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Green Chemistry based for the Synthesis of Titanium Oxide Nanoparticles Using Extracts of Azadirachta Indica

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Abstract:- The colossal significance of nanostructured materials and their implications as a coherent incentive for the exploration of novel conventional techniques. Biogenic synthesis of nanostructured materials utilizing natural herb extracts has enthralled prodigious implications owing to its rapid, clean, eco-friendly, non-toxic, cost-effective, and as a flipside pathway to several chemical and physiochemical approaches. Titanium oxide materials have been the cynosure for several propitious implications due to their low cost, availability, chemical stability, and biocompatibility. Herein, we developed an efficient green chemistry method for the synthesis of titanium oxide nanoparticles utilizing neem (*Azadirachta Indica*) extracts. The X-ray diffraction studies revealed the polycrystalline titanium oxide (rutile) structure. The spherical shape of the nanoparticles was observed in TEM and SEM images and their size ranged from 10-20 nm. UV-vis studies showed an exciton emission peak at about 380 nm while the IR transmission spectrum revealed the characteristic stretching modes of TiO_2. It is envisioned that this novel route for the synthesis ofTiO_2nanoparticles could be more beneficial in comparison to other conventional approaches.

Keywords:- *TiO_2, Neem Extracts, Titanium Iso-Propoxide, Green Chemistry, Biogenic Synthesis.*

I. INTRODUCTION

Owing to the marvelous applications and several others that are yet to be explored, an astonishing growing area of research on nanoparticles hails the rational fabrication of the nanoparticles by which the aspired functionality could be obtained. Nanoparticles with clearly described size, shape, and distribution have come to prominence for investigating the effect of morphological changes on several chemical and physical characteristics. A variety of experimental approaches including electric deposition, melt mixing, physical vapor deposition, sol-gel chemistry, metal-salt reduction, micro-emulsion confined reaction, co-precipitation, photoreduction, hydrothermal, laser ablation, etc. involving the use of capping agents have been employed for synthesis. Howbeit, the use of hazardous chemicals, non-polar solvents, synthetic additives, capping agents, and the need for an economically feasible environment-friendly method has preluded their implication and turned research towards developing benign synthesis approaches utilizing 'green chemistry' and bioprocesses [1-3]. Greener approach fabrication of nanoparticles employing naturally derived biodegradable materials for instance vitamins, enzymes, micro-organisms, plant extracts, polysaccharides, and bio-based polymers have been developed to explore the inherent applications of nanomaterials ranging from biosensing and catalysts to optics, transistors, electrical, chemical schemes and other myriad applications. Nanoparticles synthesized using this approach deliver biodegradable and biocompatible materials with enhanced catalytic activity and restrict the utilization of exorbitant, noxious chemicals.

Titanium Oxide is amidst the most immensely investigated material owing to its innocuous characteristics, thermal and chemical stability, availability, and low cost. Three distinct polymorphs viz., brookite, rutile, and anatase with band gaps of 3.2, 3.0, and 3.2*eV* have been ascribed to the binary metal oxide. Innumerable methods including hydrothermal, sol-gel route, sputtering, polyol synthesis, and precipitation among others have been reported in the synthesis of TiO_2 nanoparticles [4]. However, so far minimal indagation has been reported on the fabrication of TiO_2 nanoparticles using the green chemistry approach [5, 6]. The present work is focused on the utilization of a green chemistry approach for the synthesis of TiO_2 nanoparticles employing *Azadirachta Indica* (Neem)leaf extract. *Azadirachta Indica* belongs to the Meliaceae family. The exotic, evergreen tree is recognized for more than 200 hundred years as the popular cure-all plant, exhibiting a broad spectrum of biological activity. Neem leaves extracts to proffer paramount ascendancy over other herb plants. The phytochemicals produced by the Neem plant, specifically terpenoids and flavanones act as capping and reducing agents which aid in stabilizing the nano-structured particles [7, 8]. Recently, green synthesis of nanoparticles employing neem leave extracts has been reported for the synthesis of palladium [9], silver [10], zinc oxide [11], copper oxide [12], titanium oxide [13], manganese oxide nanoparticle [14], etc.

