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Synthesis and Characterization of TiO_2 Nanoparticles

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ABSTRACT

The ever increasing interest in Titanium Oxide (TiO_2, Titania) is motivated by its applications in solar cells, biomaterials, photo catalytic activities. Nanocrystalline titania is preferred in these applications due to chemical stability, mechanical hardness, high refractive index, excellent transmission in visible region. Titania exists in three different crystallographic phases i.e. anatase, rutile and brookite. Anatase and rutile crystallizes in tetragonal phase where as brookite has orthorhombic phase. Titania nanoparticles were synthesized via sol-gel method using $TiCl_4$ precursor. In sol-gel method ammonia was used as the gelation agent. The titania nanoparticles were then centrifuged. In order to study the effect of pH on titania nanoparticles different nanoparticles were prepared by varying the pH of the sol. As-synthesized samples were also annealed at different temperature (upto 500°C). XRD results show the formation of highly crystalline titania nanoparticles. It was found that below 400°C anatase phase dominates while annealing at high temperature results in conversion of anatase to rutile phase. With increase in annealing temperature the peak intensities corresponding to rutile phase increases. Variation in sizes of nanoparticles from 20 nm to 500 nm is observed with variation in annealing temperature and pH. Titania nanoparticles prepared in this research work were homogenous and good interconnection was formed between the particles indicating the good mechanical strength of sol-gel prepared nanoparticles.

1. INTRODUCTION

During the past few years, Titania (TiO_2) nanoparticles has attracted worldwide attraction because of its high refractive index, high dielectric constant, excellent photocatalytic abilities, high photoelectric conversion efficiency. In addition titania is low cost, environment friendly and has chemical stability (Huang 2013, Shiba 2013, Arunmetha 2013). These advantages of titania especially high refractive index and low absorbing capability have lead to its applications in solar cells and other optoelectronic devices (Ahn 2003).

Titania exist in three crystallographic phases namely anatase, rutile and brookite. Anatase (c/a >1) and rutile (c/a <1) has tetragonal structure where as brookite crystallizes in orthorhombic structure. Among these phases rutile is the thermally stable phase where as anatase and brookite both are metastable phases (Sarma 2013). It is

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transparent in the visible region and when titania is irradiated with photons of energy greater than 3 eV electron hole pairs are produced.

The control of the required phase of titania is extremely crucial in order to get the required optical properties to be utilized for optoelectronic devices. Ghamsari (2013) obtained anatase phase below 100°C with low crystallinity and at 400°C anatase to rutile transformation started where as the transformation completed at 800°C. Arunmetha (2013) used sol-gel, sonication and spray pyrolysis method TiO_2 nanoparticles synthesis. They obtained rutile phase with sol-gel with mean diameter of 76 nm with band gap of 3.168 eV, sonication method yield anatase phase with diameter of 68 nm with band gap of 3.215 eV and spray pyrolysis also resulted in anatase phase with size of 38 nm and band gap of 3.24 eV. Shalan (2013) obtained anatase phase using hydrothermal method with pH of 4 and 7 and temperature range of 100-500°C with variation in band gaps from 3.10-3.30 eV due to changes in crystallite sizes. Loryuenyong (2012) obtained anatase phase with low crystallinity under as-synthesized conditions. They observed the appearance of rutile phase at 500˚C where as completer transformation was observed at 700°C. Petrovic (2012) obtained highly crystalline anatase phase using nonhydrolitic sol–gel method at 500˚C while at 750°C both anatase and rutile phases were present. This brief over view of literature indicate that for obtaining particular phase and required optical properties of titania nanoparticles the method of synthesis and the control of synthesis conditions is exceptionally crucial.

In order to prepare titania nanoparticles various physical and chemical methods has been reported to date including sol-gel (Ghamsari 2013), sonication and spray pyrolysis (Arunmetha 2013), DC reactive magnetron sputtering (Sarma 2013), hydrothermal method (Shalan 2013). Among various methods reported to date for titania synthesis sol-gel is one of the most important and promising method due to its low cost, simplicity, low temperature reaction kinetics and most importantly its application oriented nature. The control of crystallite size, shape, phase of titania, surface structure is affected by choice of precursor, solvents, pH and temperature of sol, catalyst, sol concentration etc. (Shalan 2013, Loryuenyong 2012).

