PREPARATION AND CHARACTERIZATION OF TITANIUM DIOXIDE NANOPARTICLES BY OLYVINYLPYRROLIDONE HYDROTHERMAL PROCESSES

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ABSTRACT

In present work we report the synthesis of TiO_2 nano particles by hydrothermal process. Titianium dioxide nano particles can be prepared by various method such as chemical vapour deposition, micelle and inverse micelle method, sonochemical method and so-on out which hydrothermal process is the simplest method to synthesize titanium dioxide Nanoparticle with high purity and less crystalline size. The TiO_2 nano particles were prepared by taking Titanium tetraisopropoxide as a precursor and polyvinlpyrrolidone as a capping and reducing agent. The as-synthesized TiO_2 nano particle was characterized by X-ray Diffraction (XRD), Particle size analyser, Transmission Electron Microscopy (TEM), UV Visible Spectroscopy, Fourier transform infrared spectroscopy (**FTIR**) and TG/DTA analyses.

Keywords: TiO_2 Nanoparticles, Hydrothermal Process, XRD, TEM, FTIR, TG/DTA, PSA.

Introduction:

TiO_2 nanoparticles have attracted significant interest of materials scientists and physicists due to their special properties [1], [2] [3] and have attained a great importance in several technological applications such as bio-medical, photocatalysis [4], sensors [5], solar cells and memory devices[6],[7]. Titanium oxide Nanoparticle mainly exist in three polymeric phase that is Anatase, Rutile and Brookite. These three polymeric phases are exploited to utilize TiO2 in potential applications [8-12].

Hydrothermal method has been widely used as versatile tool for nano material synthesis. It is a facial route to prepare a highly crystalline oxide under moderate reaction condition [13-14]. It provides an effective reaction environment for the formation of nano crystalline TiO_2 with high purity, good dispersion and well controlled crystallinity with this method. The sintering process which results in a transformation from the amorphous phase to the crystalline phase can be avoided [15-17].

In the present work, we have synthesized TiO2 nanoparticles by hydrothermal method and tried to analyze the basis of their crystallinity, crystallite size, band gap and structural properties. X-ray diffraction (XRD) is used to calculate crystallite size. Transmission electron micrograph (TEM) images are shown to clearly see the crystalline tetragonal structure and the FT-IR spectra have shown the broad intense band below $1200cm^1$ due to Ti-O-Ti vibration respectively.

Experimental procedure:

Materials required

Titanium tetra isopropoxide, polyvinlpyrrolidone, ethanol, glacial acetic acid was purchased fron Aldrich. All other solvents and reagents were analytical grade quality, purchased commercially and used without any further purification.

Synthesis of Titanium dioxide nanopartcles

Titanium dioxide nanoparticles were prepared by mixing 0.1M of titanium tetra isopropoxide with 15 ml of glacial acetic acid. And then PVP solution was prepared by dissolving 0.001M of polyvinlpyrrolidone in 15 ml of ethanol. As-synthesized PVP solution is then added to TiO_2 solution drop by drop under continuous string. This solution is continuously stirred for to 2 hours to form homogenous solution. And then solution was autoclaved at 120^0 C under 15 lb pressures for 1 hours and was filtered by using Whattmann No. 1filter paper. The filtrate was neutralized by using distilled water and ethanol and then incubated for further drying. Obtained sample was calcined at 600^0 C.

Results and Discussions:

1) X-Ray Diffraction (XRD) Analysis

The XRD pattern of the as synthesized particles is shown in Figure 1.