In the present research article, we have explored the bottom-up approach utilizing oxidation/reduction reaction for the green synthesis of TiO_2nanoparticles. The bottom-up approach is the best-considered approach as precision at the atomic scale is attained. The general route to synthesize TiO_2nanoparticles involves the formation of titanium precursor solution by introducing the desired solvent. The present study utilizes Titanium isopropoxide as the precursor. The resultant nanoparticles are characterized by employing Fourier transform infrared spectroscopy, Scanning electron microscopy, X-ray diffraction, UV-visible spectrophotometry, and Transmission electron microscopy.

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II. EXPERIMENTAL

A. Chemicals and Reagents

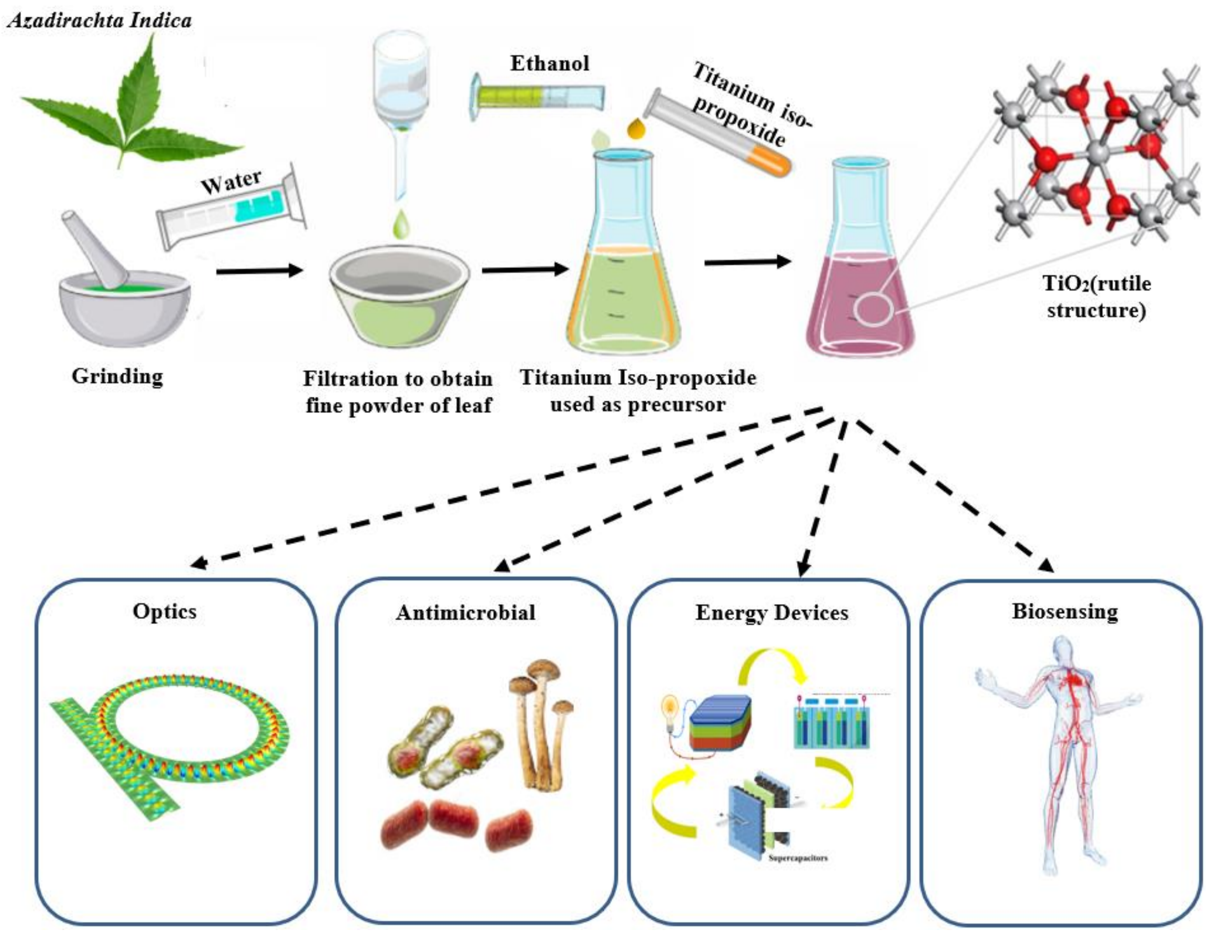
Healthy leaves of *Azadirachta Indica* were procured from Delhi, India. Titanium isopropoxide, Ethanol was supplied by Sigma Aldrich.

