

A Simple Chemical Precipitation Method of Titanium Dioxide Nanoparticles Using Polyvinyl Pyrrolidone as a Capping Agent and Their Characterization

V. P. Muhamed Shajudheen, K. Viswanathan, K. Anitha Rani, A. Uma Maheswari, S. Saravana Kumar

Abstract—In this paper, a simple chemical precipitation route for the preparation of titanium dioxide nanoparticles, synthesized by using titanium tetra isopropoxide as a precursor and polyvinyl pyrrolidone (PVP) as a capping agent, is reported. The Differential Scanning Calorimetry (DSC) and Thermo Gravimetric Analysis (TGA) of the samples were recorded and the phase transformation temperature of titanium hydroxide, $Ti(OH)_4$ to titanium oxide, TiO_2 was investigated. The as-prepared $Ti(OH)_4$ precipitate was annealed at $800^\circ C$ to obtain TiO_2 nanoparticles. The thermal, structural, morphological and textural characterizations of the TiO_2 nanoparticle samples were carried out by different techniques such as DSC-TGA, X-Ray Diffraction (XRD), Fourier Transform Infra-Red spectroscopy (FTIR), Micro Raman spectroscopy, UV-Visible absorption spectroscopy (UV-Vis), Photoluminescence spectroscopy (PL) and Field Effect Scanning Electron Microscopy (FESEM) techniques. The as-prepared precipitate was characterized using DSC-TGA and confirmed the mass loss of around 30%. XRD results exhibited no diffraction peaks attributable to anatase phase, for the reaction products, after the solvent removal. The results indicate that the product is purely rutile. The vibrational frequencies of two main absorption bands of prepared samples are discussed from the results of the FTIR analysis. The formation of nanosphere of diameter of the order of 10 nm, has been confirmed by FESEM. The optical band gap was found by using UV-Visible spectrum. From photoluminescence spectra, a strong emission was observed. The obtained results suggest that this method provides a simple, efficient and versatile technique for preparing TiO_2 nanoparticles and it has the potential to be applied to other systems for photocatalytic activity.

Keywords— TiO_2 nanoparticles, chemical precipitation route, phase transition, Fourier Transform Infra-Red spectroscopy, micro Raman spectroscopy, UV-Visible absorption spectroscopy, Photoluminescence spectroscopy, Field Effect Scanning Electron Microscopy.

I. INTRODUCTION

AMONG many semiconducting transition metal oxides, TiO_2 nanoparticles in different phases have become standard in environmental applications because they proved to be efficient, biologically and chemically inert, inexpensive,

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resistant to photo corrosion and chemical corrosion, nontoxic, highly photoactive, recyclable and have suitable band gap ($E_g = 3.2$ eV) in which its redox potential of the $H_2O/\bullet OH$ couple (-2.8 eV) lies. These properties make TiO_2 a main candidate for broad applications in photochemical solar cells, photocatalysis, chemical sensors, dielectric material of ultrathin-film capacitors, as pigments, self-cleaning surfaces and environmental purification applications [1]. TiO_2 nanoparticles exist in several forms, such as amorphous, anatase and rutile depending on fabricating conditions and further heat treatment [2], [3].

Until now, TiO_2 nanoparticles are prepared by various methods like sol-gel method [4], solid state reaction method [5], reverse microemulsion method [6], chemical vapour deposition method [7], hydrothermal method, solvothermal method, physical vapour deposition method, microwave method and sonochemical method [8]-[10]. Among the synthetic approaches co-precipitate method is considered to be one of the best techniques and potentially advantageous in comparison to other method to produce pure phase formation of compounds, low temperature preparation, highly purity and yield nanopowders [11], [12]. The present work is an attempt to prepare pure rutile phase of TiO_2 nanoparticles. The obtained results are sleeved for their thermal analysis, structure, chemical analysis, morphology and optical characterization.

II. PROCEDURE

All the chemicals reagents used in our experiments were of analytical grade, commercially purchased from Merck used as received without further purification. Nanoparticles of TiO_2 were prepared using the precursor titanium isopropoxide and isopropyl alcohol. 100 ml of isopropyl alcohol was added to 15 ml of titanium isopropoxide and stirred for 30 minutes. To this solution 0.1 gm of PVP was added and stirred for 20 minutes. For hydrolysis reaction 10 ml of deionised water was added dropwise to the mixed solution. The resulting white precipitate of $Ti(OH)_4$ is refluxed for 2 hours and then it is stirred continuously for one day. Finally, the precipitate is centrifuged with deionized water and ethanol to remove impurities. After centrifuging, the white precipitate is dried at $80^\circ C$ for one day. Finally, the as-prepared $Ti(OH)_4$ precipitate was annealed at $800^\circ C$ to obtain TiO_2 nanoparticles. The oxidation mechanism of $Ti(OH)_4$ from ambient up to $1400^\circ C$ was investigated by thermogravimetric (TG) and Differential scanning calorimeter (DSC) using Perkin Elmer, Diamond

