Hindawi
Journal of Nanomaterials
Volume 2022, Article ID 7011539, 11 pages
https://doi.org/10.1155/2022/7011539

Research Article

Photocatalytic Activity of Green Construction TiO_2 Nanoparticles from *Phyllanthus niruri* Leaf Extract

Annin K. Shimi,[1] Saikh Mohammad Wabaidur,[2] Masoom Raza Siddiqui,[2] Md Ataul Islam,[3] Kantilal Pitamber Rane,[4] and T. S. Arul Jeevan [5]

[1]*Department of Physics, Manonmaniam Sundaranar University, Tirunelveli, Tamil Nadu 627012, India*
[2]*Department of Chemistry, College of Science, King Saud University, Riyadh 11451, Saudi Arabia*
[3]*Division of Pharmacy and Optometry, School of Health Sciences, Faculty of Biology, Medicine and Health, University of Manchester, Manchester, UK*
[4]*KCE College of Engineering and Management, Jalgaon, Maharashtra 425001, India*
[5]*Department of Chemistry College of Natural and Computational Sciences, Mizan Tepi University, Tepi, Ethiopia*

Correspondence should be addressed to T. S. Arul Jeevan; jejeevan@mtu.edu.et

Received 29 December 2021; Revised 11 March 2022; Accepted 25 May 2022; Published 22 June 2022

Academic Editor: Awais Ahmed

The present research work reports the facile and green synthesis of TiO_2 nanoparticles from *Phyllanthus niruri* leaf extract using the coprecipitation method. The plant biomolecules were responsible for the nanoproduction and exhibited reduction and stabilization activity. The green synthesized TiO_2 nanoparticles were analyzed in various characterization methods. The crystalline size (23 nm) and anatase phase of TiO_2 nanoparticles were analyzed from X-ray diffraction study. The reduction and stabilization response functional group of TiO_2 nanoparticles was studied from FTIR analysis. The optical properties of TiO_2 nanoparticles were constructed from the UV-DRS technique, and their calculated bandgap is 3.16 eV. The spherical morphology and their existing materials were identified using FESEM with EDX. The catalytic activity of TiO_2 nanoparticles was examined against methylene blue dye under ultraviolet and visible light irradiation. It was detected that ultraviolet irradiation showed higher photocatalytic activity than visible light irradiation. In addition, visible light irradiation provides the above 90 percentage degradation of methylene blue dye. Hence, TiO_2 nanoparticles were proposed as a potential catalyst of photocatalytic dye degradation application and water remediation activities.

1. Introduction

Nanoscience is one of the most widely used and effective fields of research in scientific discovery. Nanotechnology has recently become a highly advanced technology with intra- and interstudy spanning chemistry, physics, biology, material science, and medicine. The production of nanometer-sized materials of various morphologies and sizes, as well as monodispersion, is an important field of research in nanoscience [1, 2]. Nanoparticles of varying sizes, shapes, and controlled disparity are synthesized by many researchers. Catalysis, optical, electric, and magnetic aspects; diagnostics; biological probes; and display devices are among the applications for metal nanoparticles [3]. The synthesis of metal and metal oxide nanoparticles is an existing field of material chemistry that has piqued interest due to applications in a wide range of fields, including air and water purification, medicine, antimicrobials, information technology, photocatalytic, antimicrobial, energy reservoirs, and biosensors [4]. Nanomaterial synthesis methods are divided into physical and chemical processes due to their enormous surface area. These procedures, however, are not ideal for medical and biological applications due to their environmental hazards. As a consequence, researchers are opting for a green synthesis method to synthesize nanomaterials although it is efficient, environmentally friendly, and cost effective [5, 6]. Green synthesis is an exciting material science approach [7–9]. Plants provide a better platform

for nanoparticle manufacturing since they do not contain hazardous compounds and provide natural capping agents [10]. Numerous organic substances are widespread in nature extracts including amino acids, proteins, polysaccharides, alkaloids, flavonoids, and phenolic compounds [11–13]. TiO_2 has become extremely prevalent in a broad spectrum of applications [14–24]. TiO_2 is an excellent material for photocatalysis and biomaterial creation [25]. Titania's biocompatibility makes it suitable for use in bone tissue engineering for bone regeneration and healing [26]. TiO_2 is a powerful catalyst that may be used to remove a variety of contaminants from the environment and has been shown to clean water and surfaces [26–34]. The Phyllanthus genus is one of the most prominent groupings of plants traded in India as a raw herbal medication [35]. The Phyllanthus genus, which belongs to the *Euphorbiaceae* family, contains over 1000 species that are found on tropical and subtropical continents like America, Africa, Australia, and Asia. The Phyllanthus genus is widely applicable in the human medical system [35–39]. *Phyllanthus niruri* has been used in traditional medicine to treat lung and skin-related diseases. The presence of various biologically active substances serves an impeccable role in the reduction, capping, and stabilization processes. These plant compounds reduced the toxicity level during the production of nanophase materials. Moreover, the plant derivatives obtained various bioactive elements that can be used in antibacterial, antifungal, and diabetic-related applications [39–47]. The bioreduction compounds of lignin, saponins, and flavonoids give the chemical-free zero-valent atom and provoke the stabilization process. In addition, these biocompounds increased microbial resistivity and are highly appreciable in liver-related diseases. The present work investigates the nanoproduction of TiO_2 nanoparticles using *Phyllanthus niruri* leaf extract. The structural, optical, and morphological entities of the synthesized nanoparticles were investigated. In addition, the photocatalytic activity of the synthesized nanoparticles was observed from ultraviolet and visible light irradiation.

2. Experimental

2.1. Materials. The titanium tetra isopropoxide (TTIP) (Sigma-Aldrich, AR grade, purity > 99 percent) was used to synthesize the TiO_2 nanoparticles. Fresh leaves of *Phyllanthus niruri* were collected from Tirunelveli, and their extract was used as a bioreductant. The methylene blue dye was purchased from HiMedia. There are no extra chemicals were used for the purification and synthesis process.

2.2. Green Synthesis of TiO_2 NPs. The *Phyllanthus niruri* leaf extract and 0.1 M TTIP solutions were used in the green synthesis of TiO_2 nanoparticles. 0.1 M TTIP solution was poured into 90 mL leaf extract under magnetic stirring. The stirring and biomolecules of the leaf extract have modified the color into white and produced precipitation. The white precipitation was centrifuged for 12000 rpm for 15 minutes two times. The obtained pellets were filtered with Whatman no. 1 filter paper and kept in an oven for 200°C at 3 hrs. Finally, the white TiO_2 nanoparticles are characterized by various analyses. The formation of TiO_2 is depicted in Scheme 1.