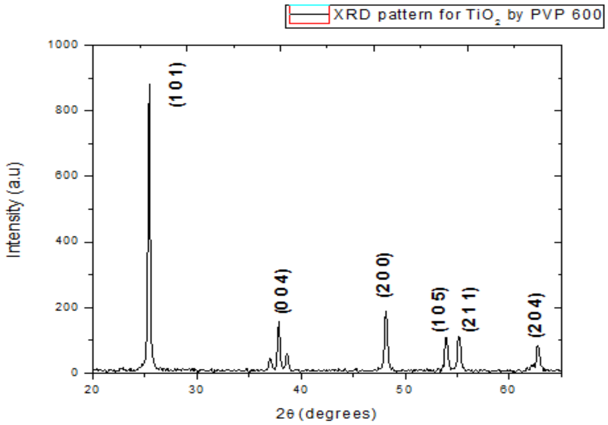

Figure 1: XRD pattern of TiO_2 nanoparticles synthesized using PVP

The planes and 2 θ values corresponding to the obtained peaks are tallied with the JCPDS data card no. 89-4921.The crystallite size (D) was determined by Scherrer's formula given below

$$D = \frac{K\lambda}{\beta \, Cos\theta}$$

Where K indicates the instrument constant which is approximately 0.9, indicates wavelength o f the X-Ray source which is 1.54Ao , ß indicates the Full Width Half Maximum (FWHM) of the peak, indicates the Bragg's angle of diffraction. The average crystallite size (D) of the as synthesized nano particles was determined to be 29.20nm.. The d - spacing (d) between the parallel p lanes corresponding to the highest intensity significant peak was obtained as 0.35nm which was obtained from the equation,

$$\frac{1}{d^2} = \frac{h^2 + k^2}{a^2} + \frac{l^2}{c^2}$$

where h,k,l indicate the plane axes and a indicates the lattice angle

Particular Size Analyser

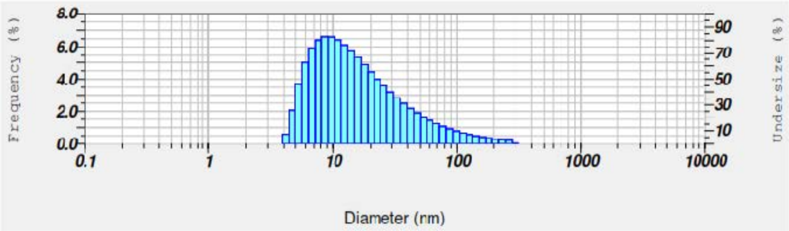

Figure 2: Particle Size Analysis for the synthesized TiO2 nanoparticles using PVP.

From the above figure 2, it can be analyzed that the average particle size is 49nm which is incoherence with the crystallite size calculated from the XRD data. In the above PSA graph, x-axis indicates the particle diameter in nano meter, left y-axis indicates the Brownian motion collision frequency of the particles and the right y-axis indicates the cumulative particle size in percentage.

UV-Visible Spectroscopy

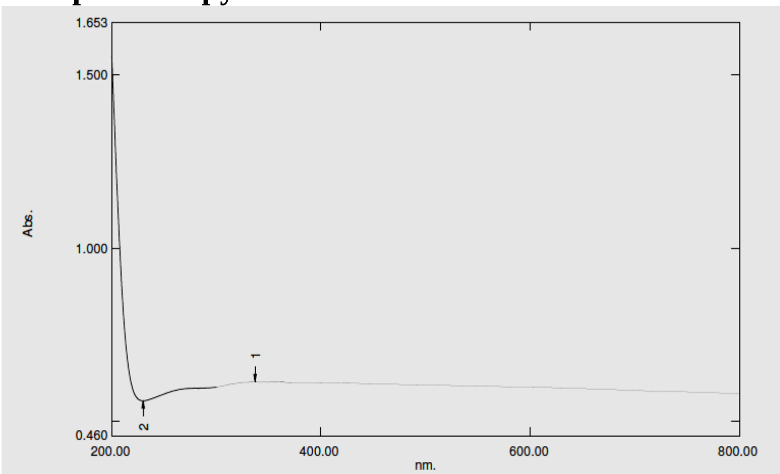

Figure 3: UV-Visible spectroscopy of the synthesized TiO2 nanoparticles using PVP

