APPLIED MATERIALS AND TECHNOLOGY

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Research Article

Sustainable fabrication of Ag_2O-doped anatase TiO_2 nanoparticles via green synthesis for enhanced photocatalysis

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ABSTRACT: In response to the growing demand for sustainable technologies for wastewater treatment, this study reports the green synthesis of Ag_2O-doped TiO_2 nanoparticles using Salix babylonica bark extract as a natural reducing and stabilizing agent. Although several plant extracts have been explored for the green synthesis of photocatalysts, the use of Salix babylonica biomass for the simultaneous synthesis and Ag_2O doping of TiO_2 nanoparticles remains scarcely investigated. The proposed synthesis route eliminates the need for hazardous chemicals and provides an environmentally friendly alternative for the production of photocatalytic materials. The synthesized samples, containing 0, 0.5, and 1 wt% Ag_2O, were characterized by thermogravimetric analysis (TGA), X-ray diffraction (XRD), Fourier-transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), energy-dispersive spectroscopy (EDS), and UV–Vis spectroscopy. The results confirmed the formation of predominantly anatase-phase TiO_2 and the successful incorporation of silver species without altering the crystalline structure of the oxide matrix. Ag incorporation promoted changes in the morphological and optical properties of TiO_2, favoring improved charge separation and enhanced light utilization. Photocatalytic activity was evaluated through the degradation of methylene blue under irradiation. The Ag_2O-doped samples exhibited superior performance compared with undoped TiO_2, with the 1 wt% Ag_2O sample showing the highest degradation efficiency. This improvement is attributed to the formation of Ag_2O/TiO_2 heterojunctions, which facilitate electron–hole separation and increase the generation of reactive oxygen species responsible for pollutant degradation. Overall, the results demonstrate that the proposed green synthesis strategy is a simple, low-cost, and sustainable approach for producing efficient photocatalysts with potential application in environmental remediation and wastewater treatment.

Keywords: *Titanium dioxide (TiO_2), Silver oxide doping, Green synthesis process, Photocatalysis, Wastewater treatment*

1. INTRODUCTION

Photocatalysis has emerged as a promising and versatile strategy for mitigating environmental pollution, particularly in the treatment of wastewater contaminated with persistent organic pollutants. Semiconductor-based photocatalysts are widely explored due to their ability to generate reactive oxidative species under light irradiation, enabling the degradation of dyes, pharmaceuticals, and other hazardous compounds. Among these materials, traditional metal oxides such as TiO_2 and ZnO remain extensively studied, while recent advances have focused on heterostructures, doped systems, and hybrid composites to enhance photocatalytic efficiency. In addition, emerging materials such as perovskites and quantum dots have gained attention due to their tunable band structures and improved charge carrier dynamics [1].

Among the available photocatalysts, TiO_2 stands out as a benchmark material owing to its chemical stability, low cost, and non-toxicity [2–4]. Its effectiveness in degrading organic pollutants has been demonstrated in various configurations, including thin films, composites, and nanostructured systems. Recent studies have

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Received: April 7, 2026
Revised: May 31, 2026
Accepted: June 10, 2026

How to cite: Portes, F. S. d. C., Oliveira, A. F., Carneiro, T. M. de C., Neto, E. T. W., Gonzalez, M. E. L., Marques M. C., Carvalho, C. H. C., (2026). Sustainable fabrication of Ag_2O-doped anatase TiO_2 nanoparticles via green synthesis for enhanced photocatalysis. Journal of Applied Materials and Technology, 8(1), 10–20. https://doi. org/10.31258/Jamt.8.1.10-20.

shown that the photocatalytic performance of TiO_2 can be significantly influenced by synthesis parameters, morphology, and post-treatment conditions, such as calcination, which directly affect crystallinity and charge transport properties [5]. Furthermore, the development of scalable deposition techniques has enabled the fabrication of TiO_2-based materials with controlled properties for environmental applications [6].

Despite these advantages, the practical application of TiO_2 is limited by its wide bandgap and the rapid recombination of photogenerated electron–hole pairs. To overcome these challenges, various modification strategies have been proposed, including doping with metallic species and the formation of heterojunctions. In this context, silver-based compounds have attracted considerable interest due to their ability to act as electron traps and improve charge separation. In particular, the incorporation of Ag has been shown to modulate the electronic structure and interfacial properties of TiO_2-based systems, enhancing their photocatalytic performance [7]. The formation of Ag_2O/TiO_2 heterojunctions can further promote efficient charge transfer and extend light absorption into the visible region [8, 9].

TiO_2 exists in three main crystalline phases, anatase, rutile, and brookite, whose formation depends on thermodynamic and kinetic factors such as particle size and surface energy [10, 11]. Among these phases, anatase is widely regarded as the most photoactive due to its favorable band structure and high surface reactivity [12]. Therefore, controlling the crystalline phase and microstructure is essential for optimizing photocatalytic performance. Previous studies have demonstrated that the combination of TiO_2 with carbon-based materials, such as graphene oxide, can further enhance photocatalytic efficiency by improving electron transport and reducing recombination rates [13]. In parallel, the development of sustainable and low-cost synthesis methods has become increasingly important in the context of green chemistry. Conventional nanoparticle synthesis routes often involve toxic solvents and hazardous reagents, which limit their environmental applicability. As an alternative, green synthesis approaches using plant extracts have emerged as eco-friendly methods that employ natural biomolecules as reducing and stabilizing agents [14].

Although significant progress has been made in the modification of TiO_2-based photocatalysts, challenges remain in developing synthesis routes that simultaneously combine sustainability, low cost, and enhanced photocatalytic efficiency. Additionally, recent studies using alternative composite systems have demonstrated the importance of synergistic effects between components in improving dye degradation efficiency [15].

From a mechanistic perspective, the photocatalytic activity of TiO_2-based materials is governed by the generation and separation of photogenerated charge carriers. Upon light irradiation with energy equal to or greater than its bandgap, TiO_2 generates electron–hole pairs (e^-/h^+). These charge carriers migrate to the surface, where they participate in redox reactions with adsorbed species. Photogenerated holes (h^+) can oxidize water or hydroxyl groups to produce highly reactive hydroxyl radicals (•OH), while electrons (e^-) reduce molecular oxygen to form superoxide radicals (O_2^-•). These reactive oxygen species are primarily responsible for the degradation of organic pollutants [4, 10–12]. However, the rapid recombination of e^-/h^+ pairs significantly limits photocatalytic efficiency [3, 9]. In this context, Ag_2O plays a crucial role by acting as an electron sink and forming a heterojunction with TiO_2, which facilitates charge separation and prolongs carrier lifetime [7–9]. This interfacial charge transfer enhances the generation of reactive species and improves overall photocatalytic performance, as widely reported for Ag-modified TiO_2 systems [5, 8].