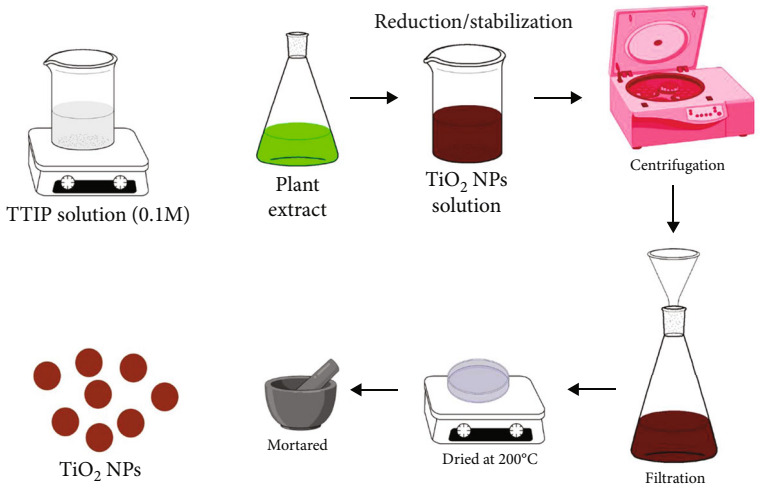
2.3. Characterization. The synthesized TiO_2 nanoparticles were evaluated by structural, optical, and morphological analyses. The crystalline property of TiO_2 nanoparticles was observed from the X-ray diffractometer (XRD) (PANalytical X-ray diffractometer, Cu-Kα radiation = 0.154 nm, angle 10°–80° and 40 kV/15 mA). The optical property of TiO_2 nanoparticles was captured from the UV Shimadzu 2700 UV-DRS spectrophotometer. The functional group and formed TiO_2 nanoparticles were recorded from the FT-IR (PerkinElmer, 400–4000 cm^{-1}, USA). The morphological entity was observed from scanning electron microscopy (HRSEM-SEM, Carl Zeiss, Germany) coupled with material identification energy-dispersive X-ray spectroscopy (EDX).

2.4. Photocatalytic Activity. The photocatalyst of TiO_2 nanoparticles was performed against visible and UV light irradiation to determine the photocatalytic MB dye degradation. The light source is an important key factor to modify the rate of degradation to degrade the organic pollutants. The 10 ppm MB (100 mL) dye solution was inoculated with a 10 mg photocatalyst. After that, the combined solution was kept in dark condition to attain the adsorption-desorption equilibrium level. Finally, the mixed solution was placed in UV and visible light circumstances. The irradiated samples were withdrawn (5 mL) in a regular interval (30 minutes) to measure the degradation efficacy of TiO_2 nanoparticles. The photocatalytic dye degradation efficacy was observed from the following equation: dye degradation efficiency = $C - C_1/C$, where C is the initial dye absorbance at time = 0, C_1 is the dye absorbance with light at time = 30 min, and t is the time.

3. Results and Discussion

3.1. X-Ray Diffraction (XRD). The X-ray diffraction pattern of the green synthesized TiO_2 nanoparticles is shown in Figure 1. The structural, crystallite size and material phases were identified from X-ray diffraction. The obtained peaks are 25.27° (1 0 1), 37.86° (0 0 4), 48.23° (2 0 0), 54.31° (1 0 5), 55.09° (2 1 1), 62.62° (1 1 8), and 75.21° (2 1 5) compared with those of the standard JCPDS card no. 78-2486 [48, 49]. The anatase phase of TiO_2 nanoparticles exhibits enhanced catalytic activity than the rutile and brookite phases. The photocatalyst TiO_2 nanoparticle crystallite size was calculated from the Debye Scherrer formula, and their calculated value is 23 nm in (1 0 1) plane at a high-intensity peak. The lowest crystallite size demonstrates the large surface area and outstanding photocatalytic activity of the synthesized materials.

3.2. FTIR Analysis. The plant active functional groups of the TiO_2 nanoparticles were analyzed by FTIR spectrum and displayed in Figure 2. The broad peak at 4000–3500 cm^{-1} specifically at 3420 cm^{-1} belongs to hydroxyl groups of O–H stretching vibration [50]. The band at 2923 cm^{-1} is attributed to C-H vibrations. The C-H vibrations are restricting



Scheme 1: Synthesis formation of TiO_2 nanoparticles.

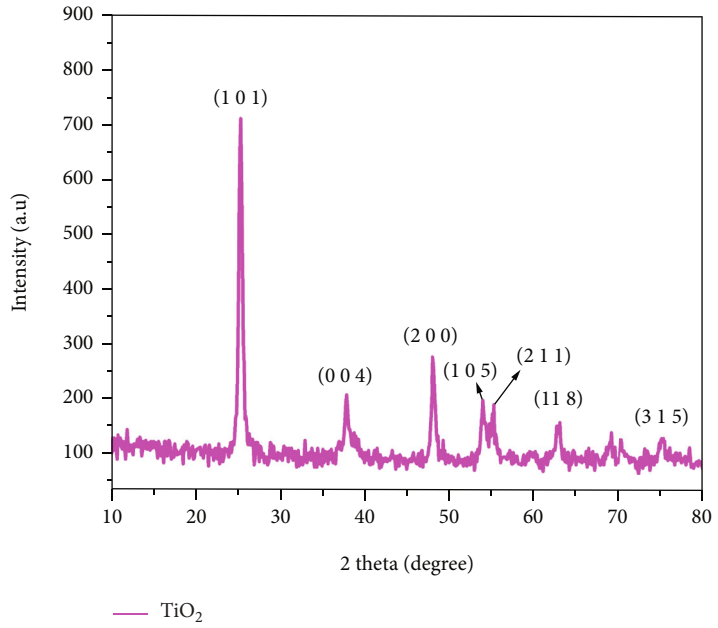


Figure 1: XRD diffraction pattern of green synthesized TiO_2 NPs.

the phase changes and promote the organic precipitation in synthesis time. Another prominent peak of TiO_2 nanoparticles is located at 1627 cm^{-1}, which can be ascribed to C=C which came from plant carbon molecules. The carbon molecules are associated with hydrogen and oxygen from the source materials. The carbon association produces the –C-O stretching and –C-H bending to the source precursors [50–53]. These compounds come from the plant extract biomolecules which can control the growth of the particles and reduction/stabilization activity. The peak at 720 cm^{-1} is attributed to the Ti-O stretching bands. The stretching modes of Ti-O-Ti all are observed at 500–700 cm^{-1} [54]. The plant bioderivatives produce the nonvalent atoms through the flavonoids, saponins, and lignin. These plant derivatives are responsible for metal and oxygen bond formation. The formed metal and oxygen elements were stabilized from plant derivatives.

3.3. UV-DRS Analysis. The optical properties of the TiO_2 nanoparticles were performed from the UV-DRS technique. The DRS spectrum is shown in Figure 3(a) which can indicate the optical reliability of the TiO_2 nanoparticles in the UV region at 390 nm. The optical transformations and their defects were determined the bandgap of the materials. There is no adsorption edge involved in the visible region which can denote the highest photonic energy. The optical bandgap values are calculated from Tauc eqn. The calculated bandgap value shows the relationship between the incident photon energy of semiconductors and absorption coefficient: $\alpha h\upsilon = A(h\upsilon - \mathrm{Eg})^n$, where α is the absorption coefficient, υ is

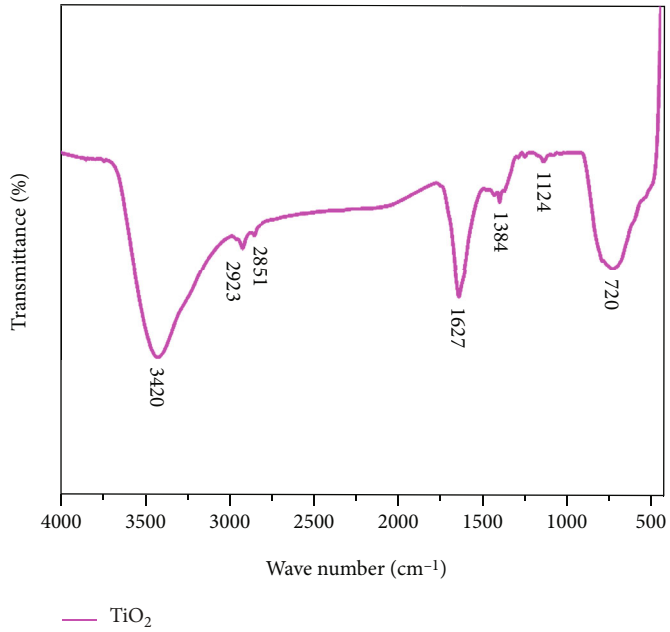


Figure 2: FTIR spectrum of green synthesized TiO_2 NPs.