B. Preparation of leaf extract

The fresh, greenish leaves of the plant *Azadirachta Indica* were washed gently and thoroughly with deionized water to eradicate dust and contaminants. In addition, the leaves were then dried for seven days in summer at room temperature under the dust-free condition to procure coarse-grained powders. The coarse powder was ground further and filtered for obtaining nanopowder of leaves.

C. Green synthesis of TiO_2 nanoparticles

The obtained leaf powder was mixed with 50ml of ethanol and refluxed for 5 hours at 50°C. To the foregoing solution, 0.4 M titanium isopropoxide was added. The solution was stirred for 5 hours at 50°C. The prepared solution was purified by repeated centrifugation at 1000 rpm for 15 minutes and washed with ethanol. After being washed in ethanol, the solution was subjected to the centrifuge again for 5 minutes at 5000 rpm. Ultimately, the solution was calcinated at 500°C for2hrs.



D. Characterization techniques

XRD measurement was carried out on D8 advance Bruker XRD by employing CuKα radiation utilizing the diffraction angle(2θ) from 0 to 70°.

The size and surface morphology of the synthesized nanoparticles was accessed using the Hitachi S-3700N instrument for SEM analysis.

High-resolution mapping images were examined using TEM for analyzing the shape and size of synthesized nanoparticles.

FTIR spectra were obtained using Perkin Elmer Spectrometer.

Characteristic UV-visible spectra of the prepared nanoparticles were recorded employinga UV visible spectrometer.

III. RESULTS AND DISCUSSIONS

X-ray diffractogram of synthesized nanostructured materials calcined at 500° C has been presented in **Fig. 1**. The prominent patterns of the developed TiO_2 nanoparticles revealed the polycrystalline behavior with preferential orientation along the (101) plane. The reflection peaks were observed at 25°, 38°, 47°, 56° and 61°attributed to (101), (004), (200), (105), and (204) planes respectively. Debye-Scherrer equation ($D=K\lambda/(\beta\cos\theta)$) was used to measure the average crystallite size .Crystallite size was found to vary from 10-50 nm range.

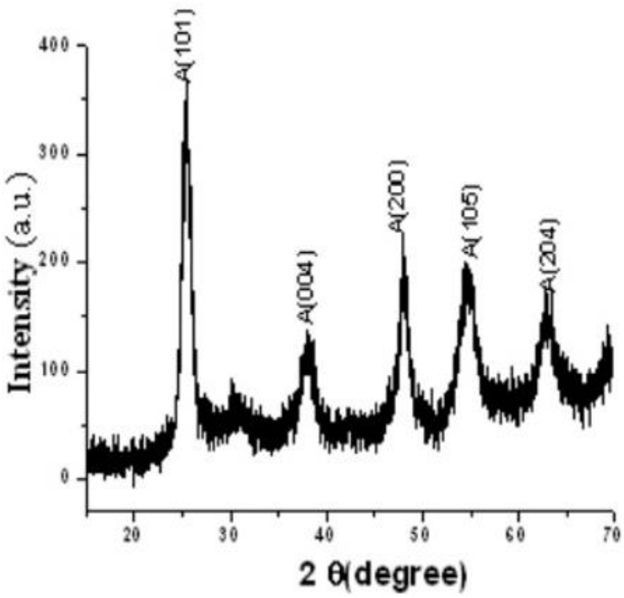


Fig 1: XRD curve showing relative intensity *vs.* 2θ of synthesized TiO_2 nanoparticles