In addition to electronic modification strategies, the synthesis route plays a fundamental role in determining the physicochemical properties of photocatalysts. Green synthesis using plant extracts has emerged as a sustainable alternative to conventional chemical methods, as it eliminates the need for toxic reagents and harsh processing conditions [13, 14]. Plant extracts are rich in bioactive compounds such as phenolics, flavonoids, and organic acids, which act as reducing, stabilizing, and capping agents during nanoparticle formation [14]. These biomolecules can influence nucleation and growth processes, enabling partial control over particle size, morphology, and surface functionality. Compared to traditional methods, green synthesis offers advantages such as lower energy consumption, reduced environmental impact, and improved biocompatibility [13]. However, it also presents challenges, including variability in extract composition, limited reproducibility, and difficulties in precisely controlling structural properties. Therefore, understanding the role of these biomolecules in the synthesis process is essential for optimizing material performance and ensuring consistency in photocatalytic applications.

Although plant-mediated synthesis of TiO_2 nanoparticles has been widely reported, most studies have focused on commonly used biomasses such as neem (Azadirachta indica), Aloe vera, and green tea extracts, which are rich in reducing phytochemicals and have demonstrated effectiveness in nanoparticle formation [16-18]. However, these investigations generally emphasize the synthesis of pure TiO_2 nanoparticles or employ conventional post-synthesis routes for metal incorporation. Consequently, the influence of alternative biomasses on the simultaneous synthesis and modification of TiO_2-based photocatalysts remains insufficiently explored.

Salix babylonica bark contains significant amounts of phenolic compounds, flavonoids, salicin derivatives, and organic acids, which can act as reducing, stabilizing, and capping agents during nanoparticle formation [19]. These biomolecules may influence nucleation and crystal growth processes, potentially affecting particle morphology, crystallinity, surface properties, and photocatalytic behavior. Despite these promising characteristics, studies employing Salix babylonica biomass for the preparation of Ag_2O-modified TiO_2 photocatalysts are still scarce.

Therefore, a scientific gap remains regarding the feasibility of using Salix babylonica extract as a sustainable precursor for the green synthesis of Ag_2O-doped TiO_2 nanoparticles and the influence of this synthesis route on photocatalytic performance. In addition, limited information is available concerning the synergistic effects between plant-mediated synthesis and the formation of Ag_2O/TiO_2 heterojunctions.

In this context, the present work reports the green synthesis of Ag_2O-doped TiO_2 nanoparticles using an aqueous extract of Salix babylonica bark as a bio-mediated reducing and stabilizing agent. Unlike previous studies that employed conventional chemical routes or focused exclusively on undoped TiO_2 systems, the proposed approach combines a renewable biomass source with Ag_2O incorporation to simultaneously promote sustainability and

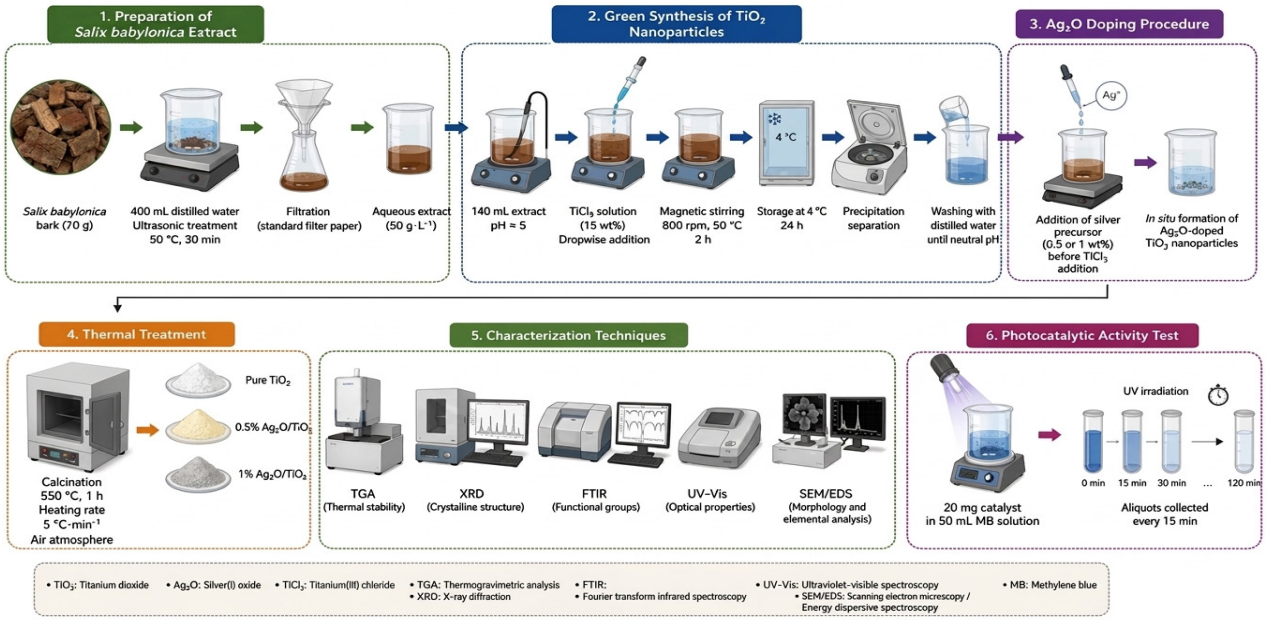

Figure 1. Schematic representation of the green synthesis route used for the preparation of pure and Ag_2O-doped TiO_2 nanoparticles using Salix babylonica bark extract.

enhanced photocatalytic activity. The influence of Ag_2O incorporation on the structural, morphological, and photocatalytic properties of the synthesized materials was systematically investigated, aiming to develop environmentally friendly photocatalysts for wastewater treatment applications.

2. MATERIALS AND METHODS

2.1. Preparation of salix babylonica extract. The aqueous extract was prepared by manually fragmenting 70 g of Salix babylonica bark, followed by immersion in 400 mL of distilled water. The mixture was subjected to ultrasonic treatment at 50 °C for 30 min to promote the extraction of bioactive compounds. Subsequently, the suspension was filtered using standard filter paper to separate the liquid extract from solid residues, and the filtrate was collected for further use.