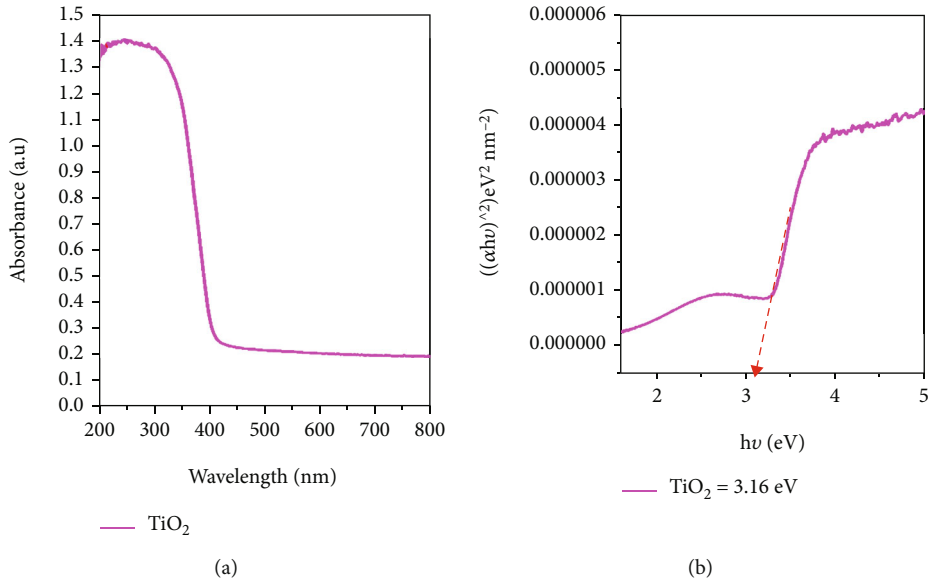
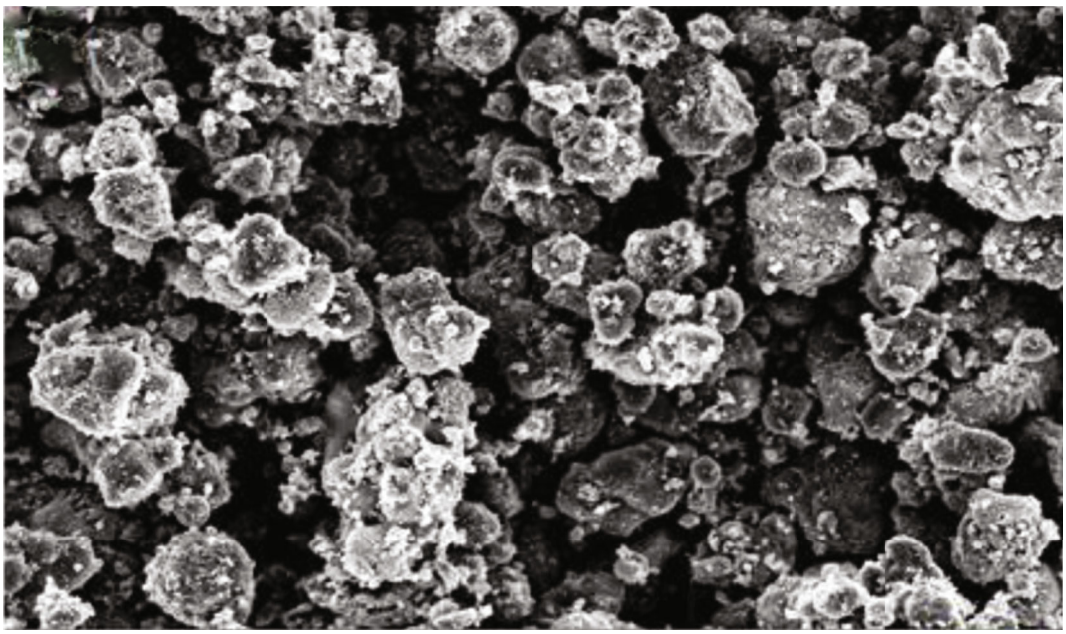


Figure 3: (a) UV-DRS absorption spectrum and (b) bandgap energy spectrum of green synthesized TiO_2 nanoparticles.

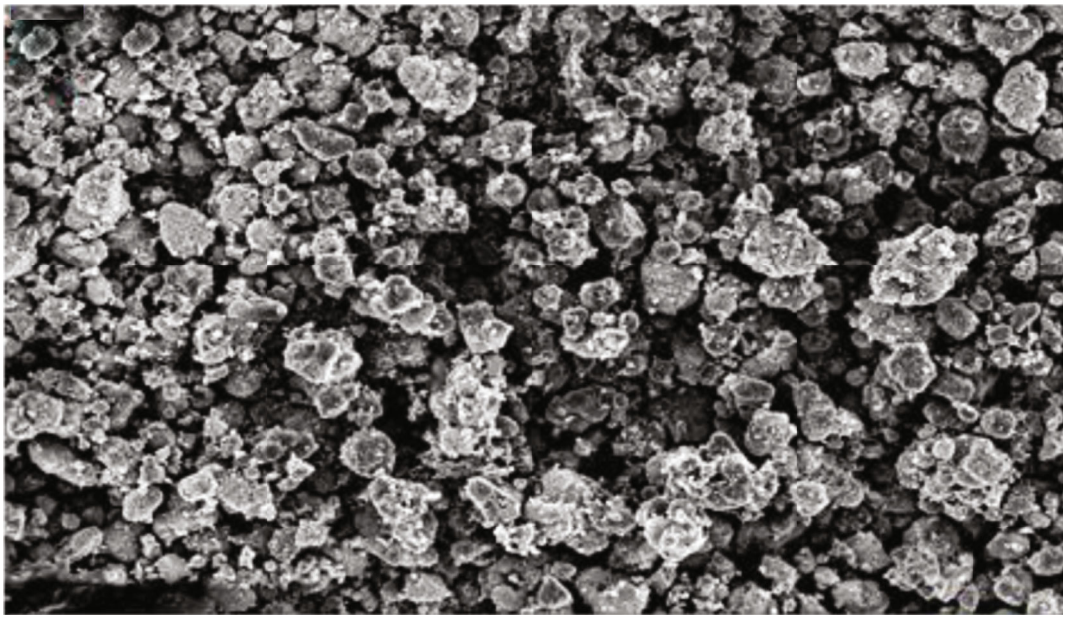
the frequency, Eg is the Bandgap, and n is the 1/2 direct bandgap semiconductor. The obtained band gap is 3.16 eV. The wide bandgap of TiO_2 nanoparticles exhibited the charge carrier formation and liberation in the photocatalytic activity [55, 56].