The formulation of the synthesized nanostructured particles was investigated using FTIR spectrais shown in **Fig 2.** is dominated by the titanium isopropoxide peaks. The characteristic stretching modes of TiO_2 are submerged in the broad transmission in the region 1000-500 cm^{-1}. The prominent peaks at ~ 560 cm^{-1} and 472 $cm^{-1}$are resolved by deconvulting the spectrum in the 600 – 400 cm^{-1} region. Furthermore, the presence of Ti-O-Tiwas confirmed by EDAX spectra of prepared samples.

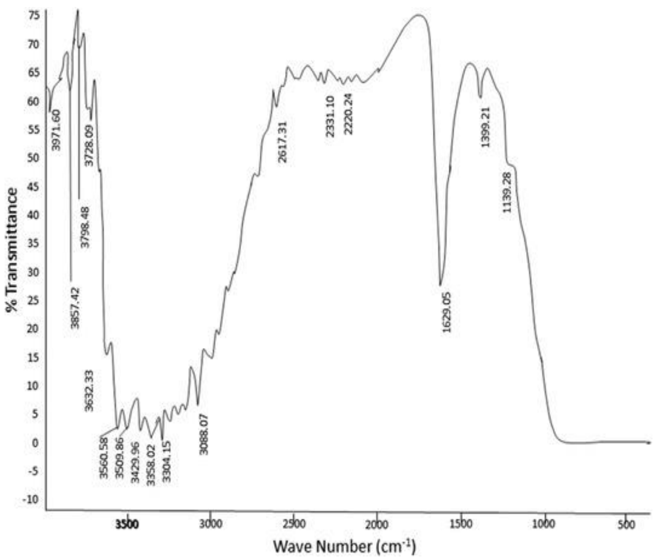


Fig. 2:FTIR spectra of TiO_2 nanoparticles

The SEM investigation suggested that the resultantTiO_2 nanoparticles were found spherical and particle size ranged from 10-50 nm which was in close covenant with that derived by the Scherrer's formula based on XRD pattern (**Fig 3**). SEM morphology elucidated the homogeneous distribution of nanoparticles with a smooth surface. This can be confidently attributed to the nature of phytochemicals present in neem that act as a capping agent.

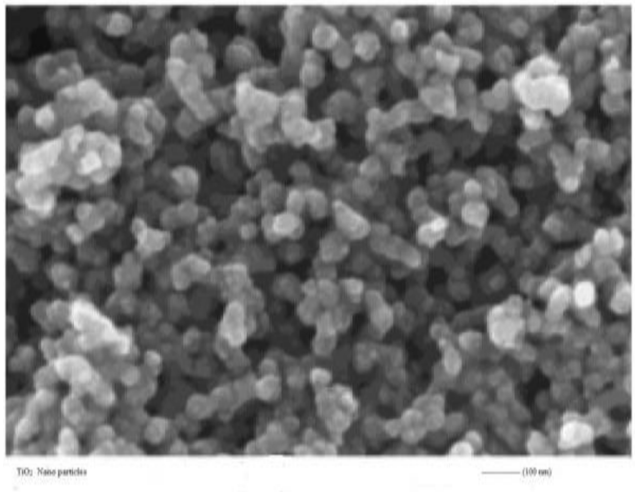


Fig 3: SEM micrographs of TiO_2 Nanoparticles

TEM micrograph is shown in **Fig 4**. The prepared nanoparticles have a particle size in the range of 15.1 nm on 5nm. The spherical and smooth surfaces of resultant nanoparticles were revealed. It can be also explicated that nanoparticles crystalline structure. The difference in the size of nanoparticles evaluated by SEM and TEM attributes to the inconsistent calibration of magnification. UV-visible absorbance spectroscopy has been corroborated to be a beneficial technique for the discernment of developed nanoparticles due to the sensitivity of the position of peak and shape of the spectra to the particle size.Fig 5shows that the UV-VIS spectrum of obtained nanoparticles recorded in 1100 – 180 nm region exhibiting exciting recombination band emission peak at 384 nm. These particles have an energy band gap of ~ 3.34 *eV*.

