Synthesis and Characterization of Controlled Size TiO_2 Nanoparticles via Green Route using *Aloe vera* Extract

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Abstract: ***Titanium dioxide is an important semiconductor material for wide range of solar energy conversion applications. However, it is limited due to its high bandgap as well as high charge carrier recombination rate under illumination. This can be overcome partly by controlling the size of the particle via green synthesis route using Aloe vera gel extraction, wherein the kinetics and thermodynamics are equally modulated. The synthesized particles were characterized using different characterization techniques such as SEM, TEM, XRD, UV-Vis, and FTIR. The outcomes of present work will help to design more pronounced synthesis protocols for production of highly mono dispersed TiO_2 nanoparticles for various electro/photoelectrochemical applications.***

Keywords:

1. Introduction

Our environment is suffering huge damage by the release of large amount of hazardous chemicals, gases or substances into the environment due to rapid industrialization and urbanization. Therefore there is an urgent to learn about the use of natural products for development of advanced functional nanomaterials [1]. Nanotechnology is the manipulation of matter on an atomic molecular and super molecular scale, ranging in dimensions 1 to 100 nm. It is one of the most active research areas in modern material science. It is the study of extremely small things and can be used across all the science fields such as chemistry, biology, physics, material science and engineering [2]. Titanium dioxide is a solid inorganic substance. It is a white color metal oxide.TiO_2 is poorly soluble, non-flammable and thermally stable. It is not classified as hazardous according to the United Nations (UN) Globally Harmonized System (GHS) of Classification and Labeling of Chemicals [3]. It can exhibit three different phases in nano- range at the different temperatures, such as anatase, rutile and brookite. Among these phases, Anatase has been proved to have extraordinary chemical and physical properties for environmental remediation [4]. It is also having high quality properties such as hydrophobicity, non-wettability and large band gap. Hence, it is used in the various industrial applications such as dye sensitized solar cell, photo catalysis, self-cleaning, charge spreading devices, chemical sensors, microelectronics, electrochemistry, anti bacterial products and textiles [5-8].

Traditionally most of the metal and metal oxide nanoparticles were routinely synthesized by various physical and chemical methods. Some of the commonly used synthetic methods are non-sputtering, solvothermal, reduction, sol-gel technique and electrochemical technique [9-12]. But these methods are costly, toxic, high pressure, high energy requirement, difficult separation and potentially hazardous. The green synthesis process is eco-friendly technique due to use of extracts of plant (leaves, flower, seed and peels), bacteria, fungi and enzymes for synthesis of titanium dioxide nanoparticles instead of large quantity of chemicals [13]. Green synthesis provides more advantages over physical methods and chemical methods because it is very cost effective, easy process and scalable for large scale production. This method does not require for high temperature, high pressure, costly equipment and hazardous chemicals.

The present work is based on the *Aloe vera* plant extract. *Aloe vera* is oldest medicinal plant ever known. It is most applied medicinal plant belonging to succulent plant species. This species is frequently cited as being used in herbal medicines since the beginning of the first century AD. It is a stemless plant growing to 60-100 cm (24-39 in) tall and the leaves are thick and fleshy, green to grey-green, with some varieties showing white flecks on the upper and lower stem surfaces [14]. *Aloe vera* gel contains a large range of vitamins such as vitamin B12, vitamin A, other B-Group vitamins, vitamin C, vitamin E, folic acid and 19 of the 20 amino acids needed by the human body. *Aloe* is a powerful detoxifier, antiseptic, tonic for the nervous system, possesses immune boosting and anti-viral properties and improves digestion. Extracts of *Aloe vera* is a proven skin healer and help the skin injuries affected by skin irritations, insect bites, burns and cuts [15]. The *Aloe vera* extract contains water soluble substances like Aloe emodin, Chrysophonal, and Helminthospor. These compounds act as reducing agents to produce TiO_2 particles from the precursor [16,17]. The nanoparticles prepared will be used in photocatalytic applications such as degradation of dye and water splitting. The chosen dye is crystal violet and chosen substrate is Ti for degradation and water splitting studies respectively. The experiments are presently in progress.