3.4. FESEM with EDX. Figure 4 shows the surface morphological and elemental analysis of green synthesized TiO_2 nanoparticles. FESEM images represent the spherical morphology with even distribution on the surface. The formed spherical shape and their smaller size particles accelerate the free radical formation. The existing plant biomolecules occupied the surface which gives the agglomerations and large grain size particles. The existing plant molecules derived the irregular distribution of the TiO_2 nanoparticles. The spherical shape is a more benefit able shape in catalytic activity than other shapes due to their large surface area [57–60]. The EDX spectrum displays the Ti and O element existence over the surface. The remaining small peaks exhibit the plant molecules which was well explained in FTIR analysis. The elemental percentages were displayed in Figure 4(d). The Ti elements occupied the major places in synthesized TiO_2 nanoparticles. The FE-SEM morphology images showed the spherical and semispherical shapes of the TiO_2 nanoparticles. The spherical shape occupied the major area of the TiO_2 nanoparticles which are attached to



1 μm
EHT = 5.00 KV
WD = 5.6 mm
Signal A = Inlens
Mag = 10.00 KX

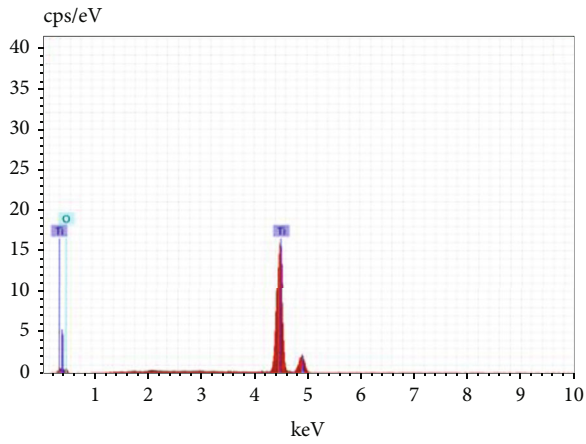
(a)



2 μm
EHT = 5.00 KV
WD = 5.6 mm
Signal A = Inlens
Mag = 5.00 KX

(b)

Figure 4: Continued.



(c)

Element	Atomic %	Weight %
Ti	59.94	81.75
O	40.06	18.25
Total	100	100

(d)

Figure 4: (a, b) FESEM images, (c) EDX spectrum, and (d) EDX table of green synthesized TiO_2 nanoparticles.

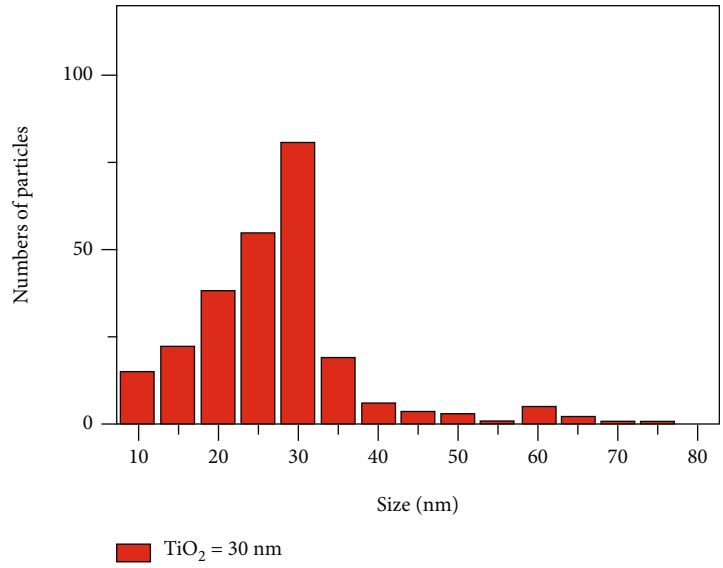


Figure 5: Histogram of green synthesized TiO_2 nanoparticles.

it shown as larger grain size particles due to their plant derivatives. The excessive plant compounds construct the layer over the TiO_2 surface and merged the two particles. Therefore, it shows semispherical and spherical shapes. The distribution of the TiO_2 nanoparticles was calculated from ImageJ software, and their values are displayed in Figure 5.

3.5. Photocatalytic Activity. The green synthesized TiO_2 nanoparticles against methylene blue dye under different light sources are shown in Figures 6(a) and 6(b). The visible light irradiation slowly increased the degradation rate due to the reactive sites of the catalyst. Above 60 minutes of visible light irradiation exhibits the higher degradation because of their OH radicals which provokes the oxidation of the dye molecules [61, 62]. The plant biomolecules sustained the electron-hole pair recombination which derived strong oxidation and reduction of dye molecules over the catalyst. This process takes 60 minutes to 90 minutes with the migration of electrons and holes of the concern bands. The ultraviolet irradiation exhibits the vigorous degradation than visible light irradiation due to their OH radicals [16–23]. The ultraviolet light provokes the electron mobilization and evoked the electron-hole pair which promotes better degradation efficiency. The 30-minute ultraviolet light irradiation of TiO_2 nanoparticles exhibited above 80% degradation. The ultraviolet irradiation (98.2%) of TiO_2 nanoparticles showed enhanced degradation efficiency than visible light irradiation (94.42%) (Figure 7(a)). The photocatalyst efficiency was calculated from the C/C_0 spectrum (Figure 7(b)) The degradation efficiency is dependent on a light source, catalyst dosage, pH, and dye concentration [63]. TiO_2 nanoparticles are extensively used in photocatalytic activity due to their wide bandgap and e-h pair restriction property. The anatase

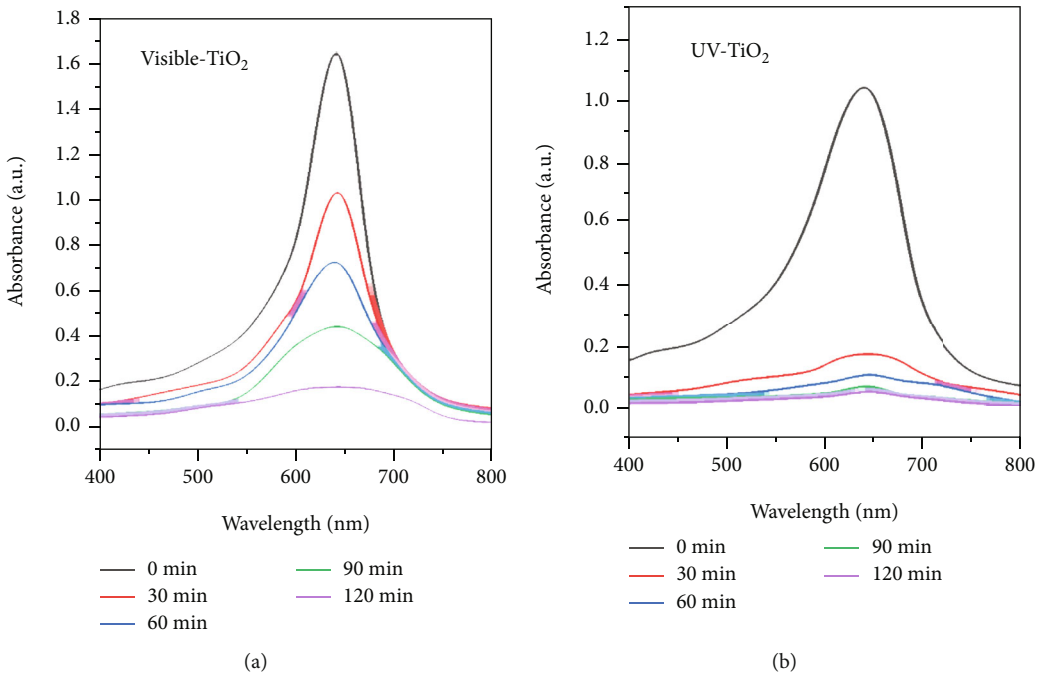


Figure 6: Photocatalytic degradation spectrum of the green synthesized TiO_2 nanoparticles.