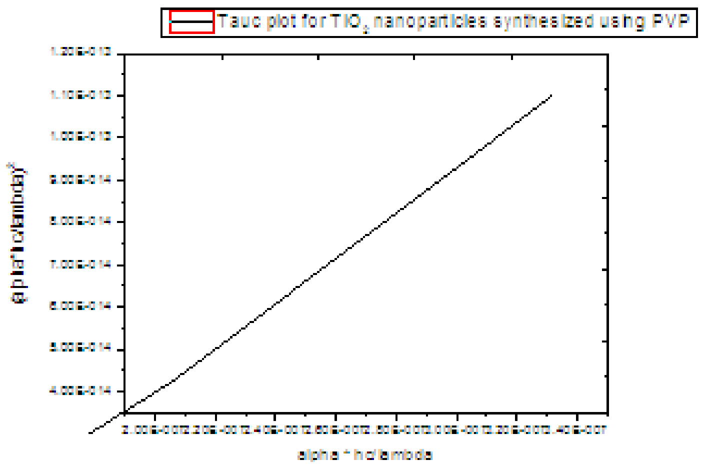

Fig 4: plot for the synthesized TiO_2 nanoparticles using PVP

Figures 3 show UV-Vis spectroscopy of the synthesized TiO2 nanoparticles using PVP. Since TiO_2 is a semiconductor material, the bandgap analysis is done using Tauc plot which are shown in the figures 4. The value where the tangent is intersecting the x-axis is considered as the bandgap which is observed as 3.5eV for the TiO_2 nanoparticles synthesized using PVP. As the particle size decreases the bandgap increases and this phenomenon can be observed in the obtained results

TG/DTA Analyses

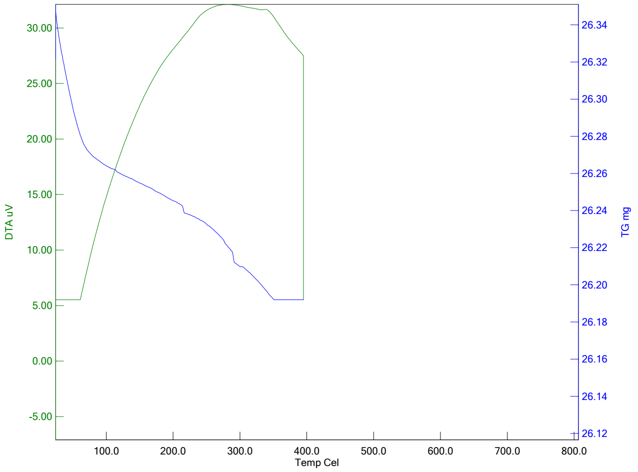

Figure 5: TG/DTA for the synthesized TiO_2 nanoparticles by PVP.

Figure 5 shows TG curve, we can observe three decomposition stages from the temperatures 25.36 to 115.62^{o}C, 187.92 to 318.72^{o}C and 350.06^{o}C to 801.37^{o}C respectively. The weight loss of the sample at the mentioned temperature ranges is 0.34%, 0.16% and 0.27% respectively. The total weight loss is contributed to approximately 0.77% which is incoherence with the above shown graph.

Transmission electron microscopy analyses

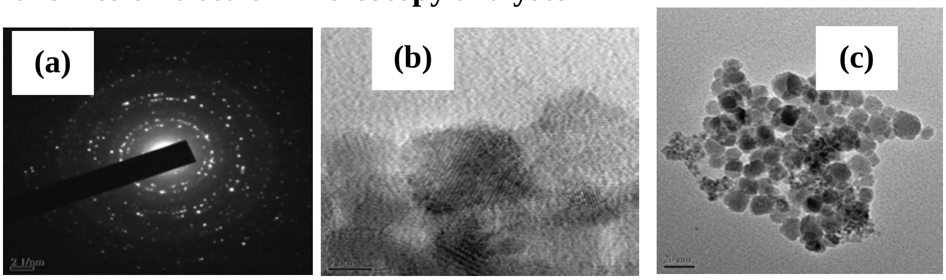

Figure 6: TEM images for the TiO_2 nanoparticles synthesized using PVP

The TEM micrographs reveal the crystalline tetragonal structure of the as synthesized TiO_2 nanoparticles which is tallied with the literature. From the figure 6a the Select area electron diffraction (saed) pattern of the as-prepared sample is completely crystalline and entirely consists of anatase phase which are in good agreement with XRD results.