2. Experiments

Preparation of Aloe vera plant extract

Fresh and healthy *Aloe vera* plant was collected from campus of JNTU Ananthapuramu, Andhra Pradesh. One of the selected leaves was cut and washed twice with tap water followed by distilled water to remove dust particles and other contaminants. 50g of the leaves was weighed using electronic weighing balance and transferred into a 500ml beaker containing 250ml distilled water. The contents were boiled for 2h at 90°C. The extract was filtered using Whatman filter paper. The filtrate was stored for the synthesis of nanoparticles.

Preparation of titanium dioxide nanoparticles

0.1 M of Titanium isopropoxide ($C_{12}H_{28}O_4Ti$) was prepared using double distilled water. Aloe vera leaves extract was added drop wise under constant stirring to achieve a solution of pH 7. The mixture was subjected to stirring for 4 hours continuously. In this process nano particles were formed and were separated using Whatman filter paper. The particles were washed with double distilled water repeatedly to remove the by-products if any. The nanoparticles were dried at 100°C overnight and calcined at 500°C for 4 hours.

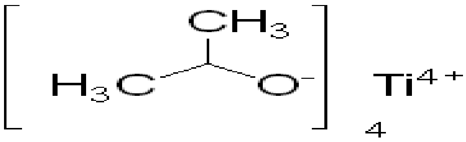

Figure 2.1: Structure of TTIP

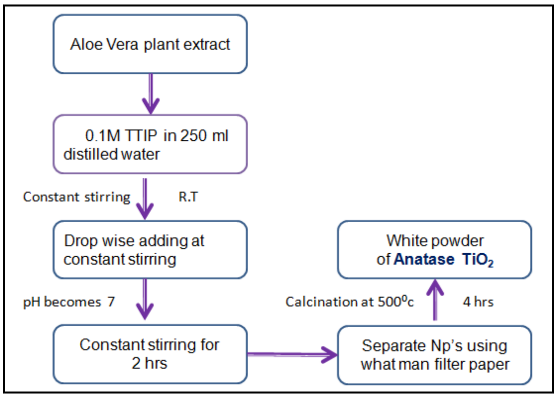

Figure 2.2: Flow chart representation of synthesis of nanoparticles

Characterization techniques

Characterization of titanium dioxide nanoparticles is necessary to establish an understanding and control of nanoparticle synthesis. Characterization was done by using the following different techniques

- X-Ray Diffractometer[XRD]
- Scanning Electron Microscope[SEM]
- Ultra Violet Visible Spectroscopy[UV-Vis]
- Fourier Transform Infrared Spectroscopy[FTIR]
- Particle Size Analyzer[PSA]

3. Results and Discussion

X-Ray Diffractogram (XRD) Analysis

The formation of titanium dioxide nanoparticles synthesized using *Aloe vera* leaves extract was supported by X-ray diffraction measurements.

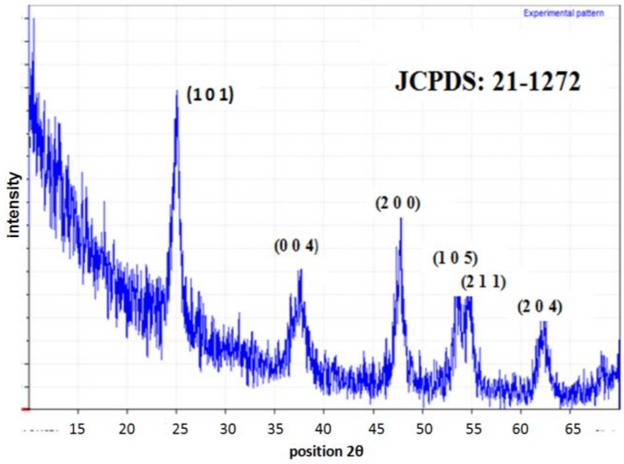

Figure 3.1: X-Ray Diffractogram ofTiO$_2$ nanoparticles

XRD analysis (Fig 3.1) showed six distinct diffraction peaks at 25.3°, 37.8°, 47.9, 54.5°, 62.8°, 69.5° and 75.1° which indexed the planes (101), (004), (200), (105),(211) and (204) respectively of the tetragonal titanium dioxide ((JCPDS No.21-1272). The average grain size formed in the green synthesis was determined using Scherrer's formula, $d = 0.89\lambda/\beta\cos\theta$ was estimated as 12 nm for the higher intense peak. The sharp peaks and absence of unidentified peaks showing that crystallite and higher purity of synthesized nanoparticles [18].

