Phytosynthesis and Characterization of TiO₂ Nanoparticles using Diospyros ebenum Leaf Extract and their Antibacterial and Photocatalytic Degradation of Crystal Violet

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ABSTRACT

Crystalline anatase titanium dioxide (TiO₂) nanoparticles (NPs) were prepared by eco friendly, facile and green synthesis of Diospyros ebenum leaf extract as reducing agent and were reported for the first time. The crystallization nature, morphology of the particles, and stability of the nanoparticles were investigated at different calcinations temperatures. The synthesized TiO₂ NPs were investigated for the performance of photodegradation of crystal violet (CV) dye under UV light irradiation. Effects of temperatures on structural properties, photocatalytic activity, and the antibacterial activity of TiO₂ NP were evaluated. This study revealed that TiO₂ NP synthesized at 600 °C exhibited high photocatalytic efficiency and dye adsorption capacity when compared to other synthesized TiO₂ NP and exhibited excellent antibacterial activity.

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1. Introduction

At present, toxic organic pollutants from the industry and domestic are a great challenging subject concerning environmental issues. In the field of nanoscience, the synthesis of nanoparticles of different sizes, chemical compositions, and controlled monodispersity is essential because they exhibit unique properties, which are not observed in bulk materials. There has been increasing
interest in applications of photocatalysts due to energy efficient, clean, and sustainable processes [1,2]. Recently, researchers have shown much interest in the synthesis and utilization of nanoparticles (NPs) in biological media [3], because of its extensive applications in the development of new technology in the field of electronics, materials science, and medicine at the nanoscale due to cost-effectiveness and eco-friendliness [4]. Synthesis of NPs using green technology (biosynthesis) is very important due to its low cost, non-toxicity, and other environmental advantages [5]. Semiconductor NPs have been an extensive topic of interest because of their wide applications in photocatalysis, gas sensors, photosensitizers, bimolecular applications, quantum devices, and optoelectronics [6–8] due to their distinctive optical and electronic properties which are due to quantum confinement effect as well as large surface area. Additionally, the plant-mediated biosynthesis of the NPs suitably is scaled up for large-scale nanoparticles synthesis without the use of high pressure, energy, temperature, and toxic chemicals [9,10]. Among the semiconductor photocatalytic materials, TiO$_2$ have been extensively used for the degradation of the intractable organic pollutants because of its non-toxicity, high efficiency, and photochemical stability. The properties of nanosized TiO$_2$ compared to bulk are found to change drastically either due to extremely large surface area or due to quantum confinement effects of charge carriers. The TiO$_2$ nanostructures can become a useful key for environmental protection like degradation of organic compounds in polluted air and waste water, energy generation, bacterial removal, membranes in the dye-sensitized solar cells, UV detectors, and fuel cells [11–13]. Recently, TiO$_2$ NPs are promising in many applications such as pigments, adsorbents, and catalytic supports [10,11]. TiO$_2$ NPs are one of the most important materials for cosmetics, pharmaceuticals, skin care warehouse, particularly to protect skin from UV rays, whiteness, solar cells, electrochemical devices, pollution control, and antibacterial coatings, opacity to products such as paints, plastics, papers, inks, food colorants, and toothpastes [14–18]. In addition, TiO$_2$ has a strong oxidizing power, and as a photocatalyst, it is certified to be the most suitable catalyst for the degradation of materials presumed to be non-degradable, which could not be degraded by existing biological treatment methods. Previous reports have found that photocatalytic properties occur on the surface of photocatalysts and adsorption of molecules improves the speed of photolysis. Diospyros ebenum (D. ebenum) or Ceylon ebony is a species of tree in the genus Diospyros and the family Ebenaceae. This plant is grown and distributed throughout India in deciduous forests. The fruits of this plant are edible; the bark is astringent [19] and its decoction is used to treat diarrhea and dyspepsia. The leaves are diuretic laxative, carminative, styptic, and the dried flowers are used to treat urinary and skin infections. Leaf extract of D. ebenum using methanol extraction contained a high total phenolic level and is a good source of antioxidant as well as antibacterial agents against Bacillus subtilis, Staphylococcus aureus, Pseudomonas aeruginosa, Salmonella typhimurium, and Enterobacter aerogenes [20].

