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INFLUENCE OF CHITOSAN ON THE SURFACE MORPHOLOGY OF TITANIUM DIOXIDE NANO PARTICLES

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ABSTRACT

Nanotechnology offers potential benefits to almost all industries and products. Titanium oxide (TiO2) nanoparticles exhibit unique physical and chemical properties which makes Titanium oxide suitable for various applications. In this work Titanium Dioxide nano particles were synthesized using a wet chemical method. The biopolymer chitosan was used as the precursor for the reaction. Synthesized nano particles were characterized using XRD, SEM, FTIR and spectroscopy. XRD was used to study the crystalline phase and size of TiO2 nano particles. Titanium Dioxide (TiO2) prepared by precipitation method showed rutile form with lower particle size at the calcination temperature 1000 0C. The X-ray diffraction and FTIR results indicate that the synthesized nanoparticles have only the rutile structure without the presence of any other phase impurities. SEM morphologies showed that TiO2 prepared by wet chemical synthesis gave spherical shaped nanoparticles of rutile TiO2. The size of the obtained nano particles comes under the range of 12 to 24 nm.

KEYWORDS: Titanium Dioxide, Synthesis, Wet chemical method, Chitosan.

INTRODUCTION

Titanium dioxide, also known as Titania, is a naturally occurring oxide of metal Titanium. Titania is a very well-known and well researched material due to the stability of its chemical structure, biocompatibility, physical, optical, and electrical properties. It is a colourless fine powder, high glossiness, low oil absorption, high weather resistance and high dispersability. Its photo catalytic properties have been utilized in various environmental applications to remove contaminants from both water and air [1]. Titanium dioxide (TiO_2) is a semiconducting transition metal oxide material which exhibits unique characteristics such as low cost, easy handling, non-toxicity and resistance to photo chemical and chemical erosion. In recent years TiO_2 has been widely used for the preparation of different types of nanomaterials, including nanoparticles, nano rods, nano wires, nanotubes, and mesoporous and nanoporous TiO_2 – containing materials [2] .

TiO_2 is a wide band gap semiconductor material which can be used for UV photo detector fabrication [3]. This material crystallizes in three major phases: rutile (tetragonal), anatase (tetragonal), and brookite (orthorhombic) [4]. Among the structures, rutile is the most stable one while anatase and brookite are meta stable phases at ambient temperature. TiO_2 nanoparticles below 40 nm, anatase seemed more stable and transformed to rutile at greater than 973 K [5]. Rutile TiO_2 has direct and indirect band gaps. Its direct band gap makes TiO_2 useful for photo detector fabrication [6]. The properties of titanium dioxide include high refractive index, light absorption, non-toxicity, chemical stability and relatively low-cost production [7-11].

Numerous methods were introduced to synthesize Titanium dioxide nano particles. The methods used for the synthesis of TiO_2 nano particles have included methods such as solvo thermal method [12], sol-gel method [13], hydrothermal method [14], direct oxidation method [15], electro deposition [16], sonochemical method [17], and microwave method [18] and other approaches, although new methods and modifications of the existing methods have been attempted with great frequency for the preparation of TiO_2 nano particles.

In this study a simple, cost effective, and environment friendly method introduced to synthesize rutile Titanium dioxide nano particles by using chitosan as a precursor via wet chemical method. It was very simple and successfully prepared the Titanium dioxide nano powder. The biopolymer Chitosan will help to control the nanoparticles size and dispersion due to the expansion during calcination. This method is suitable for large scale production of Titanium dioxide nano powder.

MATERIALS AND METHODS

Materials

Titanium tetra chloride and Urea supplied by Spectrochem, Mumbai ,India, Glacial acetic acid supplied by SD fine chem. Limited, Worli, Mumbai, Chitosan obtained from CIFT Cochin were used in the present study.

Synthesis

For the preparation of Titanium Dioxide nano particles, 50 mL Titanium tetra chloride slowly added to 200 mL distilled water in an ice cool bath. Titanium tetrachloride is a highly fuming, corrosive liquid. To get a homogeneous solution, the beaker was kept in a magnetic stirrer for 30 minutes at room temperature. Chitosan dissolved in 4% acetic acid and blended with the above solution. Bath temperature rose to 100 ^{0}C and colour of the solution gradually turns to white. The solution was kept at the same temperature till nanoparticles were completely formed. In another vessel 26 gm of urea was dissolved in 250 mL of distilled water. From the vessel 150 mL of urea solution was added to the beaker. The solution was allowed to settle down. White precipitate settles down properly. Centrifuged and washed the precipitation with water and ethanol. This centrifuging and washing was repeated for three times. It was kept for two hours calcinations in a muffle furnace at 1000 ^{0}C to burn out Chitosan and to obtain nano sized Titanium dioxide particles. The obtained powder was stored in small air tight bottles. The same procedure was used, to prepare the sample without using chitosan as precursor.