DSC-TGA set up. Significant phase transformation of $\text{Ti}(\text{OH})_4$ to TiO_2 is found to be above 400°C . And then the final product was investigated by XRD, micro Raman, FESEM, UV-Visible absorption, Photoluminescence techniques. XRD patterns of the TiO_2 samples were recorded using a Philips Xpert pro Diffractometer and using $\text{CuK}\alpha$ radiation over the diffraction angles (2θ) from 20 to 80° . The micro Raman spectra of TiO_2 nanoparticles were recorded using Horiba Labram-HR, in the range of 100 - 1400 cm^{-1} . The Nd:YAG laser operating at 200 mW power at 1064 nm was the excitation source, and a liquid nitrogen cooled Ge detector was used to record the spectrum. The room temperature FT-IR spectrum of TiO_2 nanoparticles was recorded in the range of 400 - 4000 cm^{-1} , using Shimadzu FTIR-8400S spectrometer. UV-Vis spectrophotometry and photoluminescence spectra of nanoparticles of TiO_2 were recorded using Varian, Cary 5000 spectrophotometer and JASCO FP 8200 Spectrofluorometer. The FESEM images of TiO_2 nanoparticles were recorded using Carl Zeiss Sigma HD FESEM, respectively.

III. RESULTS AND DISCUSSION

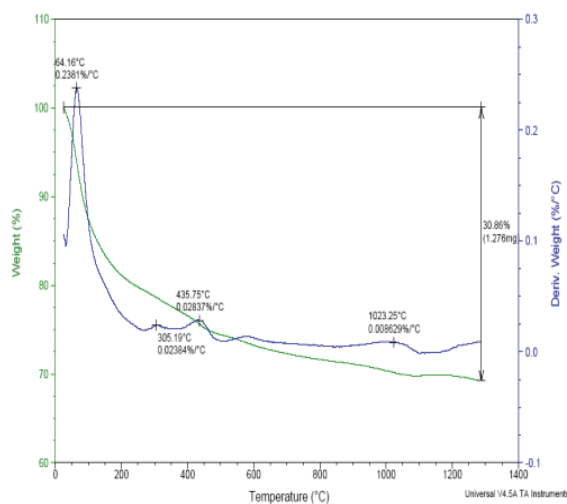


Fig. 1 DSC-TGA curves of TiO_2 nanoparticles

The differential scanning calorimeter (DSC) and thermogravimetric analysis (TGA) of nanoparticles of $\text{Ti}(\text{OH})_4$ are shown in Fig. 1. The amount of organic groups and inorganic groups before annealing was obtained by TGA curves. The TGA curve shows that the precipitated nanopowders exhibited a weight loss of 30% in the temperature range of 25 - 200°C due to the evaporation of water and organic solvent and the decomposition of titanium salts. The broad exothermic peak between 25 - 100°C is mainly attributed to the decomposition of the inorganic salts. The weight loss of 15% and the sharp exothermic peak at 100°C confirms crystallization of the prepared precipitated $\text{Ti}(\text{OH})_4$ nanopowders.

Fig. 2 demonstrates the powder XRD spectra of TiO_2 nanoparticles annealed at 800°C .

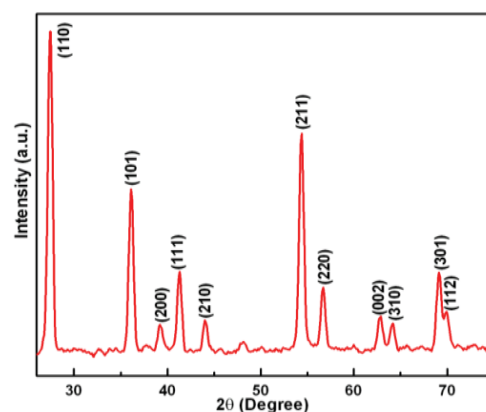


Fig. 2 XRD pattern of TiO_2 nanoparticles

The presence of a broad XRD peaks is an indication of nanocrystalline nature of TiO_2 nanoparticles. The prominent peaks exist at an angle of $2\theta = 27.44^\circ, 36.15^\circ, 39.24^\circ, 41.45^\circ, 44.07^\circ, 54.51^\circ, 56.65^\circ, 62.74^\circ, 64.16^\circ, 69.08^\circ$ and 69.82° corresponding to the reflections from (110), (101), (200), (111), (210), (211), (220), (022), (310), (301) and (112) planes of TiO_2 . The observed pattern was compared with standard JCPDS data (card no. 89-4920) and matches well with the rutile phase of titania [13]. Using full width at half maximum of predominant peak and Debye-Scherrer formula [14], the average grain size was estimated to be approximately 15 nm .