In the present work, green synthesis of crystalline TiO$_2$ NPs using fresh leaf extract of D. ebenum is reported for the first time as far as our literature survey concern. The performance of the synthesized nanoparticles was studied by photocatalyst activity and antimicrobial activity was investigated on infection causing model bacterium Escherichia coli (E. coli) [21,22].

2. Experimental
2.1. Materials
Fully matured fresh leaves of D. ebenum were collected from Bharathidasan University, Tiruchirappalli, Tamil Nadu, India using sterile polyethylene bags. The leaves were authenticated by a plant taxonomist, Department of Plant Science, Periyar University, Salem, India. D. ebenum leaves were thoroughly washed with tap water followed by distilled water to remove adhering debris and associated epifauna. After the wash, leaves were dried at room temperature for a week. The dried algal materials were macerated to make coarse powder using mortar and pestle.

2.2. Synthesis of TiO$_2$ Nanoparticles
D. ebenum leaf powder was extensively extracted in 150 ml distilled water which was used to extract the crude plant using Soxhlet apparatus at 60 °C and reflux process was continued for nearly 4 h until a dark brown colored liquid was obtained. The resultant solution was dripped in dropwise into 5 M of TTIP (Sigma Aldrich, India) thoroughly under stirring condition at room temperature for 3 h. The solution was centrifuged at 5000 rpm for about 30 min to get sediment. The resultant products were dried in vacuum oven at 80 °C for 24 h that yielded TiO$_2$ NPs powder. These TiO$_2$ NPs were post-annealed at different temperatures of 600, 500, 450, and 400 °C.

2.3. Photocatalytic Experiments
Ten mg of TiO$_2$ NPs is added to 200 mL of aqueous solution of the Crystal Violet (CV) dye. The photocatalytic decomposition of CV dye using anatase TiO$_2$ NP in solution was examined by UV–vis absorption spectroscopy. For the time intervals of 5 min, 3 mL of solution were taken for maximum absorption spectra of CV by UV–visible
spectroscopy analysis (M/s JASCO, Model V-670, U.S.A.). Time-dependent absorption was studied for the dye and charge free nanoparticles dye solutions were obtained after centrifugation at 4000 rpm for 5 min and the supernatant collected is used to examine the degradation efficiency. The dye concentration (%) after various intervals of time can be estimated using the following equation

\[
\text{Concentration of dye(%) = } \frac{C - C_0}{C} \times 100
\]

where \( C, C_0 \) are the absorbance at final and initial for various interval of times \( t \), respectively.

### 2.4. Characterizations

#### 2.4.1. XRD Analysis

From XRD measurement, crystalline phase and crystallite size of TiO\(_2\) NP were characterized using powder X-ray diffractometer (M/s PANalytical X’Pert Pro, The Netherlands), operated at voltage = 40 kV and current = 30 mA with Cu-K\(\alpha\) (\(\lambda = 1.5406 \text{ Å}\)) radiation.

#### 2.4.2. FT-IR Analysis

Functional group of the materials was confirmed by Fourier Transformation Infrared spectrometer (M/s JASCO, U.S.A.) in the transmittance mode in the range of 4000–400 cm\(^{-1}\) using KBr pellet.

#### 2.4.3. HR-TEM Analysis

The shape and size of the nanomaterials were obtained by HR-TEM (M/s JEOL, Model-6390, Japan).

#### 2.4.4. UV–vis Analysis

UV–vis absorbance spectrum of the sample was recorded by UV–vis spectrometer (M/s JASCO, Model V-670, U.S.A.). The photodegradation of crystal violet dye was measured by UV–vis spectrometer (M/s Shimadzu, Japan).

#### 2.4.5. SEM and EDX Analysis

The surface morphology of as synthesized product was analyzed by scanning electron microscopy (Carl Zesis). The energy dispersive X-ray spectrometer was performed by a (Carl Zesis) EDX spectrometer to determine the elemental composition of the samples.

### 2.5. Antimicrobial Screening of TiO\(_2\) NP on Infection Causing Bacterium

*E. coli* cultures were obtained from National Chemical Industrial Microorganisms (NCIM), Pune, India. *In-vitro* antimicrobial sensitivity study was carried out using the well diffusion method to the test samples against *E. coli* on Muller Hinton Agar (MHA) medium. A sterile cotton swab was used to inoculate the diluted bacterial suspensions (test culture suspensions prepared in sterile 0.85% saline matching an optical density of 0.5 McFarland standards corresponding to 10\(^8\) CFUs ml\(^{-1}\)) on the surface of agar plates for homogeneous growth. The 15 \(\mu\)l of test solution was poured into each well separately, and then the test sample coated disks were placed in each dish by a sterilized forceps. The plates were incubated at 37 ± 1 °C for 24–48 h. After incubation, the zone of inhibition was measured with ruler/HiAntibiotic Zone Scale-C. The assays were performed in triplicate and the average values were present. All the media, standard disks and Hi Antibiotic Zone Scale-C were purchased from Hi-Media (Mumbai, India).