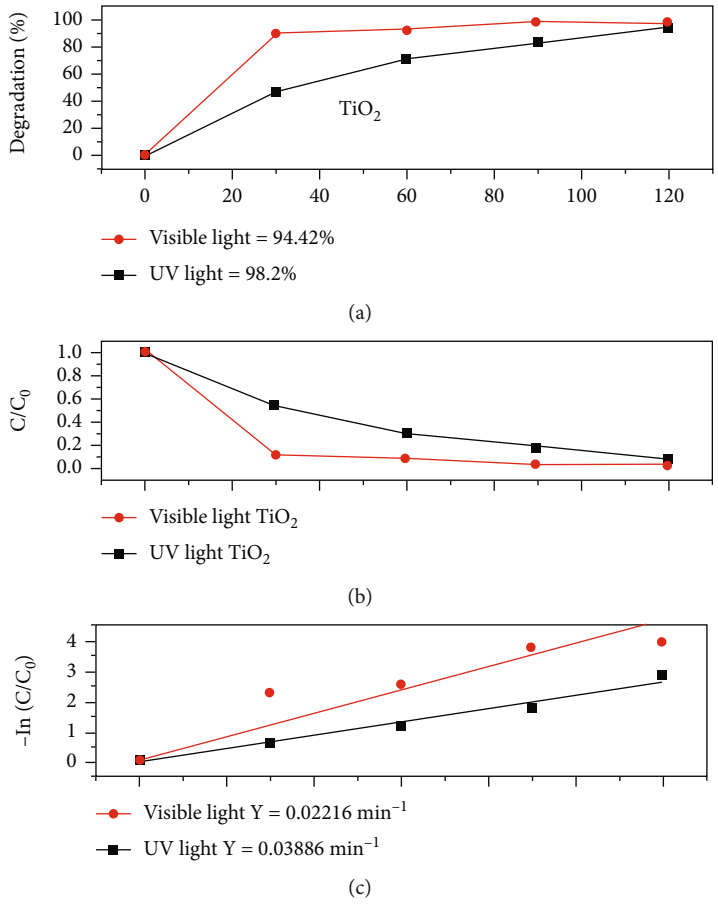


Figure 7: (a) Degradation efficacy, (b) C/C_0 absorption rate, and (c) photocatalytic degradation kinetics study of the green synthesized TiO_2 nanoparticles.

Table 1: Photocatalytic MB degradation of TiO_2 nanoparticles.

S. no	Nanomaterial	Time (min)	Source	Degradation percentage	References
1	TiO_2	120	UV-Vis	89	[70]
2	TiO_2	240	UV-Vis	70	[71]
3	TiO_2	60	UV-Vis	76	[72]
4	TiO_2	90	Solar light	90	[73]
5	Co/TiO_2	150	UV-irradiation	80	[64]
6	Mn-TiO_2	240	Visible light	88	[65]
7	TiO_2	60	UV	72.4	[66]
8	TiO_2	60	UV-Vis	90.4	[67]
9	TiO_2/PET	10	UV-vis	88	[74]
10	TiO_2	**120**	UV	**98.2**	Present work
11	TiO_2	**120**	Visible light	**94.4**	Present work

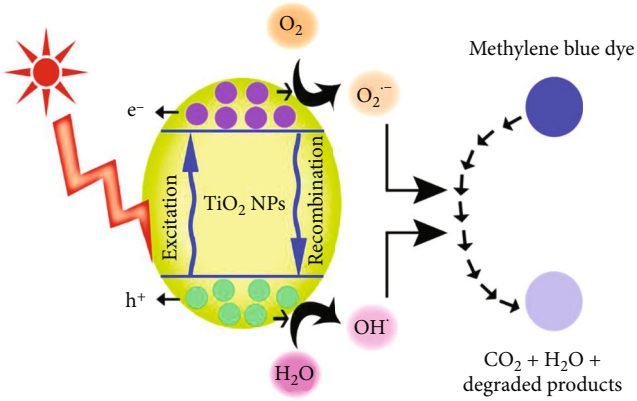


Figure 8: Photocatalytic degradation mechanism of green synthesized TiO_2 nanoparticles.

TiO_2 nanoparticles exhibited a wide bandgap (3.16 eV) and lower crystallite size and large surface area which was ensured by DRS, XRD, and FESEM analyses, respectively. The degradation rate of the catalyst was constructed from pseudo-first-order kinetics (Figure 7(c)). The kinetic equation is as follows: $-\ln(C_t/C_0) = -Kt$, where C_t is the light irradiated dye absorbance at time t, C_0 is the initial dye absorbance at time $t = 0$, and t is the activity time of degradation. The obtained pseudo-first-order kinetics delivered the ultraviolet irradiation potential which is more effective than visible light irradiation. The present work is compared with earlier published work of TiO_2 nanoparticles. The comparison of TiO_2 nanoparticle photocatalytic activity is tabulated in Table 1. The pure and doped TiO_2 photocatalytic degradation work is reported. The degradation is based on the light source, size, dopants, and surface area. The table denotes the catalytic activity of TiO_2 nanoparticles in various doping, light sources, and time. The visible light irradiation degradation is low compared to ultraviolet irradiation but the addition of metal compounds increased the catalytic efficiency. Free radicals production increased the oxidation ability of dye molecules. The radical formations are evoked in visible light irradiation [64–67]. The present visible light irradiation catalytic activity produced the superoxides and radicals which exhibited a better photocatalytic dye degradation activity than previously reported works. Therefore, the present work focused on visible and ultraviolet light irradiation and demonstrates that biogenic TiO_2 nanoparticles prove heightened degradation ability against the MB dye.

The photocatalyst mechanism of the TiO_2 nanoparticles is shown in Figure 8. The mechanism of TiO_2 nanoparticle-excited electrons traveled from the valence band to the conduction band during the illumination. The modified electrons and holes get a reduction and oxidation property. The generated charge carriers produce free radicals and superoxides. These compounds dissociated the dye molecules to noxious compounds [61, 62, 68, 69]. The UV light irradiation inhibits the e-h pair very strappingly and produces an enormous amount of free radicals than visible light irradiation. The detailed mechanism is as follows:

$$\begin{aligned} TiO_2 + hv &\longrightarrow e^-(C.B) + h^+(V.B)., \\ (H_2O \longrightarrow H^+ + OH^-) + h^+(V.B) &\longrightarrow H^+ + \cdot OH, \\ O_2 + e^-(\mathrm{C.B}) \longrightarrow O_2^- + H^+ + OH^- &\longrightarrow HO_2^{\cdot} + {}^-OH, \\ HO_2^{\cdot} + {}^-OH + h^+(\mathrm{V.B}) &\longrightarrow {}^{\cdot}OH. \end{aligned} \tag{1}$$

Based on the results, specify that the green synthesized TiO_2 nanoparticles have upgraded catalytic activity and enhanced dye adsorption behavior in ultraviolet light irradiation. Hence, the green synthesized TiO_2 nanoparticles detached the dye molecules from the aquatic surface and more powerful degradation in the ultraviolet region.

4. Conclusion

The current work reported the green production of nanoparticles from *Phyllanthus niruri* leaf extract. The plant extract using nanoparticles is an eco-friendly and noxious-free reduction to synthesize the nanophase materials. The photocatalyst of the TiO_2 structural tetragonal pattern was confirmed by XRD, and their size 23 nm was calculated using the Debye Scherrer equation. The plant derivatives and their reduction/stabilization involved biomolecules, and their functional groups were identified from FTIR spectroscopy.

