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RUTILE TITANIA NANOPARTICLES: EFFECT OF GELATIN ON THE SOL-GEL SYNTHESIS AND IT CHARACTERIZATION

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Abstract: Nanotechnology is all about making products in nanometer scale to gain greatly enhanced material properties and functionality. Metal oxide fine particles are widely used in industrial applications as catalysts, pigments, fillers and so on. This paper reports the effect of addition of gelatin on the properties of TiO_2 nanomaterials, synthesis and characterization. Rutile titanium dioxide nanoparticles were synthesized by a simple and cost-effective sol gel method using titanium isopropoxide as a precursor with 2- propanol and water as solvents. Gelatin was used as a gelling agent in the synthesis as it can provide long-term stability for nanoparticles by preventing particles agglomeration. XRD was used to study the crystalline phase and size of TiO_2 nanomaterials. The X-ray diffraction studies indicate that the synthesized nanoparticles have only the rutile structure without the presence of any other phase impurities and the sizes of TiO_2 nanoparticles synthesized without using and using gelatin are 40 nm and 20 nm respectively. Additionally, the TiO_2 nanoparticles are characterized by FTIR spectroscopy and SEM. The results indicate that gelatin solution is a reliable and cheap green gelling agent that can be used as a matrix in the sol-gel method to synthesize TiO_2 nanoparticles.

Index Terms: TiO_2 nanoparticles, rutile, sol-gel synthesis, gelatin.

I. INTRODUCTION

Nanostructure science and technology is a broad and interdisciplinary area of research and development activity that has been growing explosively worldwide in the past decade [1]. It has the potential for revolutionizing the ways in which materials and products are created and the range and nature of functionalities that can be accessed. It is already having a significant commercial impact, which will assuredly increase in the future.

Titanium dioxide, also known as Titania, is a naturally occurring oxide of titanium. TiO_2 nanomaterials are one of the attractive materials for scientists and physicists due to their properties and are widely used in many technological applications. It has the advantage of being cheap, nontoxic and stable. [2]. The properties of TiO_2 include high refractive index, high dielectric constant, chemical stability and wide band gap [3]. Due to their versatile properties, TiO_2 nanomaterials have possessed themselves vast applications, including pigments, toothpaste, paint, UV protection creams, photo-catalysis, solar cells, water and air purification, synthesis of inorganic membranes, photovoltaics, electrochromics, photochromics etc. [4, 5].

Titanium dioxide exists mainly in three crystalline polymorphos, namely, anatase, rutile and brookite. Anatase and rutile have a tetragonal structure, whereas brookite has an orthorhombic structure. Recently, oxygen deficient λ-Ti_3O_5, having a monoclinic crystal structure and photo-reversible characteristics has been discovered [6, 7]. Among the structures, rutile is the most stable one, while anatase and brookite are metastable phases at ambient temperature.

Pottier *et al* [8] synthesized nanocrytalline TiO_2 by precipitation routes, Kim *et al* [9] by microemlusion techniques, Music *et al* [10] and Bersani *et al* [11] by sol-gel methods, Melendres *et al* [12] used physical or chemical vapor deposition technique and Tang *et al* [13] synthesize by organometallic routes. Frequently hydrolysis of alkoxides is used to produce TiO_2 nanopowders.

Hwu et al observed the crystal structure of TiO_2 nanoparticles depend on the preparation method. For TiO_2 nanoparticles below 40nm, anatase seemed more stable and transformed to rutile at greater than 973K [14]. Banfield et al found that prepared TiO_2 nanoparticles had anatase and/or brookite structures, which transformed to rutile after reaching a certain particle size [15]. Once rutile was formed, it grew much faster than anatase. They found that rutile became more stable than anatase for particle size greater than 14nm. Anatase and rutile are commonly obtained by hydrolysis of titanium compounds, such as titanium tetrachloride ($TiCl_4$) [16-18] or titanium alkoxides ($Ti(OR)_4$), in solution [19-22]. Tianyou Peng et al reported the stability of anatase form up to 800 ^{0}C prepared by hydrothermal synthesis [23]. S Mahshid et al reported the formation of anatase phase by hydrolysis of titanium isopropoxide solution and nanoparticles shows anatase to rutile transformation at the temperature lower than 600 °C [24].