### 3. Results and Discussion

#### 3.1. Crystalline Structures

The crystalline structure of TiO\(_2\) NPs synthesized by *D. ebenum* leaf extract was confirmed using X-ray diffraction analysis as shown in Figure 1. The diffraction peak positions of the patterns of TiO\(_2\) are at \(2\theta = 25.32^\circ, 37.88^\circ, 47.9^\circ, 53.9^\circ, 55.10^\circ, 62.79^\circ, 68.77^\circ\), and 75.09° corresponding to the planes of (1 0 1), (0 0 4), (2 0 0), (1 0 5), (2 1 1), (2 0 4), (1 1 6), and (2 1 5), respectively, to the anatase structure of TiO\(_2\) NP (JCPDS No: 89-4921) with the lattice constant \(a = b = 3.7859 \text{ Å}, c = 9.5025 \text{ Å}\). The prepared TiO\(_2\) NP were post-annealed at different temperatures of 400, 450, 500, and 600 °C showing the anatase phase structure with well crystalline nature as shown in Figure 1(b–d). The diffraction pattern of post-annealed sample at 400 °C showed amorphous nature as shown in Figure 1(a). This result implies that the amorphous phase of TiO\(_2\) has been successfully transformed to a crystalline anatase phase by carrying out thermal treatment. The intensity of

![Figure 1. XRD patterns of TiO\(_2\) at different temperature of calcinations (a) 400°C (b) 450°C (c) 500°C, and (d) 600°C.](image-url)
the diffraction peaks became stronger with an increase in the calcinations temperature of 450, 500, and 600 °C as shown in Figure 1(b–d) which indicates in increase in crystalline nature of the sample. Debye–Scherrer’s formula is used to calculate the crystallite size from the prominent diffraction peak corresponding to (1 0 1) plane. The average crystallite size ($D_{hkl}$), dislocation density ($\delta$), and strain ($\epsilon$) are calculated using the following relations:

$$D_{hkl} = \frac{K\lambda}{\beta \cos \theta}, \quad \delta = \frac{1}{D^2}, \quad \epsilon = \frac{\beta \cos \theta}{4},$$

where $\lambda$ (1.5406Å) represents the wavelength of X-ray, $\theta$ is the diffraction angle, and $\beta$ is the full width at half maximum (FWHM) of the diffraction peak. The average crystallite size ($D_{hkl}$), FWHM, D-spacing, dislocation density ($\delta$), and strain ($\epsilon$) for the prominent diffraction peak of TiO$_2$ are shown in Table 1 for different calcinations temperatures.

### 3.2. FTIR Analysis

The identification of molecular absorption and a functional group of TiO$_2$ NP were confirmed by FTIR analysis. The functional group of TiO$_2$ NP are observed at 3410 cm$^{-1}$ due to the presence of hydroxyl alcohol group (O–H), 2810 cm$^{-1}$ (C–H) stretching of alkenes/aldehydes, 2350 cm$^{-1}$ (C=H) alkenes, 1620 cm$^{-1}$ (C–C) aromatic stretching, 1360 cm$^{-1}$ (C–H) alkenes rocking structure, 1051 cm$^{-1}$ (C–O) stretching wings of alcohols/carboxylic acids, and 450–615 cm$^{-1}$ are due to the presence of metal oxides nature of Ti–O bonding as shown in Figure 2(a–d). The fundamental absorption edges of the samples are used to estimate the band gap of the materials.

### 3.3. UV–vis Spectroscopy

UV–vis absorption spectra for analyzing the optical absorption of TiO$_2$NP are shown in Figure 4A. The maximum absorption wavelength of TiO$_2$NP annealed at different temperatures of 400, 450, 500, and 600 °C are 310, 295, 315, and 325 nm, respectively, as shown in Figure 4A(a–d). The fundamental absorption edges of the samples are used to estimate the band gap of the materials.