The optical measurement and their wide bandgap values were evident by DRS analysis. The spherical surface and elemental investigation were obtained from FESEM with EDX. The photocatalyst of TiO_2 nanoparticles was performed in ultraviolet and visible light irradiation against MB dye. The results exposed that ultraviolet irradiation of TiO_2 nanoparticles exhibited better catalytic activity than visible light photocatalytic activity. Therefore, constructed on the results of the current study, we recommended that the green synthesized TiO_2 nanoparticles are a more active and high possible catalyst in wastewater removal treatment.

Data Availability

All research data used to assist the findings of this work are included within the manuscript.

Conflicts of Interest

The authors have no conflict of interests.

Acknowledgments

The authors are grateful to the researchers supporting project no. (RSP-2021/326), King Saud University, Riyadh, Saudi Arabia.

References

[1] D. Mandal, M. E. Bolander, D. Mukhopadhyay, G. Sarkar, and P. Mukherjee, "The use of microorganisms for the formation of metal nanoparticles and their application," *Applied Microbiology and Biotechnology*, vol. 69, no. 5, pp. 485–492, 2006.

[2] S. M. Yedurkar, C. B. Maurya, and P. A. Mahanwar, "Synthesis of nanoparticles by green chemistry process and their application in surface coatings: a review," *Archives of Applied Science Research*, vol. 8, no. 5, pp. 55–69, 2016.

[3] R. Subbaiya, R. S. Lavanya, K. Selvapriya, and M. Masilamani Selvam, "Green synthesis of silver nanoparticles from Phyllanthus Amarus and their antibacterial and antioxidant properties," *International Journal of Current Microbiology and Applied Sciences*, vol. 3, no. 1, pp. 600–606, 2014.

[4] E. T. Bekele, B. A. Gonfa, O. A. Zelekew, H. H. Belay, and F. K. Sabir, "Synthesis of titanium oxide nanoparticles using root extract of kniphofia foliosa as a template, characterization, and its application on drug resistance bacteria," *Journal of Nanomaterials*, vol. 2020, Article ID 2817037, 10 pages, 2020.

[5] V. Helan, J. J. Prince, N. A. Al-Dhabi et al., "Neem leaves mediated preparation of NiO nanoparticles and its magnetization, coercivity and antibacterial analysis," *Results in Physics*, vol. 6, pp. 712–718, 2016.

[6] I. Hussain, N. B. Singh, A. Singh, H. Singh, and S. C. Singh, "Green synthesis of nanoparticles and its potential application," *Biotechnology Letters*, vol. 38, no. 4, pp. 545–560, 2016.

[7] B. E. Azar, A. Ramazani, S. T. Fardood, and A. Morsali, "Green synthesis and characterization of $ZnAl_2O_4$@ZnO nanocomposite and its environmental applications in rapid dye degradation," *Optik*, vol. 208, article 164129, 2020.

[8] S. TaghaviFardood, A. Ramazani, F. Moradnia, Z. Afshari, S. Ganjkhanlu, and F. YekkeZare, "Green synthesis of ZnO nanoparticles via sol-gel method and investigation of its application in solvent-free synthesis of 12-aryl-tetrahydrobenzo[α]xanthene-11-one derivatives under microwave irradiation," *Chemical Methodologies*, vol. 3, no. 6, pp. 696–706, 2019.

[9] S. TaghaviFardood, F. Moradnia, S. Moradi, R. Forootan, F. YekkeZare, and M. Heidari, "Eco-friendly synthesis and characterization of α-Fe2O3 nanoparticles and study of their photocatalytic activity for degradation of Congo red dye," *Nanochemistry Research*, vol. 4, no. 2, pp. 140–147, 2019.

[10] C. R. Resmi, P. Sreejamol, and P. Pillai, "Green synthesis of silver nanoparticles using Azadirachta indica leaves extract and evaluation of antibacterial activities," *International Journal of Advanced Biotechnology and Research*, vol. 4, pp. 300–303, 2014.

[11] A. Thirumurugan, P. Aswitha, C. Kiruthika, S. Nagarajan, and A. N. Christy, "Green synthesis of platinum nanoparticles using *Azadirachta indica*-an eco- friendly approach," *Materials Letters*, vol. 170, pp. 175–178, 2016.

[12] S. Dewanjee, M. Kundu, A. Maiti, R. Majumdar, A. Majumdar, and S. C. Mandal, "In vitro evaluation of antimicrobial activity of crude extract from plants Diospyros peregrina, Coccinia grandis and Swietenia macrophylla trop," *Journal of Pharmacy Research*, vol. 6, p. 773, 2007.

[13] A. K. Bhattacharjee and A. K. Das, "Phytochemical survey of few Mysore plants," *Economic Botany*, vol. 23, no. 3, pp. 274–276, 1969.

[14] K. S. Landage, G. K. Arbade, P. Khanna, and C. J. Bhongale, "Biological approach to synthesize TiO2 nanoparticles using Staphylococcus aureus for antibacterial and anti-biofilm applications," *Journal of Microbiology & Experimentation*, vol. 8, no. 1, pp. 36–43, 2020.

[15] I. Halomoan, Y. Yulizar, R. M. Surya, and D. O. B. Apriandanu, "Facile preparation of CuO- $Gd_2Ti_2O_7$ using *Acmella uliginosa* leaf extract for photocatalytic degradation of malachite green," *Materials Research Bulletin*, vol. 150, article 111726, 2022.

[16] Y. Yulizar, D. O. B. Apriandanu, and R. M. Surya, "Fabrication of novel SnWO4/ZnO using Muntingia calabura L. leaf extract with enhanced photocatalytic methylene blue degradation under visible light irradiation," *Ceramics International*, vol. 48, no. 3, pp. 3564–3577, 2022.

[17] A. Indriyani, Y. Yulizar, R. T. Yunarti, D. O. B. Apriandanu, and R. M. Surya, "One-pot green fabrication of $BiFeO_3$ nanoparticles via *Abelmoschus esculentus L* leaves extracts for photocatalytic dye degradation," *Applied Surface Science*, vol. 563, article 150113, 2021.

[18] Y. Yulizar, J. Gunlazuardi, D. O. B. Apriandanu, and T. W. W. Syahfitri, "CuO-modified $CoTiO_3$ via *Catharanthus roseus* extract: A novel nanocomposite with high photocatalytic activity," *Materials Letters*, vol. 277, article 128349, 2020.

[19] Y. Yulizar, D. O. B. Apriandanu, and F. L. Hakim, "Two-phase synthesis in n-hexane–water, characterization, and photocatalytic activity of ZnO/Bi2Sn2O7 nanocomposite," *JOM*, vol. 73, no. 1, pp. 441–449, 2021.

[20] Y. Yulizar, A. Eprasatya, D. O. B. Apriandanu, and R. T. Yunarti, "Facile synthesis of ZnO/$GdCoO_3$ nanocomposites, characterization and their photocatalytic activity under visible light illumination," *Vacuum*, vol. 183, article 109821, 2021.

[21] Y. Yulizar, D. O. B. Apriandanu, and A. P. Wibowo, "Plant extract mediated synthesis of Au/TiO_2 nanocomposite and its photocatalytic activity under sodium light irradiation," *Composites Communications*, vol. 16, pp. 50–56, 2019.

[22] Y. Yulizar, D. O. B. Apriandanu, and R. I. Ashna, "La_2CuO_4-decorated ZnO nanoparticles with improved photocatalytic activity for malachite green degradation," *Chemical Physics Letters*, vol. 755, article 137749, 2020.

[23] Y. Yulizar, E. Kusrini, D. O. B. Apriandanu, and N. Nurdini, "Datura metel L. leaves extract mediated CeO2 nanoparticles: synthesis, characterizations, and degradation activity of DPPH radical," *Surfaces and Interfaces*, vol. 19, article 100437, 2020.