***XRD analysis*:** After thoroughly cleaning the sample holder, the TiO_2 nano powder synthesized was spread on the sample holder. The sample was then placed inside the XRD machine (Model-DY-1656) and the sample was investigated to understand the phase(s) and size of the TiO_2 nano powder.

***FT-IR Analysis*:** The TiO_2 nano powder was mixed with KBr at the ratio of 1:100. The mortar and pestle was thoroughly cleaned with acetone and the mixture of TiO_2 powder and KBr was crushed. The TiO_2 powder and KBr mixture was then put into the disc which was placed on a holder placed inside the FT-IR (Shimadzu IR Affinity-1 Spectrophotometer) machine to investigate the unknown materials present in the sample.

SEM Analysis: The sample of TiO_2 nano powder was affixed to a metallic stub which is placed on the sample holder. The sample holder was then fixed on a rotatable disc inside the machine and the TiO_2 nano powders were ready for SEM. The surface morphology of the powder sample was observed on SEM (JEOL-JSM 5800) operated under low vacuum at an accelerating voltage of 25 kV to get the sharp image of the sample.

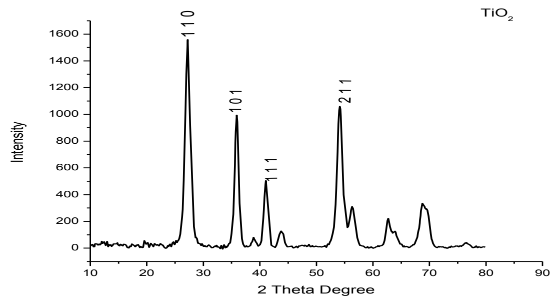
RESULTS AND DISCUSSION

XRD

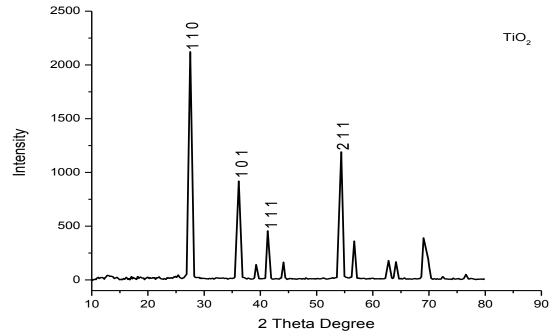
After thoroughly cleaning the sample holder, the Titanium dioxide nano powder synthesized by wet chemical method was spread on the sample holder. The sample was then placed inside the XRD machine (Model-DY-1656) and the sample was investigated to understand the phase(s) and size of the Titanium dioxide nano powder. The average crystallite size (D) of the Titanium dioxide was calculated using Debye-Scherrer equation.

$$D = \frac{0.9\lambda}{\beta \cos\theta}$$

D = shape factor, λ = x-ray wavelength, β = FWHM of diffraction peak, θ = Bragg angle.
The grain size was calculated to be 12-24 nm. Figure1.given below shows the XRD pattern of the synthesized Titanium dioxide nano powder. It was concluded that all of the peaks obtained in the XRD pattern of Titanium dioxide nano powder matched perfectly with the standard rutile structure (JCPDS file 21-1276) and the XRD pattern of Titanium dioxide of other literature. Strong peaks at 27 ^{0}, 36 ^{0}, 41 ^{0} and 54 ^{0} indicated Titanium dioxide in the rutile phase. When particle size is less than 100 nm, appreciable broadening in X-Ray Diffraction lines will occur. Diffraction pattern will show broadening because of particle size and strain.