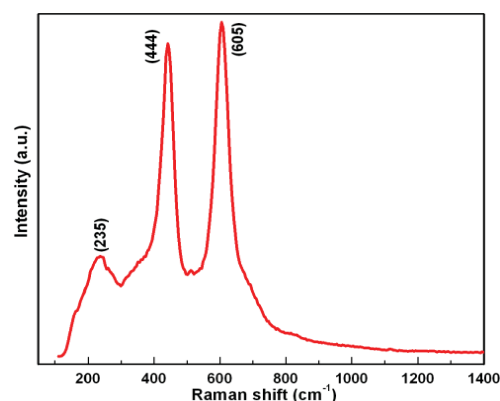


Fig. 3 Micro-RAMAN spectra of TiO_2 nanoparticles

It is tricky to find the crystal structure with XRD alone of TiO_2 nanoparticles as it overlaps with different phases such as anatase, rutile and brookite. Here, Raman spectroscopy was introduced to confirm the crystal structure for TiO_2 nanoparticles annealed at 800°C . The rutile mode has the average peak position of 444 cm^{-1} of E_g rutile mode and an average peak position of 605 cm^{-1} has A_g rutile mode [15]. Compare to nanoparticles, the bulk materials have changes due to modulation in the surrounded system. In this limited system, Raman-active modes are slightly affected among IR active, Raman active, and silent modes is blurred due to the clusters. Here, Raman active modes of prepared TiO_2 nanoparticles of rutile IR-active mode, 444 cm^{-1} which is close

to E_g Raman mode. Therefore, this could cause the red shift of our samples in asymmetric shape of the E_g peak in the Raman spectra, determining the different behaviour of E_g and A_{1g} modes [16].

Fig. 4 shows the FT-IR spectra of TiO_2 nanoparticles annealed at $800^\circ C$ in the range from $(400-4000\text{ cm}^{-1})$. The strong absorption bands observed at 555 cm^{-1} , confirms the titanium metals with no shoulder peaks. By using FT-IR analysis, the removal of unwanted ions, phase formation, organic impurities that can destroy a crystal lattice at that time of preparation was confirmed. The typical vibrations centered at 3410 and 1640 cm^{-1} , confirms the broad bands of O-H groups. FT-IR spectra were confirmed by earlier reports [17].

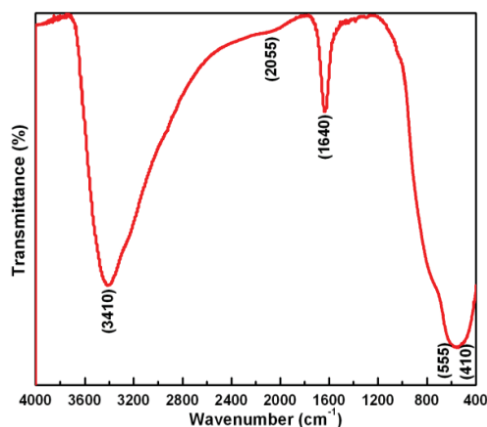


Fig. 4 FTIR spectra of TiO_2 nanoparticles

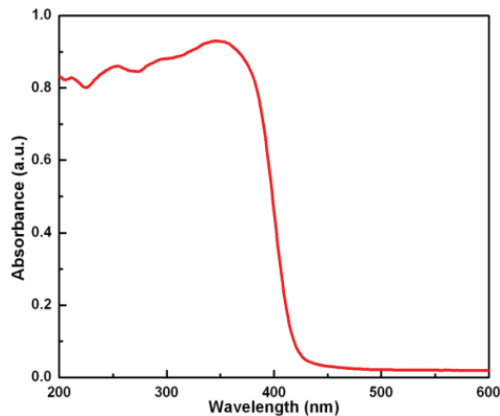


Fig. 5 Absorption spectra of TiO_2 nanoparticles

The optical absorption spectrum of TiO_2 nanoparticles annealed at $800^\circ C$ were recorded at the room temperature in the wavelength range of 200 to 600 nm is shown in the Fig. 5. The maximum absorption peak λ_{max} , of prepared TiO_2 nanoparticles is obtained at about 350 nm . The sharp peak at 350 nm in the absorption spectrum of TiO_2 nanoparticles of present study is blue shifted indicating quantum confinement effect.