The focus of the present work is to synthesize high efficient nanosized titania particles having large surface area using water-soluble gelatin as a gelling agent via sol-gel method. The gelling agent will help to control the nanoparticles size and dispersion due to the expansion during calcination. Because of its solubility in water and its ability to associate with metal ions in solution, gelatin has been used as a binder cum gel forming material in forming the shape of porous ceramics and bulks [25-27]. Furthermore, the surface morphology and size of the rutile titanium dioxide nanoparticles were identified and analyzed using different techniques such as XRD, FTIR and SEM studies.

II. MATERIALS AND METHODS

The nanoparticles were prepared by simple the sol-gel technology. All chemicals used were analytical reagents. Titanium tetraisopropoxide (Sigma Aldrich,USA), 2-propanol (Merk Speticlities Pvt. Ltd.,Mumbai), Nitric acid (s.d. fine-CHEM Ltd., Mumbai) and gelatin (s.d. fine-CHEM Ltd., Mumbai) were used as raw materials to synthesize nano TiO_2

A. Synthesis of TiO_2 nanoparticles

Nano-sized TiO_2 powder was synthesized via, a sol-gel method using titanium tetraisopropoxide (TTIP), 2- propanol and deionized water as starting materials. A fixed amount of a mixture of 2- propanol and deionized water was added in drops into TTIP solution in the molar ratio (2-propanol : TTIP : H_2O = 1:2:12) while magnetic stirring was applied at the same time. When the addition was completed, 15 wt% gelatin and nitric acid was added into the aqueous solution. pH of the solution was maintained at 2. The acid was used to restrain the hydrolysis process. The solution was stirred for 1 hour and left overnight. A two-layer solution was formed: the upper layer being, the organic by-product of the hydrolysis, and the lower layer a titanic acid gel. The gel was then collected and dried at 110 ºC for several hours, until yellow block crystals appeared. These crystals were crushed and ground into fine powder using a mortar and pestle and further calcined at 1000 ^{0}C for 2 hours. The nano powders were collected and washed first with deionized water and then with ethanol several time to remove the impurities. The characterizations were done and the reults were compared with titanium dioxide synthesized without gelatin. The hydrolysis reaction leading to the formation of TiO_2 can be represented by the following reaction:

$$\mathbf{TTIP + 2H_2O \rightarrow TiO_2 + 4C_3H_7OH}$$

B. Characterization

The structure of particles was investigated using X-ray diffraction using PANalytical, XRD machine (DY-1656). Monochromatic CuKα radiations were used as a source of 40 kV/35 mA power and the pattern was recorded in the 2θ range of 3º– 80º with a scan step of 0.02 in a scan time of 65.6seconds. IR spectrophotometer (Shimadzu, FTIR-8900, Japan) was used for obtaining IR spectra (KBr) operating in the 400–4000 cm^{-1} range. The morphology of particles was investigated using Scanning Electron Microscopy (Hitachi, JEOL-JSM 5800).

III. RESULTS AND DISCUSSIONS

A. XRD Analysis

X-ray diffraction patterns were taken to examine the crystal structure of the synthesized nano titanium dioxide particles. Crystal size was determined by measuring the broadening of a particular peak in a diffraction pattern associated with a particular planar reflection from within the crystal unit cell. It is inversely related to the FWHM of an individual peak. If the peak is broad, the crystallite size will be small and vice versa. The periodicity of individual crystallite domains reinforces the diffraction of X-ray beam, resulting in a tall narrow peak. If the crystals are randomly arranged and have low degrees of periodicity, the result is a broader peak. This is generally the case for nanomaterials.

Figure 1(a) and 1(b) represents the XRD patterns of TiO_2 prepared by sol-gel method without using gelatin and using gelatin respectively. From the XRD pattern it is clear that rutile form is observed.