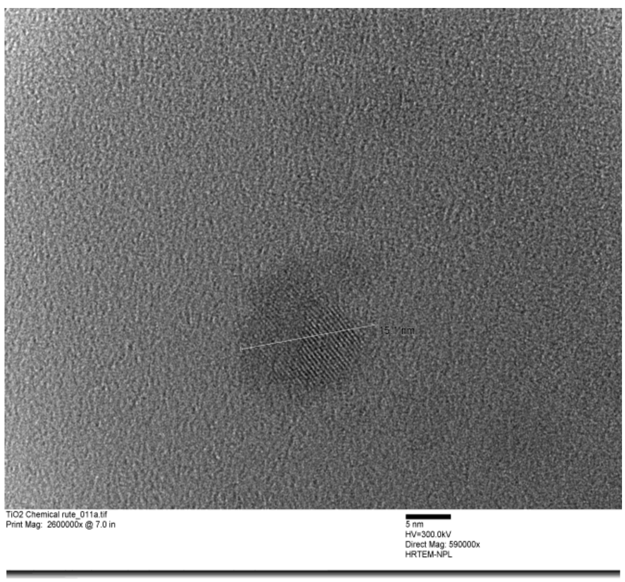


Fig4: TEM micrographs of TiO_2 Nanoparticles

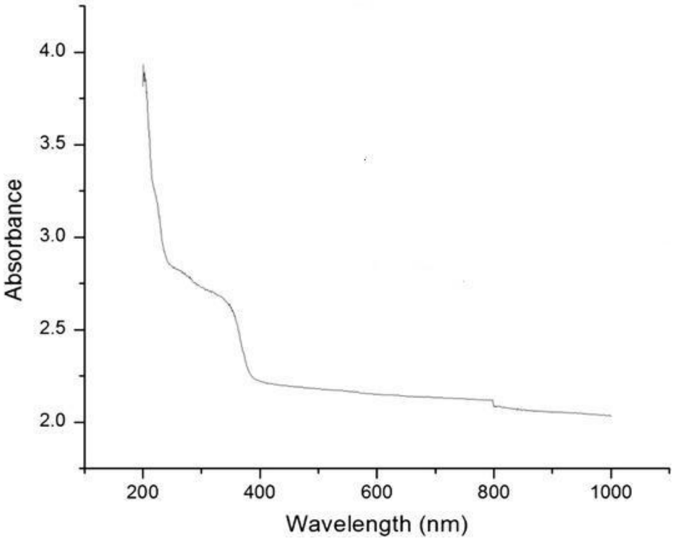


Fig5: UV-VIS absorption spectra of TiO_2 Nanoparticlesas a function of wavelength vs absorbance

IV. CONCLUSION

Biogenic synthesis ofTiO_2 nanoparticles was attained attributes to the phytochemicals and several bioactive compounds found in Azadirachta Indica. XRD pattern of the synthesized nanoparticles evinced that the particles obtained were crystalline, pure, and spherical with particle size ranging from 10-50 nm. The findings were confirmed by my mapping SEM and TEM images. Additionally, the FTIR results demonstrated that flavonoid and terpenoid compounds were acting as reducing and capping agents respectively. The size of synthesized TiO_2 nanoparticles could be controlled by stirring and altering the temperature accurately. TiO_2 nanoparticles extracted by the green chemistry method will enhance economic growth, sustainable development, and environment friendly. This study opened new ways to perform simple, cost-effective, environmentally friendly, and non-toxicroutes for the synthesis of nanoparticles.