In this paper we investigated the effect of pH on sol-gel derived titania nanoparticles. The pH of the sols are varied from 1-11 from 1 (strongly acidic) to 7 (neutral) to 11 (basic). The nanoparticles are prepared at low temperatures of 80°C and their structural and optical properties are thoroughly investigated.

2. Experimental Details

The sol of titania was synthesized locally using research grade materials that were used without further purification. Two solutions were prepared prior to the final synthesis of sol. Solution 1 was prepared by dissolving $TiCl_4$ in ethanol. The reaction is exothermic and liberates large amount of heat, as can be seen in Fig. 1, so the reaction was carried out in ice bath at temperature of 5°C. Solution 2 was prepared using acid and de-ionized water. Both the solutions were mixed together under constant stirring. The mixed solution was then stirred at 60°C for 5 hours to obtain stable sol. The sol was left for aging and was further processed after 24 hours. Sol was then heated at

70°C for several hours to obtained titania nanoparticles. 6 different sols were prepared with variation in pH of the sol from 1.0 (acidic) to 7.0 (neutral) and to 11.0 (basic). Fig. 1 shows the nanopowders obtained from TiO_2 sol under acidic, neutral and basic conditions.

Fig. 1 Experimental setup for TiO_2 nanoparticles showing exothermic reaction during synthesis

For phase analysis and structural characterization Bruker D8 Advance Diffractometer was used with λ = 1.5405 Å. S-3400N Scanning Electron Microscopy (SEM) was used to study the surface morphology and grain sizes operated at acceleration voltage of 30 kV and working distance of 7 mm. Variable Angle Spectroscopic Ellipsometer (VASE) was used to study the optical properties of TiO_2 nanoparticles.

3. Results and Discussion

Figs. 2 and 3 show XRD patterns for TiO_2 nanoparticles at different pH. The nanoparticles synthesized using sol with pH 1 are amorphous in nature (Fig. 2). Strong effect on the crystallinity was observed for rest of the nanoparticles synthesized under different pH as can be seen in Fig 3. The peaks are well matched with brookite phase (JCPDS card no. 76-1934) of titnaia with very small diffraction peaks corresponding to rutile phase (JCPDS card no. 87-0710). It is worth mentioning here that these nanoparticles are prepared at very low temperature of 80°C and brookite is metastable phase of Titania that transforms to rutile phase when annealed under suitable conditions. As the pH of the sol was increased the crystallinity of the nanoparticles increases as can be seen by the variation in peak intensities in Fig. 3.

