Effect of pH on the morphology of TiO$_2$ nanostructures

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Titanium oxide (TiO$_2$) nanostructures with different morphologies ranging from spheres, rods to sheets were prepared using solvothermal route. The effects of pH on the structural, morphological and optical properties of TiO$_2$ nanoparticles were investigated. Nanostructures are characterized using Attenuated Total Reflectance (ATR), Powder X-ray Diffractometer (XRD), Scanning electron Microscope (SEM) and UV- Visible Spectroscopy.

1. Introduction

Titanium dioxide has been one of the most studied materials for many ecological and universal applications. Titanium oxide (TiO$_2$) is available in the form of nanocrystals or nano rods having a high surface area.Titanium oxide exhibits good photo catalytic properties, hence is used in antiseptic and antibacterial compositions(1), degrading organic contaminants and germs (2) , as a UV-resistant material (3), manufacture of printing ink, self-cleaning ceramics and glass coating (4), making of cosmetic products such as sunscreen creams, whitening creams, morning and night creams (5), used in the paper industry for improving the opacity of paper (6). TiO$_2$ exists in three main phases: anatase, brookite and rutile. Precipitating nanoparticles from a solution of chemical compounds can be classified into six major categories: colloidal methods, sol – gel processing, water – oil microemulsions method, hydrothermal synthesis, solvothermal synthesis and polyol method. When compared to other techniques solvothermal synthesis has many advantages such as easy and precise control of the size, shape distribution , crystalline of the final product through adjusting the parameters such as reaction temperature, reaction time , solvent type , surfactant type, precursor type and also pH .

Solvothermal synthesis is a method for preparing a variety of materials such as metals, semiconductors, ceramics, and polymers. The process involves the use of a solvent under moderate to high pressure and temperature that facilitates the interaction of precursors during synthesis. pH is an important factor that influences the synthesis of nanoparticles by solvothermal synthesis. pH of the solution has considerable effect on morphology, size, surface area and properties of nanomaterials. Therefore, nanoparticle size can be controlled by altering the pH of the solution media. Hence, in this present study, TiO$_2$ nanostructures are prepared by solvothermal method and the effect pH on the nature of TiO$_2$ nanostructure is studied.

2. Experimental

2.1. Preparation

The Ti(OH)$_2$ colloidal suspension was prepared by hydrolysis of titanium tetra isopropoxide(TTIP). In a typical process, 3 ml of titanium tetra isopropoxide was mixed with 10

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ml of Cyclohexane. 0.1M microemulsion was prepared using Cyclohexane (10ml) and ethanol (40ml) in the presence of the surfactant, (Sodium dodecyl Sulphate). To the Microemulsion, aqueous solution of Hexamethylenetetramine (2.3gm) was added in dropwise with constant stirring. pH of the suspension was adjusted to 8,9 & 10 by the addition of aqueous ammonia and the suspension was allowed to stir for 1hr and transferred to a 250ml Teflon lined stainless steel autoclave. It was sealed tightly and maintained at 100^0 C for 1 hr. The autoclave was cooled to Room temperature; solid sample obtained was filtered, washed several times with distilled water and ethanol separately, dried at 100^0 C for 3 hrs and calcined at **700^0C** for 3 hrs. The samples were named as **T–1, T–2 & T-3** respectively for pH - 8 , 9 & 10.

2.2. Characterization

Crystallinity of the samples were identified by powder X – ray diffraction (XRD) at room temperature on a PANalyticalX'pert PRO X-ray diffractometer using Cu-Kα radiation (λ = 1.5406 Å) as X-ray source. Surface morphology of TiO_2 nanoparticles was imaged using ZEISS ultrafield emission Scanning Electron Microscope. The absorption spectra were recorded using JASCO UV-Visible spectrophotometer.