The value of optical band gap can be determined by plotting a graph of $(\alpha h\nu)^2$ vs $h\nu$ Fig. 6 and by extrapolating the linear portion of the curve to x – axis at $\alpha = 0$. The band gap value as

calculated is 3 eV and is low compared to bulk band gap value of 3.84 eV . The smaller band gap of nanoparticles of TiO_2 of present study indicates that these samples are suitable for photocatalytic applications [18].

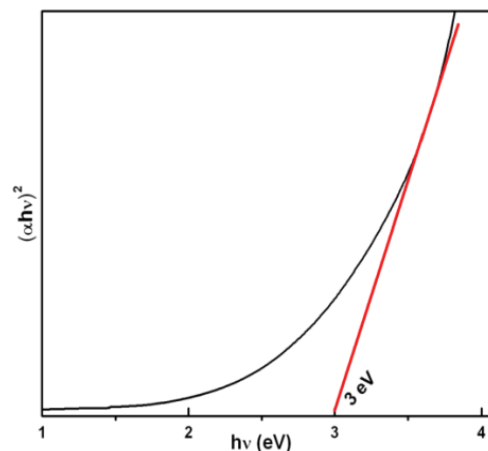


Fig. 6 Band gap of TiO_2 nanoparticles

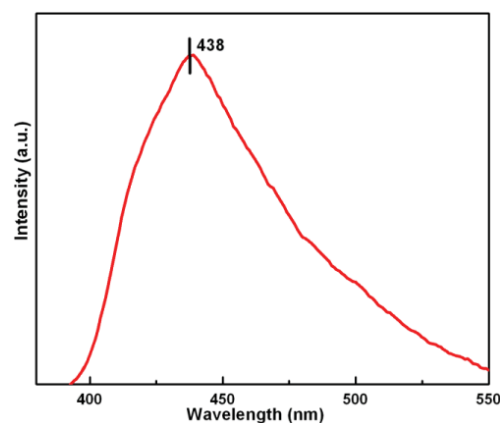


Fig. 7 Photoluminescent spectra of TiO_2 nanoparticles

In general, there is a possibility of two types of emission in semiconducting nanoparticles, the band edge (BE) emission and the surface defect emission that lie in the wavelength range below and above 500 nm respectively. The PL spectrum for TiO_2 nanoparticles is shown in Fig. 7. The emission peak observed at 438 nm (2.84 eV) in the photoluminescence spectrum cannot be ascribed to band edge emission since the band gap is around 3 eV . The above peak can be ascribed to radiative transition between shallow defect levels found near the band edges.

FESEM micrographs for TiO_2 nanoparticles annealed at $800^\circ C$ are representative in Fig. 8. FESEM is used to study the surface of the prepared TiO_2 nanoparticles. It reveals some graphs like structure, spherical shape and coarse structure with aggregate state. It is evident from the picture that the average particle size calculated using line section method is in the range of 10 nm , which is very close to the XRD grain size

value [19].

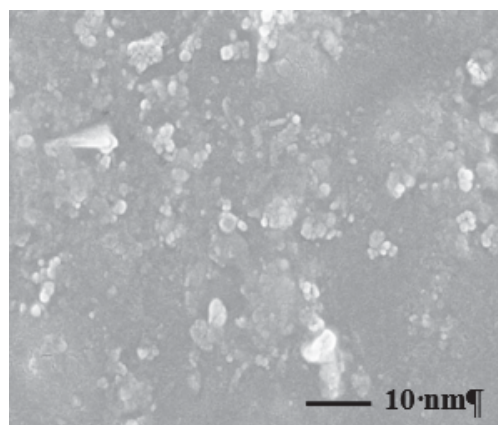


Fig. 8 FESEM photograph of TiO₂ nanoparticles

IV. CONCLUSION

In this work, we have shown fundamental aspects of rutile TiO₂ nanoparticles synthesized by using titanium tetraisopropoxide as a precursor and PVP as a capping agent by a simple chemical precipitation route. From DSC-TGA results, the decomposition of ions is confirmed. The main advantage of co-precipitate method is to achieve the rutile TiO₂ nanoparticles in a single step process without impurities and other phases. All these studies confirm the rutile phase prepared in a low temperature condition. From XRD analysis, it is clear that the prepared TiO₂ nanoparticles are in rutile phase. The asymmetric shape of the E_g peak in the Raman spectra, determined the different behaviour of E_g and A_{1g} modes. From FTIR spectra, the strong absorption bands observed at 555 cm⁻¹, confirms the titanium metals with no shoulder peaks. From the optical studies, the band gap is found to be blue shifted. Hence, it was confirmed that the prepared TiO₂ nanoparticles sample was suitable for photocatalytic application using UV light.

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