Table 1: Calculation of d-spacing values

S.No	Wave Length	COS θ	d nm
1	0.154	12	7.09
2	0.025	24	5.47
3	0.0076	26.5	13.01
4	0.0101	31	13.55

Ultra Violet (UV) Visible (VIS) Spectroscopy analysis

The absorption spectra of TiO_2 nanoparticles exhibit strong absorption below 400nm. Spectrum of TiO_2 sample at 400ºC indicates the absorption onset at around 393 nm which is in excellent agreement with band gap of anatase phase [20]. The absorption spectrum of TiO_2 nanoparticles is shown in Fig.3.2.

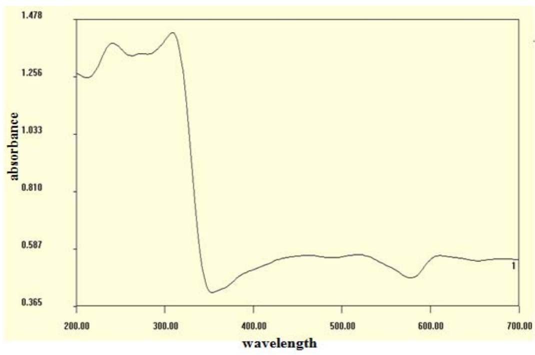

Figure 3.2: Absorption spectrum of TiO_2 nanoparticles

The band gap energy was determined based on the numerical derivative of the optical absorption coefficient. The fundamental absorption method refers to band to band transitions by using energy relation **E = hν** = h.c/ λ where C is the speed of light in vacuum (3 x 10^8 m/s), λ is the wave length of the λ=c/ν (λ=393 nm), h is Plank's constant (6.626

x 10^{-34} J.s), ν is the frequency. Band gap energy is calculated as

$$E=(6.6025 \times 10^{-34})\ (3 \times 10^{8})\ /393 = 3.196 \text{ eV}.$$

Scanning Electron Microscope (SEM) analysis

The analysis was carried out in 'Analytical Laboratory' of College of Engineering and Technology, at Osmania University, Hyderabad (TS). The grain size, shape and surface properties like morphology were investigated by the Scanning Electronic Microscopy (Fig 3.3).

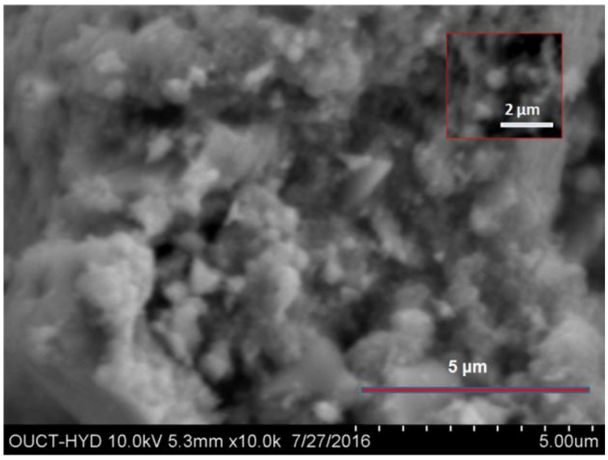

Figure 3.3: SEM images of TiO_2 nanoparticles

The SEM image was observed within the magnification of 5µm.The TiO_2 nanoparticles were showing irregular particle structure. The size was ranging from 60 nm to 80 nm [19].

Fourier Transform Infrared (FTIR) Spectroscopy analysis

The sample was submitted to FTIR at RIPER Anantapur. The spectrum is shown in the Figure 3.4.