Transform Infrared Spectroscopy (FTIR):

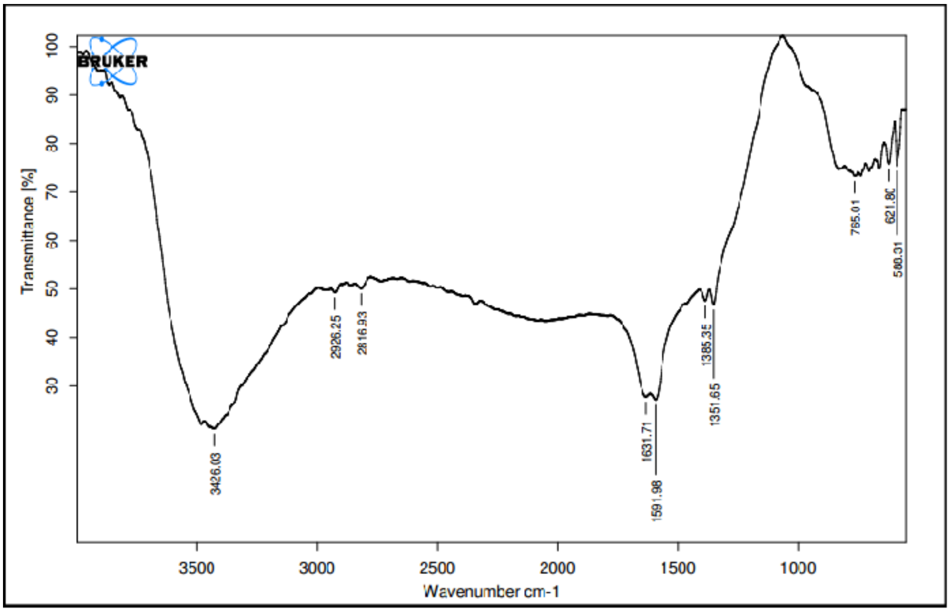

Figure 7: FTIR Spectrum for the synthesized TiO_2 nanoparticles by PVP.

The sharp band observed 3428.4 cm-1 and the broader bands at 2816.cm-1 are attributed to hydroxyl groups. The band at 1632 to 1591. Attributed C-C, the peaks at 1385.0 and 1351.2 cm-1 are due to the vibrations of CH2 group The broad band centered at 765.8- 588.2 cm–1 is likely due to the vibration of the Ti–O bonds in the form of $TiO_{2.}$

Conclusion

Titanium dioxide nanoparticles were successfully synthesized by hydrothermal process. It is studied from the XRD analysis that the crystalline size of the TiO_2 nano particles obtained shown decrease in crystalline size. The morphology of chemically synthesized TiO_2 nano particle was investigated to be tetragonal structure and further d-spacing observed was 0.35nm incoherence with the X-ray diffraction result. The mean particle sizes of chemically as-synthesized TiO_2 nano particle was analyzed by particle size analyzer and was calculated to be 49 nm and are in good agreement with crystallite sizes calculated from XRD data. The Thermo gravimetric/Differential Thermal Analysis (TG/DTA) results concluded the total weight loss to be 1.9% .The Transmission Electron Microscopy (TEM) micrographs showed that the TiO_2 nano particle is tetragonal in structure which is in coherence with the literature. The determination of the band gap was done by UV-VISIBLE SPECTROSCOPY and was found to be 4.2eV because of decrease in the particle size.

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