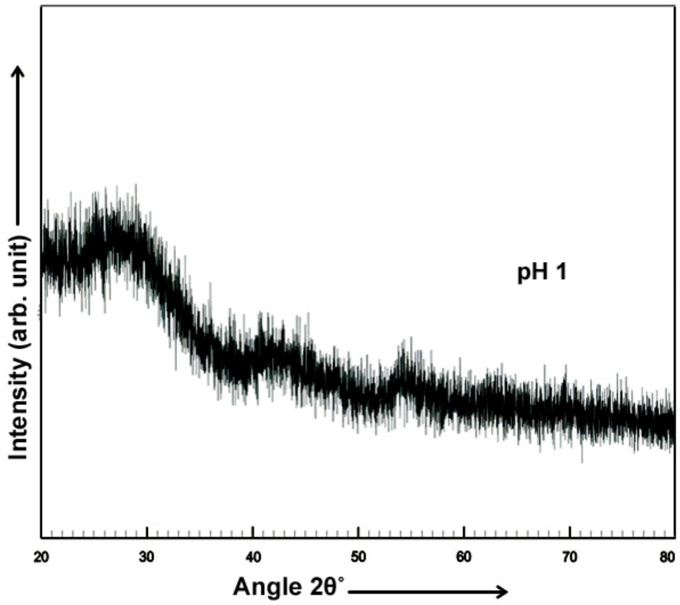

Fig. 2 XRD pattern for TiO_2 nanoparticles with pH 1

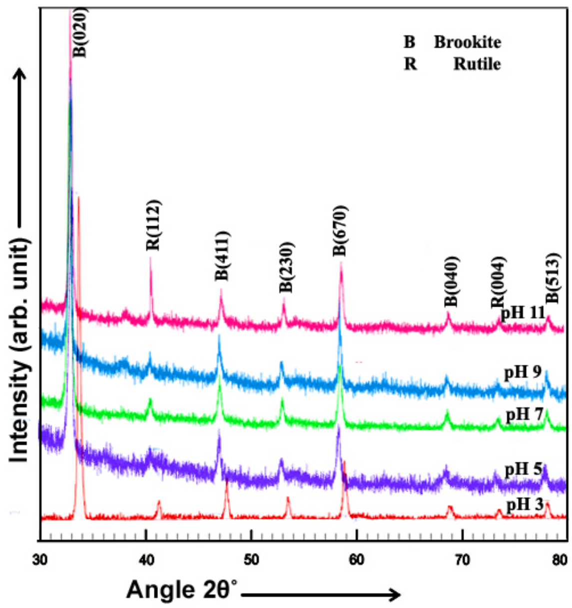

Fig. 3 XRD patterns for TiO_2 nanoparticles with variation in pH (3-11)

Fig. 4 transmission vs. wavelength curves for TiO_2 nanoparticles. Nanoparticles show high transparency in the visible and infrared region which is an important requirement for the particles to be utilized for solar cell applications. However there is a sharp reduction in transparency as the pH was reduced to 3 and then to 5 but when the pH was adjusted to 7(neutral) and basic the particles again show high transparency. The inset of Fig. 3 shows the extended region of absorption edge in the range of 380-430 nm showing the changes in band gap of nanoparticles with variation in pH.

The band gap the particles were calculated using the transmission curves using Eq. (1).

$$\alpha = \frac{1}{t}\ln\frac{1}{T} \quad (1)$$

Where T is the transmission and t is the thickness of the films. Thickness of the films is obtained using Variable Angle Spectroscopic Ellipsometer. The band gaps are then found by extrapolation of the linear region of α^2 vs. E (eV) curve. The band gap of nanoparticles with pH 1 is found to be 3.05 eV. As the pH is increased the band gaps decreases with values of 3.03 eV and 3.01 eV respectively. For neutral pH (7) nanoparticles the band gap dropped to 2.98 eV. With further increasing the pH towards basic the band gaps are found to be 2.96 eV and 3.006 eV for pH 9 and 11 respectively. Inset of Fig. 5 show that the band gap of nanoparticles decreases with increase in pH to 7 (neutral) and the further increase in pH towards basic conditions the band gap increases again.

The optical studies of titania nanoparticles were carried out using Variable Angle Spectroscopic Ellipsomter by J.A. Woollam. The data was taken at an angle of incidence of 60°. A three layered model comprising of substrate, TiO_2 film and surface roughness is used. The two layered model exclusive of the surface roughness doesn't provide a suitable fit with very high MSE (> 10). We also introduced an interface layer between the film and substrate but it was found to have least impact on fitting quality and correspondingly on optical properties. The surface roughness was approximated