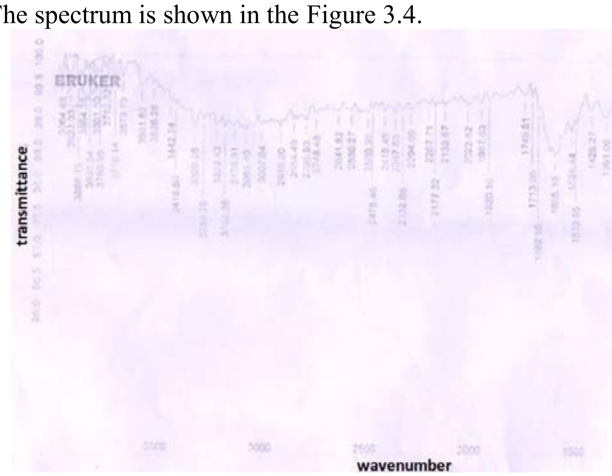

Figure 3.4: FTIR spectrum of TiO_2 nanoparticles

The spectrum of TiO_2 shows diffraction peaks corresponding to the broadband centered at 543 cm^{-1} characteristic of Ti–O bending mode of vibration which confirms the formation of metal oxygen bonding. The peak at 1682 cm^{-1} was due to O–H bending vibration of adsorbed water molecule on the surface of TiO_2 which may have crucial role in photocatalytic activity. The broad peak appearing at 3329 cm^{-1} is attributed to stretching vibration of –O–H. Also there are no other additional peaks related to organic moiety [21].

Particle Size Analyzer (PSA) analysis

The average particle size was found using Particle Size Analyzer. The particles were submitted to CNST, IST, JNTU Hyderabad. That material was dispersed completely in ethanol using ultra-sonicator. Figure 3.5 represents the histograms of the dispersed nanoparticles.

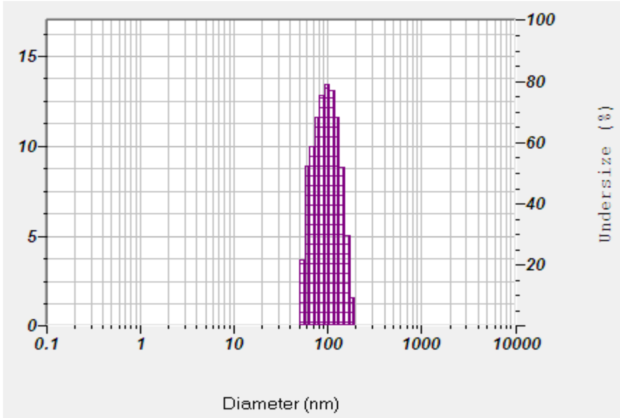

Figure 3.5: Particle size distribution of TiO_2 nanoparticles

The mean value of the histograms was taken as the average particle size. The average particle size was obtained as 30 nm. These results supported the XRD average crystallite size as 12 nm [21].

4. Conclusions

The following conclusions are drawn from the present study:

1) The TiO_2 nanoparticles were successfully synthesized using green synthesis method.
   - From XRD analysis average crystallite size of the sample was obtained 12 nm. It is observed that tetragonal structure with anatase phase was formed.
   - The average particle size was estimated as 30 nm using particle size analyzer.
   - The irregular particles were observed in SEM image.
   - Absorption spectrum of TiO_2 sample indicates the absorption onset at around 393 nm which is in excellent agreement with band gap of anatase phase (~3.2 eV).
2) This simple, cost effective, time saving and environmental friendly synthesis method gives a potential avenue for various applications.
3) The eco-friendly green chemistry approach which is sustainable, using *Aloe vera* leaf extract for the synthesis of nanoparticles will increase the economic viability of the process.

5. Future Scope

Degradation kinetics will be studied and effect of different parameters such as pH, catalyst concentration, substrate concentration and presence of electron acceptors such as hydrogen peroxide, aluminium persulfate besides molecular oxygen on degradation of crystal violet dye can be carried out. The potential of green titanium dioxide nanoparticles in carrying out water splitting reaction also may be studied and results can be compared with those of earlier studies.

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References

[1] Tamasa panigrahi, Dr. sumanjha "synthesis and characterization of silver nanoparticles using the leaf of Azadirachtaindica". Journal of Radiation Research and Applied Sciences, pp:12,(2013)

[2] Tarafdar J.C., shikha Sharma and Ramesh Raliya "Nanotechnology interdisciplinary science of applications". African journal of biotechnology vol.12(3), pp219-226,(2013)

[3] Aadarsh Mishra, Analysis Of Titanium Dioxide And Its Application In Industry, Int. J. Mech.Eng. & Rob. Res., 3(3), 7pages, 2014

[4] Rajneesh Mohan, Jana Drbohlavova and JaromirHubalek, Water-dispersible TiO_2 nanoparticles via a biphasic solvothermal reactionmethod, Nanoscale Research Letters, 8(1),4 pages, 2013.

[5] SaowalukBoonyod, WeerawanSutthisripok and LekSikong, Antibacterial Activity of $TiO_2$and Fe^{3+} doped TiO_2 Nanoparticles Synthesized at Low Temperature, Advanced Materials Research, 214, 197 2011.

