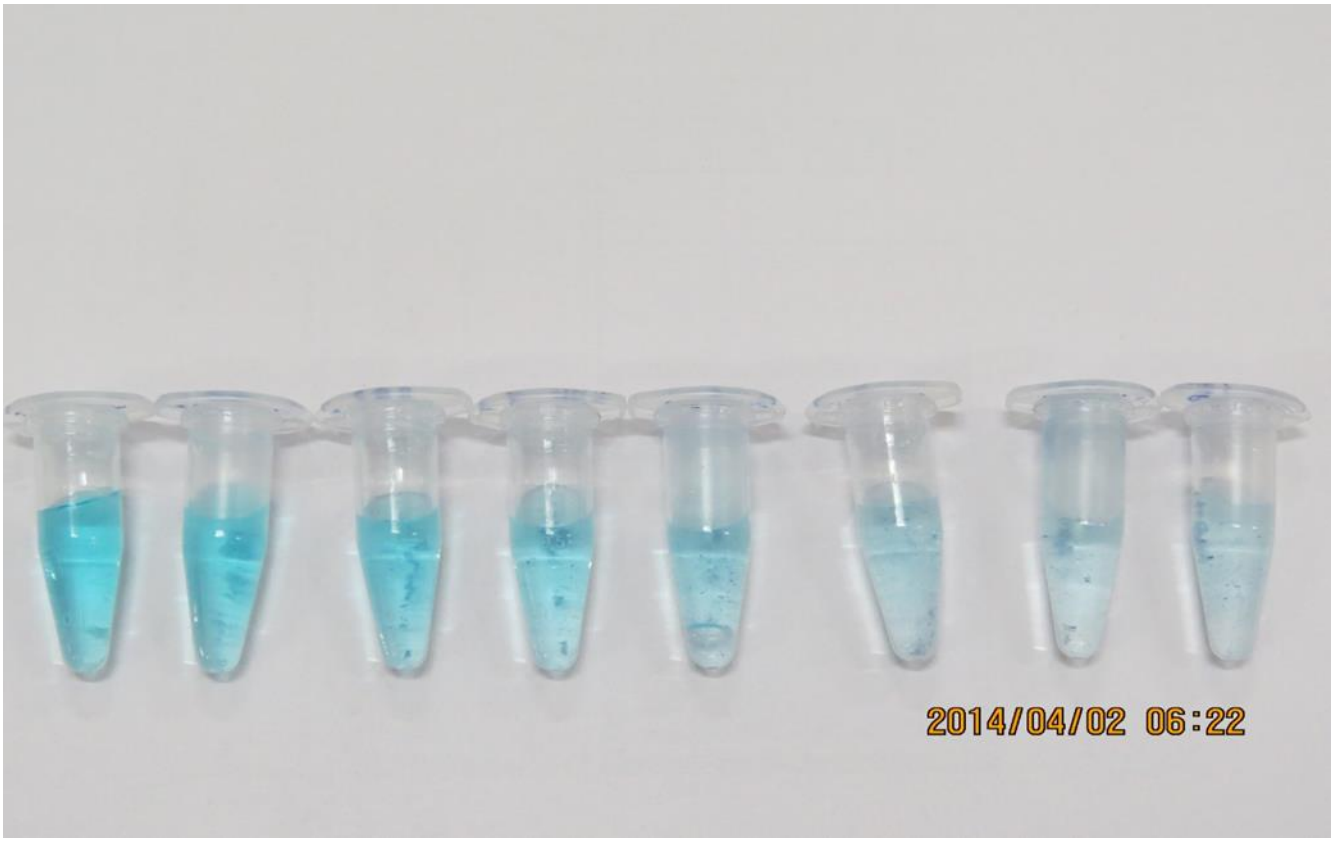


Fig. 18. Degradation of MB in presence of S-doped TiO_2 in visible light

Fig. 18 shows how the color of methylene blue solution is fading to almost white in 6 hours due to degradation by S-doped TiO_2 under the irradiation of visible light. Figure.19 and Figure.20 shows the plot of Percentage of remaining dye Vs. Time. The plot shows the decreasing concentration of MB with time. Figure.15 shows the degradation of MB with time in presence of S-doped TiO_2 sample. After 350 minutes only 8% dye remains. While Figure.16 shows that the degradation is slower with pure TiO_2 synthesized on Banana fiber template. The dye remaining in this case at 350 minutes is 30%. This result shows doping enhanced the photocatalytic activity of the S-doped TiO_2 material.