2.2. Green synthesis of TiO_2 nanoparticles. TiO_2 nanoparticles were synthesized via a green route using 140 mL of the prepared extract (50 $g{\cdot}L^{-1}$). The pH of the reaction medium was approximately 5, corresponding to the natural pH of the Salix babylonica extract after preparation. No additional pH adjustment was performed using acids or bases. This condition was maintained throughout the synthesis procedure. A solution of $TiCl_3$ (15 wt%, Riedel-de-Haën) was added dropwise under continuous magnetic stirring at approximately 800 rpm and 50 °C for 2 h. The resulting mixture was then stored at 4 °C for 24 h to allow complete precipitation. The obtained precipitate was separated and washed repeatedly with distilled water until a neutral pH was achieved, ensuring the removal of residual impurities and unreacted species. The synthesis procedure was adapted from previously reported green synthesis methodologies for TiO_2-based materials employing plant extracts as reducing and stabilizing agents. The use of the natural pH of the extract was intended to preserve the phytochemical composition responsible for the bio-mediated reduction and stabilization processes during nanoparticle formation.

2.3. Ag_2O doping procedure. For Ag_2O doping, silver precursor concentrations corresponding to 0.5% and 1% (w/w, relative to the titanium precursor) were introduced into the reaction medium before the addition of $TiCl_3$. This approach enabled the in situ formation of Ag_2O-doped TiO_2 nanoparticles during the synthesis process.

2.4. Thermal treatment. The as-synthesized materials were subjected to thermal treatment based on thermogravimetric analysis results. Calcination was carried out at 550 °C for 1 h under air atmosphere, using a heating rate of 5 $°C{\cdot}min^{-1}$. This step was performed to remove residual organic species from the plant extract and to promote crystallization of the TiO_2 phase. The overall experimental procedure employed for the preparation of pure and Ag_2O-doped TiO_2 nanoparticles is summarized in Figure 1. The schematic illustrates the preparation of the Salix babylonica extract, the green synthesis process, Ag_2O incorporation, thermal treatment, and the subsequent characterization and photocatalytic evaluation steps.

2.5. Characterization Techniques. Thermogravimetric analysis (TGA) was performed using a TGA-50 instrument (Shimadzu) to evaluate the thermal stability and determine the appropriate calcination temperature. The crystalline structure of the calcined samples was analyzed by X-ray diffraction (XRD) using an X'Pert PRO diffractometer (PANalytical), with measurements conducted over a 2θ range of 10°–80°. Optical properties were investigated by UV–Vis spectroscopy. Morphological and elemental analyses were carried out using scanning electron microscopy (SEM) coupled with energy-dispersive spectroscopy (EDS).

2.6. Photocatalytic activity tests. The photocatalytic activity of the synthesized materials was evaluated through the degradation of methylene blue under light irradiation. For each experiment, 20 mg of catalyst was dispersed in 50 mL of dye solution. The concentration changes were monitored using a UV–Vis spectrophotometer (Kasvi K37) by measuring the absorbance at the characteristic wavelength of methylene blue at regular time intervals. Aliquots were collected every 15 min during the irradiation process to evaluate the degradation profile over time.

3. RESULT AND DISCUSSION

3.1. Thermal analysis. The TGA curves of undoped and Ag_2O-doped TiO_2 nanoparticles (0, 0.5, and 1 wt%) are presented in Figure 2, providing insight into the thermal stability and decomposition behavior of the green-synthesized materials.

All samples exhibit a similar multi-step weight loss profile, indicating that the incorporation of silver does not significantly alter the overall thermal decomposition mechanism. The initial mass loss observed below 100 °C is attributed to the removal of physically adsorbed water molecules and surface moisture, which is typical for nanostructured oxides synthesized via aqueous routes [20].

A second weight loss stage occurs between approximately 150 °C and 350 °C, which can be associated with the decomposition of low-molecular-weight organic compounds derived from the Salix babylonica extract, such as phenolic and flavonoid species acting as reducing and stabilizing agents during synthesis [21]. This behavior is consistent with previous studies on plant-mediated synthesis of metal oxides, where organic residues persist after synthesis and decompose upon heating [14, 21].

The most significant mass loss is observed in the temperature range of 300 °C to 600 °C, corresponding to the thermal degradation of more stable organic constituents and carbonaceous residues strongly bound to the nanoparticle surface. This stage reflects the removal of capping agents and the progressive formation of the inorganic TiO_2 network [20]. The completion of this process indicates the transition toward a fully crystallized oxide structure.

Notably, the undoped TiO_2 sample exhibits a more pronounced mass loss compared to the Ag-doped samples, suggesting a higher content of residual organic material. In contrast, the presence of Ag appears to slightly improve the thermal stability of the system, possibly due to interactions between silver species and organic molecules or a catalytic effect that promotes earlier decomposition of organics [22, 23].

Above 600 °C, the mass stabilizes for all samples, indicating that the decomposition process is essentially complete and that the remaining material corresponds predominantly to thermally stable inorganic TiO_2. The residual mass (~50–70%) confirms the formation of oxide-based structures after removal of organic components. Based on these results, a calcination temperature of 550 °C was selected as an optimal condition to ensure the effective removal of organic residues while preserving the structural integrity of the TiO_2 framework. This thermal treatment is crucial for enhancing crystallinity, which directly influences the material's photocatalytic performance [2, 20].

3.2. Structural analysis. The XRD patterns of undoped and Ag-modified TiO_2 nanoparticles are presented in Figure 3. The diffraction peaks observed for all samples are predominantly indexed to the anatase phase of TiO_2 (JCPDS No. 21-1272), confirming the successful formation of the desired crystalline structure.

The characteristic reflections located at approximately $2\theta = 25.3°$, 37.8°, 48.0°, 54.0°, and 62.7° correspond to the (101), (004), (200), (105), and (204) planes of anatase TiO_2, respectively [24, 25]. The absence of peaks associated with the rutile or brookite phases indicates that the selected calcination temperature (550 °C) was sufficient to promote crystallization while preserving phase purity. For the Ag-doped samples (0.5% and 1%), no distinct diffraction peaks corresponding to Ag_2O or metallic Ag are clearly observed. This behavior suggests that the silver species are either highly dispersed on the TiO_2 surface, incorporated into the TiO_2 lattice, or present in concentrations below the detection limit of the XRD technique [26, 27]. Such high dispersion is often associated with improved interfacial contact and enhanced photocatalytic performance.