3. Results and discussion

3.1. X – Ray diffraction studies

Fig.1. shows the XRD pattern of prepared TiO_2 samples at different pH. For T-1, the maximum intensity peak observed at 2θ = 27.455° corresponds to (110) plane of the Rutile phase. (JCPDS File no. 78- 1510) (7). In T-2, the maximum intensity peak observed at 2θ = 25.305°, corresponds to (101) plane of the anatase phase (JCPDS File no. 21-1272) (8). In addition, a peak appeared at 30.9° corresponding to the (121) plane of the brookite phase (JCPDS file no:29-1360) is also observed in both the samples (9). Presence of mixed diffractions corresponding to anatase, rutile and brookite phases of $TiO_2$is observed for both the samples and indicates the existence of mixed phases in the prepared samples (10). The average crystallite size of prepared TiO_2nanoparticles were calculated by using Scherer's equation to the major peaks of the diffraction data (11) and the crystallite size of prepared TiO_2 at pH 8 , pH 9 and pH 10 is calculated as 25nm , 27nm and 29nm respectively. It is also observed from XRD of T-1, T-2 and T-3 that, upon increasing pH, peak broadening is observed for all the diffractions, and this could also be due to the decrease in crystallite size of the samples with pH.
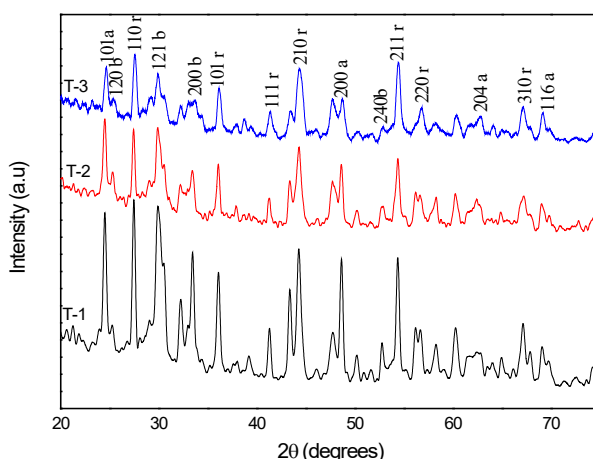

Fig. 1. X-Ray Diffraction Patterns of T-1, T-2 and T-3.

3.2. Attenuated total reflectance spectroscopic studies

ATR spectra of both the samples were recorded from 500 – 4000 cm^{-1}andare presented inFigure 2. Bands 752 cm^{-1} corresponds to O- Ti- O bonding in TiO_2 (12). Low frequency bands

between 900 & 400cm^{-1} correspond to Ti-O-Ti vibration of the metal oxide (13) network, indicating the condensation of Ti(OH)$_2$ during calcinations.
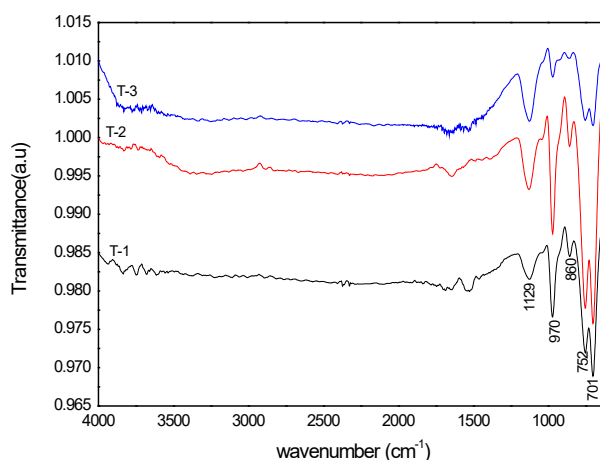

Fig. 2. ATR spectra of T-1, T-2 and T-3.

3.3. UV- Visible spectroscopy

Band gaps for the prepared samples were studied from the UV – Visible absorption spectra of the samples dispersed in ethanol (Fig.3.). Absorption edge of T-1 is found at 324 nm and the peak for T-2 is appeared at 340 nm and the peak for T -3 is found at 344 nm .The band gap energy was calculated using the formula E = hc/λ and it was found to be 3.63 eV, 3.65eV and 3.611eV. It is clear from UV that as crystallite size decreased absorption peaks become sharper and moves towards blue region. UV result is in agreement with the observed peak broadening in powder XRD pattern of T-2 (14)
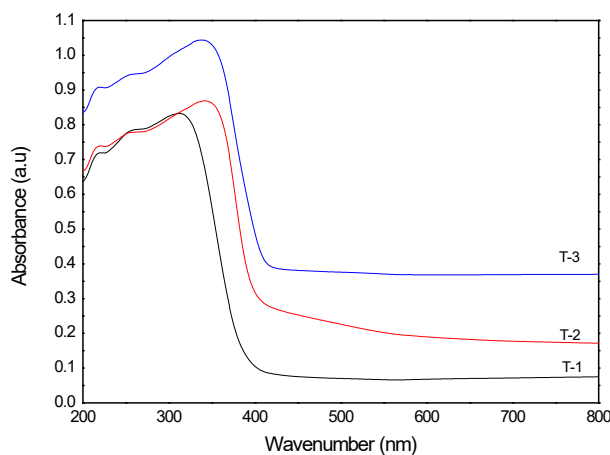

Fig. 3. UV-Visible Absorbance Spectra of T-1, T-2 and T-3.

