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ANATASE TO RUTILE PHASE TRANSFORMATION OF TiO2 NANOPARTICLES

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ABSTRACT

The anatase to rutile phase transformation of Titanium dioxide nanoparticles upon calcination is reported here. TiO2 nanoparticles are synthesized by sol gel method using titanium (IV)-n - butoxide (Ti(OC4H9)4 or Ti(OBu)4), isopropyl alcohol ((CH3)2CHOH) and conc. HNO3. The thermal stability and the decomposition of synthesized materials are studied using thermogravimetric (TG) analysis. The TGA studies show no weight loss for the sample after 400^{O}C. Hence the as prepared samples are calcined at 400 and 800^{O}C for three hours The structural characterization of the nanoparticles is done using X-ray diffraction (XRD) technique. The XRD patterns indicate that the structure of TiO2 is anatase at a calcination temperature of 400^{O}C and rutile at 800^{O}C. The X-ray diffraction studies show an increase in the intensity of diffraction peaks, decrease in FWHM and increase in crystallite size. The crystallite size values obtained are 11.3 and 58 nm for the anatase and rutile samples respectively. The optical absorption of these nanoparticles are investigated

using UV-Visible and photoluminescence (PL) spectroscopic methods. The optical absorption spectra of TiO2 sample exhibited strong absorption in the UV region. The band gap energy values obtained are 3.43 and 3.00 eV for the anatase and rutile samples respectively, in close agreement with the values obtained in other studies. The samples exhibit a strong and wide PL signal from 400 to 500 nm and a shoulder peak at 377 nm with an excited wavelength of 300 nm. Both the samples exhibit similar type of PL signal with no significant change in the curve shape. The emission intensity of anatase is higher than that of rutile sample. This study reports the successful transformation from anatase to rutile phase of TiO2 nano particles synthesized by sol gel method.

Keywords: TiO2 nanoparticles, anatase & rutile phase, sol-gel technique, phase transformation.

INTRODUCTION

With the advent of nanotechnology, the use of NPs in electronics, antimicrobial materials, cosmetics, sunscreens, and medication delivery systems has increased dramatically. Titanium dioxide nanoparticles, also known as ultrafine titanium dioxide or nanocrystalline titanium dioxide. Microcrystalline titanium dioxide or titanium dioxide are titanium dioxide particles with a diameter less than 100 nm. The metastable anatase phase of titanium dioxide produces nanoscale particles due to its lower surface energy than the equilibrium rutile phase. Surfaces of ultrafine titanium dioxide with anatase structures are useful as an addition in building materials such as anti-fogging coatings and self-cleaning windows due to their photocatalytic sterilising capabilities.

TiO2 is a significant compound due to its exceptional catalytic and semiconducting properties. It's also chemically stable, non-toxic,

and biocompatible. Nano TiO_2 is a powerful oxidising agent with a large surface area and, as a result, high photocatalytic activity. The refractive index of titanium dioxide (TiO_2) nanoparticles is 2.4. It is used in a variety of applications such as pharmaceuticals, coatings, inks, plastics, food, cosmetics, and textiles.

Anatase, Rutile, and Brookite are the three crystalline phases of titanium dioxide. Rutile and anatase are two of the three common TiO_2 polymorphs (crystal forms) used to make TiO_2 nanoparticles. TiO_2 nanoparticles, as opposed to large TiO_2 particles, are transparent rather than white. TiO_2 has unique electrical and diffusion path properties. TiO_2 nanoparticles are typically broad band gap semiconductors with Eg-values ranging from 3.0 to 3.2 eV and high UV absorbance.

Sol-gel, flame hydrolysis, co-precipitation, impregnation, and chemical vapour deposition processes are used to create TiO_2 nanoparticles. Researchers are particularly interested in the biosynthesis of titanium dioxide nanoparticles because it is a low-cost, environmentally friendly, and repeatable method.The sol-gel process is a wet-chemical method for producing high-quality metal-oxide-based nanomaterials. It is used in the production of TiO_2 nanoparticles. X-ray diffraction, UV-Vis spectroscopy, photoluminescence, and thermogravimetric analysis are all methods of characterization. When heated, anatase to rutile phase transformation can be seen. We successfully produced and transformed TiO_2 nanoparticles from anatase to rutile phase in this study. Its properties should also be studied using various

MATERIALS AND METHODS

Materials

All the chemicals used for the synthesis of titanium dioxide are of analytic reagent grade. The specific reagents used for the synthesis of titanium dioxide include titanium (IV)-n - butoxide ($Ti(OC_4H_9)_4$ or $Ti(OBu)_4$), 97%, Sigma-Aldrich), isopropyl alcohol ($(CH_3)_2CHOH$), 99%, Merck) and conc. HNO_3 (99.9%, Merck). Distilled water is used throughout the synthesis.