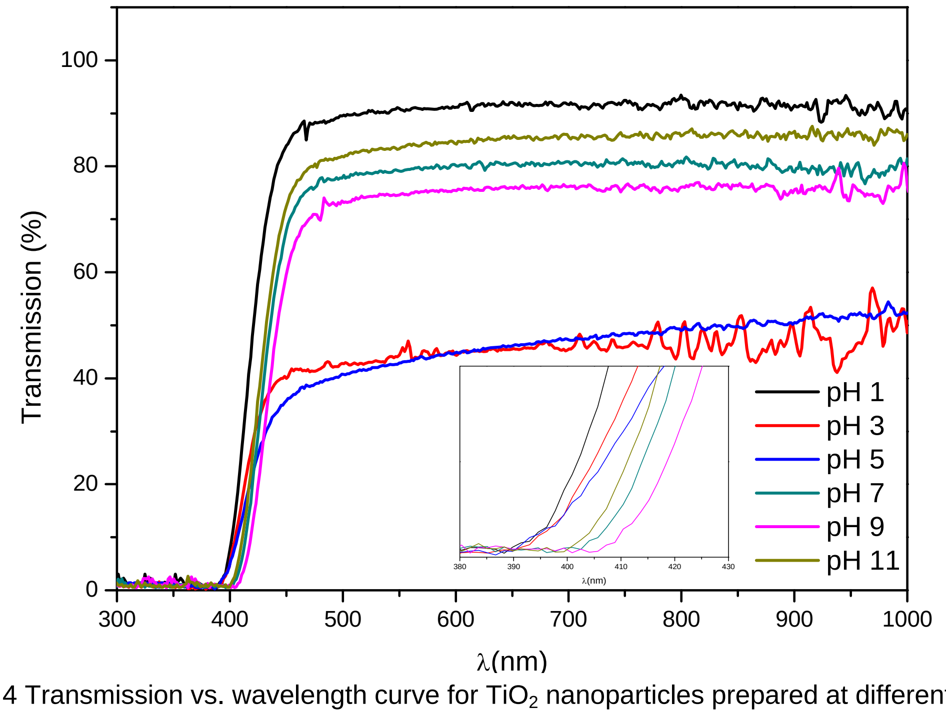

Fig. 4 Transmission vs. wavelength curve for TiO_2 nanoparticles prepared at different pH