As the crystallite size increases, the diffraction peak becomes narrower as in the case of TiO_2 prepared without gelatin. Broadening of peak is observed in the case of TiO_2 prepared using gelatin, is an indication of reduction in crystallite size. For TiO_2 nanoparticles synthesized by both routes, the reflections were obviously observed at 2θ angles around 27 ^{0} (110), 36 ^{0} (101), 41 ^{0} (111), 54 ^{0} (211), 56 ^{0} (220) and 69 ^{0} (301). All the diffraction peaks were in good agreement with the JCPDS file for TiO_2 (JCPDS 21–1276), which can be indexed to the tetragonal structure of rutile TiO_2. The strong and sharp diffraction peaks indicated that the TiO_2 nanoparticles were well crystallized.

The average crystallite sizes of synthesized samples were calculated from the full width at half maximum (FWHM) of the peaks using Debye-Scherrer formula:

$$\mathbf{D = 0.9\lambda / \beta \cos \theta}$$

where, D - crystallite size, λ - wavelength of CuKα radiation, β - corrected full width at half maximum (FWHM) of the diffraction (hkl) peak, θ – Bragg's angle of the X-ray diffraction peak. The average crystalline size of TiO_2 nano particles without using gelatin was in the range of 15 - 25 nm and for titania nanoparticles synthesized using gelatin, the average crystalline size was found to be in the range of 35 – 40 nm. Figure 1(a) and 1(b) shows XRD pattern of TiO_2 nano particles without gelatin and with gelatin respectively.

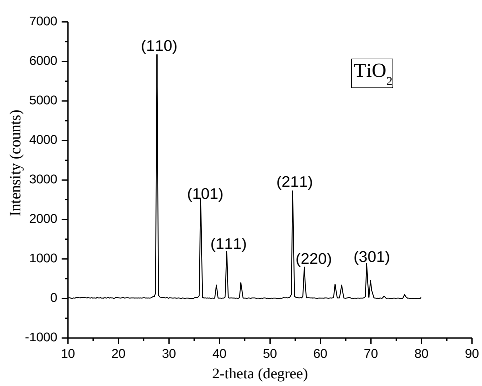

Fig:1(a). XRD of nano TiO_2 without gelatin

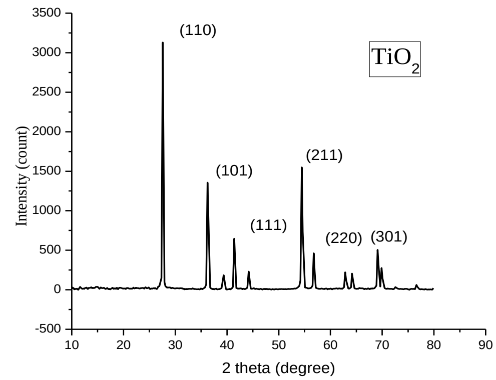

Fig: 1(b). XRD of nano TiO_2 using gelatin

B. FTIR analysis

Figure 2(a) and 2(b)) shows the FTIR spectra of TiO_2 nanoparticles synthesized via sol-gel method without gelatin and using gelatin respectively in the range of 400–4000 cm^{-1}. Titanium dioxide powder and KBr mixture (1:100) was crushed thoroughly and 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 characteristic frequencies present in the sample In this curve, a broad absorption band between 400 cm^{-1} and 800 cm^{-1} are due to bending and stretching vibrations of Ti-O-Ti. The peaks centered around 1600 cm^{-1} and 3500 cm^{-1} are the characteristic of stretching and bending vibration of the hydroxyl group. The absence of a characteristic peak around 2900 cm^{-1} regarding C–H stretching band indicates that all organic compounds were removed from the samples after calcinations. Both samples of TiO_2 exhibit similar vibration patterns. However, the only difference between the two kinds of powders was in the depth of the bands.