Synthesis of TiO2 NPs

The precursor solution is a combination of titanium (IV)-n-butoxide ($Ti(OBu)_4$) and isopropyl alcohol with a ratio of 1:2. This solution was then dropped into a distilled water solution while being stirred. A sol was generated after 3 hours of hydrolysis at room temperature and stirring. Finally, the produced sol was dried for 20 hours at 60! to get TiO_2 powder. The powder samples were then calcined for 3 hours in a furnace at 400! and 800!.

RESULT AND DISCUSSION

Figure 1 shows the thermogravimetric analysis of TiO2 NPs. The TG curve indicates that the weight loss of the as prepared sample occurred from 500 to 400 ! . This may be related to the decomposition of the residual titanium butoxide and organic compounds. This suggests that the synthesized sample decomposed completely by 400! to become titanium dioxide

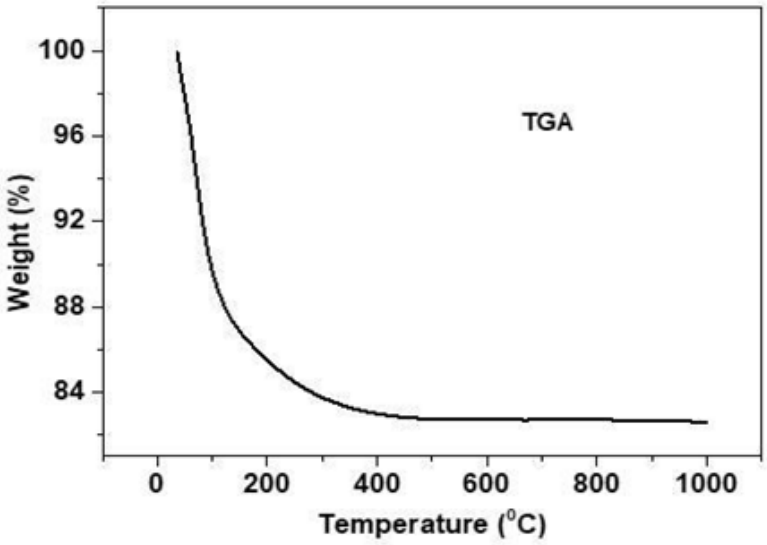

Fig: 1 TGA curve of TiO2

The XRD patterns show that TiO2 has an anatase structure at 400°C and a rutile structure at 800°C. The anatase ph ase found at 2è values of 25.357, 37.888, 48.024, 54.9, and 62.768 matches the convention al XRD pattern (JCPDS files No. 21-1272). The rutile phase of TiO2 is represented by the peaks at 2è values of 27.468, 36.095, 41.258, 44.076, 56.659, and 69.036 and is consistent with the conventional XRD pattern (JCPDS files No. 21-1276). When the calcination tempe rature is raised from 400°C to 800°C, a phase change from anatase to rutile occurs.