[24] J. Abdul, S. Salman, K. H. Ibrahem, and F. A. Ali, "Effect of culture media on biosynthesis of titanium dioxide nanoparticles using Lactobacillus crispatus material and methods: results and discusion," *International Journal of Advanced Research*, vol. 2, no. 5, pp. 1014–1021, 2014.

[25] C. Jayaseelan, A. A. Rahuman, S. M. Roopan et al., "Biological approach to synthesize TiO_2 nanoparticles using *Aeromonas hydrophila* and its antibacterial activity," *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, vol. 107, pp. 82–89, 2013.

[26] R. Joerger, T. Klaus, and C. G. Granqvist, "Biologically produced silver-carbon composite materials for optically functional thin-film coatings," *Advanced Materials*, vol. 12, no. 6, pp. 407–409, 2000.

[27] W. M. Tolles and B. B. Rath, "Nanotechnology, a stimulus for innovation," *Current Science*, vol. 85, no. 12, pp. 1746–1759, 2003.

[28] A. Vishnu Kirthi, A. Abdul Rahuman, G. Rajakumar et al., "Biosynthesis of titanium dioxide nanoparticles using bacterium *Bacillus subtilis*," *Materials Letters*, vol. 65, no. 17–18, pp. 2745–2747, 2011.

[29] C. Gélis, S. Girard, A. Mavon, M. Delverdier, N. Paillous, and P. Vicendo, "Assessment of the skin photoprotective capacities of an organo-mineral broad-spectrum sunblock on two ex vivo skin models," *Photodermatology, Photoimmunology & Photomedicine*, vol. 19, no. 5, pp. 242–253, 2003.

[30] S. Hussain, X. Yang, M. K. Aslam et al., "Robust TiN nanoparticles polysulfide anchor for Li-S storage and diffusion pathways using first principle calculations," *Chemical Engineering Journal*, vol. 391, article 123595, 2020.

[31] S. Hussain, A. J. Khan, M. Arshad et al., "Charge storage in binder-free 2D-hexagonal $CoMoO_4$ nanosheets as a redox active material for pseudocapacitors," *Ceramics International*, vol. 47, no. 6, pp. 8659–8667, 2021.

[32] S. Hussain, M. Hassan, M. S. Javed et al., "Distinctive flower-like $CoNi_2S_4$ nanoneedle arrays (CNS-NAs) for superior supercapacitor electrode performances," *Ceramics International*, vol. 46, no. 16, pp. 25942–25948, 2020.

[33] S. Hussain, N. Ullah, Y. Zhang et al., "One-step synthesis of unique catalyst Ni_9S_8@C for excellent MOR performances," *International Journal of Hydrogen Energy*, vol. 44, no. 45, pp. 24525–24533, 2019.

[34] S. Hussain, M. S. Javed, S. Asim et al., "Novel gravel-like $NiMoO_4$ nanoparticles on carbon cloth for outstanding supercapacitor applications," *Ceramics International*, vol. 46, no. 5, pp. 6406–6412, 2020.

[35] D. K. Ved and G. S. Goraya, *A Text Book of Demand and Supply of Medicinal Plants in India*, NMPB, New Delhi and FRLHT„ Bangalore, India, 2008.

[36] D. W. Unander, G. L. Webster, and B. S. Blumberg, "Usage and bioassays in *Phyllanthus* (Euphorbiaceae). IV. Clustering of antiviral uses and other effects," *Journal of Ethno-Pharmacology*, vol. 45, no. 1, pp. 1–18, 1995.

[37] G. L. Webster, "Classification of the Euphorbiaceae," *Annals of the Missouri Botanical Garden*, vol. 81, no. 1, pp. 3–32, 1994.

[38] B. Joseph and S. J. Raj, "An overview: pharmacognostic Properties of Phyllanthus amarus Linn," *International Journal of Pharmacology*, vol. 7, no. 1, pp. 40–45, 2010.

[39] G. Ravikant, R. Srirama, U. Senthilkumar, K. N. Ganeshaiah, and R. Umashaanker, "Genetic Resources of Phyllanthus in Southern India: Identification of Geographic and Genetic Hot Spots and Its Implication for Conservation," in *Phyllanthus Species*, Scientific Evaluation and Medicinal Applications, pp. 97–118, CRC Press, 2011.

[40] A. K. Khanna, F. Rizvi, and R. Chander, "Lipid lowering activity of *Phyllanthus niruri* in hyperlipemic rats," *Journal of Ethnopharmacology*, vol. 82, no. 1, pp. 19–22, 2002.

[41] J. Meena, R. A. Sharma, and R. Rolania, "A review on phytochemical and pharmacological properties of Phyllanthus amarus Schum. and Thonn," *International Journal of Pharmaceutical Sciences and Research*, vol. 9, no. 4, pp. 1377–1386, 2018.

[42] K. Narendra, J. Swathi, K. M. Sowjanya, and A. Krishna Satya, "Phyllanthus niruri: a review on its ethno botanical, phytochemical and pharmacological profile," *Journal of Pharmacy Research*, vol. 5, no. 9, pp. 4681–4691, 2012.

[43] S. Shanavas, A. Priyadharsan, S. Karthikeyan et al., "Green synthesis of titanium dioxide nanoparticles using *Phyllanthus niruri* leaf extract and study on its structural, optical and morphological properties," *Materials Today: Proceedings*, vol. 26, pp. 3531–3534, 2020.

[44] A. Panneerselvam, J. Velayutham, and S. Ramasamy, "Green synthesis of TiO2 nanoparticles prepared from Phyllanthus niruri leaf extract for dye adsorption and their isotherm and kinetic studies," *IET Nanobiotechnology*, vol. 15, no. 2, pp. 164–172, 2021.

[45] M. Sathish Kumar, M. Saroja, and M. Venkatachalam, "Characterization and antimicrobial activity of green synthesized zinc sulphide nanoparticles using plant extracts of Phyllanthus niruri," *International Journal of Chemical Sciences*, vol. 15, no. 2, pp. 123–130, 2017.

[46] K. Singh, M. Panghal, S. Kadyan, U. Chaudhary, and J. P. Yadav, "Green silver nanoparticles of Phyllanthus amarus: as an antibacterial agent against multi drug resistant clinical isolates of Pseudomonas aeruginosa," *Journal of Nanobiotechnology*, vol. 12, no. 1, p. 40, 2014.

[47] W. W. Andualem, F. K. Sabir, E. T. Mohammed, H. H. Belay, and B. A. Gonfa, "Synthesis of copper oxide nanoparticles using plant leaf extract of Catha edulis and its antibacterial activity," *Journal of Nanotechnology*, vol. 2020, Article ID 2932434, 10 pages, 2020.

[48] M. D. Purkayastha, T. P. Majumder, M. Sarkar, and S. Ghosh, "Carrier Transport and Shielding Properties of Rod-Like Mesoporous TiO2–SiO2 Nanocomposite," *Radiation Physics and Chemistry*, vol. 192, article 109898, 2021.

[49] Y. Huang, J. Liang, M. Xu et al., "Stereotaxically constructed graphene modification of CuO-Cu2O/TiO2 microspheres for boosted lithium and sodium storage performance," *Journal of Electronic Materials*, vol. 51, no. 1, pp. 47–56, 2021.

[50] A. Chinnathambi, S. Vasantharaj, M. Saravanan et al., "Biosynthesis of TiO 2 nanoparticles by Acalypha indica; photocatalytic degradation of methylene blue," *Applied Nanoscience*, vol. 11, pp. 1–8, 2021.