Competing Interest
Nothing to declare

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Acronyms
FTIR-Fourier Transform Infrared Spectroscopy
XRD-X-ray diffraction
UV-VIS-Ultraviolet visible
SEM-Scanning electron microscopy
TEM-Transmission electron microscopy
TiO_2-Titanium Oxide

REFERENCES

[1]. Adil, S. F., Assal, M. E., Khan, M., Al-Warthan, A., Siddiqui, M. R. H., & Liz-Marzán, L. M. (2015). Biogenic synthesis of metallic nanoparticles and prospects toward green chemistry. *Dalton Transactions*, *44*(21), 9709-9717.
[2]. Iravani, S. (2011). Green synthesis of metal nanoparticles using plants. *Green Chemistry*, *13*(10), 2638-2650.
[3]. Singh, J., Dutta, T., Kim, K. H., Rawat, M., Samddar, P., & Kumar, P. (2018). 'Green'synthesis of metals and their oxide nanoparticles: applications for environmental remediation. *Journal of nanobiotechnology*, *16*(1), 84.
[4]. Muniandy, S. S., Kaus, N. H. M., Jiang, Z. T., Altarawneh, M., & Lee, H. L. (2017). Green synthesis of mesoporous anatase TiO 2 nanoparticles and their photocatalytic activities. *RSC advances*, *7*(76), 48083-48094.
[5]. Shukla, A. K., & Iravani, S. (2017). Metallic nanoparticles: green synthesis and spectroscopic characterization. *Environmental Chemistry Letters*, *15*(2), 223-231.
[6]. Nabi, G., Khalid, N. R., Tahir, M. B., Rafique, M., Rizwan, M., Hussain, S., ... & Majid, A. (2018). A Review on Novel Eco-Friendly Green Approach to Synthesis TiO 2 Nanoparticles Using Different Extracts. *Journal of Inorganic and Organometallic Polymers and Materials*, *28*(4), 1552-1564.
[7]. Rajendaran, K., Muthuramalingam, R., & Ayyadurai, S. (2019). Green synthesis of Ag-Mo/CuO nanoparticles using Azadirachta Indica leaf extracts to study its solar photocatalytic and antimicrobial activities. *Materials Science in Semiconductor Processing*, *91*, 230-238.
[8]. Verma, A., & Mehata, M. S. (2016). Controllable synthesis of silver nanoparticles using Neem leaves and their antimicrobial activity. *Journal of radiation Research and applied sciences*, *9*(1), 109-115.
[9]. Amrutham, S., Maragoni, V., & Guttena, V. (2020). One-step green synthesis of palladium nanoparticles using neem gum (Azadirachta Indica): characterization, reduction of Rhodamine 6G dye and free radical scavenging activity. *Applied Nanoscience*, 1-7.
[10]. Chand, K., Abro, M. I., Aftab, U., Shah, A. H., Lakhan, M. N., Cao, D., ... & Mohamed, A. M. A. (2019). Green synthesis characterization and antimicrobial activity against Staphylococcus aureus of silver nanoparticles using extracts of neem, onion and tomato. *RSC advances*, *9*(30), 17002-17015.
[11]. Biofriendly and competent domestic microwave assisted method for the synthesis of ZnO nanoparticles from the extract of Azadirachta Indica leaves P. Saravanan a , K. SenthilKannan b , M. Vimalan c , S. Tamilselvan a,⇑ , D. Sankar
[12]. Nagar, N., & Devra, V. (2018). Green synthesis and characterization of copper nanoparticles using Azadirachta Indica leaves. *Materials Chemistry and Physics*, *213*, 44-51.

[13]. Thakur, B. K., Kumar, A., & Kumar, D. (2019). Green synthesis of titanium dioxide nanoparticles using Azadirachta Indica leaf extract and evaluation of their antibacterial activity. *South African Journal of Botany*, *124*, 223-227.

[14]. Moorthy, S. K., Ashok, C. H., Rao, K. V., & Viswanathan, C. (2015). Synthesis and characterization of MgO nanoparticles by Neem leaves through green method. *Materials Today: Proceedings*, *2*(9), 4360-4368.