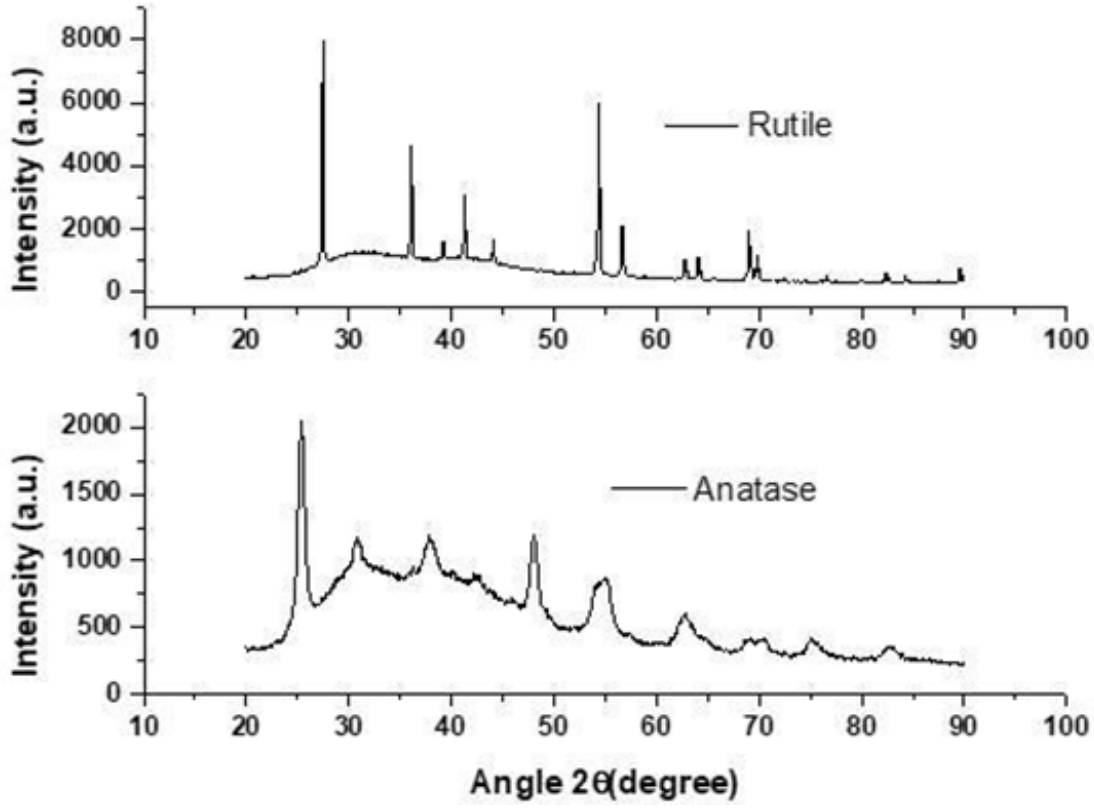

Fig: 2 XRD pattern of anatase and rutile TiO2 NPs

From this figure, it is observed that diffraction peaks become intense and their FWHM decreases on heating the sample from 400oC to 800oC, indicating an increase in crystallite size. The crystallite sizes of the samples are calculated from the line broadening of the diffraction peaks using Scherrer formula,

D=kë/âcosè

Where D represents the average crystallite size.k = 0.89 (Scherrer constant), ë = 1.5406 Å (wavelength of the X-ray Cu Ká radiation), è the diffraction angle of the peak and â represents the full-width at half-maximum (FWHM) of the peaks. The values obtained were 11.3 and 58 nm for the anatase and rutile samples respectively.

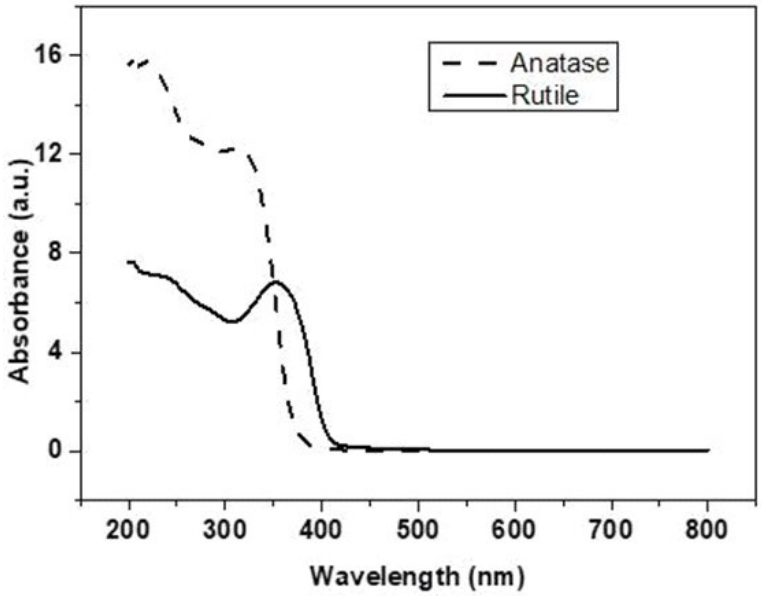

Fig: 3 UV-Vis absorption spectra of anatase and rutile TiO2 nanoparticles

Both samples have high UV absorption followed by an absorption hump between 300 and 400 nm. The electron transfer from the valence band to the conduction band is represented by UV absorption (band–band transition). The existence of Ti3+ vacancies created during annealing may explain the clearer hump in the rutile sample. During the phase change from anatase to rutile, a red shift occurs.

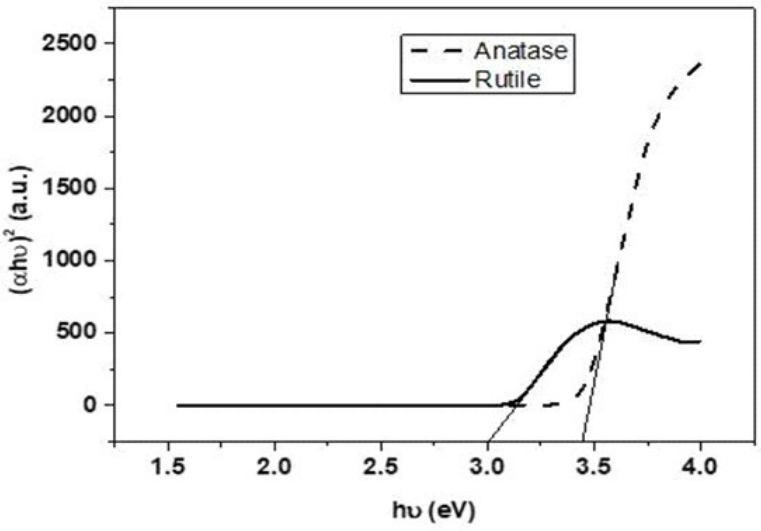

Fig: 4 Tauc Plot of TiO2 nanoparticles

Direct bandgap (Ed) of samples is determined by fitting absorption data to direct transition equation,