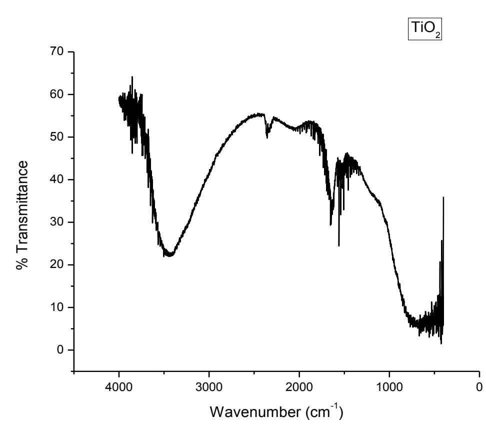

Fig: 2(a). FTIR spectrum of nano TiO_2 without gelatin

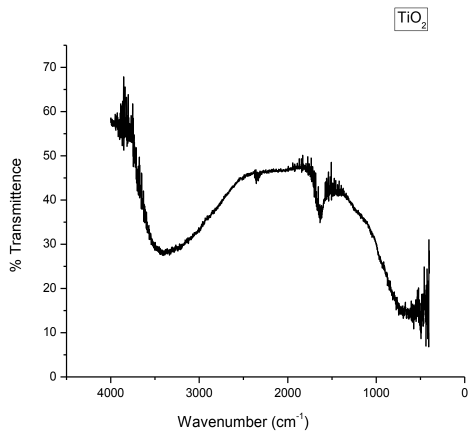

Fig: 2(b). FTIR spectrum of nano TiO_2 using gelatin

C. SEM Analysis

Scanning electron microscope is a very useful tool for studying morphology of nano powders Scanning electron micrographs of TiO_2 prepared by sol gel method without using gelatin and using gelatin are given in figure 3(a) and 3(b) respectively. By employing gelatin morphology of TiO_2 changes. In figure 3(b) small particles are observed for nano TiO_2 when compared with figure 3(a). Large particles are seen due to the high temperature of calcination. Use of gelatin provides long-term stability for nanoparticles by preventing particles agglomeration.

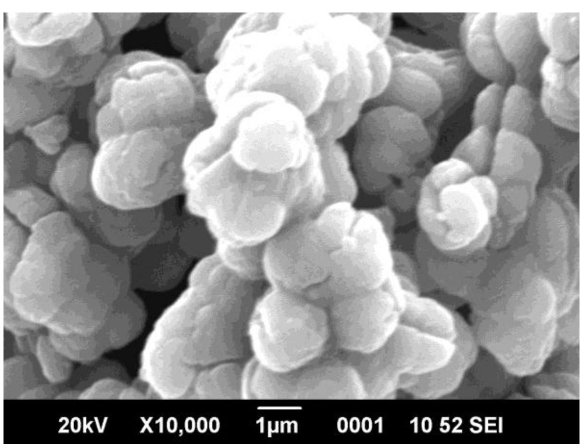

Fig: 3(a). SEM of nano TiO_2 without gelatin

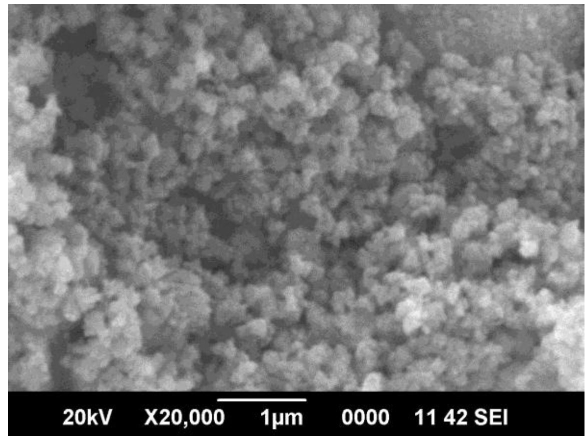

Fig: 3(b). SEM of nano TiO_2 using gelatin

IV CONCLUSIONS

Rutile titania nanoparticles were synthesized with and without water-soluble gelatin by the sol-gel method. From XRD and FTIR results, it is clear that synthesized titania naoparticles exhibited the rutile structure. XRD and SEM results indicate that using gelatin solution as a matrix improves the crystallinity and decreases the size of particles. The particle sizes of the TiO_2 nanoparticles, with and without gelatin solution were 40 nm and 20 nm, respectively. A broad absorption band between $400\,cm^{-1}$ and $800\,cm^{-1}$ in the FTIR spectrum is an indication of the bending and stretching vibrations of Ti-O-Ti. The effect of gelatin on the surface morphology of TiO_2 nano particles is clear from the SEM analysis. The results confirm that gelatin is an appropriate gelling agent for synthesizing titania nanoparticles using sol-gel method. The current simple, cost-effective and environmental friendly synthesis method using water-soluble gelatin can be extended to prepare nanoparticles of other interesting materials.

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