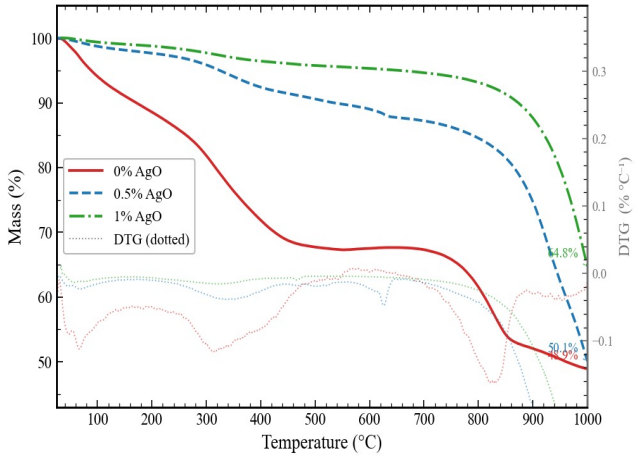

Figure 2. TGA curves of green-synthesized TiO_2 nanoparticles with different Ag_2O doping levels (0, 0.5, and 1 wt%). The profiles reveal a multi-step weight loss associated with (i) removal of adsorbed moisture below 100 °C, (ii) decomposition of organic compounds from the Salix babylonica extract between 150–350 °C, and (iii) degradation of more stable carbonaceous residues in the 300–600 °C range. The reduced mass loss observed for Ag-doped samples suggests improved thermal stability and possible interactions between silver species and residual organic components.

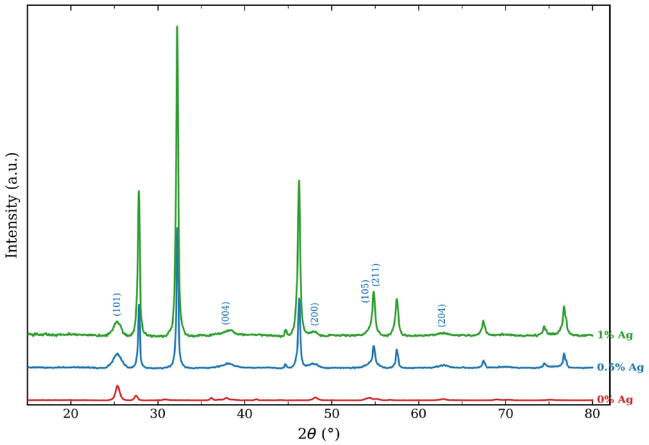

Figure 3. XRD patterns of TiO_2 nanoparticles with different Ag contents (0, 0.5, and 1 wt%). The diffraction peaks are predominantly indexed to the anatase phase (JCPDS No. 21-1272), confirming the formation of crystalline TiO_2. No secondary phases, such as rutile, are observed. The absence of well-defined peaks associated with Ag-based species suggests their high dispersion and/or low concentration within the samples. A slight increase in peak intensity for Ag-doped samples indicates improved crystallinity upon silver incorporation.

Interestingly, a slight increase in peak intensity and sharpening is observed with increasing Ag content, particularly for the (101) plane, indicating an improvement in crystallinity. This may be attributed to the role of Ag species in facilitating crystal growth during thermal treatment, possibly by influencing nucleation kinetics or reducing structural defects [28]. Additionally, no significant peak shift is detected, suggesting that Ag does not substitute Ti^{4+} ions in the lattice to a considerable extent, which is consistent with the difference in ionic radii and typical behavior of surface-deposited noble metals [26]. Instead, the formation of surface heterojunctions between TiO_2 and Ag-based species is more likely.

Minor reflections that may be associated with Ag-containing phases (such as AgCl or Ag_2O) are weak and not well-resolved, reinforcing the hypothesis of low concentration and/or nanometric dispersion. This structural feature is particularly relevant for photocatalytic applications, as it favors charge separation without significantly disturbing the TiO_2 crystal structure.

Overall, the XRD results confirm that Ag incorporation does not compromise the anatase framework, while subtly enhancing crystallinity and potentially promoting the formation of efficient heterojunctions, which are essential for improved photocatalytic activity.

3.3. FTIR analysis. The FTIR spectra of undoped and Ag_2O-doped TiO_2 nanoparticles are presented in Figure 4, providing insight into the surface chemistry and the presence of residual organic species derived from the green synthesis route. A broad absorption band observed in the region of 3200–3600 cm^{-1} is attributed to O–H stretching vibrations, which are associated with hydroxyl groups and adsorbed water molecules on the surface of TiO_2 nanoparticles [29]. The presence of these hydroxyl groups is particularly relevant for photocatalytic applications, as they play a key role in the generation of reactive hydroxyl radicals (•OH).

In the region around 2800–3000 cm^{-1}, bands corresponding to C–H stretching vibrations are observed, indicating the presence of organic residues originating from the Salix babylonica extract [30]. These biomolecules act as reducing and stabilizing agents during synthesis, and their partial persistence after calcination suggests incomplete removal or strong interaction with the nanoparticle surface.

A distinct band near ~1600–1700 cm^{-1} is assigned to C=O stretching vibrations or bending modes of adsorbed water molecules, further confirming the presence of organic functional groups and surface-bound species [29, 30]. These features are consistent with plant-mediated synthesis routes, where phenolic and flavonoid compounds contribute to nanoparticle formation and stabilization

In the low wavenumber region (below ~700 cm^{-1}), a strong absorption band is observed, which is characteristic of Ti–O–Ti lattice vibrations, confirming the formation of the TiO_2 framework [24, 29]. This result is in good agreement with the XRD analysis, which also confirmed the formation of crystalline anatase TiO_2, reinforcing the successful synthesis of the oxide structure through the green route.

Comparatively, the intensity of organic-related bands (C–H and C=O) decreases slightly with increasing Ag content, suggesting that the incorporation of silver may facilitate the removal or transformation of organic residues during calcination. This behavior is consistent with the catalytic role of silver species in promoting thermal decomposition processes [31].