3.4. Field emission scanning electron microscopic analysis

Fig.4. shows FE-SEM micrographs of the TiO$_2$ nanostructures prepared by hydrothermal method at pH 8, 9& 10 . The morphology appears like nanorods, with rectangular cross section (15). The thickness of the nanorod decreases as the pH increases. This decrease in thickness could be the reason for peak broadening appeared in powder XRD and observed blue shift in UV – Visible absorption spectroscopy.
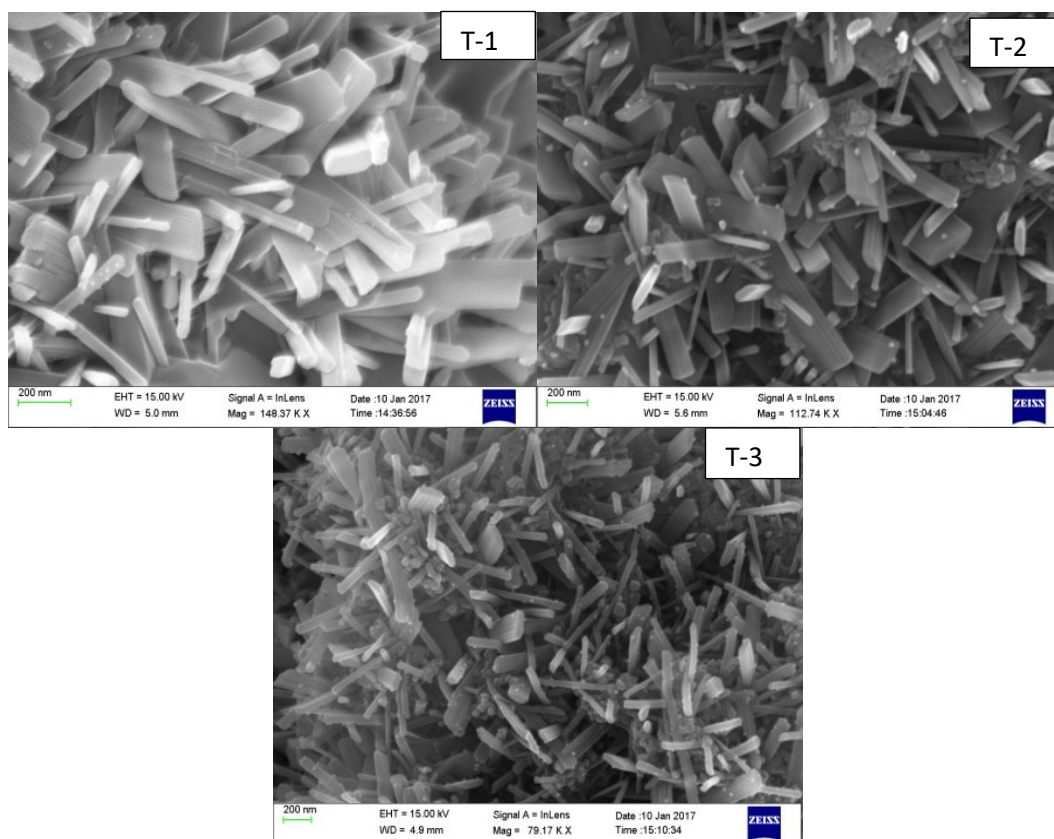
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Fig. 4. FE SEM image of TiO₂ nanostructures.

4. Conclusion

TiO$_2$ nanorods were prepared by hydrothermal method at different pH conditions (pH – 8 , 9 & 10) . Upon increase pH crystallite size decreases, band gap increases. Presence of rutile, anatase and brookite mixed phase for the prepared TiO$_2$ is identified from powder XRD .

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