[51] S. S. Bahri, Z. Harun, S. K. Hubadillah et al., "Review on recent advance biosynthesis of TiO2nanoparticles from plant-mediated materials: characterization, mechanism and application," *IOP Conference Series: Materials Science and Engineering*, vol. 1142, no. 1, article 012005, 2021.

[52] M. Saleem, M. Y. Naz, S. Shukrullah, S. Ali, and S. T. A. Hamdani, "Ultrasonic biosynthesis of TiO2 nanoparticles for improved self-cleaning and wettability coating of DBD plasma pre-treated cotton fabric," *Applied Physics A*, vol. 127, no. 8, 2021.

[53] R. Aswini, S. Murugesan, and K. Kannan, "Bio-engineered TiO2nanoparticles usingLedebouria revolutaextract: larvicidal, histopathological, antibacterial and anticancer activity," *International Journal of Environmental Analytical Chemistry*, vol. 101, no. 15, pp. 2926–2936, 2021.

[54] A. Fall, I. Ngom, M. Bakayoko et al., "Biosynthesis of TiO2 nanoparticles by using natural extract of Citrus sinensis," *Materials Today: Proceedings*, vol. 36, pp. 349–356, 2021.

[55] K. Lingaraju, R. B. Basavaraj, K. Jayanna et al., "Biocompatible fabrication of TiO2 nanoparticles: antimicrobial, anticoagulant, antiplatelet, direct hemolytic and cytotoxicity properties," *Inorganic Chemistry Communications*, vol. 127, article 108505, 2021.

[56] M. K. Singh and M. S. Mehata, "Temperature-dependent photoluminescence and decay times of different phases of grown TiO2 nanoparticles: carrier dynamics and trap states," *Ceramics International*, vol. 47, no. 23, pp. 32534–32544, 2021.

[57] L. Zhou, Z. Shen, S. Wang et al., "Construction of quantum-scale catalytic regions on anatase TiO_2 nanoparticles by loading TiO_2 quantum dots for the photocatalytic degradation of VOCs," *Ceramics International*, vol. 47, no. 15, pp. 21090–21098, 2021.

[58] G. Nabi, A. Majid, A. Riaz, T. Alharbi, M. A. Kamran, and M. Al-Habardi, "Green synthesis of spherical TiO2 nanoparticles using Citrus limetta extract: excellent photocatalytic water decontamination agent for RhB dye," *Inorganic Chemistry Communications*, vol. 129, article 108618, 2021.

[59] K. S. Khashan, G. M. Sulaiman, F. A. Abdulameer et al., "Antibacterial activity of TiO2 nanoparticles prepared by one-step laser ablation in liquid," *Applied Sciences*, vol. 11, no. 10, p. 4623, 2021.

[60] K. Mallikarjuna, S. V. P. Vattikuti, R. Manne et al., "Sonochemical synthesis of silver quantum dots immobilized on exfoliated graphitic carbon nitride nanostructures using ginseng extract for photocatalytic hydrogen evolution, dye degradation, and antimicrobial studies," *Nanomaterials*, vol. 11, no. 11, p. 2918, 2021.

[61] K. N. Pandiyaraj, D. Vasu, R. Ghobeira et al., "Dye wastewater degradation by the synergetic effect of an atmospheric pressure plasma treatment and the photocatalytic activity of plasma-functionalized Cu–TiO_2 nanoparticles," *Journal of Hazardous Materials*, vol. 405, article 124264, 2021.

[62] J. Singh, S. Juneja, R. K. Soni, and J. Bhattacharya, "Sunlight mediated enhanced photocatalytic activity of TiO_2 nanoparticles functionalized CuO- Cu_2O nanorods for removal of methylene blue and oxytetracycline hydrochloride," *Journal of Colloid and Interface Science*, vol. 590, pp. 60–71, 2021.

[63] S. Sagadevan, J. A. Lett, G. K. Weldegebrieal et al., "Enhanced gas sensing and photocatalytic activity of reduced graphene oxide loaded TiO_2 nanoparticles," *Chemical Physics Letters*, vol. 780, article 138897, 2021.

[64] P. Monazzam and B. F. Kisomi, "Co/TiO2 Nanoparticles: Preparation, Characterization and Its Application for Photocatalytic Degradation of Methylene Blue," *Desalination and Water Treatment*, vol. 63, pp. 283–292, 2017.

[65] R. Chauhan, A. Kumar, and R. P. Chaudhary, "Structural and photocatalytic studies of Mn doped TiO_2 nanoparticles," *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, vol. 98, pp. 256–264, 2012.

[66] L. Gnanasekaran, R. Hemamalini, R. Saravanan, K. Ravichandran, F. Gracia, and V. K. Gupta, "Intermediate state created by dopant ions (Mn, Co and Zr) into TiO_2 nanoparticles for degradation of dyes under visible light," *Journal of Molecular Liquids*, vol. 223, pp. 652–659, 2016.

[67] P. Karuppasamy, N. R. N. Nisha, A. Pugazhendhi, S. Kandasamy, and S. Pitchaimuthu, "An investigation of transition metal doped TiO_2 photocatalysts for the enhanced photocatalytic decoloration of methylene blue dye under visible light irradiation," *Journal of Environmental Chemical Engineering*, vol. 9, no. 4, article 105254, 2021.

[68] M. R. Bindhu, T. D. Willington, M. R. Hatshan, S. M. Chen, and T. W. Chen, "Environmental photochemistry with Sn/F simultaneously doped TiO2 nanoparticles: UV and visible light induced degradation of thiazine dye," *Environmental Research*, vol. 207, article 112108, 2021.

[69] E. T. Helmy, E. M. Abouellef, U. A. Soliman, and J. H. Pan, "Novel green synthesis of S-doped TiO_2 nanoparticles using *Malva parviflora* plant extract and their photocatalytic, antimicrobial and antioxidant activities under sunlight illumination," *Chemosphere*, vol. 271, article 129524, 2021.

[70] M. Aravind, M. Amalanathan, and M. Mary, "Synthesis of TiO2 nanoparticles by chemical and green synthesis methods and their multifaceted properties," *SN Applied Sciences*, vol. 3, no. 4, pp. 1–10, 2021.

[71] D. Achudhan, S. Vijayakumar, B. Malaikozhundan et al., "The antibacterial, antibiofilm, antifogging and mosquitocidal activities of titanium dioxide (TiO_2) nanoparticles green-synthesized using multiple plants extracts," *Journal of Environmental Chemical Engineering*, vol. 8, no. 6, article 104521, 2020.

[72] R. J. Barnes, R. Molina, J. Xu, P. J. Dobson, and I. P. Thompson, "Comparison of TiO2 and ZnO nanoparticles for photocatalytic degradation of methylene blue and the correlated inactivation of gram-positive and gram-negative bacteria," *Journal of Nanoparticle Research*, vol. 15, no. 2, 2013.

[73] K. S. Saranya, V. V. T. Padil, C. Senan et al., "Green synthesis of high temperature stable anatase titanium dioxide nanoparticles using gum kondagogu: characterization and solar driven photocatalytic degradation of organic dye," *Nanomaterials*, vol. 8, no. 12, p. 1002, 2018.

[74] S. A. Yasin, J. A. Abbas, M. M. Ali, I. A. Saeed, and I. H. Ahmed, "Methylene blue photocatalytic degradation by TiO2 nanoparticles supported on PET nanofibres," *Materials Today: Proceedings*, vol. 20, pp. 482–487, 2020.