[6] DejanVerhovsek, NikaVeronovski, Urska Lavrencic Stangar, Marko Kete, Kristina Zagarand MiranCeh, The Synthesis of Anatase Nanoparticles and the Preparation of Photocatalytically Active Coatings Based on Wet Chemical Methods for Self-Cleaning Applications, International Journal of Photo energy, ID 329796, 10 pages, 2012.

[7] Ibrahim Dar. M., Aravind Kumar Chandiran, Michael Gratzel, Mohammad K. Nazeeruddin and Srinivas rao A. Shivashanka, Electronic Supplementary Information Controlled synthesis of TiO_2 nanoparticles and nanospheres using a microwave assisted approach for their application in dye-sensitized solar cells, The Royal Society of Chemistry, 7 pages, 2013.

[8] ZeljkoSenic, Sonja Bauk, MajaVitorovicTodorovic, NatasaPajic, AleksandarSamolov and DusanRajic, Application of TiO_2 Nanoparticles for Obtaining Self-Decontaminating Smart Textiles, Scientific Technical Review, 61(3-4), 63 2011.

[9] Balantrapu, Krishna, and Dan V. Goia. "Silver nanoparticles for printable electronics and biological applications." Journal of materials research 24.09 (2009): 2828-2836).

[10] Saxena, Antariksh, R. M. Tripathi, and R. P. Singh. "Biological synthesis of silver nanoparticles by using onion (Allium cepa) extract and their antibacterial activity." Dig J Nanomater Bios 5.2 (2010): 427-432.

[11] Rodriguez-Sanchez, L., M. C. Blanco, and M. A. Lopez-Quintela. "Electrochemical synthesis of silver nanoparticles." The Journal of Physical Chemistry *B* 104.41 (2000): 9683-9688.

[12] Taleb, A., C. Petit, and M. P. Pileni. "Synthesis of highly monodisperse silver nanoparticles from AOT reverse micelles: a way to 2D and 3D self-organization." Chemistry of Materials 9.4 (1997): 950-959.

[13] Vijaylaxmee Mishra, Richa Sharma, Nakuleshawar DutJasuja and Deepak Kumar Gupta, A Review on Green Synthesis of Nanoparticles and Evaluation of Antimicrobial Activity, International Journal of Green and Herbal Chemistry, 3(1), 081 2014.

[14] Yuvasree. P., Nithya. K. and Neelakandeswari.N., Biosynthesis of Silver Nanoparticles from Aloe Vera Plant Extract and its Antimicrobial Activity Against Multidrug Resistant Pathogens, Proceedings of the International Conference on Advanced Nanomaterials & Emerging Engineering Technologies, Pp 84-86, (2013).

[15] Rajeswari. R., Umadevi. M., SharmilaRahale. C., Pushpa. R., Selvavenkadesh. S.,Sampath Kumar. K.P. and DebjitBhowmik, Aloe Vera: The Miracle Plant Its Medicinal and Traditional Uses in India, Journal of Pharmacognosy and Phytochemistry, 1(4), 118 2012.

[16] Kavanagh, F., "Analytical Microbiology. F. Kavanagh (ED)", VOL II, Academic Press New York, and London, P: 11,1972.

[17] Zhang LL, Jiang YH, Ding YL, Povey M, York D., "Investigation into the antibacterial behaviour of suspensions of ZnO nanoparticles zno nanofluids". J.Nanopart. Res; 9:479–489, 2007.

[18] PusitPookmanee and SukonPhanichphant, Titanium dioxide powder prepared by a sol gel method, Journal of Ceramic Processing Research, 10(2), 167 2009.

[19] G Ouyang, KWang and X Y Chen, TiO_2 nanoparticles modified polydimethylsiloxane with fast response time and increased dielectric constant, Journal of Micromechanics And Micro engineering, 22, 9 pages 2012.

[20] Ashok. CH. And VenkateswaraRao. K., ZnO/TiO_2 nanocomposite rods synthesized by microwave-assisted method for humidity sensor application, Superlattices and Microstructures, 76, 46 2014.

[21] Khade, G. V., et al. "Green synthesis of TiO_2 and its photocatalytic activity."Journal of Materials Science: Materials in Electronics 26.5 (2015): 3309-3315.