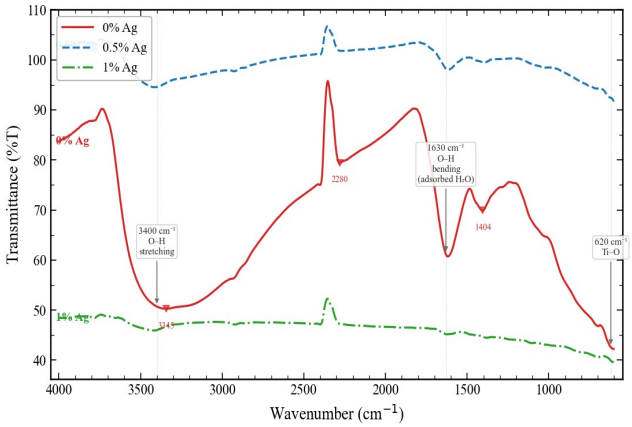

Figure 4. FTIR spectra of undoped and Ag_2O-doped TiO_2 nanoparticles (0, 0.5, and 1 wt%). The broad band at 3200–3600 cm^{-1} is attributed to O–H stretching of surface hydroxyl groups and adsorbed water. Bands in the 2800–3000 cm^{-1} region correspond to C–H vibrations, while the peak near 1600–1700 cm^{-1} is associated with C=O stretching and/or bending modes of adsorbed water. The strong absorption below 700 cm^{-1} is assigned to Ti–O–Ti lattice vibrations, confirming the formation of the TiO_2 framework. The decrease in intensity of organic-related bands in Ag-doped samples suggests partial removal of residual biomolecules.

3.4. Morphological analysis. The morphology and surface characteristics of the synthesized TiO_2 nanoparticles were investigated by SEM, as shown in Figure 5 (a–c). The undoped TiO_2 sample (Figure 5a) exhibits a morphology composed of irregularly shaped and highly agglomerated nanoparticles. This agglomeration is commonly observed in TiO_2 synthesized via wet chemical and green routes, and is mainly attributed to high surface energy and the presence of residual organic species from the plant extract.

Upon Ag incorporation, noticeable morphological changes are observed. For the sample containing 0.5 wt% Ag (Figure 5b), the formation of brighter regions distributed across the surface becomes evident. These features are associated with silver-containing species, which present higher electron density and therefore appear brighter under SEM imaging.

With further increase in Ag content to 1 wt% (Figure 5c), these bright domains become more pronounced and uniformly distributed, suggesting improved dispersion of Ag species over the TiO_2 surface. This homogeneous distribution is particularly relevant for photocatalytic applications, as it favors the formation of interfacial contact between TiO_2 and Ag_2O, promoting efficient charge separation.

The presence of Ag appears to slightly reduce particle agglomeration, possibly due to the interaction between silver species and surface functional groups, which can modify nucleation and growth processes during synthesis. The elemental composition of the samples was further confirmed by EDS, as presented in Figure 6. The spectrum of undoped TiO_2 shows only Ti and O signals, while the doped samples clearly exhibit the presence of Ag peaks, confirming the successful incorporation of silver into the material. These results are consistent with the XRD analysis, which suggested high dispersion of Ag species without the formation of detectable secondary crystalline phases.

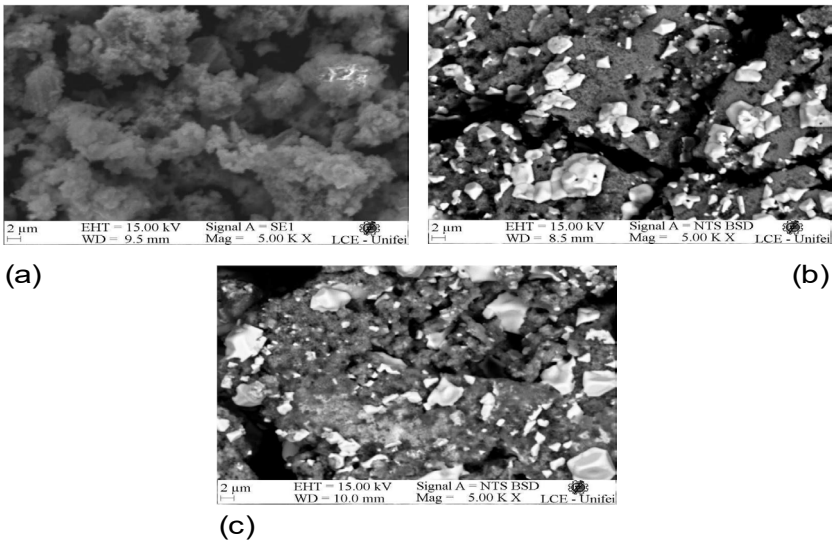

Figure 5. SEM images of TiO_2 nanoparticles with different Ag contents: (a) 0 wt%, (b) 0.5 wt%, and (c) 1 wt%. The undoped sample exhibits agglomerated nanoparticles with irregular morphology. The incorporation of Ag leads to the appearance of brighter regions associated with silver-containing species, which become more pronounced and uniformly distributed with increasing Ag content, indicating improved dispersion over the TiO_2 surface.

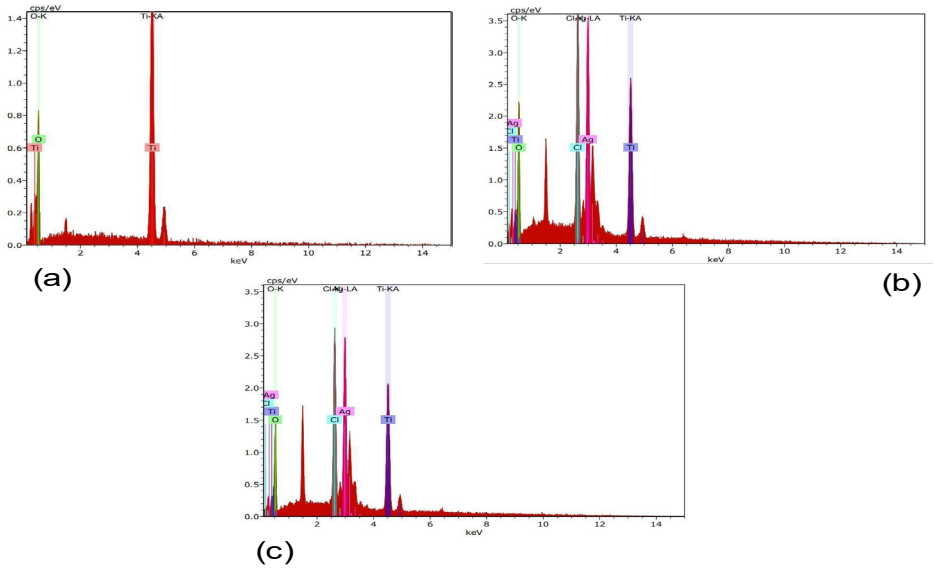

Figure 6. EDS spectra of TiO_2 nanoparticles with varying Ag content: (a) 0 wt%, (b) 0.5 wt%, and (c) 1 wt%. The undoped sample shows only Ti and O signals, while the Ag-doped samples exhibit characteristic silver peaks, confirming the successful incorporation of Ag into the TiO_2 structure. The increase in Ag signal intensity with higher doping levels indicates the progressive incorporation of silver species.