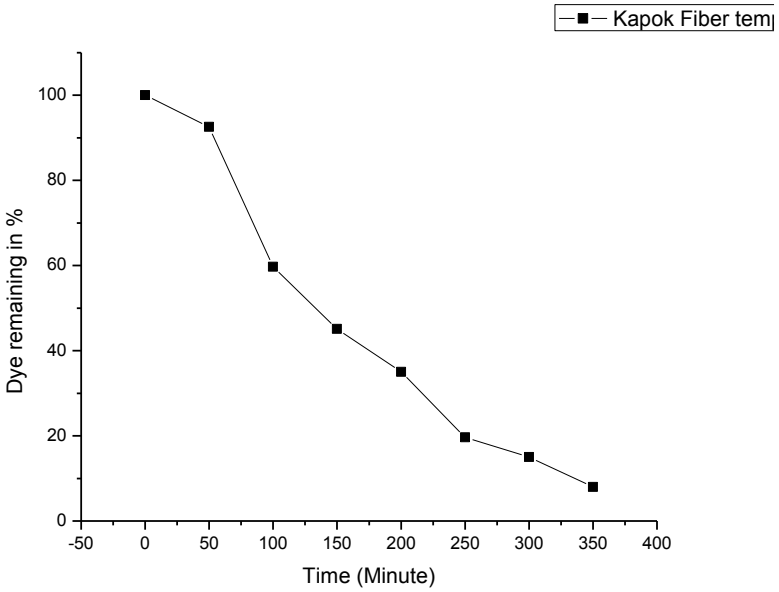


Fig.19. Degradation Plot of MB by S-doped TiO_2 synthesized on Kapok fiber template

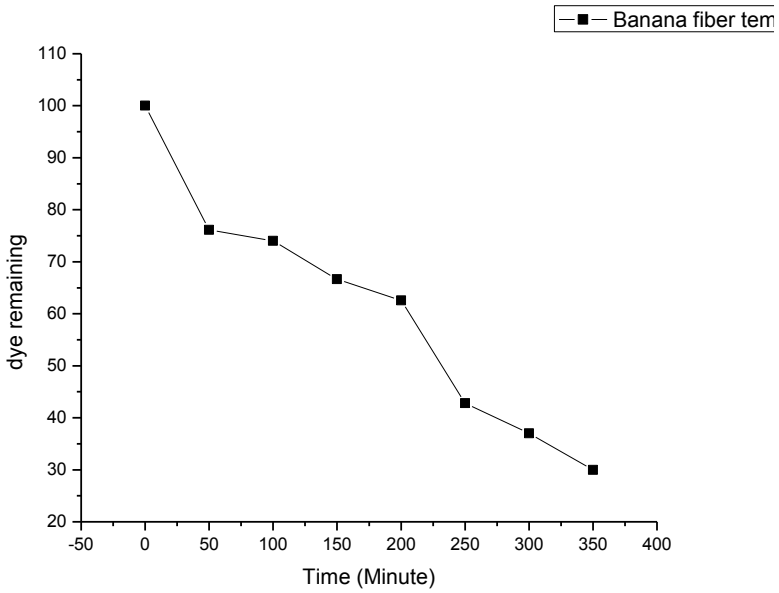


Fig. 20. Degradation Plot of MB by pure TiO_2 synthesized on Banana fiber template

Chapter 5

Conclusion

5.1 CONCLUSION:

High surface area nano-structured S-doped TiO_2 and pure TiO_2 were synthesized by a facile method using Kapok fiber and Banana fiber as sacrificial templates. The method of synthesis without any requirement of surfactant was simple and time saving. It was found that the material synthesized was purely anatase even when the calcination temperature exceeds 600^0 C. TiO_2 synthesized at calcination temperature $750\ ^0$ C was found to be purely anatase. The nanostructures obtained replicates the structure of the templates. The hollow tubular structures indicates high specific surface area. The specific surface area of the TiO_2 synthesized on Kapok fiber template by calcination at $450\ ^0$ C was found to be four times the commercial TiO_2 (P25) available in the market. The material obtained is very light and white in color. The effect of doping and high surface area is reflected in the photocatalytic study. Under the irradiation of visible light, Methylene Blue was degraded from dye percentage of 100% to 8% in 350 minutes. Banana fiber is proved as an easily available and economical template material for synthesis of tubular nanostructures of TiO_2.