(a)

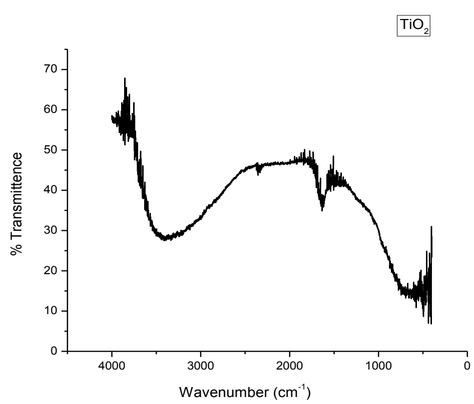


(b)

Figure1. XRD spectrum of TiO_2 nanoparticles samples: Synthesized TiO_2 nanoparticles using chitosan as precursor (a); Synthesized TiO_2 nanoparticles without using chitosan as precursor (b)

FOURIER TRANSFORM INFRARED (FT-IR) SPECTROSCOPY

The Titanium Dioxide nano powder was mixed with KBr at the ratio of 1:100. The mortar and pestle was thoroughly cleaned with acetone, the mixture of Titanium dioxide nano powder and KBr was crushed. The Titanium dioxide powder and KBr mixture was then put into the disc which was placed on a holder placed inside the FT-IR (Shimadzu IR Affinity-1 Spectrophotometer) machine to investigate the unknown materials present in the sample. FT-IR analysis confirmed that the Titanium dioxide nano powder synthesized had the characteristic peak. Figure 2 shows the FTIR Spectra of synthesized Titanium dioxide nanoparticles. A sharp peak at 1588.85 cm^{-1} confirmed that the Titanium dioxide nano powder obtained was rutile. FT-IR analysis also evidenced that the powder consisted of Titanium dioxide itself.



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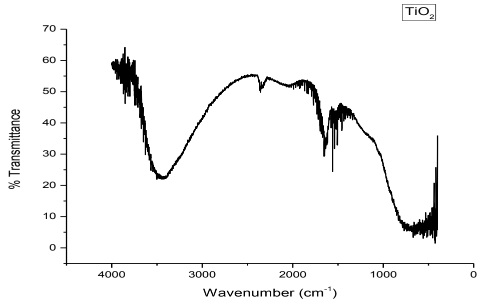
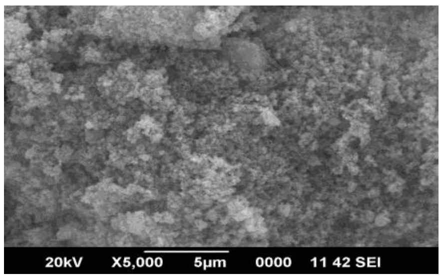


(b)

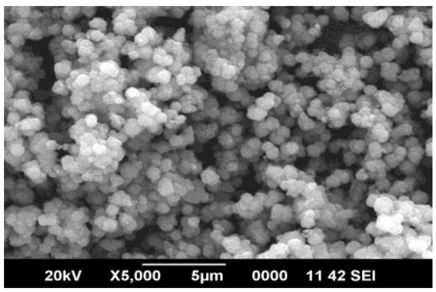
Figure 2. FTIR Spectra of TiO_2 nanoparticles samples: Synthesized TiO_2 nanoparticles using chitosan as precursor (a); Synthesized TiO_2 nanoparticles without using chitosan as precursor (b)

SCANNING ELECTRON MICROSCOPY

Scanning electron microscope is a very useful tool for studying morphology of nano powders. The surface morphology of the powder sample were observed on SEM (JEOL-JSM 5800) operated under low vacuum at an accelerating voltage of 20 kV to get the sharp image of the sample. Clear nanostructures can be seen having grain size of ~ 24 nm. SEM images of the nanoparticles prepared via wet chemical route are shown in Figure 3. So it is clear that the nanoparticles seen by SEM image consist of a number of crystallites with rutile structure. SEM images of the nanoparticles (Figure 3) show that they are approximately in spherical form and their sizes are different. Figure 3(a) shows grain size is very small and clustered. In figure 3(b) we can see large spherical sized particles.



(a)



(b)

Figure 3. SEM images of TiO_2 nanoparticles samples: Synthesized TiO_2 nanoparticles using chitosan as precursor (a) and Synthesized TiO_2 nanoparticles without using chitosan as precursor (b)

CONCLUSION

This work deals with the synthesis of nano particles of Titanium Dioxide using wet chemical method by employing Chitosan as the precursor and without using chitosan as precursor. Titanium dioxide nano particles were successfully synthesized and the estimated particle size distribution of synthesized TiO_2 nano particles has 12-24 nm according to Debye Sherrer relation. The obtained Titanium dioxide was characterized by XRD, FTIR, and SEM. XRD analysis showed that the Titanium dioxide nano powder synthesized had more stable rutile phase and the nanoparticles get more crystal- line by annealing at higher temperatures. FT-IR analysis confirmed that the Titanium dioxide nano powder obtained had the characteristic peaks. SEM images confirmed that the synthesized Titanium dioxide nano powder have rutile phase and the grain size decreases by using chitosan as precursor.

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