To further investigate the elemental distribution within the synthesized materials, EDS elemental mapping analyses were performed for the undoped and Ag_2O-doped TiO_2 samples, as shown in Figures 7–9. The undoped TiO_2 sample (Figure 7) exhibits only Ti and O signals distributed throughout the analyzed region, confirming the formation of titanium oxide particles and the absence of silver species. The elemental maps obtained for the 0.5 wt% Ag_2O-doped TiO_2 sample (Figure 8) reveal the presence of Ti, O, and Ag across the entire analyzed area. The Ag-Lα map demonstrates that silver species were successfully incorporated into the material through the in situ green synthesis route. No evidence of pronounced Ag-rich agglomerates was observed, suggesting an effective dispersion of the dopant within the TiO_2 matrix. A similar behavior was observed for the 1 wt% Ag_2O-doped TiO_2 sample (Figure 9), where the Ag signal remained distributed throughout the analyzed region. The higher intensity of the Ag map compared to the 0.5 wt% sample is consistent with the increased silver content employed during synthesis. The relatively homogeneous distribution of Ag supports the effectiveness of the doping procedure and indicates the successful formation of Ag-modified TiO_2 photocatalysts. These results corroborate the EDS spectra and provide additional evidence for the incorporation of silver species into the synthesized materials.

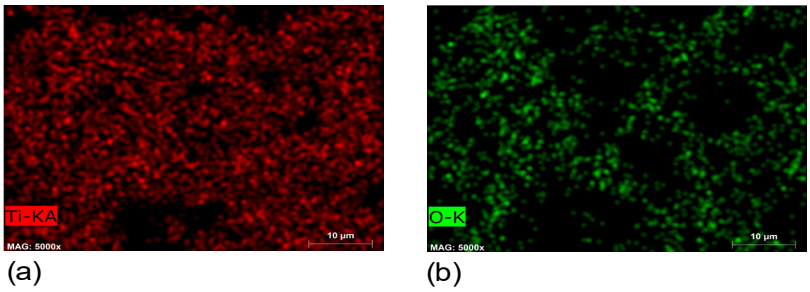

Figure 7. EDS elemental mapping of the undoped TiO_2 sample: (a) Ti-Kα distribution and (b) O-Kα distribution. The elemental maps confirm the presence of titanium and oxygen throughout the analyzed region, consistent with the formation of TiO_2 particles.

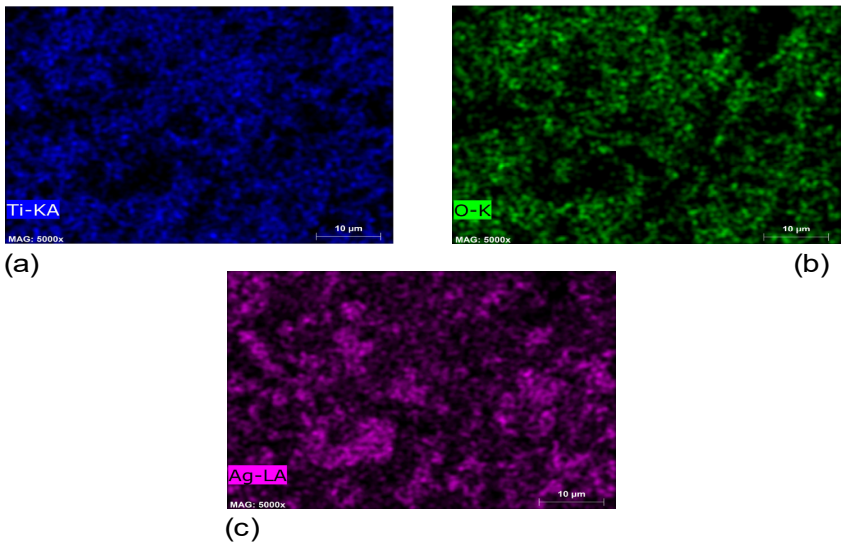

Figure 8. EDS elemental mapping of the 0.5 wt% Ag_2O-doped TiO_2 sample: (a) Ti-Kα distribution, (b) O-Kα distribution, and (c) Ag-Lα distribution. The elemental maps confirm the presence of Ti, O, and Ag throughout the analyzed region, indicating successful incorporation of silver species into the TiO_2 matrix and a relatively uniform distribution of the dopant.

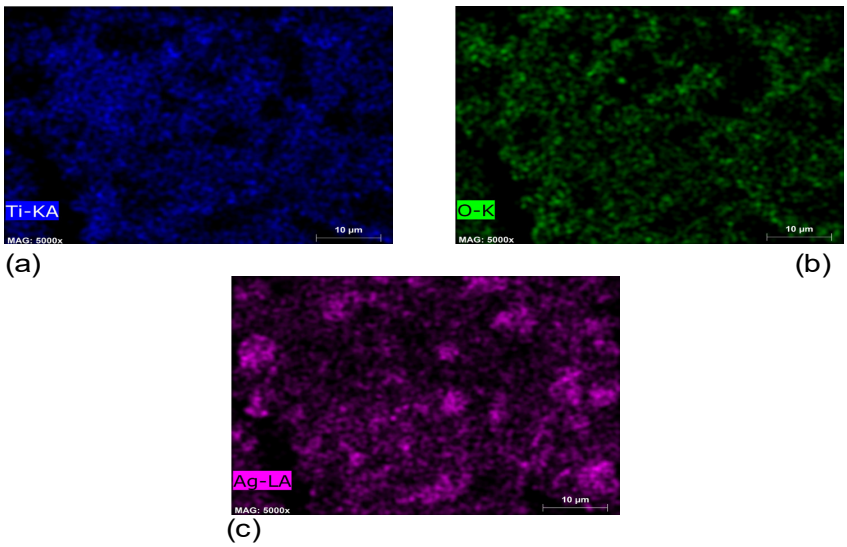

Figure 9. EDS elemental mapping of the 1 wt% Ag_2O-doped TiO_2 sample: (a) Ti-Kα distribution, (b) O-Kα distribution, and (c) Ag-Lα distribution. The elemental maps confirm the presence of Ti, O, and Ag throughout the analyzed region, indicating successful incorporation of silver species and a homogeneous distribution of the dopant within the TiO_2 matrix.