$$áhõ = Ed(hõ - Eg)^{½}$$

where á is optical absorption coefficient, hõ photon energy and a constant. Band gap of the samples have been measured by plotting as a function of photon energy hí and extrapolating linear portion of the curve to absorption equal to zero. The anatase and rutile samples had band gap energies of 3.43 and 3.00 eV, respectively. In general, rutile has a lower bandgap (about 3.05eV) than anatase phase and is the most thermostable form of TiO2. Figure 5 shows a strong and wide PL signal from 400 to 500 nm, as well as a shoulder peak at 377 nm and an excited wavelength of 300 nm. The shoulder peak is caused by direct recombination of electrons in the conduction band with holes in the valence band. The surface trap states are responsible for the emission peak at 470 nm. Both examples show a similar sort of PL signal with no discernible difference in curve form. The intensity of anatase emission is greater than that of rutile sample. The oxygen vacancy concentration increases as particle size decreases, and hence absorbance across the UV and visible range increases. Higher temperature annealing reduces the intensity of emission by decreasing defect centres of rutile phase

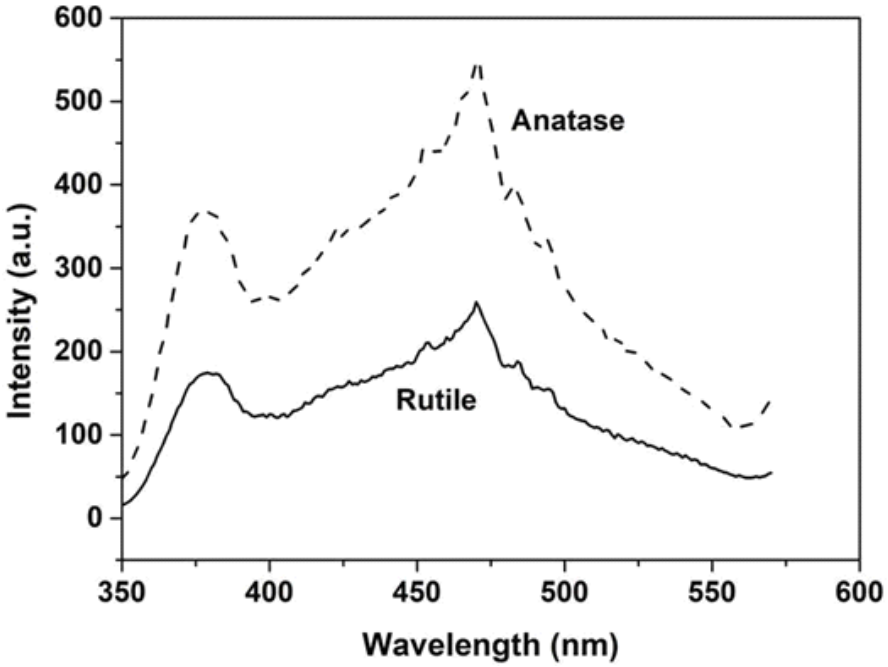

Fig:5 PL spectra of TiO2 nanoparticles

CONCLUSION

The sol-gel technique was used to successfully synthesise TiO2 NPs. The TGA experiments reveal that the sample loses no weight after being heated to 400^{O}C. As a result, the as-prepared samples are heated for three hours at 400 and 800^{O}C. X-ray diffraction investigations demonstrate a rise in the intensity of diffraction peaks, a decrease in FWHM, and an increase in crystallite size. The anatase and rutile samples had crystallite sizes of 11.3 and 58 nm, respectively. The optical absorption spectra of TiO2 sample showed high absorption in the UV range. A hump is visible between 300 and 400 nm, which is more visible in the rutile sample.The band gap energy values obtained for the anatase and rutile samples are 3.43 and

3.00 eV, respectively, which are in close agreement with the values obtained in other samples. The samples exhibit a strong and wide PL signal from 400 to 500 nm and a shoulder peak at 377 nm with an excited wavelength of 300 nm. Both examples show a similar sort of PL signal with no discernible difference in curve form. The intensity of anatase emission is greater than that of rutile sample.

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