The optical band gap of the material was estimated from Tauc’s relation [25]

$$(a h\nu) = A (h\nu - E_g)^p$$

where $(h\nu)$ is the photon energy, $E_g$ is the optical band gap of the material. $A$ is a constant and $p = 1/2$ (or) 2 for the direct (or) indirect band gap material. The direct optical band gap was calculated values from $(a h\nu)^2$ vs. $h\nu$ plot by extrapolating the linear portion of the curve to $h\nu$ axis. From Figure 4B, it can be inferred that there is an increase in band gap of TiO$_2$-NPs as the annealing temperature increases.

### Table 1. Crystalline structure characterization of synthesized TiO$_2$.

| TiO$_2$ (°C) | 2θ (h k l) | FWHM (radian) | D-spacing (nm) | Crystallite size | Dislocation density ($\delta$) x (10$^6$) lines/m$^2$ | Strain ($\epsilon$) x 10$^{-3}$ |
|--------------|------------|----------------|----------------|------------------|-----------------------------------------------|-------------------------------|
| 400          | 25.32      | 0.2600         | 3.75           | 24.0             | 9.1                                           | 0.94                          |
| 450          | 25.32      | 0.2600         | 3.51           | 24.0             | 9.1                                           | 0.94                          |
| 500          | 25.32      | 0.2600         | 3.52           | 30.1             | 9.1                                           | 0.94                          |
| 600          | 25.32      | 0.2600         | 3.51           | 33.3             | 9.1                                           | 0.94                          |
3.4. Structural Analysis

3.4.1. Scanning Electron Microscope
The morphology of annealed TiO$_2$ NPs was analyzed by scanning electron microscope (SEM) studies. SEM images (Figure 5) confirm the spherical/sphere-like tiny nanoparticles fine and agglomerated in nature, the nanoparticles are uniformly distributed throughout the sample, and the sizes of the particles are small. There is no change in morphology of TiO$_2$NP even after the increase in annealing temperature but there is a change in average grain size of materials. EDS spectra show the presence of Ti and O in the synthesized powder. The atomic weight percentage of Ti and O are tabulated in Table 2 for the annealed samples. Also the structure and the crystallite size of TiO$_2$NP were studied by HR-TEM (Figure 6).

3.4.2. Transmission Electron Microscopy (TEM) Analysis
Figure 6 illustrates the TEM micrographs of synthesized TiO$_2$ NP annealed at 600 °C temperature. The particles were spherical in shape with a narrow dimension ranging from 10 to 12 nm of crystallite size. The anatase phase of (1 0 1) lattice plane is clearly seen in the Figure 6(c) for TiO$_2$NP for annealed at 600 °C. The d-spacing was calculated from the TEM image as 3.10, 3.15, and 3.25 nm as shown in Figure 6(c). The average d-spacing is found as 3.15 nm, which was matched with the crystallite d-spacing obtained from XRD analysis as 3.20 nm. The anatase TiO$_2$NPs is further confirmed by Raman spectra. The SAED diffraction pattern also confirms the presence of anatase phase having the lattice fringe spacing for (1 0 1), (0 0 4 ), and (2 0 0) Miller planes as shown in Figure 6(b).
The absorption spectra at 590 nm for CV dye at different time intervals have been studied with catalyst and without catalyst. Figure 7 shows the selective UV–vis absorption spectral changes of CV dye during the photocatalytic degradation performance without the catalyst and with catalyst TiO$_2$-NPs at different annealed temperatures under UV light irradiation for 10 ppm of dye concentration [23,26]. The major maximum absorption peak of CV dye solution at 590 nm gradually diminishes with the increase in time of exposure to UV light radiation and the weak peaks at 310 nm also tediously decreases with increase in time of exposure to radiation that indicates the presence of TiO$_2$ maximum absorbance spectra as shown in Figure 7. The plots clearly demonstrate that the

From the SAED pattern, it is evident that the synthesized nanoparticles are in anatase phase.