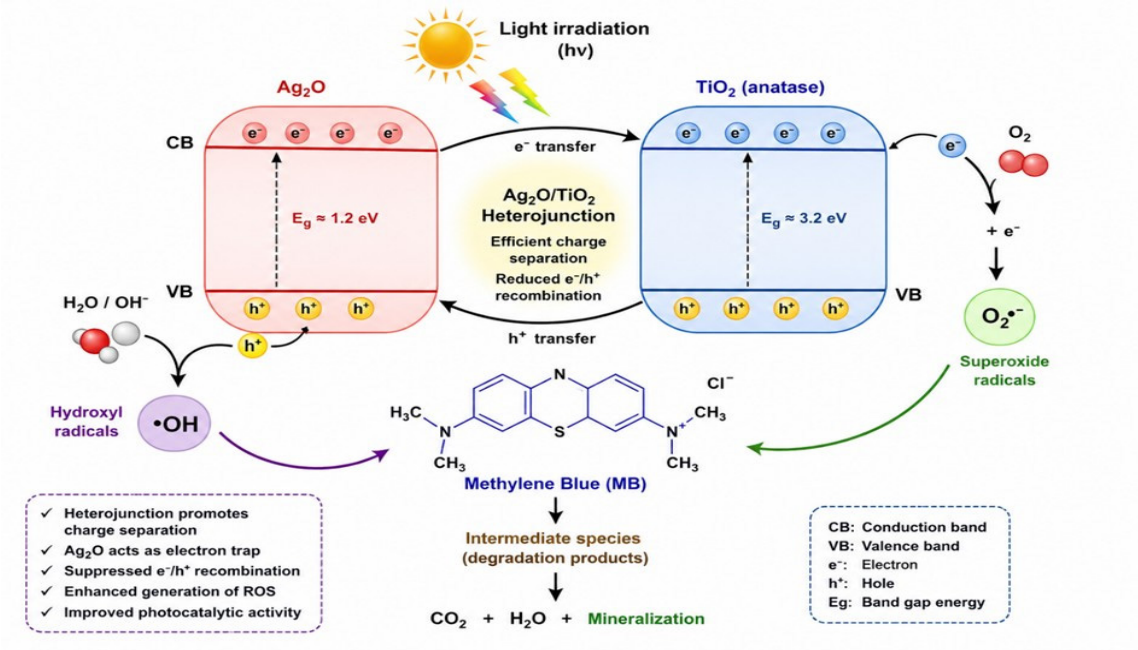

Figure 10. Proposed photocatalytic mechanism for methylene blue degradation over the Ag_2O/TiO_2 heterojunction system under light irradiation.

Table 1. Relative concentration (C_t/C_0) of methylene blue during photocatalytic degradation using TiO_2 nanoparticles with different Ag doping levels (0, 0.5, and 1 wt%) under light irradiation. Measurements were taken at selected time intervals (0, 5, and 20 min) to evaluate the initial degradation performance.

Irradiation Time (min)	C_t/C_o (%) – 0 wt% Ag	C_t/Co (%) – 0.5 wt% Ag	C_t/Co (%) – 1wt% Ag
0	100.0	100.0	100.0
5	26.3	9.1	6.3
20	19.9	3.6	2.7

3.5. Photocatalytic activitys. The photocatalytic performance of the synthesized materials was evaluated through the degradation of methylene blue under light irradiation, as summarized in Table 1. The results clearly demonstrate that Ag incorporation significantly enhances the photocatalytic efficiency of TiO_2, particularly in the initial stages of the reaction.

After 5 minutes of irradiation, the undoped TiO_2 sample shows a substantial decrease in dye concentration (26.3%), while the Ag-doped samples exhibit markedly higher degradation efficiencies, reaching 9.1% and 6.3% for 0.5% and 1% Ag, respectively. This trend becomes even more pronounced after 20 minutes, where the residual concentration decreases to 19.9% for pure TiO_2, compared to 3.6% and 2.7% for the doped samples. The enhanced photocatalytic activity can be attributed to the formation of Ag_2O/TiO_2 heterojunctions, which facilitate charge separation and reduce electron–hole recombination [32, 33]. This behavior is widely reported for Ag-modified TiO_2 systems, where silver acts as an electron sink, improving interfacial charge transfer efficiency [27, 32].

Additionally, the rapid decrease in dye concentration within the first minutes suggests fast reaction kinetics, which is desirable for practical wastewater treatment applications [33]. This effect is consistent with the structural and morphological analyses, where Ag species were found to be well-dispersed over the TiO_2 surface, promoting efficient photocatalytic activity.

It is important to note that the photocatalytic evaluation was conducted at selected time intervals (0, 5, and 20 min), focusing on the initial degradation behavior. Despite the limited number of data points, the results clearly indicate a significant improvement in photocatalytic performance upon Ag incorporation, particularly at higher doping levels.

The superior photocatalytic activity observed for the 1 wt% Ag_2O-doped TiO_2 sample can be explained by the synergistic interaction between Ag_2O and TiO_2. While pure TiO_2 exhibits high photocatalytic potential, its performance is often limited by the rapid recombination of photogenerated electron–hole pairs [3, 9, 24]. The incorporation of Ag_2O promotes the formation of a heterojunction at the Ag_2O/TiO_2 interface, facilitating charge separation and reducing recombination losses [7–9, 32]. In this configuration, photogenerated electrons can be transferred between the semiconductor phases, increasing the lifetime of charge carriers and enhancing the generation of reactive oxygen species responsible for methylene blue degradation (Figure 10) [26, 32]. The XRD patterns revealed that all samples remained predominantly in the anatase phase after Ag incorporation, with no significant shifts in diffraction peak positions or evidence of phase transformation. These results indicate that the crystal structure of TiO_2 was preserved during the doping process and suggest that the improved photocatalytic activity is primarily associated with interfacial electronic effects rather than structural modifications. Furthermore, EDS analysis confirmed the presence of Ag in the synthesized materials, supporting the successful formation of Ag-modified TiO_2.