References:

(1) **Yiding Liu, James Goebl and Yadong Yin,** Templated synthesis of nanostructured materials, Chem. Soc. Rev., 2013, 42, 2610.

(2) **Xiaobo Chen** and **Samuel S. Mao**, Titanium Dioxide Nanomaterials: Synthesis, Properties, Modifications, and Applications, Chem. Rev. **2007,** 107, 2891-2959.

(3**) Miguel Pelaeza, Nicholas T. Nolanb, Suresh C. Pillai b, Michael K. Seeryc, Polycarpos Falarasd, Athanassios G. Kontosd, Patrick S.M. Dunlope, Jeremy W.J. Hamiltone, J. Anthony Byrnee, Kevin O'Sheaf, Mohammad H. Entezarig, Dionysios D. Dionysiou**, A review on the visible light active titanium dioxide photocatalysts for environmental applications. Applied Catalysis B: Environmental 125 (2012) 331– 349.

(4) **Fujishima, A.; Honda, K.** Nature 1972, 37, 238.

(5) **Gupta Shipra Mital & Tripathi Manoj,** A review of TiO2 nanoparticles, Chinese Science Bulletin, June 2011, Vol.56 No.16: 1639–1657.

(6**) Gratzel M**. Nature 2001, 414, 338.

(7) **Gratzel M**. J. Photochem. Photobiol. A 2004, 164, 3.

(8**) Gratzel M.** MRS Bull. 2005, 30, 23.

(9) **A. Mills, S. Le Hunte**, Journal of Photochemistry and Photobiology A 108 (1997) 1–35.

(10) **P. Suppan,** Chemistry and Light, Royal Society of Chemistry, Cambridge, 1994.

(11) **A. Testino, I.R. Bellobono, V. Buscaglia, C. Canevali, M. D'Arienzo, S. Polizzi, R. Scotti, F. Morazzoni,** Journal of the American Chemical Society 129 (2007) 3564–3575.

(12) **Lorant Szatmarya** *et al*, Sulphur doped nanoparticles of TiO2, Catalysis Today 161 (2011) 23–28.

(13**) Chongyin Yang, Zhou Wang, Tianquan Lin, Had Yin, Xujie Lü, Dongyun Wan, Tao Xu, Chong Zheng, Jianhua Lin, Fuqiang Huang, Xiaoming Xie, and Mianheng Jiang**. Core-Shell

Nanostructured “Black” Rutile Titania as Excellent Catalyst for Hydrogen Production Enhanced by Sulfur Doping. Just Accepted Manuscript. Publication Date (Web): 28 Oct 2013.

(14) **Tao Zheng, Ze Tian, Boat Su, and Ziqiang Lei**, Facile Method To Prepare TiO2 Hollow Fiber Materials via Replication of Cotton Fiber, Ind. Eng. Chem. Res. 2012, 51, 1391–1395.

(15) **Yian Zheng** *et al*, Kapok fiber oriented-polyaniline nanofibers for efficient Cr (VI) removal, Chemical Engineering Journal 191 (2012) 154– 161

(16) **Youngbaek Kim**, Small Structures Fabricated Using Ash-Forming Biological Materials as Templates, Biomacromolecules 2003, 4, 908-913.

(17) **Xiaobo Chen and Samuel S. Mao**, Titanium Dioxide Nanomaterials: Synthesis, Properties, Modifications, and Applications, Chem. Rev. 2007, 107, 2891-2959.

(18) **Bernd Wickleinab and German Salazar-Alvarez**, Functional hybrids based on biogenic nanofibrilsand inorganic nanomaterial, J. Mater. Chem. A, 2013, 15469.

(19) **Zhongbing Huang***et al*, Preparation and characterization of the biomineralized zinc oxide particles in spider silk peptides, Journal of Colloid and Interface Science 325 (2008) 356–362.

(20) **Rui-Qin Sun** *et al*, Synthesizing nanocrystal-assembled mesoporous magnesium oxide using cotton fibres as exotemplate.