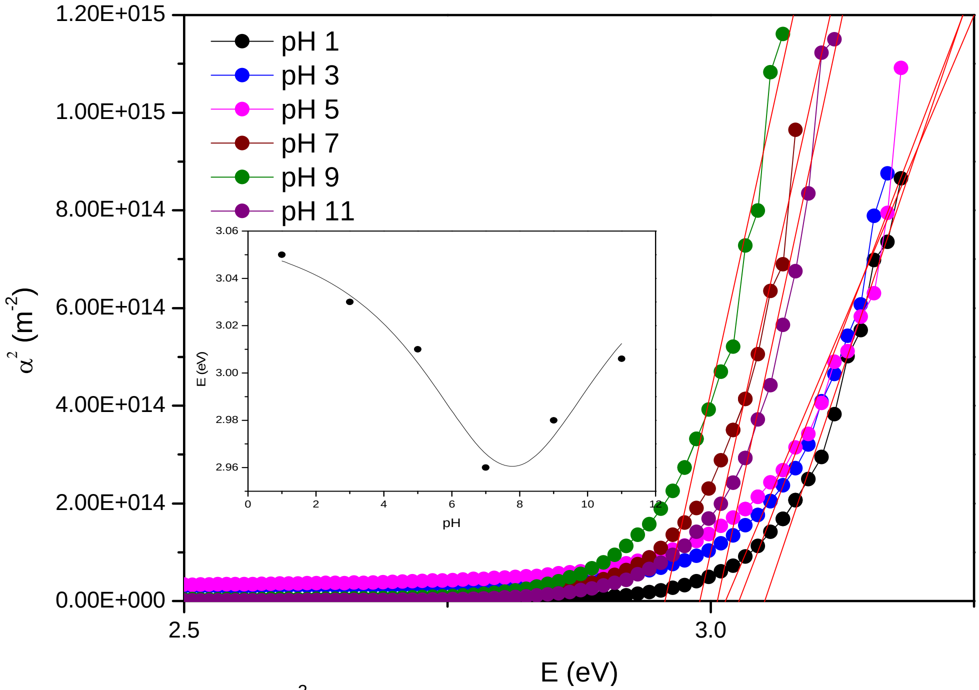

Fig. 5 α^2 vs. energy curve for TiO_2 nanoparticles

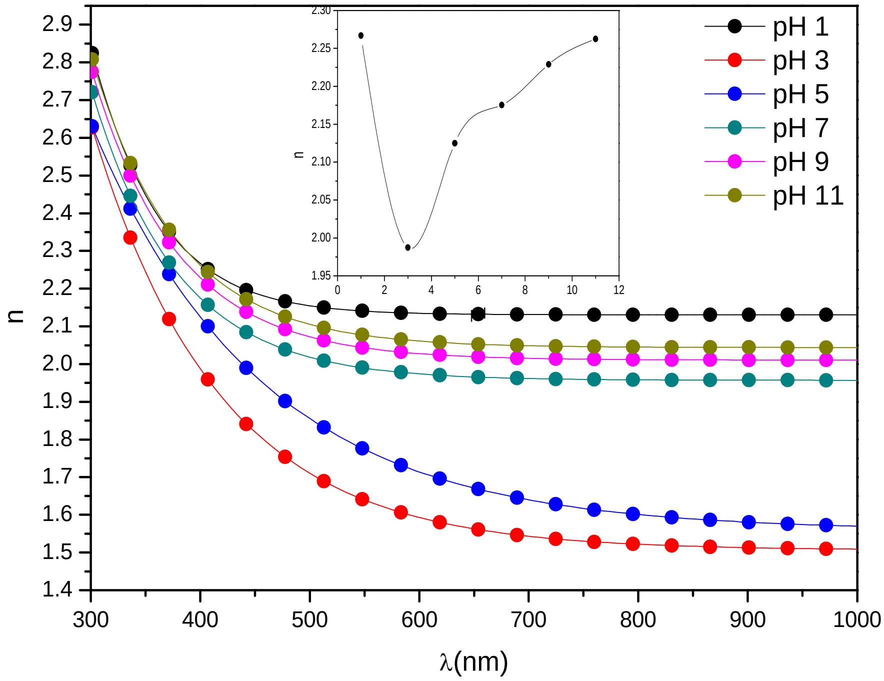

Fig. 6 Refrcative index vs. wavelenght curves for TiO_2

through Maxwell Effective Medium Approximation (EMA) where a mixture of 50% voids/air and 50% TiO_2 was used.

Fig. 6 show refractive index and extinction coefficient for TiO_2 nanoparticles prepared with variation in pH. The refractive index decreases with increase in wavelength representing normal dispersion behavior. High refractive index indicates highly dense nanoparticles without cracks and/or porous structure. With increase in pH from 1 to 3 here a reduction in refractive index from 2.82 to 2.62 (at λ = 300 nm). With further increase in pH the refractive index increases. The refractive index values for nanoparticles with pH 5, 7, 9 and 11 are 2.64, 2.73, 2.79, 2.81 at λ = 300 nm respectively. Fig. 7 show extinction coefficient for TiO_2 nanoparticles showing normal dispersion behavior. Sharp decrease in extinction coefficient at wavelength of 350 nm show onset of absorption.

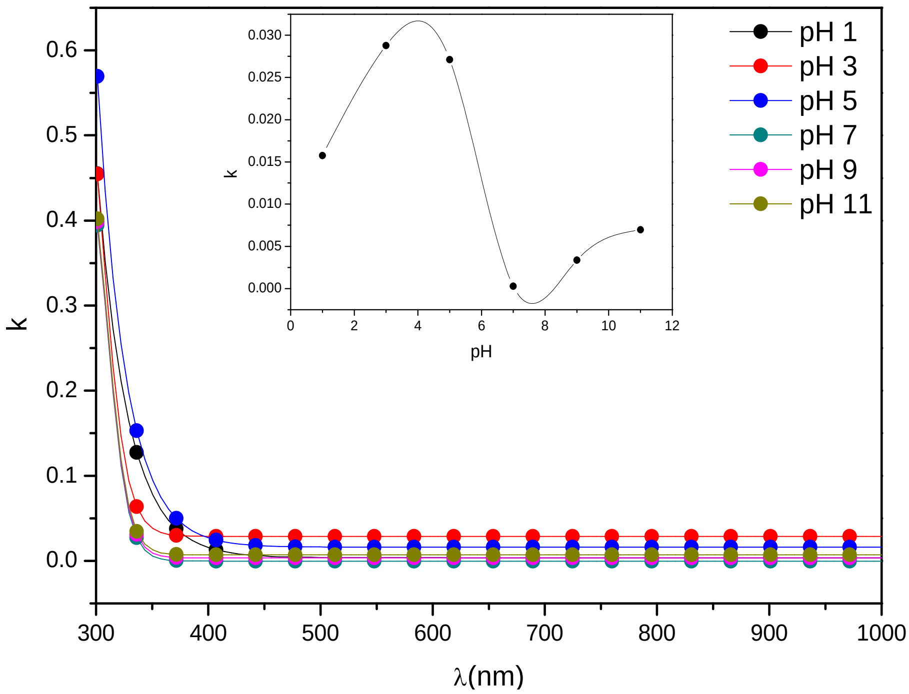

Fig. 7 Extinction Coefficient as a function of wavelength

3. CONCLUSIONS

Titania nanoparticles are prepared via sol-gel method and effect of variation in pH on structural and optical properties is studied. XRD results show the formation of highly crystalline titania nanoparticles except at pH 1. The nanoparticles are prepared at low temperatures and show brookite phase along with some contribution from rutile phase. The crystallinity of nanoparticles increases as the pH of the particles increases. the band gaps are found in the range of 2.96-3.03 eV. Titania nanoparticles prepared in this research work were homogenous and good interconnection was formed between the particles indicating the good mechanical strength of sol-gel prepared nanoparticles.

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