Similar improvements have been reported for Ag_2O/TiO_2 systems, where silver-containing species act as electron trapping centers

Table 2. Comparison of methylene blue (MB) photocatalytic degradation performance of TiO_2-based photocatalysts reported in the literature.

Photocatalyst	Pollutant	Removal (%)	Irradiation Time (min)	Reference
Pure TiO_2	MB	80.1	20	This work
0.5 wt% Ag_2O/TiO_2	MB	96.4	20	This work
1 wt% Ag_2O/TiO_2	MB	97.3	2.7	This work
Ag^+-doped TiO_2	MB	>99	180	[34]
Ag-doped TiO_2 thin films	MB	~35	300	[35]
TiO_2-Ag nanoparticles	MB	97.25	-	[36]

and promote more efficient charge transfer across the heterojunction [22, 28, 32, 33]. Additionally, Ag_2O may contribute to extending light absorption toward the visible region due to its narrower band-gap compared to TiO_2, further increasing photocatalytic efficiency [7, 26, 28]. Therefore, the enhanced methylene blue degradation observed for the 1 wt% Ag_2O-doped sample is mainly attributed to improved charge separation, reduced electron–hole recombination, and enhanced generation of reactive oxygen species [22, 26, 32, 33].

A possible photocatalytic mechanism for the Ag_2O/TiO_2 system is proposed based on the experimental results and previous literature reports. Upon irradiation, both TiO_2 and Ag_2O can absorb photons and generate electron–hole pairs. Due to the formation of the Ag_2O/TiO_2 heterojunction, the photogenerated charge carriers are efficiently separated at the interface, reducing electron–hole recombination. Electrons transferred through the heterojunction react with dissolved oxygen molecules to produce superoxide radicals ($O_2^{\bullet-}$), while photogenerated holes oxidize surface hydroxyl groups or water molecules, generating hydroxyl radicals (•OH). These highly reactive species are responsible for the oxidation and degradation of methylene blue molecules into smaller intermediates and ultimately into CO_2 and H_2O.

In addition to heterojunction formation, silver-containing species may act as electron trapping centers, further suppressing charge recombination and increasing the lifetime of photogenerated carriers. Consequently, the concentration of reactive oxygen species available for photocatalytic reactions increases, resulting in enhanced degradation efficiency. The superior performance observed for the 1 wt% Ag_2O-doped TiO_2 sample suggests that this composition provides a more favorable balance between charge separation and interfacial charge transfer, leading to improved photocatalytic activity.

3.6. Comparison with literature. To evaluate the performance of the synthesized photocatalyst, the photocatalytic degradation efficiency obtained in this work was compared with similar TiO_2-based and Ag-modified photocatalysts reported in the literature. Table 2 summarizes representative studies involving methylene blue degradation under different experimental conditions.

Although direct comparison between photocatalytic studies should be interpreted with caution due to differences in catalyst dosage, irradiation source, dye concentration, and reaction conditions, the results obtained in the present work demonstrate that the green-synthesized Ag_2O-doped TiO_2 photocatalyst exhibits competitive performance compared to similar systems reported in the literature. Furthermore, the proposed synthesis route offers additional advantages associated with the use of Salix babylonica extract as a renewable and environmentally friendly reducing and stabilizing agent. The enhanced photocatalytic activity observed for the 1 wt% Ag_2O-doped TiO_2 sample is consistent with previous reports demonstrating that Ag incorporation promotes charge separation and improves the generation of reactive oxygen species. These findings indicate that the developed material represents a promising alternative for wastewater treatment applications while maintaining the benefits of a sustainable synthesis route.

Particularly, the 1 wt% Ag_2O-doped TiO_2 sample achieved 97.3% methylene blue degradation within only 20 min of irradiation, demonstrating highly competitive photocatalytic performance compared to Ag-modified TiO_2 systems reported in the literature. While direct comparisons are complicated by differences in experimental conditions, the short irradiation time required to achieve high degradation efficiency highlights the effectiveness of the proposed green synthesis approach based on Salix babylonica extract.

4. CONCLUSION

Silver oxide-doped titanium dioxide (Ag_2O-doped TiO_2) nanoparticles were successfully synthesized via a sustainable green route using Salix babylonica bark extract as a bio-reducing and stabilizing agent. The adopted methodology proved effective in producing nanostructured materials predominantly in the anatase crystalline phase, as confirmed by XRD analysis.

Thermal and spectroscopic analyses (TGA and FTIR) revealed the presence of residual organic species derived from the plant extract, which were effectively reduced after calcination at 550 °C, leading to the formation of a stable TiO_2 framework. The incorporation of Ag did not alter the crystalline phase but contributed to improved crystallinity and surface characteristics.

Morphological evaluation by SEM indicated that the materials are composed of agglomerated nanoparticles with irregular morphology, while the presence of Ag was evidenced by the appearance of well-dispersed bright regions on the TiO_2 surface. This was further confirmed by EDS analysis, which verified the successful incorporation of silver without introducing additional impurities.

The photocatalytic results demonstrated a significant enhancement in the degradation of methylene blue for Ag-doped samples, particularly at higher doping levels. This improvement is attributed to the formation of Ag_2O/TiO_2 heterojunctions, which promote efficient charge separation and reduce electron–hole recombination, thereby increasing photocatalytic efficiency. Although the present study demonstrates the beneficial effect of Ag_2O incorporation on the photocatalytic degradation of methylene blue, additional investigations involving operational parameters such as catalyst dosage, initial dye concentration, solution pH, and catalyst reusability are

necessary to further optimize the process and assess its applicability under different operating conditions. These aspects will be addressed in future studies.

Overall, the proposed green synthesis route represents a low-cost and environmentally friendly strategy for producing efficient photocatalysts. The combination of structural stability, improved surface properties, and enhanced photocatalytic performance highlights the potential of Ag_2O-doped TiO_2 nanoparticles for application in wastewater treatment. Future work should focus on detailed kinetic studies, long-term stability evaluation, and optimization of synthesis parameters to further improve reproducibility and performance.

ACKNOWLEDGEMENTS

The Brazilian agency CAPES and Fapemig (Grant APQ-03495-25) for their financial support.

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DECLARATIONS

Conflict of interest The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

AVAILABILITY OF DATA

The All data supporting the findings of this study are included within the manuscript. Any additional data related to this work is available from the corresponding author upon reasonable request.

AI DISCLOSURE STATEMENT

The authors declare that Generative AI tools were used solely to enhance image resolution and quality, without generating any new scientific content. All figures and data originate from the authors' own research.

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