### 3.5. Photocatalyst

The photocatalytic activity of annealed TiO$_2$ is evaluated by degradation of CV dye under UV light of wavelength 354 nm. The absorption spectra at 590 nm for CV dye at different time intervals have been studied with catalyst and without catalyst. Figure 7 shows the selective UV–vis absorption spectral changes of CV dye during the photocatalytic degradation performance without the catalyst and with catalyst TiO$_2$-NPs at different annealed temperatures under UV light irradiation for 10 ppm of dye concentration [23,26]. The major maximum absorption peak of CV dye solution at 590 nm gradually diminishes with the increase in time of exposure to UV light radiation and the weak peaks at 310 nm also tediously decreases with increase in time of exposure to radiation that indicates the presence of TiO$_2$ maximum absorbance spectra as shown in Figure 7. The plots clearly demonstrate that the

### Table 2. Atomic weight percentage of Ti and O.

| Calcination temperature (°C) | Ti (%) | O (%) |
|------------------------------|--------|-------|
| 400                          | 51.67  | 48.33 |
| 450                          | 62.93  | 37.07 |
| 500                          | 66.61  | 33.39 |
| 600                          | 68.60  | 31.40 |

From the SAED pattern, it is evident that the synthesized nanoparticles are in anatase phase.

### Figure 5. SEM micrographs and EDS spectrum of TiO$_2$ NP annealed at (A) 400 °C, (B) 450 °C, (C) 500 °C and (D) 600 °C.

### Figure 6. HR-TEM images of TiO$_2$ NP annealed at 600 °C (A) 20 nm (B) 10 nm inset SAED Patterns (C) 5 nm with d-spacing.
Crystalline phase, surface area, and hierarchical structures can affect photocatalytic efficiency. Initially, concentration effect of TiO$_2$ on the rate of degradation is performed with different thermally annealed TiO$_2$NP (400 °C to 600 °C) were investigated and compared with the synthesized TiO$_2$NP. The rate of degradation increases with an increase in post-annealed TiO$_2$NP better than the annealed TiO$_2$-NP increases the rate of degradation efficiency and directly proportional to exposure time. Figure 7(a–e) shows a series of graphs indicating a characteristic activity of photodegradation of CV dyes by different crystallite size of nanoparticles obtained by annealing the TiO$_2$NP at different temperatures of 400, 450, 500, 550, and 600 °C, were compared with bulk TiO$_2$NP.

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as-prepared TiO₂-NP. The degree of photodegradation is mainly due to the absorption of photons with higher energies than that the band gap of pure/bare TiO₂-NP leading to the generation of electrons and hole pairs of TiO₂-NP. The charge separation was followed by migration of these photogenerated carriers in TiO₂-NP and surface chemical reactions between the carriers with various compounds. The holes and electrons recombination take place with each other without participating in any chemical reactions. In TiO₂-NPs mechanism for the degradation of crystal violet, the photocatalytic reaction initiates from the electron–hole pairs generation upon light irradiation [27,28]. From the photocatalytic activity, it is clear evident that the photodegradation of dye performance is increased much for higher annealed sample and even better than the as-prepared as shown in Figure 7(a–e). Pseudo first-order kinetic reaction of the calcined at 400, 450, 500, and 600 °C samples are given in the Figure 8 which confirms the kinetic reaction and degradation of efficiency.

3.6. Antibacterial Activity

The antibacterial activities of solutions containing different concentrations of TiO₂-NPs were shown in gram-negative bacteria. The different concentrations such as 10, 20, 30, and 40 μg of TiO₂-NPs were used for antimicrobial activity assay. The maximum antibacterial zone in case of 100 μg/ml concentration of the synthesized TiO₂-NPs was found as 16 mm against E. coli. This suggests that TiO₂-NPs from D. ebenum possess antibacterial potential against gram-negative bacteria E. Coli. The result also shows that the zone of inhibition was increased when increasing the concentration of TiO₂-NPs. The results of the antibacterial assay are shown in Figure 9 and Table 3.

4. Conclusion

TiO₂-NPs having polycrystalline nature had been synthesized using D. ebenum leaf extract and it was used for the photodegradation of dyes and antimicrobial studies of E. coli bacterium. The results showing enhancement in photodegradation of dyes is due to TiO₂ crystallite size which lead to higher surface and adsorptive nature. Increase in band gap and an optical property were confirmed by UV studies and supports the quantum confinement of particles which was added an advantage for optimizing and increasing the rate of photodegradation of dyes. This work will lead to an eye opener to a new opportunity in the exploration of TiO₂-NPs and promotes their practical application in clean and renewable energy and environmental concern. The influence of native defects was investigated on photocatalytic activity and dye adsorption using TiO₂-NPs surface. We found that a lower concentration of nonradioactive defects induced a higher photocatalytic activity.

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Disclosure statement

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